

Measurement of structural and optical band gaps of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x = 4$ and 6) nanomaterials

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The sulphides of cadmium and zinc are widely used materials due to their suitable energy band gaps. Their energy band gap depends on the particle size. The materials have been prepared using a simple solution of CdCl_2 and ZnCl_2 mixed in proper ratio without use of thiophenol. Precipitate of CdZnS is obtained by passing H_2S , liberated from heated thiourea through this solution. It is confirmed by X-ray diffraction (XRD) and optical band gap estimation that materials prepared are nano-materials. The optical band gap of these materials has been determined in order to establish a relationship between energy band gap of bulk and nanomaterial. It has been noticed that optical band increases with the increase of Zn concentration in CdZnS .

Keywords: Nanoparticle, Absorption spectra, Chemical method, Energy band gap, Grain size

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1 Introduction

There is a great interest to study the optical and electronic transport properties of nanometre-sized semiconductor particle¹, which show a significant difference from bulk materials. The synthesis and characterization of nanoparticles of cadmium and zinc chalcogenides have become an area of intense research activity over the last few years²⁻⁴. Several methods⁵⁻⁷ have been reported for preparation of nanocrystal of cadmium and zinc chalcogenides such as sputtering, electro-chemical deposition, co-precipitation method etc. A reduction in particle size strongly influences the crystallinity, structural stability and electrical and mechanical properties. In cadmium chalcogenides, it is possible to engineer the band gap over a wide range depending upon the concentration of Cd and Zn in the CdZnS system. Lot of efforts have been made to study binary chalcogenides from the viewpoint of producing nanoparticles. However, very few attempts have been made in ternary CdZnS nanomaterials.

In this paper, simple chemical method to prepare $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$ and $\text{Cd}_{0.4}\text{Zn}_{0.6}\text{S}$ nanomaterials has been reported. The optical and structural properties of these materials have been investigated and compared with their counterparts in the respective properties in the bulk materials.

2 Experimental Details

Samples of $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$ and $\text{Cd}_{0.4}\text{Zn}_{0.6}\text{S}$ materials have been prepared by chemical method using

cadmium chloride, zinc chloride and H_2S . In this method, an appropriate ratio of cadmium chloride and zinc chloride was taken in solution form (1 M). This solution was mixed thoroughly using magnetic stirrer for 20 min. H_2S gas produced by heating thiourea was then passed through this solution. From this reaction, a precipitate of $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$ and $\text{Cd}_{0.4}\text{Zn}_{0.6}\text{S}$ was obtained. The precipitate obtained was filtered and dried in open atmosphere. When the precipitate was completely dried, it was then crushed to fine powder by grinding in a mortar.

Materials thus prepared were characterized by using XRD. X-ray diffractogram of these materials were taken by using Philips PW-1729 X-ray diffractometer using the discrete $\text{Fe K}\alpha$ line (Figs 1 and 2). Particle size was determined from the width of XRD peaks using Scherrer formula⁸ as given below:

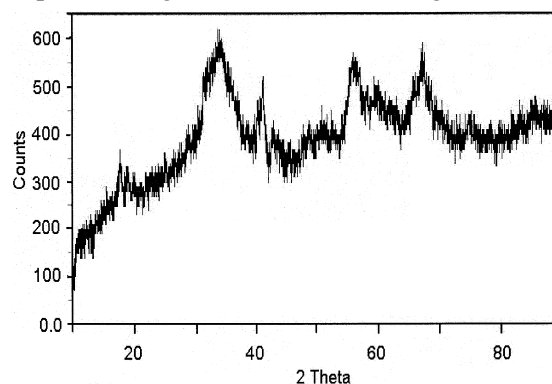
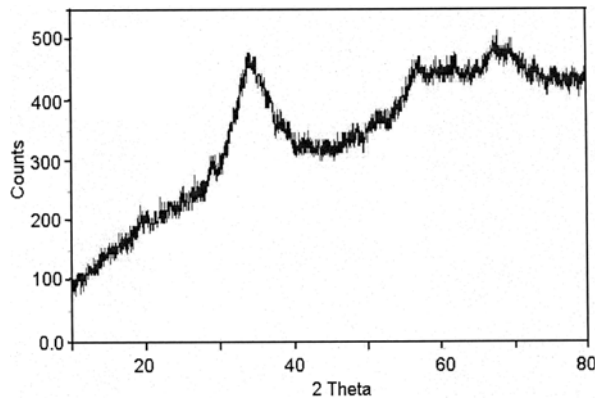
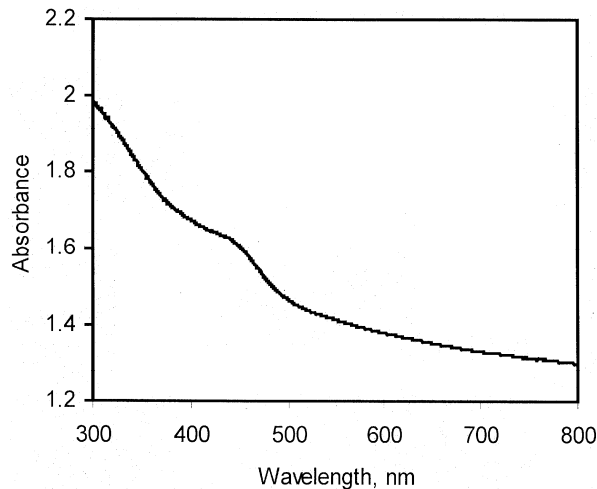


Fig. 1—XRD of sample $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$

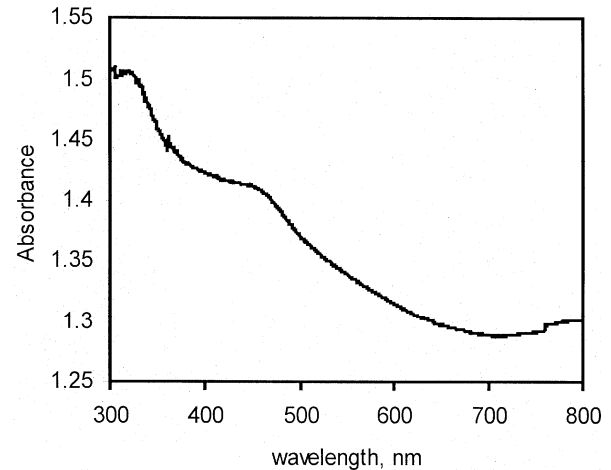
Fig. 2—XRD of sample $\text{Cd}_{0.4}\text{Zn}_{0.6}\text{S}$ Fig. 3—Absorption spectra of $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$

$$d = 0.94 \lambda / \beta \cos \theta \quad \dots(1)$$

where β is the full width half maximum (FWHM), θ is the diffraction angle, d is the average crystallite domain size perpendicular to the reflecting planes and λ is the wavelength of X-rays. For particles smaller than 100 nm, FWHM should be corrected by using FWHM for large grain silicon sample⁹.

$$\beta_{\text{corrected}} = [\text{FWHM}_{\text{sample}}^2 - \text{FWHM}_{\text{Si}}^2]^{1/2} \quad \dots(2)$$

The absorption spectra of these samples have been recorded at the room temperature using a spectrophotometer. For these spectra, the sample powders are to be dissolved in glycerin using the magnetic stirrer. Figures 3 and 4 show the absorption spectra of these materials. The energy band gap of these materials was estimated using the Tauc relation^{10,11}.

Fig. 4—Absorption spectra of $\text{Cd}_{0.4}\text{Zn}_{0.6}\text{S}$

$$\alpha h\nu = A(h\nu - E_g)^n \quad \dots(3)$$

where α absorption coefficient, $h\nu$ the photon energy, E_g the band gap, $n=1/2$ for direct band gap transition and A is constant which is different for different transitions.

For bulk form of these materials (thick films) $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ was prepared by screen-printing with sintering method. The reflection spectra of these films were used to estimate the energy band gap of these materials¹².

3 Results and Discussion

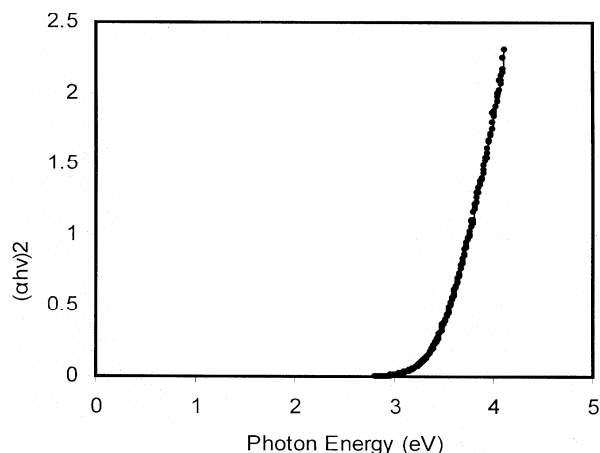
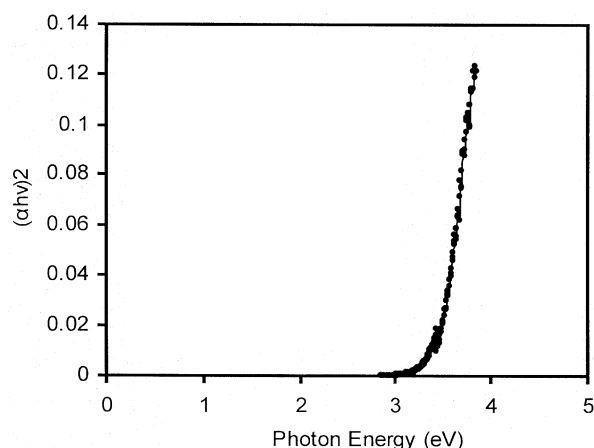
Diffraction patterns of powder of samples are shown in Figs 1 and 2 at room temperature. Figure 1 shows the XRD of $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$. There are no extra peaks of other phase except the reported phase of $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$. Therefore, it is clear from the X-ray data that the sample is a single phase Z-type structure. Broad diffraction peaks are exhibited by $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$ powder. The peak broadening is generally attributed to coherent diffracting grain size. This is easily understood as arising from the small and finite size of the crystallites. For calculation of the grain size of this sample, $\beta_{\text{corrected}}$ is used taking FWHM of silicon as 0.15° . The estimated X-ray grain size of this sample is 2.6 nm obtained from the FWHM of peak corresponding to $2\theta=33.32^\circ$.

Figure 2 shows the XRD of $\text{Cd}_{0.4}\text{Zn}_{0.6}\text{S}$. The XRD pattern from $\text{Cd}_{0.4}\text{Zn}_{0.6}\text{S}$ apparently exhibits only five broad peaks. The estimated X-ray grain size of this sample is 2.9 nm based on the FWHM of the broad peak, centered at 33.99° .

The optical absorption spectra of $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$ and $\text{Cd}_{0.4}\text{Zn}_{0.6}\text{S}$ are shown in Figs 3 and 4. For absorption

Table 1—Band gap for bulk and nanomaterials

Samples	Band gap (eV) (bulk)	Band gap (eV) (nano)
Cd _{0.6} Zn _{0.4} S	2.75	3.41
Cd _{0.4} Zn _{0.6} S	2.95	3.47

Fig. 5—Energy band gap determination of Cd_{0.6}Zn_{0.4}SFig. 6—Energy band gap determination of Cd_{0.4}Zn_{0.6}S

spectra, these samples are dissolved in glycerin with the help of magnetic stirrer for half an hour at room temperature to lead homogeneous colloidal solution. The absorption spectra of these colloidal solutions were recorded using a spectrophotometer at room temperature. It is evident from Figs 3 and 4 that the two samples show absorption edges which are blue shifted with respect to the bulk CdZnS, arising from quantum confinement effects in the nanoparticle.

The energy band gap is measured with the help of absorption spectra, a graph $(\alpha h\nu)^2$ versus $h\nu$ is plotted as shown in Figs 5 and 6. The extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the energy band. The energy band gaps for bulk (thick films) and nanomaterials are listed in Table 1.

The shift in the band gap of nanoparticle due to quantum confinement has the quantitative form¹³.

$$\Delta E_g = E_g^{\text{nano}} - E_g^{\text{bulk}} = \hbar^2 \pi^2 / 2MR^2 \quad \dots(4)$$

where R is the radius of particle and M is the effective mass of the system.

Eq. 4 could be used to estimate the particle size. The corresponding average particle sizes of Cd_{0.6}Zn_{0.4}S and Cd_{0.4}Zn_{0.6}S are 3.2 nm and 3.6 nm at room temperature, which are higher than that of particle sizes of 2.6 nm and 2.9 nm as determined from X-ray diffractograms. This difference is due to the approximate value of M that is taken as 1.919×10^{-31} Kg, M should be taken for CdZnS system instead of CdS system⁷ and also due to the fact that X-ray diffractograms were recorded for the freshly prepared materials, whereas absorption spectra of these materials were recorded after a gap of six months. Increased value of grain size as obtained from energy band gap is a consequence of grain growth with time.

4 Conclusions

It is possible to produce Cd_{0.6}Zn_{0.4}S and Cd_{0.4}Zn_{0.6}S nanomaterials using a simple chemical method without using a chemical as a clapping agent. XRD and optical band gap data have been obtained to confirm the nano size of these materials. It is also observed that in Cd_{0.6}Zn_{0.4}S and Cd_{0.4}Zn_{0.6}S grain growth rate is almost the same. There are indications that the band gaps vary with the composition of Zn in the sample. As the particle size depends upon the composition, an increase in the band gap is observed with the increase in the size of the grain.

References

- 1 Alivisatos A P, *J Phys Chem*, 100 (13) (1996) 226.
- 2 ACC & Trindade T, *Curr Opinoin Solid State Mater Sci*, 6 (2002) 347.
- 3 Rao C N R, Kulkarni G U, Thomas P J & Edwards P P, *Chem Eur J*, 8 (2002) 29.
- 4 Pileni M P, *Nature Mater*, 2 (2003) 145.
- 5 Arai T, Yoshida T & Ogawa T, *J Appl Phys*, 26 (1987) 396.
- 6 Salata O V, Dobson P J, Hull P J & Huthinson J L, *Thin Solid Films*, 251 (1994) 1.
- 7 Benerjee R, Jayakrishnan R & Ayyub P, *J Phys: Condens Mater*, 12 (2000) 10647.

- 8 Guinier A, *X-Ray Diffraction* (San Francisco: Freeman), (1963).
- 9 Boulch F, Schouler M C, Donnadiou P, Chaix J M & Djurado E, *Image Anal Stereol*, 20 (2001) 157.
- 10 Tauc J, *Amorphous & liquid Semiconductors* (J Tauc Edi, New York: Plenum), (1974).
- 11 Joshi G P, Saxena N S, Sharma T P, Dixit V & Misra S C K, *Indian J Pure & Appl Phys*, 41 (2003) 462.
- 12 Kumar V, Singh V, Sharma S K & Sharma T P, *Optical Materials*, 11 (1998) 29.
- 13 Mandal S K, Choudhari S & Pal A K, *Thin solid Films*, 350 (1999).