Temperature dependence of absorption band edge of CdTe nanocrystals in glass

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Abstract. CdTe nanocrystals were grown in borosilicate glass by two-step heat treatment process. Their average radii between 2.98 ± 0.07 and 6.15 ± 0.32 nm are determined by using effective mass approximation in the strong confinement limit. The changes in the band gap of CdTe nanocrystals with temperature in the range from 300 to 775 K are found to be between −5.43 × 10$^{-4}$ and −3.78 × 10$^{-4}$ eV K$^{-1}$ by using Varshni’s empirical temperature-dependent band gap energy change relation. The difference between temperature dependence of band gap energy for CdTe nanocrystals and that of bulk CdTe crystal is proposed to be due to electron–phonon coupling which is stronger in nanocrystals. We also report a method to estimate glass transition temperature on the basis of analysis of temperature dependence of absorption band edge of CdTe nanocrystals in glass.

Since the early 1980s, semiconductor nanocrystals embedded in liquids, polymers, crystals, etc have been very promising materials in the fields of optoelectronic device fabrication [1], telecommunication [2] and medical treatment [3]. These nanometer-size semiconductors offer some advantages over bulk semiconductors and other low-dimensional structures of the same composition (quantum wells and wires) due to unique quantum confinement effect observed in all three space dimensions. For example, the tunability of absorbed and emitted light wavelengths is excellent in these structures.

Size- and stoichiometry-dependent band gap energy of II–VI binary and ternary semiconductor nanocrystals, such as CdS, CdSe and CdS$_x$Se$_{1-x}$, have been well investigated. However, temperature-dependent band gap energy has not been studied extensively. Nomura and Kobayashi [4] reported temperature shift of first exciton band between 70 and 293 K for

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Cd$_{0.12}$Se$_{0.88}$ nanocrystals in glass in a strong confinement regime. Absorption band edge shift of Cd$_{x}$Se$_{1-x}$ (0.25 \(\leq x \leq 0.89\)) nanocrystals in glass in a weak-confinement regime below room temperature (300 K) was also reported by Surendran et al [5]. Kunets et al studied the optical band gap shift between 4.2 and 500 K for CdS$_{0.13}$Se$_{0.87}$ in the weak-confinement regime and CdS$_{0.32}$Se$_{0.68}$ nanocrystals in the strong confinement regime [6]. Temperature shift of the energetic position of first exciton band of CdS nanocrystals between 4 and 295 K in liquid and their band edge shift in glass between 300 and 900 K were investigated, respectively, by Vossmeier et al [7] and Yükselici and Persans [8].

In this work, temperature-dependent band gap energy of CdTe nanocrystals in glass between room temperature (300 K) and 950 K is studied. We report a method to estimate glass transition temperature on the basis of analysis of temperature dependence of absorption band edge of CdTe nanocrystals in glass.

CdTe nanocrystals were grown from commercially available RG850 Schott filter glass via well-known melt followed by two step heat treatment process. RG850 Schott filter glass was sliced to dimensions of $10 \times 10 \times 2$ mm$^3$ by a diamond saw. A number of these small samples were melted at 1273 K for 15 min and quenched rapidly to room temperature, then treated at 823 K for 16 h and at 863 K for various hours up to 24 h. One of the samples was treated at 823 K for 16 h and then at 953 K for 24 h to grow larger size nanocrystals. Thus, CdTe nanocrystals of different average size and size distribution, and high volume fraction were formed in borosilicate glasses [9].

The optical transmission spectra of the samples were recorded between 300 and 950 K by using a setup illustrated in figure 1. The actual temperature near the sample was monitored by a thermocouple placed within 2.5 cm of the sample. Light from a tungsten halogen lamp powered by a constant current/voltage source was focused by using a pair of plano-convex lenses onto the sample which is placed horizontally on a technical ceramic disk with an opening at the center, in the middle of a tube furnace oriented vertically. The transmitted light, with

**Figure 1.** Optical transmission setup for high temperatures.
The room temperature optical absorption spectra for CdTe nanocrystals in borosilicate glasses.

The Gaussian peak in each absorption spectrum results from the lowest electron–hole pair transitions in CdTe nanocrystals embedded in glass matrix and often called the first exciton peak. The average CdTe nanocrystal radius in each glass sample can be calculated by using a relation deduced from an effective mass model as follows [10]:

$$\Delta E [\text{eV}] = \frac{\hbar^2 \pi^2}{2\mu m_o R_{\text{ave}}^2 [\text{nm}^2]} \approx \frac{0.376}{\mu R_{\text{ave}}^2 [\text{nm}^2]} \quad (1)$$

where $\Delta E$ is the blue shift of the first-exciton peak energy relative to the bulk band gap energy (1.44 eV for bulk CdTe at room temperature [11]), $\mu$ the reduced mass of an electron–hole pair in units of electron rest mass ($m_o$) and $R_{\text{ave}}$ the average nanocrystal radius. As seen in figure 2, the lowest transition energy for the bulk crystal of 1.44 eV is blue shifted when the size is reduced which is due to quantum confinement effect [12]. We employ equation (1) to calculate the average nanocrystal radii in the samples from their absorption blue shifts.
A comprehensive study on growth kinetics of CdTe nanocrystals in glass published elsewhere [9] shows that particles in glass sample(s) treated at 863 K for 6 (sample 1), 8 (sample 2) and 16 (sample 3) h undergo diffusion-limited growth and, at 863 (sample 4) and 953 (sample 5) K for 24 h coarsening, respectively.

In figure 3, the band gap energy is plotted against temperature for both CdTe nanocrystals in glass and bulk CdTe (labeled as Bulk in the figure) which is obtained from a two-oscillator model [13].

The band gap energy of CdTe nanocrystals in each temperature for five samples are found by extrapolating the straight-line portion of squared absorption coefficient between $\alpha^2 = 0.3$ and 1 cm$^{-2}$ to $\alpha^2 = 0$ energy axis. We present temperature-dependent absorption band edge of CdTe nanocrystals in glass in figure 3. The temperature is altered between 300 and 775 K (reversible range) for samples 1–4 and increased beyond the reversible range for samples 1 and 2.

Reversible changes in figure 3: we first discuss the reversible range where particle growth is negligible. As seen from figure 3, the band gap energy of CdTe nanocrystals decreases linearly with increasing temperature between 300 and 775 K. The temperature shifts observed in figure 3 are reversible within that range, that is, data points taken by either increasing (white symbols) or lowering (black symbols) the temperature almost overlap as shown in the same
Table 1. Average nanocrystal radius ($R_{\text{ave}}$), zero temperature band gap energy ($E_g(0)$), Varshni’s $\alpha$ parameter for CdTe nanocrystals in glass and for bulk CdTe crystal.

| Sample | $R_{\text{ave}}$ (nm) | $E_g(0)$ (eV) | $\alpha$ (eV K$^{-1}$) |
|--------|-----------------------|---------------|------------------------|
| 1      | 2.98 ± 0.07           | 1.923         | 4.73E $-4$             |
| 2      | 3.15 ± 0.08           | 1.880         | 5.19E $-4$             |
| 3      | 3.38 ± 0.08           | 1.823         | 5.43E $-4$             |
| 4      | 3.48 ± 0.09           | 1.801         | 5.35E $-4$             |
| 5      | 6.15 ± 0.32           | 1.514         | 3.78E $-4$             |
| Bulk   | 1.502                 | 3.24E $-4$    |                        |

Temperature-dependent band gap energy parameters of CdTe nanocrystals are obtained by using Varshni’s empirical relation as follows [14]:

$$E_g(T) = E_g(0) - \alpha \frac{T^2}{(\theta_D + T)},$$  \hspace{1cm} (2)

where $E_g(0)$ is the zero temperature band gap energy, $\theta_D$ the Debye temperature (160 K for bulk CdTe [13]) and $\alpha$ Varshni’s proportionality constant between band gap energy and temperature $(T)$ for $\theta_D \ll T$. By employing $\theta_D = 160$ K, we calculate from equation (2), $E_g(0) \approx 1.9–1.8$ eV, $\alpha = 4.7–5.5 \times 10^{-4}$ eV K$^{-1}$ for samples 1–4 and $E_g(0) \approx 1.5$ eV, $\alpha \approx 3.8 \times 10^{-4}$ eV K$^{-1}$ for sample 5 (see Table 1 for exact values). Varshni’s parameters for bulk CdTe are calculated from the two-oscillator model [13] for the temperature range of 300–775 K which predicts well band gap changes of semiconductors (see figure 3). The parameter $\alpha$ for CdTe nanocrystals is found to be of the same order of magnitude as that of the bulk. However, a slight increase is evident for CdTe nanocrystals in glass as shown in table 1. This difference will be explained in the next paragraph.

Both thermal expansion of the lattice and electron–phonon coupling play an important role in temperature dependence of band gap energy of bulk semiconductor crystals. For semiconductor nanocrystals, however, there might be two more reasons as well: (i) the mechanical strain between nanocrystals and surrounding matrix and (ii) quantum confinement effect for charge carriers in nanocrystals [15]. The band gap variation due to the mechanical strain is caused by a thermal strain and surface tension. In this paper, we presumed that the mechanical strain is only due to the thermal strain. On the other hand, the strength of electron–LO phonon couplings in nanocrystals differs from bulk semiconductor due to the quantum confinement. The difference between $(\partial E_g/\partial T)$ of a semiconductor nanocrystal and that of its bulk state in the limit of $T \to \infty$ can be given using empirical band gap change relations (i.e. equation (2) etc) as follows [16]:

$$\lim_{T \to \infty} \left[ \left( \frac{\partial E_g}{\partial T} \right)_\text{nano} - \left( \frac{\partial E_g}{\partial T} \right)_\text{bulk} \right] = 2k_B(S_{\text{bulk}} - S_{\text{nano}}) + \left( \frac{\partial E_g}{\partial T} \right)_\text{qc} + \left( \frac{\partial E_g}{\partial T} \right)_\text{ts},$$  \hspace{1cm} (3)

where subscripts ‘qc’ and ‘ts’ stand for the quantum confinement and the thermal strain, respectively. $S_{\text{bulk}}$ and $S_{\text{nano}}$ are dimensionless constants which are related to the electron–phonon coupling strengths for bulk semiconductor and nanocrystal, respectively.
(effective coupling constants; 1.68 for bulk CdTe [17]) and $k_B$ is the Boltzmann constant. In this high temperature limit, equation (3) can be written, using Varshni’s relation, as follows:

$$(\alpha_{\text{bulk}} - \alpha_{\text{nano}}) = 2k_B(S_{\text{bulk}} - S_{\text{nano}}) + \left(\frac{\partial E_g}{\partial T}\right)_{qc} + \left(\frac{\partial E_g}{\partial T}\right)_{ts},$$

where

$$\left(\frac{\partial E_g}{\partial T}\right)_{qc} = -\frac{\hbar^2\pi^2}{\mu R_{ave}^2} \bar{\beta}$$

and

$$\left(\frac{\partial E_g}{\partial T}\right)_{ts} = -\left(\frac{\partial E_g}{\partial P}\right) \left[3B_0 \frac{\partial}{\partial T} \left(\frac{\Delta a}{a_0}\right)\right] = -\left(\frac{\partial E_g}{\partial P}\right) \left[3B_0(\beta_{\text{glass}} - \bar{\beta})\right].$$

Equation (4) can be rearranged as in equation (7) using the simplifications: $\Delta \alpha = \alpha_{\text{nano}} - \alpha_{\text{bulk}}$ and $\Delta S = S_{\text{nano}} - S_{\text{bulk}}$.

$$\Delta S = \left(\frac{1}{2k_B}\right) \left[\Delta \alpha - \frac{\hbar^2\pi^2}{\mu R_{ave}^2} \bar{\beta} + \left(\frac{\partial E_g}{\partial T}\right)_{ts}\right].$$

The changes in Varshni’s $\alpha$ parameter ($\Delta \alpha$) and coupling strength ($\Delta S$) of our nanocrystals relative to their bulk states are plotted as a function of average nanocrystal radius in figures 4(a) and (b), respectively. The coupling strength is larger for CdTe nanocrystals whose radii are smaller than bulk exciton Bohr radius ($R < a_B$, that is, strong confinement regime is active). However, the strength change increases up to average CdTe nanocrystal radius of $\approx 3.38 \pm 0.08$ nm (for 16 h at 863 K), then decreases toward to bulk value for larger nanocrystals. It can be seen that the strength change increases in these nanocrystals before the coarsening sets in. This might be due to the change in surface configuration and size distribution of nanocrystals after that instance. In consequence of this, there is always a critical value for radius for CdTe nanocrystals which results in the largest band gap change with temperature and electron–phonon coupling in these nanocrystals before the coarsening is at work. Our results for Varshni’s $\alpha$ parameter for different average CdTe nanocrystal radii are consistent with findings in a recent study of Sedrakian et al. [20] who reported that there is a maximum for the $\alpha$ parameter of CdS$_x$Se$_{1-x}$ nanocrystals in silicate glass whose radii are smaller than 5 nm.

Irreversible changes in figure 3: we now discuss the irreversible range between 775 and 950 K, where particle growth is significant. The temperature-dependent band gap variation of CdTe nanocrystals in glass is shown for above 775 K for samples 1 and 2. The absorption band edge of CdTe nanocrystals in glass shifts to red with temperature, but more rapidly after the temperature of 848 K. The deviation from Varshni’s fit above 848 K is due to growing nanocrystals in glass.
The variation in Varshni’s parameter ($\alpha (eV/K) \times 10^4$) for CdTe Nanocrystals in glass (a) and the variation in effective electron–phonon coupling constant ($S$) for CdTe Nanocrystals in glass (b) are shown in Figure 4. The changes in $\alpha$ (a) and coupling strength (b) for CdTe nanocrystals dependent on their average radii. The lines between data points are for the eye to follow.

The nanocrystals in a glass can be grown above the transition temperature of that glass since the motion of ions and molecules in glass is possible above this temperature [21]. Therefore, the transition has to occur between 848 and 875 K. The transition temperature of this glass is determined with the DTA method. The transition temperature point ($T_g$) calculated from the endothermal peak in DTA graph is 854 K. As seen from Figure 5, the glass transition temperature range obtained from band edge shift is consistent with the DTA and DSC (differential scanning calorimetry; not shown here) measurements. However, the transition temperature point given by the Schott firm (827 K [22]) is out of this range. This difference is reasonable because of the nature of the transition temperature itself. The glass transition temperature is not a fixed point and varies with instrumental factors (furnace size, furnace shape, furnace atmosphere, sample-holder material, heating rate, cooling rate, etc) and sample characteristics (particle size, degree of crystallinity, amount of sample, etc) when it is determined from the DTA curve [23]. Therefore, the small semiconductor nanocrystals in glass can be used to determine the transition temperature of that glass exactly by means of the quantum confinement effect. We thus established a method to estimate glass transition temperature on the basis of analysis of temperature dependence of absorption band edge of CdTe nanocrystals in glass.

In conclusion, the two-step heat treatment process enables us to grow CdTe nanocrystals in borosilicate glass whose radii are between $2.98 \pm 0.07$ and $6.15 \pm 0.32$ nm. The reversible band edge red shift of nanocrystals with temperature is studied using Varshni’s empirical relation. The band gap change of CdTe nanocrystals between 300 and 775 K is found to be between $-5.43 \times 10^{-4}$ and $-3.78 \times 10^{-4}$ eV K$^{-1}$. The slight increase in band gap change for nanocrystals relative to the bulk is attributed to the strength of phonon–exciton coupling in nanocrystals. The band gap change of these nanocrystals with temperature offers us the opportunity to determine the transition temperature range of CdTe doped borosilicate glass which is consistent with...
Figure 5. The absorption band edge shift of CdTe nanocrystals for sample 1 (open circles) with temperature is shown together with DTA curve (solid curve). The transformation temperature point of this glass \( T_g \) obtained from DTA measurement is 854 K. The double headed arrow shows the transformation temperature range obtained from band edge shifts of CdTe nanocrystals in the strong confinement with temperature which is consistent with that of the DTA curve. The sample weight is about 8 mg, the heating rate is 10 K min\(^{-1}\) and \( N_2 \) flow rate is 20 ml min\(^{-1}\) for DTA measurement.

DTA measurement. The range at which the slope of the absorption band edge energy against temperature curve changes dramatically points out the glass transition temperature.

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