

# Structural and optical studies of confined ZnS nanoparticles synthesized by chemical precipitation method

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**Abstract:** ZnS nanoparticles were synthesized by chemical precipitation method at room temperature. From X-ray diffraction (XRD) pattern, the crystallite size evaluated to be 2 nm to 4 nm. Scanning electron microscopy (SEM) showed agglomerated grains with random shape. EDAX spectra indicated the presence of Zn and S elements in the samples. High Resolution Transmission Electron Microscopy (HRTEM) images revealed the nanocrystalline nature of the sample with distinct grain boundaries having average particle size of 3nm. The band gap energies were estimated by diffused reflectance spectra (DRS) of the ZnS samples were found to be higher than the band gap of the bulk ZnS. Photoluminescence spectra (PL) is observed to be broad and an emission occurred at a lower energy value than that corresponding to the excitonic emission band due to quantum confinement

**Keywords:** Nanoparticles, exciton, Bohr radius, Confinement

## 1. Introduction

Controlled physical and optical properties can be obtained from quantum sized semiconducting particles. Conversion from bulk to nanoparticles revealed high quantum perfunctory properties and improved surface atoms which increases the chemical procedure of a material. Zinc sulphide (ZnS) is an important II-VI semiconductor good optically eminence material with wide directband gap,  $E_g=3.68\text{eV}$  (336nm) and is a broadly used semiconductor [1]. ZnS nanoparticles exhibit wider energy gap, high thermal stability, surface effect, quantum confinement effect etc Due to its peculiar properties of optical, luminescence and photochemistry, ZnS NP have versatile potential applications in ultraviolet light-emitting diodes[2], solar cells, field emitters, injection lasers, infrared windows[3], photocatalysts, flat-panel displays, thin film electroluminescent devices[4]. It is a potentially important material to be used as a window layer in solar cells [5]. Several techniques have been used to produce ZnS nanoparticles such as screen printing, electro deposition, molecular beam epitaxy (MBE) and physical vapour deposition. Above mentioned synthesis methods require highly advanced instruments and cost. Considering all these aspects in view, we have carried out a systematic process of synthesizing ZnS nanoparticles showing strong confinement by a simple and cost-effective chemical process at room temperature [6].

## 2. Experimental details

ZnS powder samples were prepared by chemical route of precipitation method. 1% Wt of Sodium sulfide ( $\text{Na}_2\text{S}$ ) (sigma Aldrich India) and Zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (sigma Aldrich India) were separately dissolved in de-ionized water and stirred. Initially the aqueous solution of 1% Wt of Sodium sulfide added drop wise with the aqueous solution of Zinc nitrate 0.1mole concentration and same amount of sodium sulfide added to 0.3mole and 0.5mole concentration of Zinc nitrate at room temperature, maintained at constant stirring speed by using magnetic stirrer. The formation of the white precipitate indicates the presence of ZnS particles. The resultant solutions were well dissolved by using magnetic stirrer for 5h at room temperature. The co-precipitated solutions were centrifuged at 5000 rpm for 30 min to separate undesired agglomerates and washed with de-ionized water and ethanol. Finally, the samples were dried for one hour at  $150^\circ\text{C}$  to eliminate residual gas, water impurities and to obtain fine powder of ZnS particles. All the reactions of the synthesis were carried out at room temperature and under ambient condition using de-ionized water as a solvent for its inherent advantages of being simple and eco-friendly.

## 3. Characterizations

X-ray diffraction carried out using PAN analytical X-ray diffractometer and surface morphology of the samples analysed by using Scanning electron microscope (JEOL JSMS 800-V). High resolution transmission electron microscope (HRTEM) images of the ZnS recorded with help of Philips TECNAI F20 microscope. Elemental composition of the samples found by using of energy dispersive analysis of X-rays (JEOL Model JED -2300). Optical reflectance spectra of the ZnS sample were measured using a HITACHI-U 3210 UV-VIS spectrometer. The functional groups present were identified from Fourier transform-infrared (FTIR) spectroscopy using a Thermo Nicolet Avatar 370 with a spectral range of  $4000\text{--}500\text{cm}^{-1}$  and resolution of  $4\text{ cm}^{-1}$ . From photoluminescence studies (PL) synthesis conditions, shape, size and energetic position of the surface states analyzed by spectrofluorometer (JOBIN YVON FLUROLOG-3-11)

## 4. Results and discussion

### 4.1. X-ray diffraction (XRD)

X-ray diffraction technique is used to find out the crystallite size and structure of ZnS nanoparticles. The XRD spectrum of ZnS nanoparticles prepared at three different concentrations (0.1m, 0.3m & 0.5m) the results are shown in Figure 1, where three broad peaks observed in the XRD patterns at around 28.66°, 47.99° and 56.66° for 0.1mole, 28.60°, 47.90° and 56.35° for 0.3mole and 28.30°, 47.60° and 56.05° for 0.5mole concentration respectively. In the spectrum, most of the peaks can be indexed to those of the ZnS zinc blende structure (cubic lattice). The three main peaks corresponding to the planes (111), (220) and (311) indicated cubic phase[7]. This is in agreement with the standard JCPDS data [05-0566]. It can be observed that these peaks are broad compared to the bulk ZnS confirmed the nano crystalline nature of the samples and implying that the sizes of ZnS nanoparticles were very small. The increment in diffracted angle indicates particle size contraction may be due to confinement, higher surface to volume ratio[7] From X-ray diffraction pattern, mean particle size has been calculated by using Scherrer formula[8]

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where  $\theta$  is the Bragg angle and  $\lambda$  is the X-ray wavelength. Here  $K=0.9$  for spherical shape (evidence from HRTEM). For calculation  $\beta$  is observed by zooming the peak position using origin graphic software. The calculated size is found to be 2. nm for 0.1mole concentration, 3.50 nm ( $\pm 0.1$  nm) for 0.3mole concentration, 4.00 nm for 0.5mole concentration respectively.

### 4.2. Scanning electron microscopy (SEM)

Scanning electron microscope is a convenient characterization to study the microstructure of the sample. The SEM micrographs of 0.1mole, 0.3mole, 0.5mole ZnS NPs are recorded very different morphologies (Fig. 2). The samples showed agglomerated grains with random shape and the distributions of grains are of irregular shape through all the regions. The size of the grain increased due to the agglomeration of the grains with increasing mole concentration.

### 4.3. Energy dispersive X-ray spectroscopy (EDX)

The system works as an-integrated feature of a SEM and it is used for the elemental identification of the samples. The EDAX spectra indicate the presence of Zn and S elements in the samples (Fig. 3). From the EDAX spectra, it is seen that the intensities of Zn and S peaks are affected by low mole concentration.[9]

### 4.4. High resolution transmission electron microscopy (HRTEM)

The morphology and the size distribution of the synthesized ZnS NPs were characterized using the HRTEM. The HRTEM images of ZnS NPs prepared at 0.1 mole (Fig.4), 0.3 mole (Fig.5) and 0.5 mole (Fig. 6) samples depict that the particles are mono disperse, less spherical in shape and dense with the tendency of agglomeration[10]. It also indicates the nanocrystalline nature of the sample with distinct grain boundaries having average crystallite size of 3nm. The NPs have also seen with clear lattice fringes showing the well crystallized nature. The three rings seen in the selected area electron diffraction can be indexed to (111), (220), and (311) lattice planes of cubic ZnS[11]. The selected area electron diffraction (SAED) corresponding to the intense peaks observed in the XRD spectrum. The size is also nearly consistent with the size obtained from XRD observations (Table 1).

### 4.5 Fourier transform-infrared (FTIR) spectroscopy

The FTIR spectra of synthesized ZnS nanoparticles has been compared with reported values of different stretching and bending modes in standard references[12]. The results are shown in Figure 7, the measurement of the spectrum of powdered sample yields the bands, which are in good agreement with the reported values. The changes in the observed values are due to the formation of nano phase. The broad spectrum observed around 3468-3509 $\text{cm}^{-1}$  corresponds to valence vibrations of the occluded water and the spectrum observed around 1112-1375 $\text{cm}^{-1}$  are due to the oxygen stretching and bending frequency. The additional weak bands and shoulders at 1613, 1615 and 1617 $\text{cm}^{-1}$  may be due to the micro structural formation of the sample. 1102 and 1100 $\text{cm}^{-1}$  band modes indicated the presence of resonance interaction between vibrational modes of sulphide ions in the crystal. The peak at 616  $\text{cm}^{-1}$  is due symmetric bending and assigned to the ZnS band (i.e., corresponding to sulphides). These peaks (near 600  $\text{cm}^{-1}$ ) are attributed to the formation of ZnS NPs.

### 4.6. Diffused reflectance spectra (DRS)

The optical properties of the as-synthesized ZnS nanoparticles were determined by UV-Vis spectroscopy measurements (Fig. 8). The diffused reflectance spectrum of ZnS nanoparticles of 0.1 mole concentration sample exhibits a reflectance at around 316.25nm with a band gap of 3.92eV, 0.3 mole concentration samples shows an reflectance at around 324.74nm with the band gap of 3.81eV and 0.5 mole concentration sample shows an reflectance at around 332.38nm with the band gap of 3.73eV. The peak has been blue shifted in comparison with the bulk ZnS value of 3.6eV (339 nm) and this is achieved due to increase band-gap energy (quantum confinement effect) of the ZnS nanoparticles [13] implying that the sizes of the ZnS nanoparticles are smaller than Bohr radius of the exciton in bulk ZnS[14]

### 4.7. Photoluminescence spectra

In the present investigation, the photoluminescence spectra of ZnS were recorded at room temperature. Photoluminescence spectra are observed to be broad and an emission occurred at a lower energy value than that corresponding to the excitonic emission band.

This could be ascribed to the recombination of the charge carriers trapped in the surface states [15]. The photoluminescence emission spectra of ZnS is found to exhibit an emission peak centered at different ranges of wavelength for three different concentration. (Fig.9). The emission band of 0.1 mole concentration present at 340 nm is originated at deep level related to native defects of ZnS.

## 5. Conclusion

Nanoparticles of ZnS have been successfully synthesized by a simple precipitation reaction. The FTIR peak at  $616\text{ cm}^{-1}$  indicates symmetric bending of ZnS band and formations of nano phase of sample. XRD and SEAD patterns confirmed the nanocrystalline in cubic structure. HRTEM images of the samples revealed the formation of ZnS quantum dots with size within the range of 2-4 nm. Optical studies indicate an increase in band gap energy with decrease of particle size which supports the formation of ZnS nanoparticles. The ZnS nanoparticles have strong quantum confinement effect as the optical band gap increases significantly from 3.73 eV to 3.92 eV compared to bulk value of 3.68 eV. The photoluminescent spectra of ZnS nanoparticles showed of the emission peak at 340nm. This may be due to the quantum confinement effect of the nanoparticles. small particle size, narrow size distribution and surface defects. Due to small particles size increased band gap energy of synthesized ZnS nanoparticles. Hence we suggested that these samples will be used as a window layer in solar cells.

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**TABLE. 1: Variation of NPs size with energy band gap of ZnS**

Mole concentration of the ZnS	NPs Size from XRD (nm)	NPs Size from HRTEM (nm)	Band gap energy (eV)
0.1 mole	2.20	2.90	3.92
0.3 mole	3.50	3.78	3.81
0.5 mole	4.00	4.20	3.72

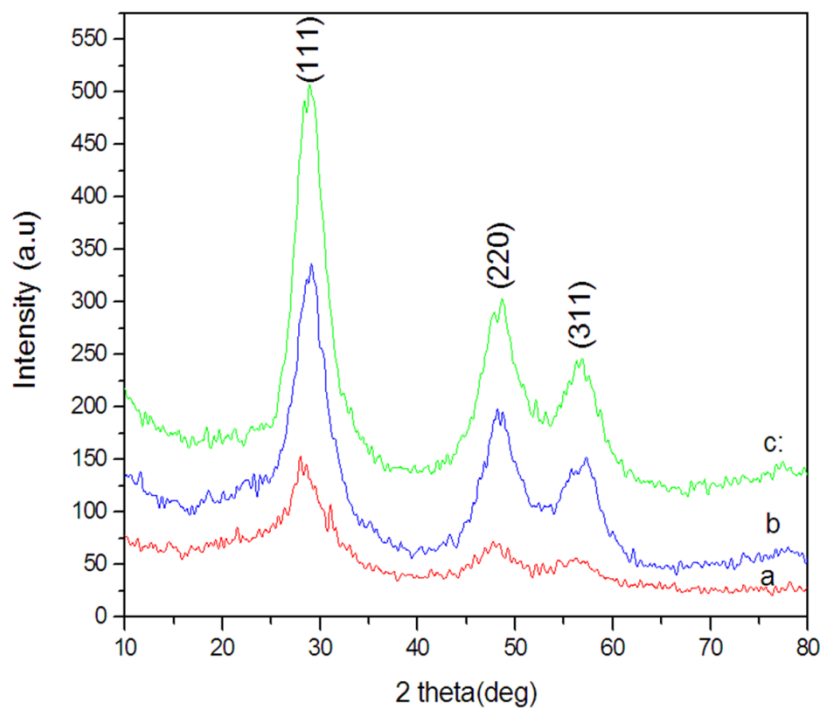
**FIGURE LEGEND**

Fig. 1: X-ray diffraction pattern of ZnS NPs of (a) 0.1 mole (b) 0.3 mole and (c) 0.5 mole Concentration

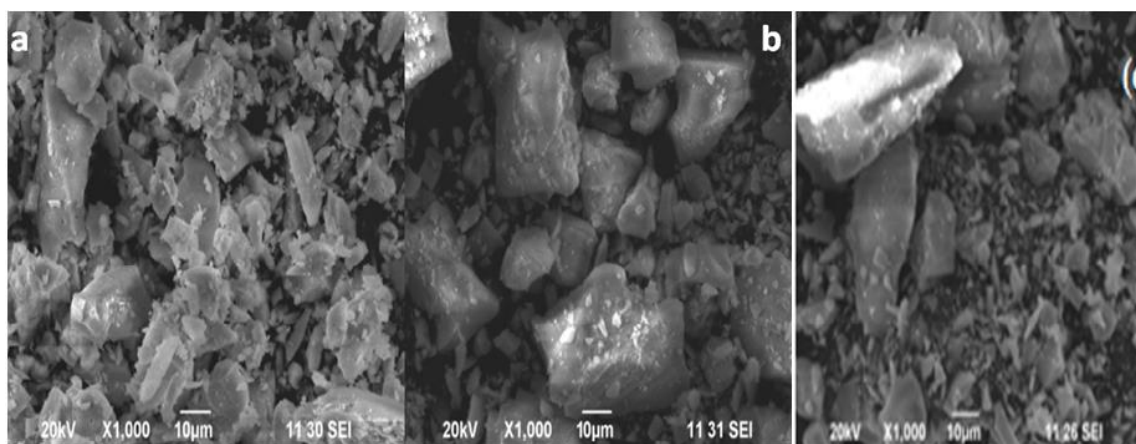


Fig. 2: SEM micrographs of ZnS NPs of (a) 0.1mole, 0.3mole and (b) 0.5 mole concentration

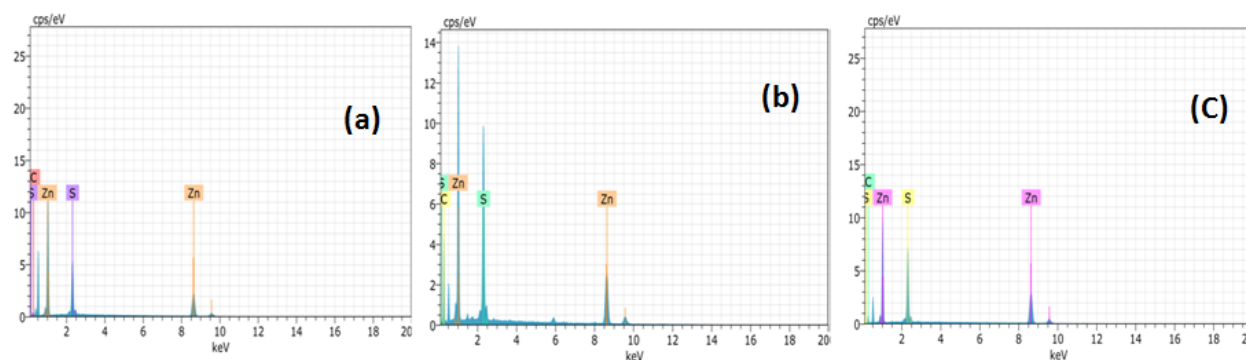


Fig. 3: EDAX spectra of ZnS NPs of (a) 0.1mole and (b) 0.5 mole

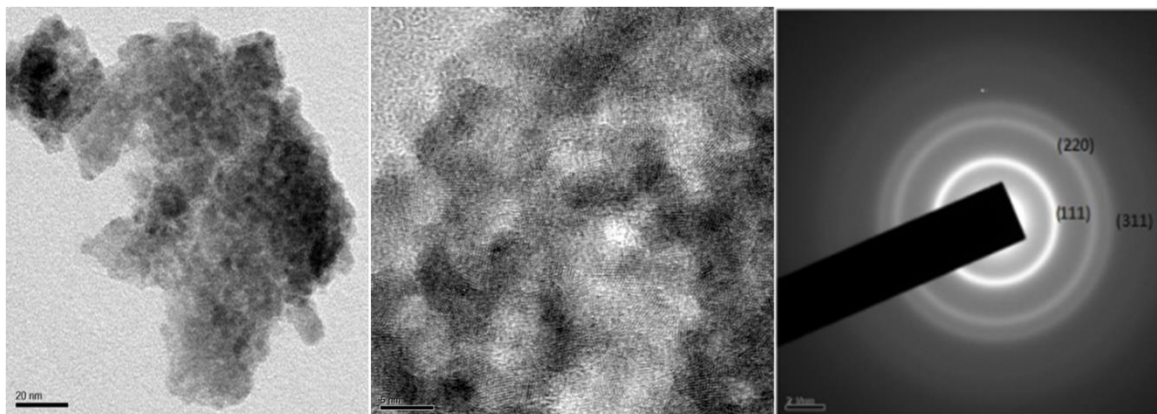


Fig. 4: HRTEM image &SEAD pattern of ZnS NPss of 0.1 mole concentration

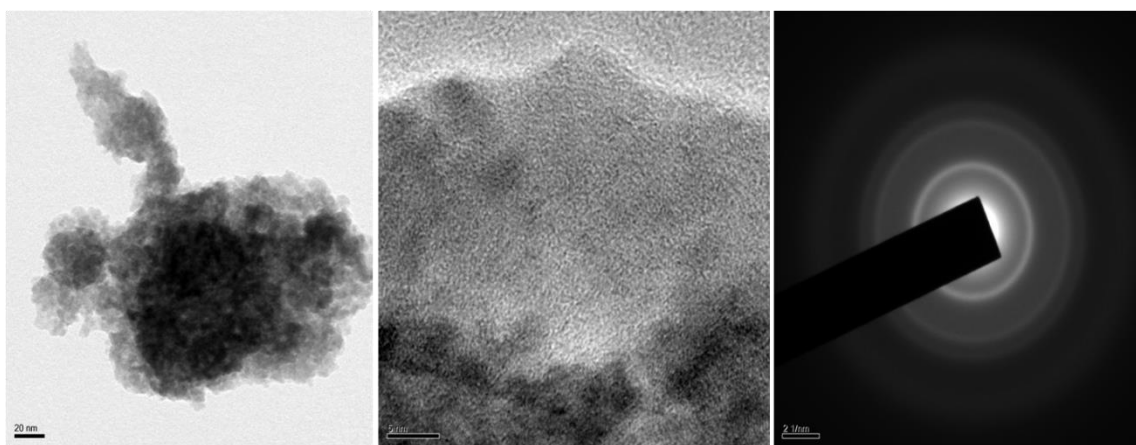


Fig. 5: HRTEM image &SEAD pattern of ZnS NPs of 0.3 mole concentration

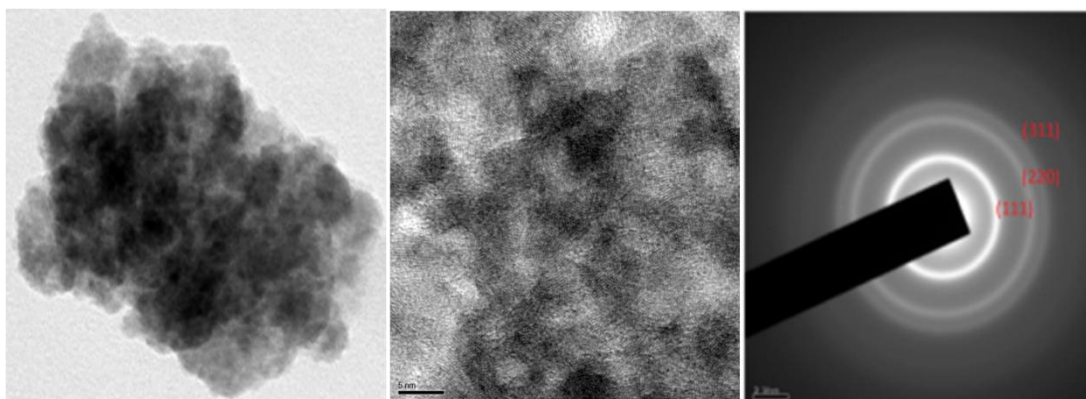


Fig. 6: HRTEM image &SEAD pattern of ZnS NPs of 0.5 mole concentration

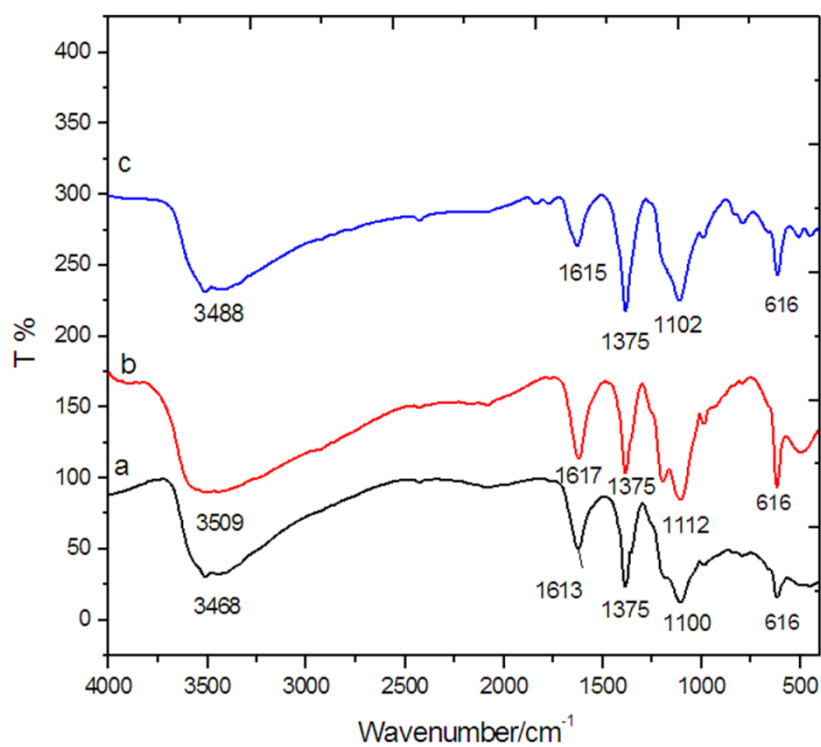


Fig. 7: FT-IR spectra of ZnS NPs of (a) 0.1 mole (b) 0.3 mole and (c) 0.5 mole concentration

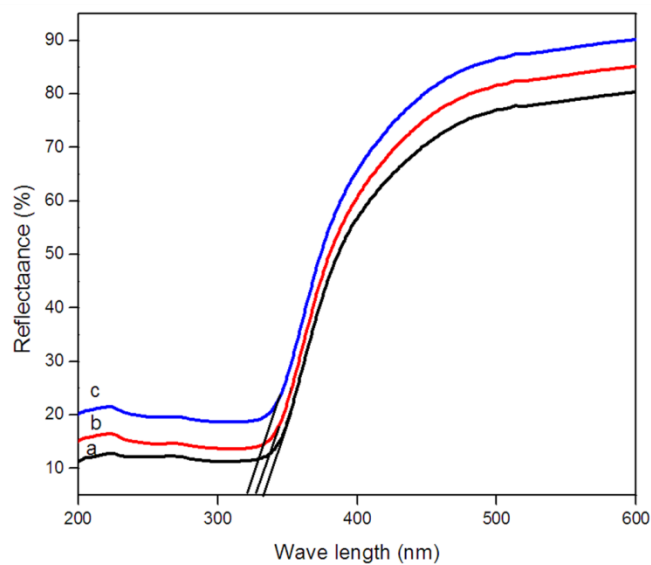


Fig. 8: Diffused reflectance spectra and band gap determination of ZnS NPs of (a) 0.5 mole (b) 0.3 mole and (c) 0.1 mole concentration

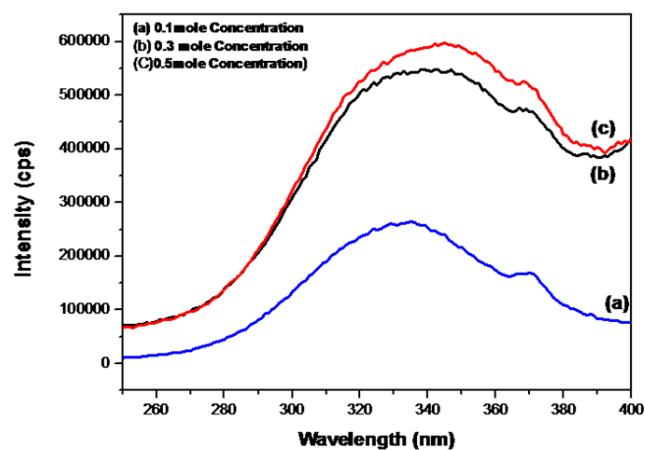


Fig.9: PL spectra and band gap determination of ZnS NPs of (a) 0.5 mole (b) 0.3 mole and(c) 0.1 moleconcentration