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Studies on absorption spectra of mixed zinc–cadmium sulphide microparticles stabilized in AOT–heptane–water and CTAB–chloroform–water inverse micellar systems

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Abstract

Ultrafine particles composed of mixed crystals of $Zn_xCd_{1-x}S$ can be generated in situ in AOT–heptane–water and CTAB–chloroform–water microemulsions using an ultrasonic processor. The microcrystallites exhibit the "quantum size effect". The composition of mixed sulphides and the water content (pool size) of inverted micelles can be varied systematically and the band gap energies of the semiconductor particles can be determined from the photoabsorption thresholds (edges). The experimental results reveal that a homogeneous solid solution of two sulphides is formed in CTAB–chloroform–water system. A method is proposed for determining the bulk optical dielectric constants of solid solutions of two semiconductors employing the Brus equation.

Keywords: Absorption spectra; Zinc–cadmium sulphide microparticles; Inverse micellar systems

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1. Introduction

Microcrystalline semiconductor particles are not thermodynamically stable and require some sort of kinetic stabilization. Organised surfactant assemblies such as vesicles or reverse micelles may be used as the incorporation media of these particles [1–4]. These ultrasmall particles with diameters ranging from between 1 and 10 nm possess properties which lie in the region of transition between the molecular level and the bulk phase. The size-dependent development of bulk electronic properties (quantum size effect) in semiconductor crystallites can be understood in terms of an expression proposed by Brus [5]:

$$E(R) = E_g + \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{\epsilon R} \tag{1}$$

E_g represents the bulk band gap energy, $E(R)$ stands for the band gap energy of the semiconductor particle having radius R, m_e^* and m_h^* denote the effective masses of the electron and hole and ϵ designates the bulk optical dielectric constant of the semiconductor. It is evident from Eq. (1) that ϵ of a semiconductor can be determined from the intercept of the straight line obtained by plotting $R\,\Delta E_g$ against $1/R$ where ΔE_g is the difference between $E(R)$ and E_g.

The radius of inverted micelles is dependent on the water content, defined by $W = [H_2O]/([AOT]$ or $[CTAB])$. The particle size can be changed by altering the values of W. The average particle diameter also depends on the relative amounts of M^{2+} and S^{2+} [6]. In the present work, the composition and radius of mixed crystals of $Zn_xCd_{1-x}S$ have been varied systematically. The band gap energies of the semiconductor particles have been determined from the absorption edges. The homogeneity–heterogeneity of the mixed sulphides has been ascertained from $E(R)$ vs. x plots. R has been related to W and finally the ϵ values of solid solutions of zinc–cadmium sulphide have been determined using the Brus equation.

2. Experimental details

14 μl of 0.5 M M^{2+} (M^{2+} represents Zn^{2+} and Cd^{2+} ions in various proportions) was added to 10 ml of deoxygenated AOT–heptane–water or CTAB–chloroform–water inverse micellar solution. It was followed by addition of 14 μl of 0.5 M Na_2S solution. The mixing of the two solutions was achieved by an ultrasonic processor (Vibronics, Processor PI) which generates intense shockwaves at the rate of 25 000 s^{-1}. The microemulsion was purged with nitrogen during addition of Na_2S solution to prevent oxidation of S^{2-} by dissolved oxygen. The size of the clusters of $Zn_xCd_{1-x}S$ is

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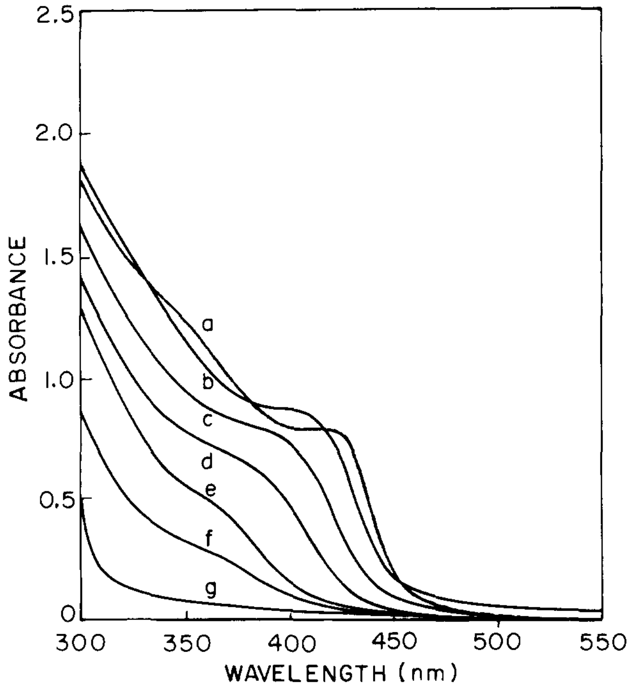

Fig. 1. Absorption spectra of $Zn_xCd_{1-x}S$ stabilized in ATO–heptane–water: $W=5$ and $x=0$, 0.14, 0.25, 0.50, 0.75, 0.86 and 1 for spectra a, b, c, d, e, f and g respectively.

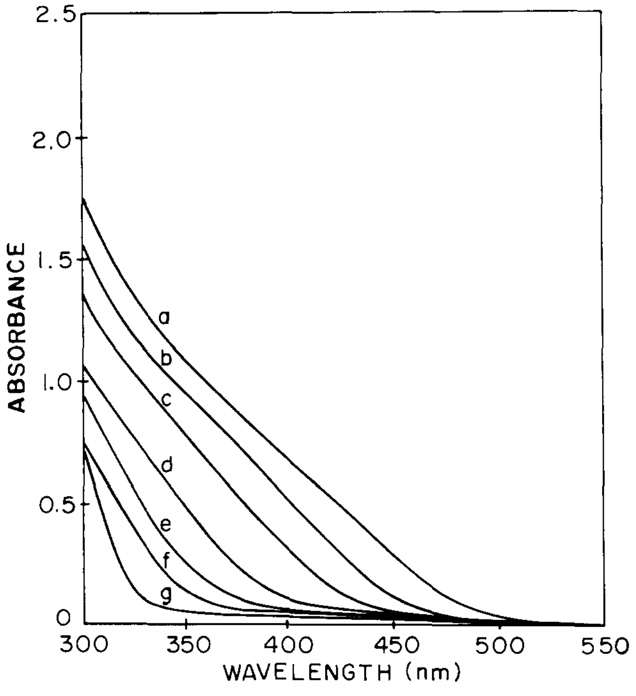

Fig. 2. Absorption spectra of $Zn_xCd_{1-x}S$ stabilized in CTAB–chloroform–water: $W=3.5$ and $x=0$, 0.14, 0.25, 0.50, 0.75, 0.86 and 1 for spectra a, b, c, d, e, f and g respectively.

somewhat dependent on the size of the reaction vessel, sonication time and quantity of the colloidal solution to be prepared. Therefore, attempts were made to keep these factors unchanged. The diameter of the waterpool has been varied by changing the concentration of added water in the system.

The absorption spectra of the semiconductor particles were recorded with a Hitachi U-3200 spectrophotometer. Fig. 1 represents the absorption spectra of $Zn_xCd_{1-x}S$ stabilized in AOT–heptane–water and Fig. 2 indicates the same in CTAB–chloroform–water.

3. Results and discussion

The band gap energies of mixed crystallites of $Zn_xCd_{1-x}S$ in AOT–heptane–water and CTAB–chloroform–water are presented as functions of x and W in Tables 1 and 2 respec-

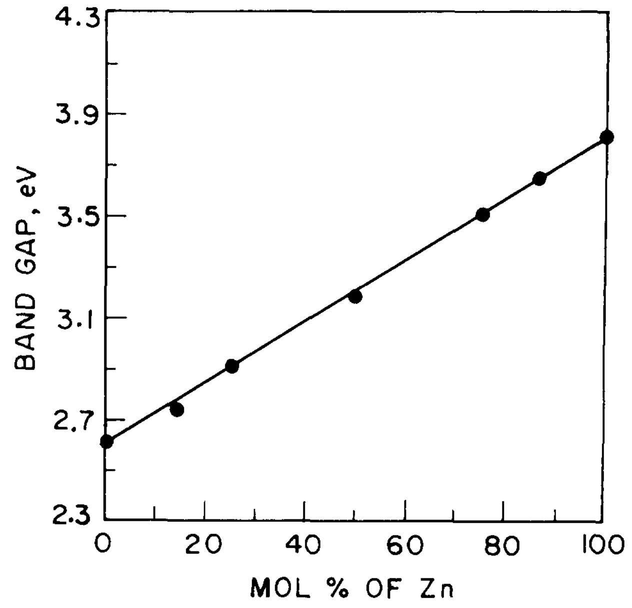

Fig. 3. Dependence of band gap energy of $Zn_xCd_{1-x}S$, stabilized in CTAB–chloroform–water ($W=3.5$), on concentration of Zn (molar per cent).

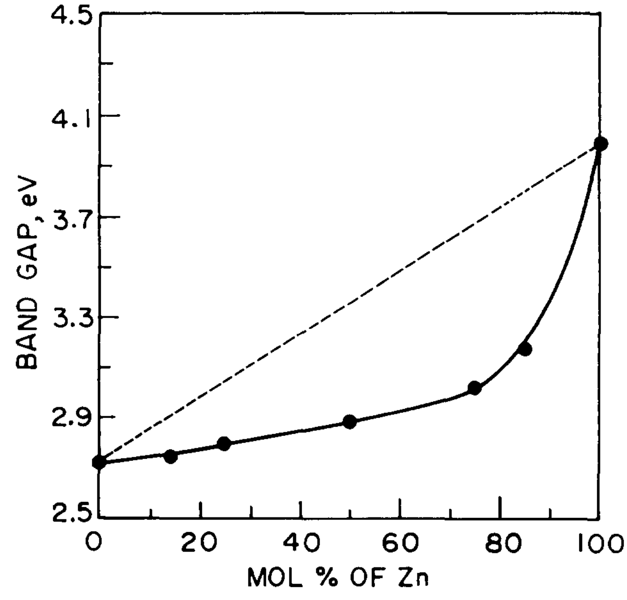

Fig. 4. Dependence of band gap energy of $Zn_xCd_{1-x}S$, stabilized in AOT–heptane–water ($W=5$), on concentration of Zn (molar per cent).

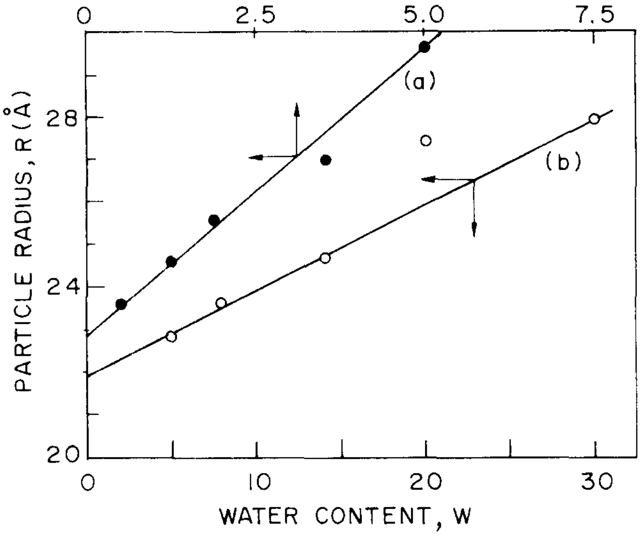

Fig. 5. Variation in particle radius R_{CdS} with water content W in (a) CTAB–chloroform–water and (b) AOT–heptane–water.

tively. ΔE_g denotes the band gap shift. The band gap energy of homogeneous solid solutions of two semiconductors lies between those of the contributing species and is for an ideal solution given by

$$E = xE_1 + (1-x)E_2 \tag{2}$$

where x is the mole fraction of the component with band gap energy E_1, and E_2 is the band gap energy of the other component. Fig. 3 indicates that $E(R)$ of $Zn_xCd_{1-x}S$, stabilized in the CTAB–chloroform–water system, is a linear function of x as predicted by Eq. (2). Fig. 4 reveals that the $E(R)$ vs. x curve of $Zn_xCd_{1-x}S$ stabilized in AOT–heptane–water exhibits negative deviation from ideality, indicating an inhomogeneous nature of the mixed crystallites. The departure from ideal behaviour may be ascribed to the binding of Zn^{2+} and Cd^{2+} ions to different extents on the negatively charged interface of AOT–water within the pool (as the binding constants of the two ions are different).

The linear dependence of the particle radius and water content of AOT–heptane–water (Fig. 5) may be expressed by the equations

$$R_{CdS}\ (\text{Å}) = 0.21W + 21.8 \tag{3a}$$

$$R_{ZnS}\ (\text{Å}) = 0.47W + 20.4 \tag{3b}$$

while the same relations for CTAB–chloroform–water may be represented as

$$R_{CdS}\ (\text{Å}) = 1.36W + 22.9 \tag{4a}$$

$$R_{ZnS}\ (\text{Å}) = 2.55W + 25.2 \tag{4b}$$

In a given pool R_{ZnS} and R_{CdS} have been determined using the Brus equation with experimentally determined values of ΔE_g and the reported values of ϵ, m_e^* and m_h^* for CdS and ZnS [7,8]. The radius R_M of $Zn_xCd_{1-x}S$ stabilized in CTAB–chloroform–water has been evaluated from the following linear relation:

$$R_M = xR_{ZnS} + (1-x)R_{CdS} \tag{5}$$

The dielectric constants ϵ_M of mixed $Zn_xCd_{1-x}S$ have been determined from the intercepts of the straight lines obtained by plotting $R_M\,\Delta E_g$ against $1/R_M$. The intercepts of the mean straight lines have been computed by the method of least squares. The values of the ϵ_M, as a function of x, have been compiled in Table 3.

Table 1
Band gap energies of $Zn_xCd_{1-x}S$ as a function of x and W in AOT–heptane–water

x	0	0.14	0.25	0.50	0.75	0.86	1
$W=5$							
$E(R)$ (eV)	2.73	2.76	2.81	2.89	3.03	3.18	4.00
ΔE_g[a] (eV)	0.33	0.18	0.09	−0.14	−0.32	−0.30	0.34
ΔE^*[b] (eV)	–	−0.15	−0.24	−0.48	−0.65	−0.64	–
$W=8$							
$E(R)$ (eV)	2.70	2.72	2.76	2.79	2.85	3.70	3.94
ΔE_g (eV)	0.30	0.14	0.04	−0.24	−0.50	0.22	0.28
ΔE^* (eV)	–	−0.16	−0.28	−0.53	−0.78	−0.06	–
$W=14$							
$E(R)$ (eV)	2.67	2.70	2.71	2.73	3.55	3.65	3.88
ΔE_g (eV)	0.27	0.12	−0.01	−0.30	0.20	0.17	0.22
ΔE^* (eV)	–	−0.14	−0.26	−0.55	−0.03	−0.06	–
$W=20$							
$E(R)$ (eV)	2.60	2.64	2.69	3.18	3.48	3.65	3.82
ΔE_g (eV)	0.20	0.06	−0.03	0.15	0.13	0.17	0.16
ΔE^* (eV)	–	−0.13	−0.22	−0.03	−0.04	−0.00	–

$[Zn_xCd_{1-x}S] = 7\times10^{-4}$ M, $([Zn^{2+}]+[Cd^{2+}])/[S^{2-}] = 1$, $[AOT] = 0.058$ M.

[a] $\Delta E_g = E(R) - E_g$, $E(R)$ denotes the observed band gap energy in the pool and E_g represents the bulk band gap energy of a homogeneous solid solution having the same composition as that in the pool. The bulk band gap energies of ZnS and CdS are 3.66 eV and 2.4 eV respectively.

[b] $\Delta E^* = E(R) - E^*(R)$ and $E^*(R)$ symbolizes the ideal band gap energy for a homogeneous solid solution in the pool and as such ΔE^* may be considered as a measure of deviation from ideality (inhomogeneity).

Table 2
Band gap energies of $Zn_xCd_{1-x}S$ as a function of x and W in CTAB–chloroform–water

x	0	0.14	0.25	0.50	0.75	0.86	1
$W=0.50$							
$E(R)$ (eV)	2.70	2.89	3.06	3.40	3.65	3.74	3.94
ΔE_g (eV)	0.30	0.31	0.34	0.37	0.30	0.26	0.28
ΔE^* (eV)	–	0.01	0.05	0.08	0.02	−0.02	–
$W=1.25$							
$E(R)$ (eV)	2.67	2.87	3.05	3.33	3.60	3.70	3.88
ΔE_g (eV)	0.27	0.29	0.33	0.30	0.25	0.22	0.22
ΔE^* (eV)	–	0.03	0.08	0.05	0.02	0.00	–
$W=2.00$							
$E(R)$ (eV)	2.64	2.82	2.95	3.27	3.55	3.67	3.82
ΔE_g (eV)	0.24	0.24	0.23	0.24	0.20	0.19	0.16
ΔE^* (eV)	–	0.01	0.01	0.04	0.02	0.02	–
$W=3.50$							
$E(R)$ (eV)	2.61	2.74	2.92	3.18	3.50	3.65	3.82
ΔE_g (eV)	0.21	0.16	0.20	0.15	0.15	0.17	0.16
ΔE^* (eV)	–	−0.04	0.01	−0.03	−0.02	0.00	–
$W=5.00$							
$E(R)$ (eV)	2.56	2.70	2.89	3.14	3.43	3.55	3.76
ΔE_g (eV)	0.16	0.12	0.17	0.11	0.08	0.07	0.10
ΔE^* (eV)	–	−0.03	0.03	−0.02	−0.03	−0.04	–

$[Zn_xCd_{1-x}S]=7\times10^{-4}$ M, $([Zn^{2+}]+[Cd^{2+}])/[S^{2-}]=1$, $[CTAB]=0.232$ M.

Table 3
$R_M\,\Delta E_g$ as a function of $1/R_M$ of mixed crystalline solid solutions of $Zn_xCd_{1-x}S$ in CTAB–chloroform–water system

x	$W=0.50$		$W=1.25$		$W=2.00$		$W=3.50$		$W=5.00$		ϵ_M
	$R_M\,\Delta E_g$ (eV Å)	$1/R_M$ [a] (Å^{-1})	$R_M\,\Delta E_g$ (eV Å)	$1/R_M$ (Å^{-1})	$R_M\,\Delta E_g$ (eV Å)	$1/R_M$ (Å^{-1})	$R_M\,\Delta E_g$ (eV Å)	$1/R_M$ (Å^{-1})	$R_M\,\Delta E_g$ (eV Å)	$1/R_M$ (Å^{-1})	
0.14	7.409	0.0418	7.290	0.0398	6.382	0.0376	4.434	0.0361	3.704	0.0324	2.39
0.25	8.203	0.0414	8.432	0.0391	6.279	0.0366	5.655	0.0354	5.410	0.0314	4.71
0.50	9.121	0.0406	7.950	0.0377	6.948	0.0345	4.440	0.0338	3.746	0.0294	2.27
0.75	7.553	0.0397	6.863	0.0364	6.120	0.0327	4.639	0.0323	2.902	0.0276	3.46
0.86	6.604	0.0394	6.129	0.0359	5.949	0.0319	5.353	0.0318	2.606	0.0269	5.79

[a] $\epsilon=5.7$ and 5.13, $m_e^*=0.17m_0$ and $0.205m_0$ and $m_h^*=0.7m_0$ and $0.51m_0$ for CdS and ZnS respectively.

The same calculation for $Zn_xCd_{1-x}S$ stabilized in AOT–heptane–water has not been tried owing to inhomogeneity of the mixed semiconductor particulates.

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