Original Research Article

Composition dependent structural and optical properties of nanocrystallites $Zn_xCd_{1-x}S$

ABSTRACT

In this work a novel chemical reduction method at room temperature is described to synthesize nanocrystalline ZnS, CdS, $Zn_xCd_{1-x}S$. The method is cheap and cost effective. The grown nanoparticles are characterized by XRD, TEM, EDX, UV-VIS absorption and PL study. CdS formation is supported by the systematic splitting of x-ray diffraction peak at lower angle and the peaks are identified. ZnS peaks are also identified comparing with ICDD data. EDX analysis shows two other phases **$Zn_{0.8}Cd_{0.2}S$, $Zn_{0.5}Cd_{0.5}S$** The particle sizes are in the range 4-8 nm. The band gap changes with change of composition. Also at each composition the band gap is greater compared to bulk band gap. This indicates quantum confinement takes place. The band gap energy of nanoparticles can be tuned to a lower energy by increasing the Cd content, indicating the formation of the alloyed nanoparticles. . PL peak shifts towards higher wavelength as Cd content increases. The peak corresponds to transition associated with surface state.

Keywords: ***$Zn_xCd_{1-x}S$, nanoparticles, structural properties, Optical properties, Photoluminescence***

1. INTRODUCTION

The synthesis and characterization of semiconductor nanoparticles have attracted much interest because of their novel properties as a consequence of the large number of surface atoms and the three-dimensional confinement of the electrons [1-7]. Altering the size of the particles alters the degree of the confinement of the electrons and affects the electronic structure of the solid, especially the band gap edges.

Among a variety of semiconductor materials, the binary metal chalcogenides of group II-VI have been extensively studied [1-16]. For example, nanocrystalline thin films of ZnS and CdS are attractive materials in photoconducting cells and optoelectronic devices such as solar cells and photodetectors [17-19].

Alloying of semiconductors is one of the simplest techniques used for tailoring the energy band gap, lattice parameter, electronic and optical properties [20] generally in alloys; the lattice parameter varies linearly with composition and follows the Vegard's law.

Among the different ternary II-VI semi-conductors, ZnxCd1-xS has been widely used as a wide band gap material in heterojunction solar cells [21–23], photoconductive devices [24], high-density optical recording and for blue or even ultraviolet laser diodes [25-29].

In this paper, we report a novel chemical reduction route to synthesize ZnS, CdS and $Zn_xCd_{1-x}S$ nanocrystals at room temperature

2. EXPERIMENTAL SECTION

Typically, an appropriate amount of sulfur powder was added to a flask containing 50 mL of tetrahydrofuran (THF). After being stirred using magnetic stirrer for 5 min, the mixture becomes a colorless transparent solution. A stoichiometric amount of $ZnCl_2$ was added to the flask and a black suspension formed upon stirring. After the addition of $NaBH_4$, the suspension turned light green. After the mixture was stirred for 3h, a white precipitate formed. Then the precipitate was centrifuged and dried at room temperature.The sample is now ready for characterization. For the preparation of nanocrystalline CdS, the process was the same as above except that anhydrous $CdCl_2$ was used instead of $ZnCl_2$. For the preparation of Zn $_x$ Cd $_{1-x}$ S stoichiometric anhydrous $ZnCl_2$ and $CdCl_2$ powders were used according to the molar ratios in the target compounds Zn $_{0.7}$ Cd $_{0.3}$ S, Zn $_{0.5}$ Cd $_{0.5}$ S. The X-ray powder diffraction (XRD) was obtained using a Rigaku MiniFlex-II X-ray Diffractometer using CuK_α radiation. Transmission electron microscope (TEM) images were obtained using the JEOL JEM-200 TEM operated at 200 kV. UV-VIS absorption spectra were recorded using a Shimadzu Pharmaspec-1700 spectrophotometer with a 1-cm quartz cell at room temperature. Colloid solutions in ethanol were prepared ultrasonically for the UV-VIS and the photoluminescence (PL) measurements. The Photoluminescence of ZnS, CdS and Zn $_x$ Cd $_{1-x}$ S nanoparticles were measured using Perkin Elmer LS 55 Fluorescence Spectrometer.

3. RESULTS AND DISCUSSION

Fig. 1 shows the x-ray diffraction peaks of the as prepared ZnS, CdS and different Zn $_x$ Cd $_{1-x}$ S samples. Samples are taken in the powder form and the measured angle is within 20-60 degree. Results show well defined peaks in each case and the peak positions gradually change with composition of the samples. All XRD patterns show obvious size broadening effect. In case of CdS the half width of the first peak is maximum indicating that particle size is minimum which is also confirmed by TEM pattern. For CdS the XRD pattern can be indexed as a wurtzite phase structure with strongly characteristic (100),(002),(101),(102),(110),(103)and (112) peaks , while for ZnS XRD pattern mainly reflects its zincblende character [(111),(220)and (311) peaks] with some wurtzite character [such as the exixtence of a vague (103)],which indicates either that the ZnS particles have a zincblende structure with some wurtzite stacking faults or that most particles have a zincblende structure with others having a wurtzite structure. As for the $Zn_xCd_{1-x}S$ nanocrystals the diffraction peaks in the XRD patterns gradually shift to larger angels and a phase transition from wurtzite to zincblende occurs with an increase of Zn content. This continuous peak shifting of the nanocrystals also indicates that there is no phase separation or separated nucleation of ZnS or CdS in the $Zn_xCd_{1-x}S$ nanocrystals.

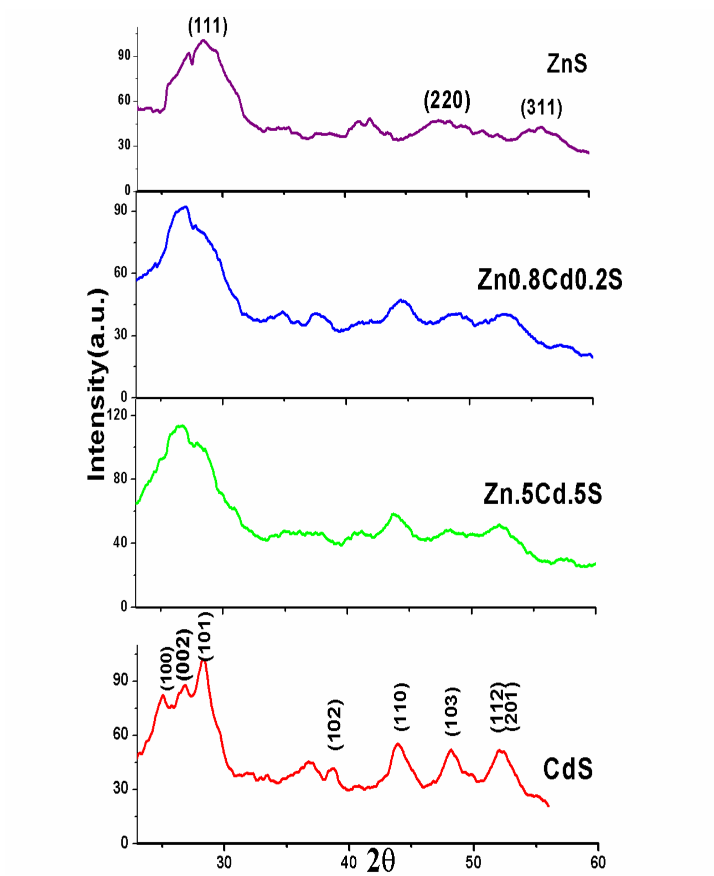
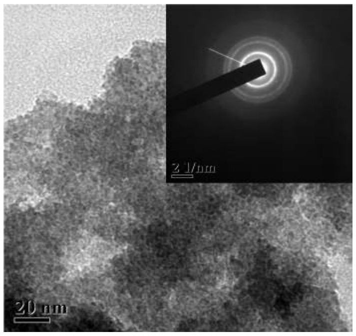


Figure.-1 The XRD pattern of the as prepared samples.



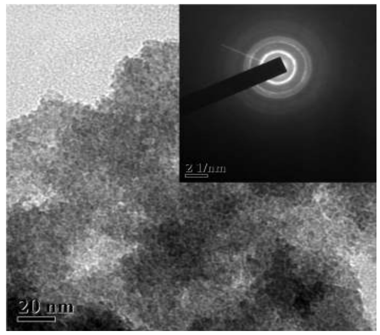
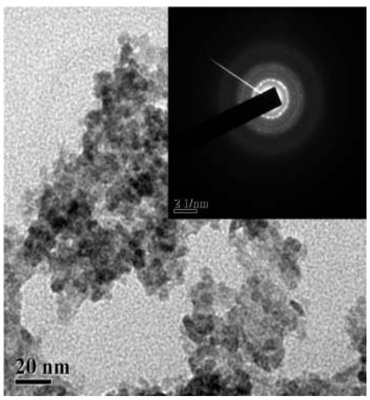


Fig. 2(a) Fig. 2(b)



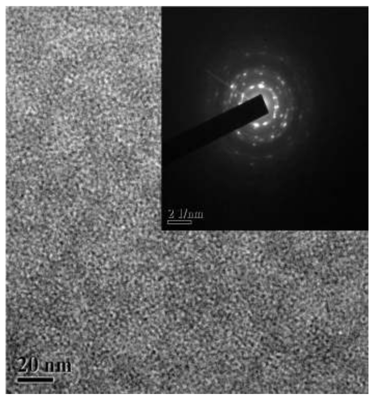


Fig. 2(c) Fig. 2(d)

Figure :-2 The TEM pattern of as synthesized (a) ZnS (b) $Zn_{0.8}Cd_{0.2}S$ (c) $Zn_{0.5}Cd_{0.5}S$ (d) CdS

Samples are well dispersed in ethanol by ultrasonification and it is placed on the carbon coated grid for TEM measurement.Fig.2 (a, b, c, d) shows TEM pattern of the as prepared samples. The particle size is measured in each case from the photograph.

TEM analysis indicates that the particles are in the nano range for different samples. Particle size for ZnS is found to be 4 nm. Particle size gradually increases with increase of Cd content. But in case of CdS particle size is reduced. Also from TED pattern it is observed that in case of CdS diffraction dots predominates ring. Hence CdS nanoparticles show single crystalinity. Other three phases show polycrystalline nature.EDX analysis show the composition of the obtained material. There is difference of the target material and the obtained material for the composition $Zn_{0.8}Cd_{0.2}S$.

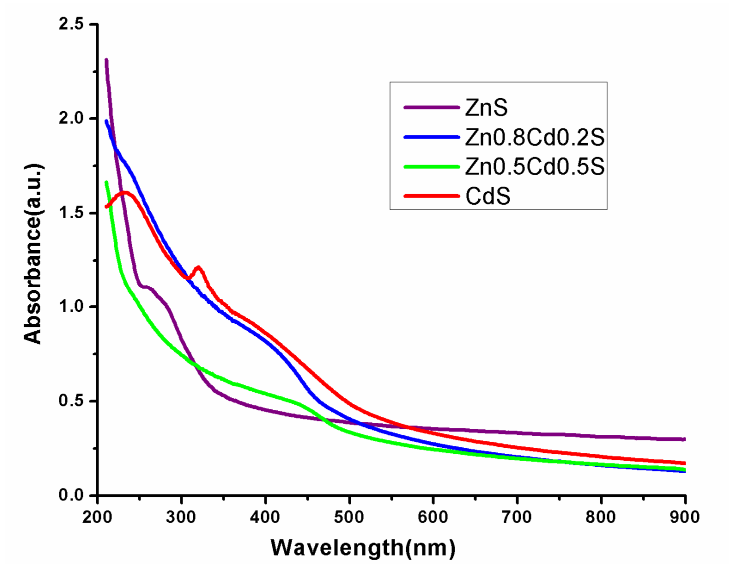


Figure.-3 Optical absorption spectra of different samples.

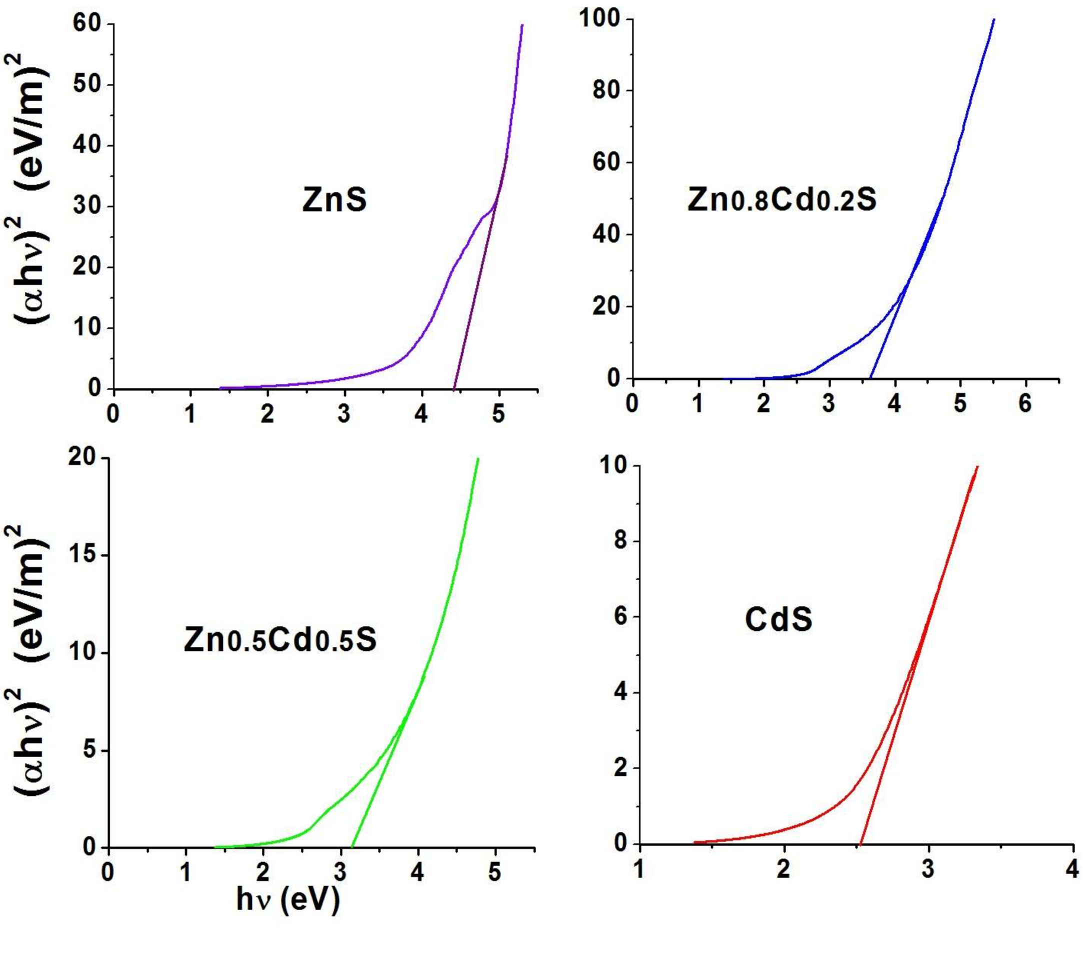


Figure.-4 The band gap determination curve for different samples.

Optical absorption of the dispersed samples are taken using a spectrophotometer and the data is recorded in the range of 200-900 nm.Fig.3 displays the absorption spectra of the different samples. Optical absorption coefficient (α) is calculated at each wave length. The band gaps of the as-prepared nanoparticles are determined from the relation

$$(\alpha h\nu)^2 = C(h\nu - E_g)$$

Where *C* is a constant. E_g is the band gap of the material and α is the absorption coefficient.

Fig. 4 shows the plot of $(\alpha h\nu)^2$ vs. energy ($h\nu$) and it is used to determine band gap in each case.

From the optical absorption study it is found that The band gap of $Zn_xCd_{1-x}S$ are decreases with increase of Cd content and are close to the band gap determined by C.S. Pathak et al[30] and K. Nagamani et al [31].The decrease of band gap is attributed to the increase of particle size as well as the stoichiometric variation of Cd with respect to Zn. But in each sample band gap is found to be greater than the bulk band gap. This clearly indicates quantum confinement takes place in each sample [32].

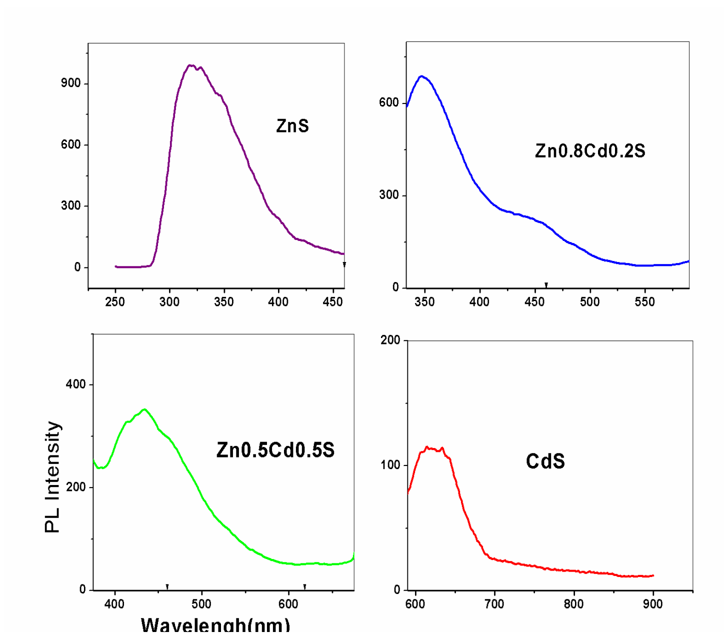


Figure.-5 The photoluminescence spectra of as synthesized samples.

Fig .5 displays the PL spectra of the samples dispersed in ethanol.PL peaks are shifted to higher wavelength as Cd content increases.

Table 1. Summarisatiion Table

Target Material	*Obtained Material*	*PL PEAK(nm)*	*Particle Size(nm)*	*BAND GAP (eV)*
ZnS	**ZnS**	**320**	**4**	**4.46**
$Zn_{0.7}Cd_{0.3}S$	**$Zn_{0.8}Cd_{0.2}S$**	**348**	**5.4**	**3.59**
$Zn_{0.5}Cd_{0.5}S$	**$Zn_{0.5}Cd_{0.5}S$**	**435**	**8.0**	**3.11**
CdS	**CdS**	**621**	**4.5**	**2.54**

4. CONCLUSION

The above results reveal that ZnS, CdS and $Zn_x Cd_{1-x} S$ nanoparticles are successfully obtained at room temperature and the compositions have been controlled. It is observed that by changing the ratio of $ZnCl_2$, $CdCl_2$ in the reactants the two phases $Zn_{0.8} Cd_{0.2} S$ and $Zn_{0.5} Cd_{0.5} S$ are obtained.The control of the composition of $Zn_x Cd_{1-x} S$ nanoparticles may lead to the development of ideal materials for short wavelength diode laser applications.

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