STUDY OF STRUCTURAL AND OPTICAL PROPERTIES OF ZnS NANO PARTICLES SYNTHESIZED BY CBD METHOD

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Abstract: In this work we report the growth of ZnS nanoparticls embeded in polyvinyl alcohol (PVA) matrix. The nanoparticles have been synthesized by chemical bath deposition method at different P^H . The prepared nanoparticles have been characterized by X-ray diffraction(XRD),UV-Vis absorption, SEM and photoluminescence (PL) techniques. X-ray diffraction patterns indicate the formation of cubic phase of ZnS nanocrystals at all P^H.UV-vis results showed a blue shift.

Keywords: ZnS nanoparticle, XRD, Optical band gap, Thin film.

I. Introduction:

Nanostructured semiconductors have been extensively studied for their unique characteristics that can not be obtained from conventional macroscopic materials.ZnS is an important II-IV semiconductor having a wide direct band gap of 3.65 eV in the bulk.Among all semiconductor ,zinc sulphide (ZnS) is an interesting material with many applications in various fields such as optoelectronics, photocatalysis , solar energy conversion, projection television, fluorescence microscopy etc[1] . ZnS nanostructure in the form of thin film, powder and colloid prepared using various methods such as evaporation [2], sputtering[3], wet chemical[4,5], sol-ge[l6,7], spray pyrolysis[8] were investigated in detail.Shayestch et al[9] have reported the effect of P^H on structural and optical properties of ZnS nanoparticles embedded in PVA matrix. Ben Nasr et al[10] have studied the effect of P^H on the properties of ZnS thin films.Borah et al[11] have reported the structural and optical properties of ZnS nanoparticlesembedded in polymeric matrix. Many researchers studied ZnS nanoparticles for their unique characteristics which is not possible to obtain from conventional macroscopic structures.

II. Experimental:

ZnS nanoparticles were synthesized using Polyvinyl alcohol (PVA) as a matrix by Chemical Bath Deposition method. PVA being good solute to multiple phase system and it provides uniform gaps that are very close to each other and distributes in the form of array. 2 wt% solution of PVA ,0.1M zinc acetate prepared by dissolving $(CH_3COO)_2Zn2H_2O$ in distilled water was added and stirring at 60ºC for 3h using magnetic stirrer . The sample under preparation at different P^H was kept for 12 hours for complete dissolution to get a transparent solution. To this solution 0.1M Na_2SxH_2O was added and stirred at room temperature. Finally the whole solution appears completely milky. The size of the particle is controlled by changing pH value of the whole solution. Similar procedure were used to prepare ZnS nano particles in powder form. To achieve powder form the precipitates were washed several times with distilled water to remove the impurities. After washing precipitates were dried at room temperature and grinded to obtain fine structure.

III. Characterization :

Powder X-ray diffraction (XRD) pattern of prepared ZnO nanoparticle is recorded by a Philips X-ray Diffractrometer (X'Pert Pro) with Cu $K_{\alpha 1}$ radiation (λ=1.5406 Å). Before data collection the diffractometer is calibrated with a standard silicon sample. The instrumental broadening is corrected by Warren rule[12] .
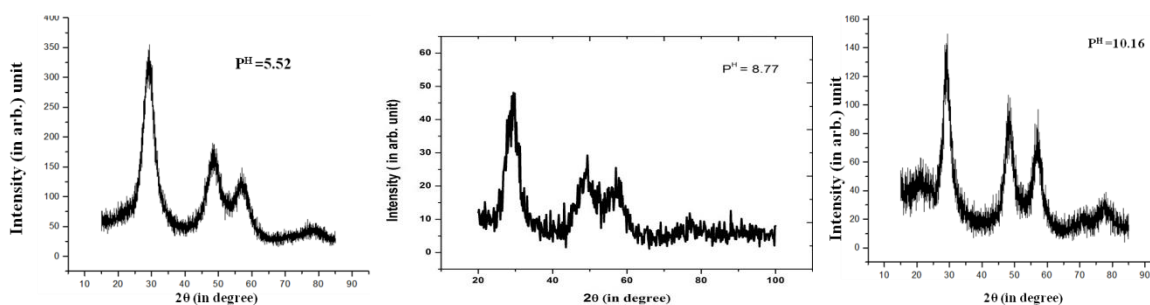

Fig.1. X-ray diffraction (XRD) patterns of the prepared ZnS nanoparticles (powder) at different P^H

The XRD spectrum of ZnS1,ZnS2 and ZnS3 apparently exhibit weak and broad peaks, suggesting small crystallite sizes of cubic phase (JCPDS card, No. 5-0566). Again it is seen that when pH decreases peaks are more broadened and shifted to higher diffraction angle with decreasing crystal size. The grain sizes of the nanocrystallites (diameter D) prepared at three different P^H was determined from the full width at half maximum (β) of the (111),(200) and(311) peaks by using the Scherrer formula [13]

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

Where λ is the wavelength of radiation used, θ is the Bragg angle and K=0.9 for spherical shape. It is seen that as the value of p^H is increased the particle size is also increased (Table 1).

Table 1 :Particle size calculated from Scherrer formula

pH	Particle size(nm)
5.52	4.45
8.77	17.13
10.16	26.91

One of the important luminescence material is ZnS. In the visible spectral region it is transparent and its exciton binding energy is 40 eV. In Fig. 2 photoluminescence emission spectra of samples at different p^H are shown. A strong peak around 290 nm is observed for all nanoparticles prepared at three different p^H. The sample with p^H 5.52 yield maximum PL intensity. The band gap energy is calculated from the PL peak which equal to about 4.27 ev.
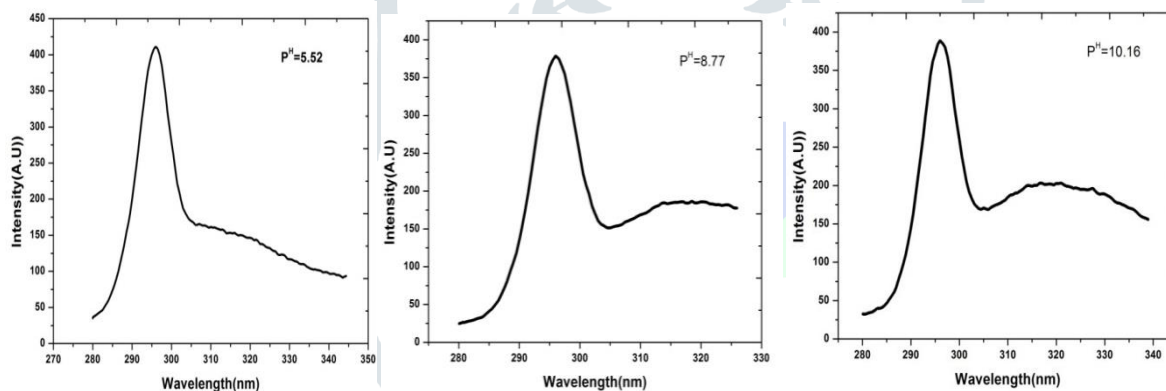

Fig.2. Room temperature PL emission spectra of ZnS nanoparticles at different P^H

Fig. 3. Shows UV-vis absorbance spectra as a function of wavelength at different p^H. It is evident from the Figures that absorption edge is shifted to lower wavelength i.e. absorption spectra show a blue shift from the bulk absorption.

The optical band gap of the prepared ZnS nanoparticles are determined from the Tauc plot of $(\alpha h\nu)^2$ versus $(h\nu)$ (Fig. 4.) which is around 5.78 ev. The band gap of ZnS nanopaticles is higher than the band gap of bulk ZnS.
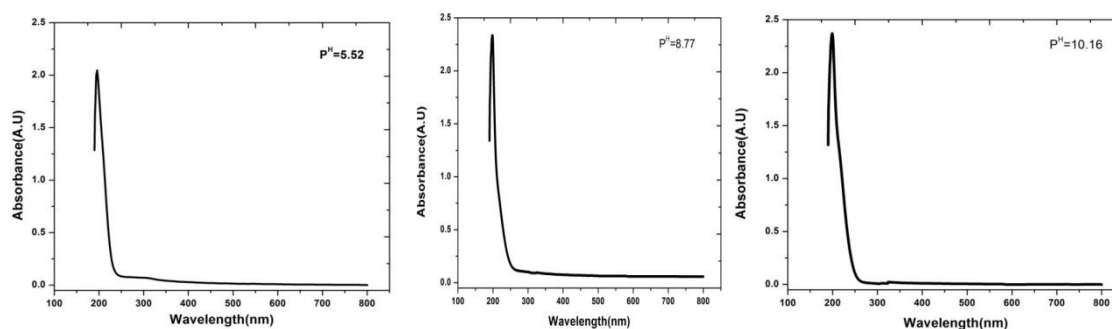

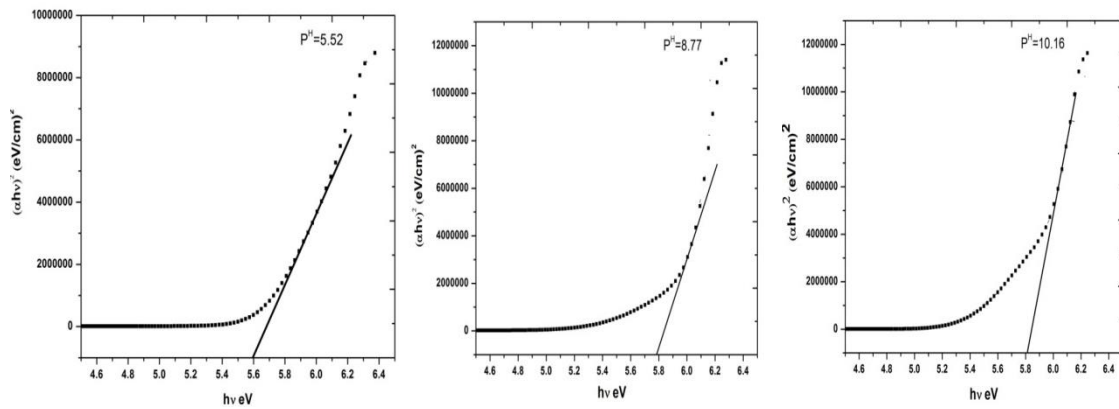Fig. 3. UV-Vis absorbance as a function of wavelength for ZnS samples with different P^H

Fig. 4. Plot for determination of direct band gap of ZnS nanoparticle at different P^H
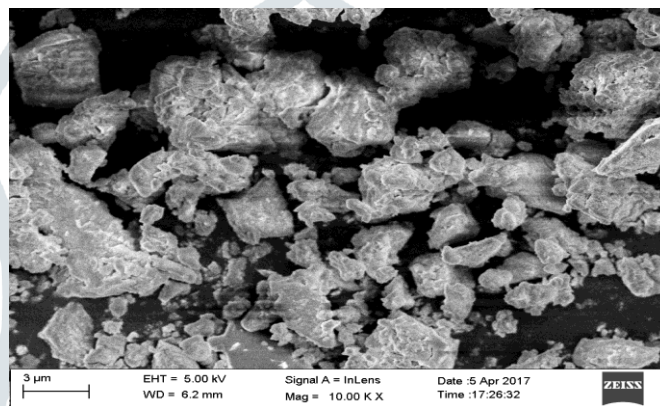

Fig. 5. SEM image of ZnS nanoparticle

Surface structure and morphology of prepared ZnS nanoparticles were studied by SEM. The SEM photograph of the ZnS sample with p^H= 5.52 (fig.5) shows the formation of uniform sample.

IV. Conclusion:

ZnS nanoparticles have been synthesized successfully by Chemical Bath Deposition method. The size of the nanoparticles was controlled by changing the p^H and as expected the particle sizes are increased with the increase in p^H value. From the XRD results it was confirmed that all prepared ZnS nanoparticles show cubic phase in all p^H range. From the PL spectra it was found that intensity of PL emission is dependent on p^H of precursors. The band gap of the nanoparticles are dependent of the various defects associated with the nano structures. The effect of defects are not considered on the calculation of the band gaps by Tauc plot. So, there is a slight variation in the band gap enegry of the nano particles measured by PL and UV-vis absorption method. UV-vis absorption results show a blue shift.

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