

PACS numbers: 68.37.Hk, 42.70.Qs, 81.07.b, 81.16.Be

SYNTHESIS AND CHARACTERISATION OF $Cd_xZn_{1-x}S$ NANOCOMPOSITES

**M. Ragam¹, K. Prem Ananth¹, P. Parasakthi¹, M. Thiribuvan¹, K. Prema¹,
R. Karuppaian¹, N. Sankar¹, K. Ramachandran²**

¹ Department of Physics,
Yadava College, Govindarajan Campus,
Thiruppalai, Madurai 625 014, India
E-mail: ragamyc1983@yahoo.com

² School of Physics,
Madurai Kamaraj University,
Madurai-21, Tamilnadu, India

Cd_xZn_{1-x}S nanoparticles have been synthesized using hydrothermal method. Structural characterization was done by XRD where the lattice structure gradually changes from hexagonal to cubic with increasing percentage of Zn in Cd_xZn_{1-x}S nanoparticles. Optical spectroscopy provided evidence that the absorption edges of those nanoparticles can be varied from blue to UV. The nanoparticles exhibit emission peaks that shift to shorter wavelength with increasing percentage of Zn in the compounds Cd_xZn_{1-x}S. The control of the composition of Cd_xZn_{1-x}S nanoparticles may lead the development of ideal materials for short wavelength diode laser applications.

Keywords: SEMICONDUCTORS, HYDROTHERMAL SYNTHESIS, OPTICAL PROPERTIES, SCANNING ELECTRON MICROSCOPY, CADMIUM ZINC COMPOSITES.

(Received 04 February 2011, in final form 20 March 2011)

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]. 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, which are tunable with particle size. Among a variety of semiconductor materials, the binary metal chalcogenides of group II-IV have been extensively studied [2]. They have outstanding potential applications, owing to their nonlinear optical and luminescence properties [3], quantum size effect [4], and other important physical and chemical properties [5]. Nanocrystalline CdS and ZnS are attractive materials in photo conducting cells and optoelectronic devices such as solar cells and photodetectors [6]. Also the related ternary compounds $Cd_xZn_{1-x}S$ are promising materials for high density optical recording and for blue or even ultraviolet laser diodes. These applications are based on the quantum well structures of $Cd_xZn_{1-x}S$, which exhibits fundamental absorption edges that can be varied from green to UV [7].

A facile, easy controlled and economical method was described in this article. We used simple inorganic raw materials to synthesize a series of nano-sized $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ samples involved in hydrothermal process. The central objective of the present study is to understand the growth behavior of ZnS-CdS nanoparticles, the optical and structural properties have been studied, and the results indicate that the absorption edges of those nanoparticles can be varied from blue to UV, while the emission peak can be adjusted from 470 to 690 nm which shows it has potential applications as wide band gap window materials.

2. EXPERIMENTAL

2.1 Chemicals

Chemicals were all of analytical reagent grade quality and used without further purification. Deionized and doubly distilled water were used throughout this study.

2.2 Synthesis

In a typical synthesis, 0.003 mol of $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.003 mol of $\text{Zn}(\text{AC})_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 41.67 mL of ethylene glycol to form a clear solution after stirring for 15 min at room temperature. 0.006 mol of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ were added into 20.34 mL of ethylene glycol which was then stirred to form a homogeneous solution. The above solutions were mixed and were then transferred into an autoclave with an inner Teflon lining and maintained at 140 °C for 3 h. The yellow precipitate was harvested by centrifugation and washed several times with deionized water and ethanol to remove possible cations and anions before being dried in oven at 80 °C for 6 h.

2.3 Characterization of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ nanocomposites

Products were characterized by X-ray diffraction (XRD) recorded on a X-ray diffraction (PANalytical X'pert PRO X-Ray Diffractometer) with Cu $k\text{-}\alpha$ ($\lambda = 1.54060 \text{ \AA}$) as the source of incident radiation. UV-Vis spectra were recorded on a Shimadzu UV Spectrophotometer in the spectral range 200 - 900 nm at room temperature. The room temperature PL spectra are recorded using Perkin-Elmer LS-55 fluorescence spectrophotometer. Scanning Electron Microscopy (SEM) picture of these particles were taken using JEOL, JSM-840 microscope

3. RESULTS AND DISCUSSION

3.1 Crystal Structure and Morphology

Fig. 1. shows X-ray diffraction pattern of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ nanoparticles. It is clear that XRD patterns of the nanoparticles exhibits prominent peaks at scattering angles (2θ) of 26.548, 43.37, and 51.91 which could be indexed to scattering from the (002), (110) and (112) planes respectively, of the hexagonal $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ crystal lattice. From the spectra it is clear that at lower Cd/Zn ratios, the crystal structure is similar to that of the cubic ZnS lattice. The (111) reflection is the main reflection observed from the ZnS sample, and this reflection is shifted to lower 2θ angle and the intensity of

the reflection gradually decreases when the Cd concentration in the nanoparticles increases. This phenomenon was also observed by Laukaitis et al.

From the half width of the XRD peaks, the average particle size is tabulated in Table 1. based on Scherrer equation ($D = 0.9\lambda/B \cos\theta$), where D is the crystal diameter, λ is the X-ray wavelength 1.5408 Å and θ is the diffraction angle. But it is known that the accuracy of Scherrer formula for particle size below 5 nm is questionable as instrumental broadening of the diffractometer will mask. And so dislocation density and strain are calculated and tabulated in Table 1. These sizes are taken as only guideline values.

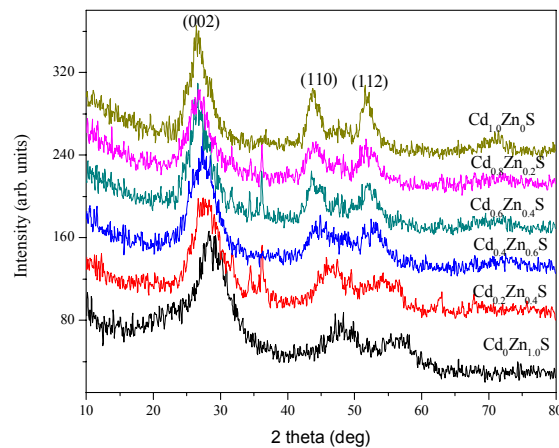


Fig. 1 – XRD spectra for Cd_xZn_{1-x}S ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) nanoparticles

Table 1– Structural parameters of Cd_xZn_{1-x}S nanocomposites

Samples	Particle size (nm)	Dislocation density (lines/m ²)	Strain
Cd ₀ Zn _{1.0} S	2.1	2.14×10^{17}	0.02
Cd _{0.2} Zn _{0.8} S	2.4	1.61×10^{17}	0.017
Cd _{0.4} Zn _{0.6} S	2.2	1.94×10^{17}	0.020
Cd _{0.6} Zn _{0.4} S	2.3	1.79×10^{17}	0.018
Cd _{0.8} Zn _{0.2} S	2.5	1.62×10^{17}	0.073
Cd _{1.0} Zn ₀ S	3.5	7.99×10^{16}	0.012

3.2 SEM Analysis

Fig. 2. shows the SEM images of Cd_xZn_{1-x}S nanocrystals. Well-crystallized particles with estimated particle sizes of 30 - 40 nm were observed. The sample is composed of a large quantity of spherical nanoparticles with uniform size, shape and large specific surface area, it can significantly improve electron transfer rate which contribute to the high photo catalytic activity.

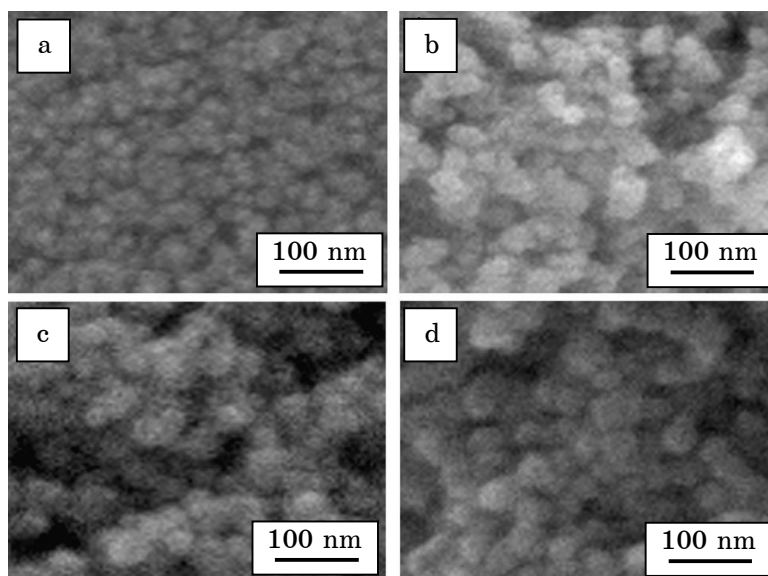


Fig. 2 – SEM image of $Cd_xZn_{1-x}S$ ($x = 0.2, 0.4, 0.6, 0.8$) nanoparticles

3.3 UV-Vis Analysis

The optoelectronics properties were investigated by ultraviolet-visible absorption spectra using the Shimadzu UV Spectrophotometer in the spectral range 200 - 900 nm at room temperature Fig. 3. shows the UV absorption spectra of $Cd_xZn_{1-x}S$ nanoparticles solutions along with those of the pure ZnS nanoparticles and CdS nanoparticles solutions. ZnS nanoparticles have an absorption peak at 302 nm, while CdS shows its absorption shoulder peak at 477 nm, the wavelengths corresponding the bandgaps of 4.11 eV for ZnS and 2.60 eV for CdS respectively. The blue shifts in the absorption edge bands have been interpreted in terms of quantum size effects [8] which are tabulated in table 2.

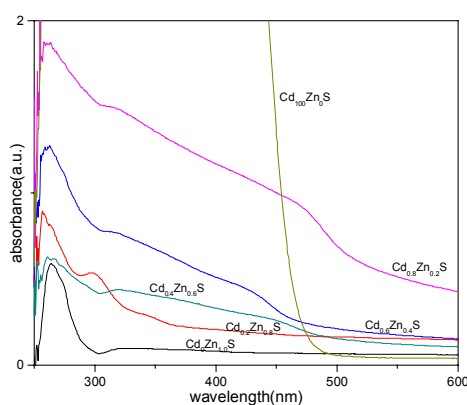


Fig. 3 – UV-Vis spectra of $Cd_xZn_{1-x}S$ ($x = 0.2, 0.4, 0.6, 0.8$) nanoparticles

The absorption spectra of nanoparticles were found to lie between those of pure CdS and ZnS nanoparticles solutions. And the absorption edge bands of nanoparticles systematically redshifted from 302 nm to 450 nm with increasing the content of Cd in $Cd_xZn_{1-x}S$ nanoparticles which indicates the adsorption edges of those nanoparticles can be varied from blue to UV. This is very similar to the result obtained by Shengnan Zu et al. [8].

Table 2 – Optical parameters of $Cd_xZn_{1-x}S$ nanocomposites

Nanoparticles	Absorption edge (nm)	Bandgap (eV)
$Cd_0Zn_{1.0}S$	302	4.11
$Cd_{0.2}Zn_{0.8}S$	324,288	4.07
$Cd_{0.4}Zn_{0.6}S$	492,305	3.29
$Cd_{0.6}Zn_{0.4}S$	471,301	3.37
$Cd_{0.8}Zn_{0.2}S$	499,302	3.30
$Cd_{1.0}Zn_0S$	477	2.60

3.4 PL Analysis

The photoluminescence spectra of the $Cd_xZn_{1-x}S$ nanocrystals in Fig. 4 shows three peaks around 620 nm, 660 nm and 670 nm, lying between those of pure CdS and ZnS nanoparticles. The emission band around 480 nm for ZnS nanoparticles arises from the recombination through surface localized state [9]. For the distinct peak at 620 nm shows the electron hole recombination after relaxation, while emission around 660 nm is due to the trap state emission [10].

An interesting feature in these spectra is that once the composite nanoparticles form, the band edge emission of CdS nanoparticles will disappear. Therefore, the PL bands of $Cd_xZn_{1-x}S$ nanoparticles as in Fig. 4. are caused by trap state emission [10]. In our system, PL band position is red shifted as the Cd content increases, which is consistent with the results of UV absorption, confirming the formation of nanoparticles. And the position of emission peaks can be adjusted from 460 to 670 nm when increasing the Cd content in the $Cd_xZn_{1-x}S$ nanoparticles.

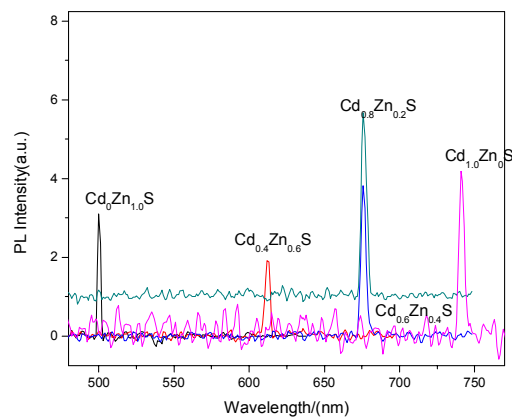


Fig. 4 – PL spectra of $Cd_xZn_{1-x}S$ ($x = 0.2, 0.4, 0.6, 0.8$) nanoparticles

4. CONCLUSION

In conclusion, we have developed a novel and simple method by hydrothermal process to produce nano sized $\text{Cd}_x\text{Zn}_{1-x}\text{S}$. The obtained nanocrystals present homogenous alloyed structure and uniform spheres. Lattice structure of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ changes from cubic to hexagonal as x goes from 0 to 1. The optical properties of nano $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ can be modulated by tuning their compositions with a wide range which has the prospect for solar energy utilization due to the variable optical properties.

REFERENCES

1. A. Henglein, *Chem. Rev.* **89**, 1861 (1989).
2. M.L. Steigerwald, L.E. Brus, *Acc. Chem. Res.* **23**, 183 (1990).
3. M.G. Bawendi, M.L. Steigerwald, L.E. Brus, *Annu. Rev. Phys. Chem.* **41**, 477 (1990).
4. Y. Wang, N. Herron, *J. Phys. Chem.* **95**, 525 (1991).
5. S. Gorer, J.A. Ganske, J.C. Hemminger, R.M.J. Penner, *Am. Chem. Soc.* **120**, 9584 (1998).
6. J. Britt, C. Ferekides, *Appl. Phys. Lett.* **62**, 2851 (1993).
7. T. Taguchi, Y. Endoh, Y. Nozue, *Appl. Phys. Lett.* **59**, 3434 (1991).
8. S. Zu, Z. Wang, B. Lie, X. Fan, G. Qian, *J. Alloy. Compd.* **476**, 689 (2009).
9. S. Wageh, S.M. Liu, T.Y. Fang, X.R. Xu, *J. Lumin.* **102**, 768 (2003)
10. Y. Li, F. Huang, Q. Zhang, *J. Mater. Sci.* **35**, 5933 (2000).
11. G. Laukaitis, S. Lindross, S. Tamulevicius, M. Leskela, M. Rackaitis, *Appl. Surf. Sci.* **396**, 161 (2000).