Structural and optical properties of ZnO nanoparticles synthesized by CBD method using different precursors

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Abstract: *In this work we report synthesis of ZnO nanoparticles by Chemical Bath Deposition method. Two samples were synthesized using two different precursors.PVA was used as capping agent. The prepared samples were characterised to study the structural and optical properties.XRD result shows the formation of nanostructured ZnO. Optical band gap was calculated utilizing UV-vis spectra. Room temperature PL spectra showed one near-band-edge emission peak and another broad defect related visible emission peak.*

Key words: ZnO nanoparticles, XRD, UV-Vis spectroscopy, PL, SEM

1. Introduction:

Nanomaterials play important role in different fields of technology because of their different structural, optical and electronic properties from their bulk counterparts. Out of many semiconductor nanomaterials, ZnO is an important II-VI wide band gap semiconductor nanomaterial as it has varity of applications like UV absorption, antibacterial treatment[1],UV light emitters[2], photocatalyst[3] and in different industrial products. ZnO nanomaterials have been synthsized by various methods such as thermal decomposition, sol-gel method, gas-reaction, hydrothermal synthesis and so on[4-8].Among these methods chemical bath deposition method is preferable because of its good control of morphology, composition, crystalinity and purity. Also it is low cost method for large scale production. In this work ZnO nanoparticles are prepared using two different precursors. Characterisations of the samples are done for studying structural and optical properties of prepared ZnO.

2. Experimental Details:

Two samples of ZnO nanoparticles are prepared through Chemical Bath Deposition method. For the synthesis of first sample (ZnO 1)100 ml of 0.2 mol $Zn(NO_3)_2.6H_2O$ solution is stirred continuously for 30 min at 60ºC (first solution). 2wt% of PVA is stirred continuously for 30 min at 60ºC (second solution). Now to the first solution NH_4OH is added drop by drop until the pH of the solution drops to the value of 7. Now a milky solution of ZnO is formed (third solution). Then second solution is added to the third solution and the mixture is stirred continuously for 1 hour at 60ºC. The whole solution is kept over night to settle down. Finally the precipitation is filtered and washed

several times to dissolve the impurities and dried at 60ºC for 12 hours in an oven. Second sample (ZnO 2) is also synthesised in the similar way. But the first solution is prepared with $(CH_3COO)_2Zn2H_2O$ instead of $Zn(NO_3)_2$.$6H_2O$.

3. Sample characterisation:

For the determination of crystallite sizes and phase identification of prepared ZnO nanoparticles X-ray diffractogram is taken using Phillips X'Pert Pro Powder X-ray Diffractometer with Cu Kα_1 radiations of wavelength 1.5406Å. The Diffractometer is calibrated with standard silicon sample. Optical absorption spectra of the prepared samples are recorded using Hitachi UV-vis –JVIR spectrometer. Photo luminescence measurements of the samples are performed by JASCO spectrophotometer at room temperature. Excitation light source was xenon lamp. Zeiss Field Emission Scanning Electron Microscope is used to study the surface morphology of the prepared ZnO nanoparticles.

4. XRD Analysis:

Phase structures of the prepared samples are studied by analysing the XRD data. The peak positions (2θ) of XRD are compared with the standard ICDD data base. Fig.1 shows the XRD patterns of the samples. The hexagonal wurzite structure of the samples ZnO 1and ZnO 2 is confirmed from the presence of peaks such as (100), (002), (101), (110), (103), (200) and (112) in the XRD[9,10]. The grain size D of the samples is calculated using Scherrer's equation [11]

$$D = \frac{k\lambda}{\beta_{hkl}cos\theta}$$

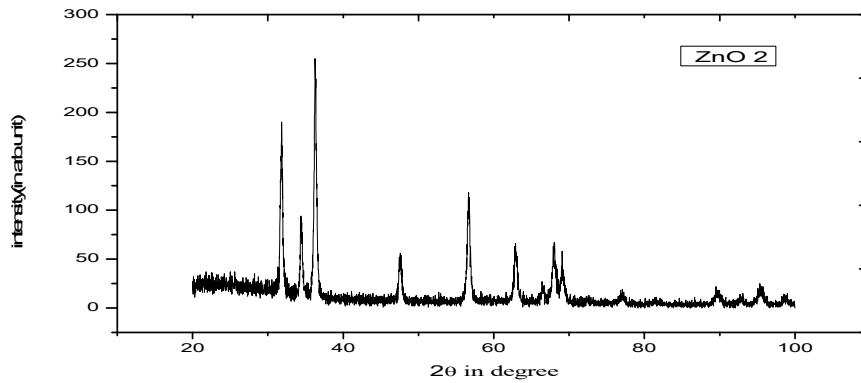where β is FWHM, θ is the Bragg's angle of different peak and λ is the X-ray wavelength. k is the shape factor (0.9).
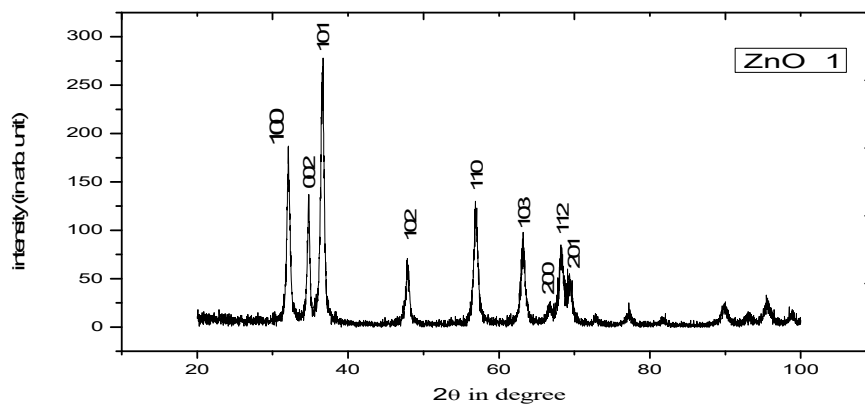
Fig.1. XRD pattern of prepared ZnO 1 and ZnO 2

Instrumental broadening arises due to slit width of kα1 and k α2 line. The instrumental broadening of βhkl corresponding to each diffraction peak of the ZnO samples was corrected using following equation[12]

$$\beta_{hkl} = [(\beta_{hkl})^2_{Measured} - (\beta_{hkl})^2_{Instrumental}]$$

The broadening of XRD peaks are due to particle size and strain mainly. When the crystallite sizes are measured with Scherrer's equation the broadening due to particle size and strain are considered. So the crystallite sizes measured with Scherrer's equation is an approximate size of crystallites. To separate the strain broadening, the Williamson-Hall (W-H) method is employed.

Fig.2 shows the Williamson-Hal l(W-H) plot of samples ZnO 1 and ZnO 2. For W-H plot β_{hkl} is plotted vs 4sinθ for all peaks of XRD of the samples.
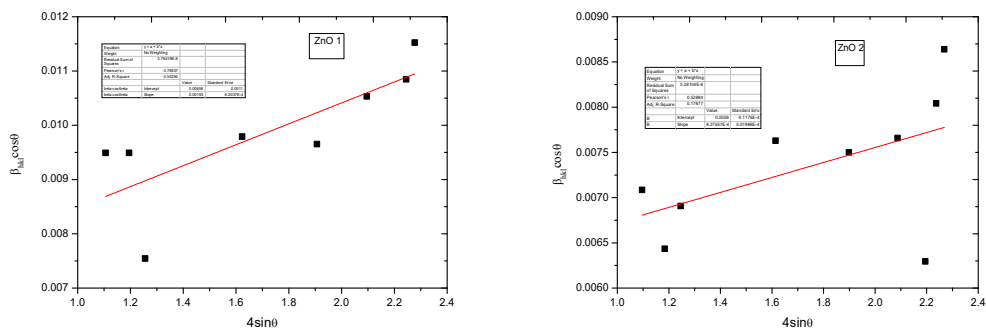

Fig.2. W-H plot for ZnO 1 and ZnO 2

The broadening of XRD peaks are due to small crystallite size and lattice distortion. But the effect of crystalline size on the line broadening is different from effect of strain and imperfections. The strain associated with the ZnO samples is calculated using following equation[13]

$$\varepsilon = \frac{\beta_{hkl}}{4tan\theta}$$

Average crystallite size of the samples is calculated averaging the crystallite sizes obtained from all peaks and from the slope of the linear fit of W-H plot[13]. Strain is calculated from the y-intercept of the fit crystallite size of the samples calculated from W-H plot using the following equation

$$\beta_{hkl} = \frac{k\lambda}{Dcos\theta} + 4\varepsilon tan\theta$$

Table 1 and 2 show the structure parameters of ZnO 1and ZnO 2 samples and crystallite size (D) determined using Sherrer's equation and W-H plot.

Table: 1. Structure parameters and crystallite size of ZnO 1 sample

Plane	2θ(in degree)	FWHM(in degree)	D(in nm) using Sherrer's equation	Average crystallite size(in nm)	Average crystallite size(in nm) from W-H plot	Strain
(100)	32.097	0.565	14.607	14.212	21.13	0.00193
(002)	34.765	0.452	18.380			
(101)	36.598	0.590	14.162			
(102)	47.888	0.605	14.362			
(110)	56.935	0.686	13.163			
(103)	63.196	0.729	12.781			
(112)	68.273	0.797	12.033			

Table: 2. Structure parameters and crystallite size of ZnO 2 sample

Plane	2θ (in degree)	FWHM (in degree)	D (in nm)	Average crystallite size(in nm)	crystallite size(in nm) from W-H plot	Strain
(100)	31.804	0.422	19.569	19.028	23.50	0.00827
(002)	34.440	0.385	21.552			
(101)	36.295	0.416	20.072			
(102)	47.590	0.477	18.175			
(110)	56.659	0.488	18.485			
(103)	62.917	0.514	18.104			
(112)	68.016	0.555	17.242			

5. UV-Vis analysis :

Optical properties of the samples ZnO1 and ZnO 2 are studied by UV –Vis spectroscopy. Fig.3 shows the UV absorption spectra of the two samples. Sample ZnO 1 exhibits a strong absorption peak at λ = 300.5nm (4.12eV) which is blue shifted compared to bulk ZnO absorption (λ = 376nm; 3.3 eV) and is attributed to the confinement effects[14]. For sample ZnO 2 absorption peak is observed at λ~ 380nm which is close to intrinsic bandgap of ZnO.

The optical band gap E_g is determined from the Tauc model[15]:

$$\alpha h\upsilon = A(h\upsilon - Eg)^n$$

Where A is a constant, hυ is photon the energy, α is the optical absorption coefficient, Eg is the optical band gap energy and n is aparameter associated with the type of electronic transitions. ZnO has a direct band gap for which $n = \frac{1}{2}$. Fig.4 shows Tauc plot for samples ZnO 1 and ZnO 2. Optical band gap energy is obtained from the intercept of $(\alpha h\upsilon)^2$ vs $h\upsilon$[16].Table.3 shows optical band gap energy for ZnO 1 and ZnO 2 .
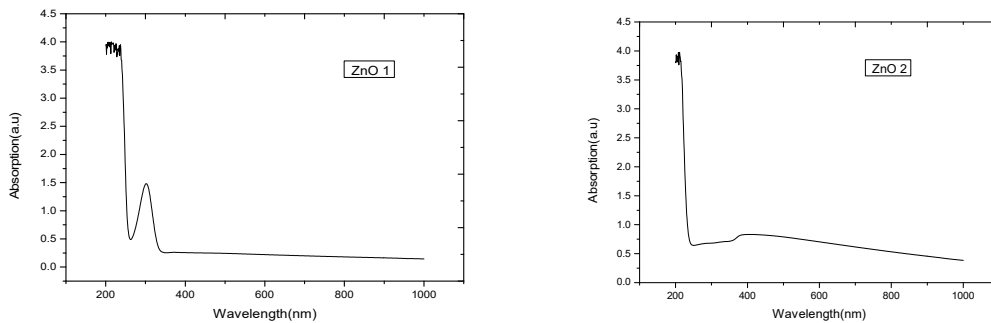

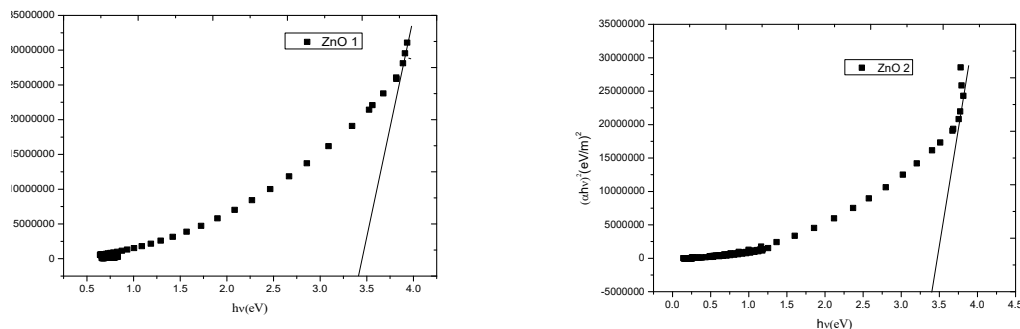
Fig.3. UV absorption spectra of ZnO 1 and ZnO 2

Fig.4. Tauc plot 0f samples ZnO 1 and ZnO 2

Table. 3. Optical band gap energy of ZnO 1 and ZnO 2.

Sample	Optical band gap energy
ZnO 1	3.40
ZnO 2	3.39

Optical band gap energy is size dependent. With the increase in optical band gap energy there is decrease in size of the semiconductor[17]

6.   Photoluminescence (PL) study:

Photoluminescence originates from the recombination of the surface states[18].Generally PL spectrum exhibits two emissions. A near –band-edge UV emission and a broad defect related visible emission.Fig.5 shows PL spectra of samples ZnO 1 and ZnO 2. In the PL spectrum of ZnO 1 a strong emission peak is observed at 409 nm (~3.03eV) which can be attributed to near-band-edge emission. And in the PL spectrum of ZnO 2 near- band-edge emission peak is observed at 383.5nm (3.23eV).Other defect related emissions are also observed in both of the spectra.
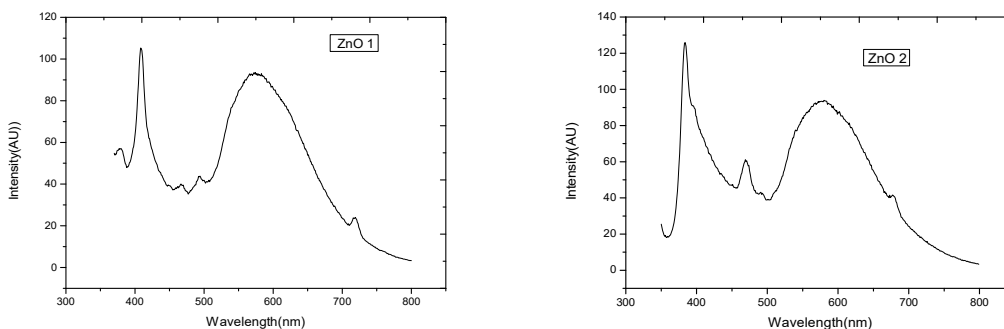

Fig.5. PL spectra of ZnO 1 and ZnO 2

7.   Surface morphology study:

Fig. 6 shows the SEM imags of ZnO 1 and ZnO 2 samples. Shape of the ZnO 1 sample is found to be nearly spherical and that of ZnO 2 sample is cylindrical.Surfaces of the samples are found to be smooth and uniform.
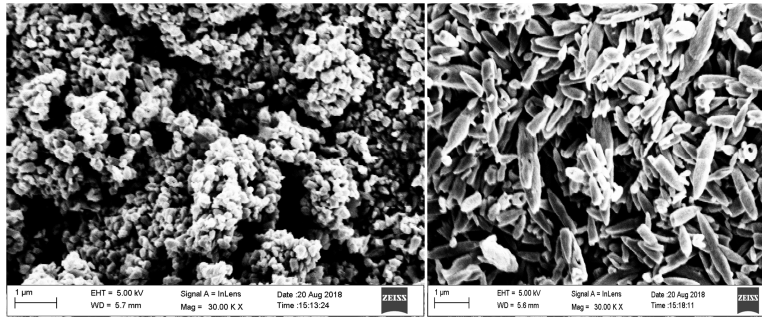
Fig.6. SEM imags of ZnO 1 and ZnO 2

8. Conclusion:

ZnO nanoparticles have been synthesized successfully by Chemical Bath Deposition method. Two samples are synthesized using two different precursors. Size of the nanoparticles is calculated using Scherrer's formula and from the W-H plot. Microstrain associated with the nanoparticles is also calculated by W-H plot. Optical band gap energy is calculated from Tauc plot. PL spectra showed one near-band-edge emission peak and another broad defect related visible emission peak. SEM image showed the surface morphology of the samples. Shape of ZnO 1 sample is found to be nearly spherical and that of ZnO 2 was found to be cylindrical.

Acknowledgement

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