Chapter 4

Thermo-optic studies on CdSe quantum dots based materials

Details of the thermo-optic studies of CdSe based nanomaterials are described in this chapter. We have applied two thermo-optic methods for the characterization of the samples in which thermal lens study give information about thermal diffusivity property of the material. Characterization of the samples has also been carried out using Photo acoustic technique. Both of these studies give the details about the nonradiative property of the samples.

Results of this chapter are published in :

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4.1 Introduction

In recent years, thermo-optic method has emerged as an effective research and analytical tool for the characterization of materials due to its dependence on optical absorption coefficient. This study includes group of techniques used to measure the optical absorption and thermal properties of the samples. The basic idea behind these techniques is the change in thermal state of the sample resulting from nonradiative relaxation following the absorption of a pulsed or chopped optical radiation [1-9].

The detected PT signal depends on the optical absorption coefficient at the incident wavelength as well as on how heat diffuses through the sample [10-14]. Dependence of PT signal on how heat diffuses through the specimen allows the investigation of transport and structural properties such as thermal diffusivity, thermal effusivity, thermal conductivity, voids, etc. The unique feature of PT methods is that the detected PT signal depends only on the absorbed light and it is independent of transmitted or scattered light. Among the two relaxation processes for the deexcitation of the states, nonradiative relaxation occurs in thermo-optic methods while radiative emission leads to the studies on conventional spectroscopy. Nonradiative process leads to the heating of the sample and the corresponding thermodynamic properties can be studied [13-15]. The merit of these methods also lies in the extremely sensitive detection technique used here in comparison with conventional transmission methods.

PT methods based on the measurement of the strength of the lens formed due to the refractive index changes are called thermal lens spectroscopy (TLS). This technique has proven to be an appreciated method to study the thermo-optical properties of transparent materials such as glasses, liquid crystals and polymers. TLS method is useful for the determination of thermal diffusivity, thermal conductivity, the temperature coefficient of the refractive index leading to change in the optical path length, optical absorption coefficient and fluorescence quantum efficiency. Since this is an isolated sensing technique, measurement of samples in isolated environment presents no extra difficulties.
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In PT methods another important parameter that can be exploited is the pressure change associated with the transient temperature change in the specimen. Pressure transducers such as microphones and piezoelectric crystals are commonly used for the detection of pressure waves associated with a rapid sample heating. The branch of PT method based on the detection of these pressure waves is known as opto acoustic or photo acoustic (PA) technique [16-19]. A detailed description of this technique is given in the 2nd chapter.

Our interest is to study the thermo-optic changes which occurs in the QDs since they are highly sensitive to the light-matter interactions. The measurement of the heat transfer through diffusion in a liquid medium containing CdSe QDs and its composites at different conditions is also done.

4.2 Thermal lens study of CdSe QDs based samples

Thermal lens spectrometry (TLS) is one of the important PT techniques which depends on temperature gradient generated by absorption of electromagnetic radiation and subsequent non-radiative relaxation of the excited molecules. For thermal lens studies, the schematic experimental set up and explanations are same as described in the 2nd chapter in figure 2.2. Sample was taken in a cuvette of 1 cm path length for making the measurements. A low frequency mechanical chopper with 3 Hz is used to modulate the intensity of the pump beam until the abbreviate free TL peak-to-peak signal is maximum [20-21]. The probe beam from the He-Ne laser which passes collinearly with pump beam(532nm) experiences divergence due to thermally induced negative refractive index gradient in the sample and the beam shape expands in the presence of thermal lens. The change in intensity at the centre of the probe beam spot in the far field is measured using a fast photo detector from which the relative intensity and initial slope is measured. Photograph showing the thermal blooming of the probe beam is given in figure 4.1. The data are analyzed by using the procedure reported earlier [22]. Time
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Figure 4.1: Photograph showing probe beam cross-section (a) without pump beam and (b) with pump beam.

dependent probe beam intensity follows the expression [23-24].

\[ I(t) = I_0 [1 - \theta (1 + \frac{t_c}{2t})^{-1} + \frac{\theta^2}{2} (1 + \frac{t_c}{2t})^{-2} - 1] \]  \hspace{1cm} (4.1)

Here, the parameter \( \theta \) is related to the thermal power radiated as heat and can be obtained with

\[ I = \frac{I_0 - I_\infty}{I_\infty} \]  \hspace{1cm} (4.2)

and

\[ \theta = 1 - \sqrt{1 + 2I} \]  \hspace{1cm} (4.3)

where \( I_0 \) is the initial intensity and \( I_\infty \) is the intensity after the steady state. A detailed curve fitting of this experimental data to equation (4.1) gives the time constant \( t_c \) of the thermal decay process. Finally the thermal diffusivity \( D \) of the sample can be calculated from the equation

\[ t_c = \frac{\omega^2}{4D} \]  \hspace{1cm} (4.4)

where \( \omega \) is the beam radius at the sample position and \( t_c \) is the time response to attain the steady state TL signal.

4.2.1 Size dependent variation of thermal diffusivity of CdSe based QDs

CdSe QDs are prepared by a modified aqueous method using reflux. We have selected four samples with different particle sizes for the study,
namely \(C_1=4.62\text{nm}, C_2=4.88\text{nm}, C_3=4.96\text{nm}\) and \(C_4=5.16\text{nm}\). Figure 4.2 represents a typical TL pulse train measured at 3Hz and figure 4.3 represents the thermal decay of CdSe sample \(C_2\) at an input power of 136 mW.

Similar TL signal evolution obtained for CdSe QDs of different sizes \((C_1, C_2, C_3\) and \(C_4)\) and their corresponding \(t_c\), \(\theta\), and \(D\) are tabulated in Table 4.1. Thermal diffusivity plotted against the size of the CdSe QDs is shown in figure 4.4. Thermal diffusivity is mainly controlled by the size and shape of the NPs. Particle size is an important parameter controlling thermal properties of nanofluids. There are reports based
on variation of thermal diffusivity with particle size[25-26]. The range of particle size in our experiment lies between 4nm-6 nm. The general trend in our experimental data is that the thermal diffusivity of CdSe nanofluid decreases with increasing particle size in the fluid. This trend is theoretically supported by Brownian motion of NPs and liquid layering around these. The reduction of D in our experiment with increased particle size is attributed to the convection velocity

\[ V = \sqrt{\frac{18k_B T}{\pi \rho d^3}} \]  

which drops drastically due to the cube dependence on particle size. Where d=particle size, \( \rho \)=density of the medium, and \( k_B T \)=thermal energy. Therefore if the particle size is very small, Brownian motion is strong and if the particles are large, Brownian motion is severely arrested [22]. Thus the observed decrease in the thermal diffusivity with

<table>
<thead>
<tr>
<th>sample</th>
<th>Particle size (nm)</th>
<th>( \theta )</th>
<th>( t_c ) (s)</th>
<th>[ D \times 10^{-3} \text{ (cm}^2/\text{s}) ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁</td>
<td>4.62</td>
<td>-2.07</td>
<td>0.05</td>
<td>0.63</td>
</tr>
<tr>
<td>C₂</td>
<td>4.88</td>
<td>-2.89</td>
<td>0.05</td>
<td>0.61</td>
</tr>
<tr>
<td>C₃</td>
<td>4.96</td>
<td>-12.65</td>
<td>0.08</td>
<td>0.41</td>
</tr>
<tr>
<td>C₄</td>
<td>5.16</td>
<td>-5.70</td>
<td>0.13</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 4.1: Particle size, time constant and diffusivity of CdSe QDs prepared by reflux method.
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Increased particle size can be attributed due to the increase in Brownian velocity. Also it can be concluded that CdSe with very small particle size, transports heat rapidly through it and cause high thermal diffusivity.

4.2.2 Thermal lens studies of CdSe based nanofluids with different pH.

In this experiment, CdSe nanofluids are prepared by rapid microwave irradiation method 2nd chapter. The pH of the corresponding colourless solution was adjusted by adding 1M NaOH. We have selected samples with different pH values. The samples taken for optical characterization were named as pH 3.7, pH 4.7, pH 7.6, and pH 8.9. Figures 4.5 & 4.6 show the absorption and fluorescence spectra of the prepared CdSe samples with different pH at room temperature. It can be clearly seen that the absorption and luminescence peaks of the CdSe QDs were red-shifted with increasing value of pH. It is observed that sample with pH less than 4.7, there is a sign of agglomeration and for higher pH sample shows much less intensity with large FWHM.

![Figure 4.5: Absorption spectra of the prepared CdSe QDs with different pH.](image)

Figure 4.5 shows the pH effects of the reaction solution on the fluorescent properties of CdSe QDs. The unique structure of MSA plays an important role in reducing the surface trap states of CdSe QDs and the two carbonyl groups of MSA can provide better stability than other thiol compounds [27-28].

Figure 4.7 represents the Particle size distribution and auto correlation function g2(T) vs. delay time for the measurement of hydro dynamic...
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Figure 4.6: Fluorescence spectra of the prepared CdSe Quantum dots with different pH.

particle size (d) of CdSe sample by DLS method.

Figure 4.7: (a) Particle size distribution and (b) Auto correlation function g2(T) vs. delay time by DLS method.

It shows that the average size of the nanoparticles formed are within 10 nm range. Figure 4.8 represents the thermal decay at an input power of 136mW. The experiment was repeated for CdSe nanofluids with various pH values. Typical results are shown in figure 4.9. The beam spot size at the sample position is 0.225mm. Finally, the thermal diffusivity D of the sample was calculated from the equation (4.4). Similarly TL signal evolution were obtained for CdSe QDs of different pH values and their
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Figure 4.8: Fitting of the data of sample (PH- 9.6) with probe beam intensity as a function of time with fit parameters $I_0 = 0.252$, $\theta = 36.22$ and $t_c=1.94$ s.

corresponding cluster size or hydrodynamic particle size $(d)$, $t_c$, $\theta$, and diffusivity $(D)$ with an error $\pm 0.03$ were obtained and are tabulated in Table 4.2.

<table>
<thead>
<tr>
<th>pH</th>
<th>$d$ (nm)</th>
<th>$\theta$</th>
<th>$t_c$ (ms)</th>
<th>$D \times 10^{-5}$ cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.7</td>
<td>8.4</td>
<td>467.97</td>
<td>12.907</td>
<td>0.24</td>
</tr>
<tr>
<td>4.7</td>
<td>10</td>
<td>0.98</td>
<td>0.01</td>
<td>4520</td>
</tr>
<tr>
<td>7.6</td>
<td>10.1</td>
<td>13.24</td>
<td>0.79</td>
<td>3.98</td>
</tr>
<tr>
<td>8.9</td>
<td>10.3</td>
<td>103.10</td>
<td>4.9</td>
<td>0.64</td>
</tr>
<tr>
<td>9.6</td>
<td>8.5</td>
<td>36.22</td>
<td>1.94</td>
<td>1.62</td>
</tr>
<tr>
<td>10</td>
<td>9.2</td>
<td>463.52</td>
<td>48.23</td>
<td>0.06</td>
</tr>
<tr>
<td>11</td>
<td>7.9</td>
<td>465.01</td>
<td>30.07</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 4.2: Observations of thermal diffusivity changes of CdSe QDs prepared at different pH

The observed (figure 4.10) reduction in $t_c$ at optimum pH can be the effect of shortening of the mean free path of the phonons which is confirmed from Table 4.2. As the pH value is increased continuously, the mean free path of the phonon in the solid increases the value of $t_c$ and thermal diffusivity get reduced. From the figure it is observed that, at an optimum pH, $t_c$ value is very small compared to that at other
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Figure 4.9: TL fitting of data of CdSe QDs with different pH values.

Figure 4.10: (a) Observed $t_c$ of CdSe QDs plotted against pH and (b) Thermal diffusivity of CdSe QDs plotted against pH.

pH values. A large enhancement of thermal diffusivity is also observed (from figure 4.10.(b)) with sample pH $\sim$ 4.7. When the QDs are dispersed into water, the overall behaviour of the particle-water interaction depends on the properties of the particle surface. Experimental results also indicate that the stabilities of these nanofluids are influenced by pH values. Derjaguin theory [29-30] explains the aggregation of aqueous dispersions quantitatively and describes the force between charged surfaces interacting through a liquid medium. It combines the effects of the van der Waals attraction and the electrostatic repulsion due to the so called double layer of counter ions. According to this, when the pH is increased
to the optimized value, ($\sim 4.7$) the surface charge increases because of the more frequent attacking of the surface hydroxyl groups and phenyl sulfonic group by potential-determining ions ($H^+$, $OH^-$ and phenyl sulfonic group). This leads to an increase of the electrostatic repulsion force between the particles, and the suspensions show significantly reduced agglomeration and enhanced mobility, ultimately improving the heat transport [31-32]. When the pH is equal to the isoelectric point (IEP), which is the optimized pH ($\sim 4.7$) in our case the QDs tend to be unstable, form clusters, and precipitate, where IEP, is the pH at which a particular molecule or surface carries no net charge. The repulsive forces among metal oxides are zero and QDs coagulate together at this pH value. The resulting big clusters formed at IEP will trap water and the structures of trapped water are varied due to the strong atomic force among QDs. Water is packed well inside and volume fraction of the QDs will be larger.

In addition, shapes of clusters containing trapped water will not be spherical but rather has irregular structure like chains. Such structure favors thermal transport because they provide a long link [33]. Therefore, the overall thermal conductivity and hence thermal diffusivity of nanofluids are enhanced. When the pH is too large, the concentration of the pH adjustment reagent (NaOH) in the system increases, which causes the compression of the electrical double-layer. At pH $\geq 10$, surface charge of QDs increases, which creates repulsive forces between QDs. As a result of this effect, substantial clustering of QDs is prevented.

**Zeta ($\zeta$) potential studies based on different pH of CdSe nanofluids**

Zeta ($\zeta$) potential is a measure of the magnitude of the electrostatic or charge repulsion or attraction between particles in a liquid suspension. We calculated the variation of $\zeta$ potential and cluster radius or hydrodynamic particle size ($d$) of the QDs (table 4.2) as a function of pH by using DLS measurement. The effect of charge on the clustering process with varying pH has also been plotted in figure 4.11 which shows that an almost neutral charge is obtained at optimum pH. Therefore, it looks reasonable to infer that optimizing pH or high surface charge facilitates heat transport through increased transport efficiency. We also attempt
to link the concept of this interesting phenomena of change in thermal diffusivity with pH from the emission intensity in figure 4.6. We have the total relaxation cross section $\sigma_T = \sigma_R + \sigma_{NR}$, where $\sigma_R$ is the radiative relaxation and $\sigma_{NR}$ is the nonradiative relaxation crosssection so that $\sigma_{NR} = \sigma_T - \sigma_R$. From figure 4.6: (b) the observation of maximum fluorescence intensity at optimum pH value indicating maximum fluorescence quantum yield and minimum thermal energy generated in the medium. Our calculation showed that maximum fluorescence quantum yield is obtained at pH $\sim$4.7, where the probe beam (TL signal) intensity is minimum. It is also observed from figure 4.6. This enhanced radiative process will reduce the heat evolved through nonradiative process. This may cause reduction of $t_c$, which is the time taken to transport heat, and hence enhancement of the magnitude of diffusion coefficient. The major advantages of such materials is that they can be used both as coolant and insulator by adjusting the corresponding pH values. At low pH ($\sim$4.7), it acts as a good coolant which can be used to diffuse heat energy to the surroundings, and at high pH they can be efficient materials to trap thermal energy and act as good insulators.

4.2.3 Thermal lens studies on CdSe-metal nanofluids

Microwave rapid heating is used for the synthesis of CdSe QDs and metal NPs. For the preparation of hybrid CdSe-metal NPs, different volume ratios of colloidal Ag/Au NPs are mixed with fixed volume of colloidal
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CdSe QDs. Sharp excitonic peak in figure 4.12(a) indicates mono dispersion of the CdSe QDs and these emissions are basically from excitonic (1S_e → 1S_h) transitions. Surface plasmon resonance (SPR) peaks around 415 nm confirm the presence of Ag. The 520 nm peak in figure 4.12(c) confirms the presence of Au NPs. The shape and position of surface plasmon (SP) absorption depend on particle size, shape and the dielectric constant of the surrounding medium. The sharpness of the peaks indicates that the particle size is fairly uniform.

From figure 4.13, it is clear that by adding a particular volume fraction of metal NPs to the CdSe nanofluid, an increase in the PL emission is
observed. This emission may rely on energy transfer from the QDs to metal NPs which could be de-excited through radiative plasmon relaxation [34-36]. From figure 4.13:(b) it is clear that, at low values of volume ratio of Au NPs an additional strong band is observed in $\sim 700$ nm spectral region and at higher ratio this is quenched and the emission peak coincide with that of CdSe QDs. This exciton-plasmon interactions can give rise to modified emission properties like enhancement and quenching as seen in figure 4.13. Generally, the interplay between metal NPs and QDs involves two major phenomena: the first one is an enhancement of the local excitation field, and the second one is the modification of the radiative and nonradiative decay rates of the QDs, inducing a change of fluorescence lifetime and quantum yield. The competition between these processes results in two contradictory observations as reported in the literature: quenching of luminescence or on the contrary it’s enhancement. Different parameters play a determinant role in the quenching and enhancement mechanisms but their influence is still debated. Particularly, the spectral position and the influence of the localized surface plasmon resonance (LSPR) compared to the absorption and emission maximum of luminescent species is very decisive.

Quenching of emission and shortening of exciton lifetime in the QD - NP superstructures can be explained using a typical model based on the exciton-plasmon resonance taking place when emission peak of excitons in QDs and absorption peak of the plasmons in NPs display a spectral overlap. In a QD- NP complex, oscillators corresponding to excitons in QDs and plasmons in metal NPs couple via. simple Coulomb forces. Since QD - NP complexes are in liquid, they are randomly oriented with respect to the incident electric field [37-38]. Figure 4.14 shows TEM images of monodispersed CdSe QDs, AgNPs and Au NPs. By using the non-contact TL technique with optical interactions of material we are able to extract the thermal properties of material mainly the thermal diffusivity. The theoretical curves in figure 4.15 calculated using equation (4.1) agree very well with experimental data, which give the thermal diffusivity value for the sample at an input power of 136 mW. Finally the thermal diffusivity $D$ of the sample can be calculated using the equation (4.2). Similarly TL signal evolution were obtained for CdSe-metal nanofluid of different volume ratios and their corresponding diffusion
coefficients are obtained and plotted in figure 4.15. From figure 4.16, it is clear that the heat diffusion constant has enhanced at an optimum volume of metal NPs and it gets reduced with further addition of it. NPs composed of various materials (such as Au, Ag, and semiconductors) can efficiently release heat under optical excitation.

The mechanism of heat release under laser excitation can be explained as follows: the laser electric field strongly drives mobile carriers inside the QDs, and the energy gained by carriers gets converted into heat. Then the heat diffuses away from the QDs and leads to an elevated temperature of the surrounding medium making the nanofluid an effective coolant. Heat generation becomes especially strong in the case of metal NPs in the regime of plasmon resonance where a collective motion of a large number of electrons occur. In the case of semiconductor QDs, the heat generation rate is much weaker since heat dissipation occurs through an interband absorption process with the creation of mobile electron and hole (exciton) pairs followed by possible radiative process [39-40]. The heating effect can be strongly enhanced in the presence of several NPs. Mechanisms of interaction between NPs that could enhance the heating process are accumulative effect and Coulomb interaction. The accumulative effect comes from the addition of heat fluxes generated by single NPs [41-42]. Coulomb interaction effects leads to the partial screening of electric fields inside the NP. The total heat dissipation can increase or decrease, depending on the incident light polarization. If the NPs are in solution and randomly oriented, the average heat generation can be enhanced or reduced depending on the screening effect which
become concentration dependent. It is also suggested that, clustering of metal NPs can significantly affect the total heat generation and diffusion. This effect may also cause the variation of thermal diffusivity of CdSe-Au /CdSe-Ag complexes. Most of the studies based on the measurement of thermal diffusivity of metal nanofluids using TLS [23-24, 43-44] reported the enhancement of thermal diffusivity with metal NP in dye colloidal system. In our study we report, the heat and charge transport mechanism of QD-metal nanohybrid (NH) which can be optimized with properties of QDs and metal. The emission properties of the QD-metal nanofluid can be tuned and can also be used as an effective coolant under optimum conditions.

4.3 Photo acoustic measurements of CdSe QDs based nanofluids

Over the years numerous techniques have been developed for the optical investigation of highly scattering and opaque materials, the most common of which are diffuse reflectance [45], attenuated total reflection, internal reflection spectroscopy [46] and scattering [47]. But all these
methods have their specific limitations. During the past few years, another optical technique has been developed to investigate the optical properties of those materials that are unsuitable with the conventional transmission or reflection methodologies. This technique, called photo acoustic spectroscopy (PAS), deals with the effect of generation of acoustic waves in the specimen after illumination with a chopped or pulsed optical radiation.

PA effect was discovered by Graham Bell in 1880, when he noticed that the incidence of modulated light on a diaphragm connected to a tube produced sound [47-49]. Extensive study of photo acoustic effect in liquids and gases showed that the intensity of acoustic signal depends on the absorption of light by the material. Thereafter in the nineteenth century, it was known that the heat of a gas in a closed chamber produces pressure and volume change in this gas and during the next years many theories were developed to explain the PA effect [50-53]. According to Rayleigh this effect was due to the movement of the solid diaphragm, and Bell believed that the incidence of light on a porous sample expanded its particles, producing a cycle of air expulsion and re absorption in the sample pores. These ideas were opposed by Preece by pointing that the expansion/contraction of the gas layer inside the photo acoustic cell is the cause of the phenomenon. Mercadier explained the effect correlated
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with the thermal diffusion mechanism in which the periodic heating of the sample is transferred to the surrounding gas layer, generating pressure fluctuations. At present, the invention of sensitive and compact microphone made this area of study an interesting one. Ever since the theory of PA effect in solids was developed by Rosencwaig and Gersho, this technique has been effectively used in diverse areas of physics, chemistry and medicine [52-55].

Main difference of PA effect from other spectroscopic methods is that this is an indirect method wherein the incident energy is in the form of optical photons, which interacts with the material under investigation. The measurement is not through the subsequent detection and analysis of some of the photons, but rather through a direct measure of the energy absorbed by the material. Local warming of the sample matrix arises due to the non-radiative relaxation processes such as collisions with other molecules. Pressure fluctuations are then generated by thermal expansion, which can be detected in the form of acoustic or ultrasonic waves. In a typical experiment the sample is illuminated with an intensity modulated monochromatic radiation. If any of the incident photons are absorbed by the sample, internal energy levels within the sample are excited. Upon subsequent de-excitation of these energy levels, all or part of the absorbed photon energy is transformed into heat energy through nonradiative de-excitation processes. In PAS, we measure the acoustic signal produced by the pressure variations due to this internal heating of the sample. Hence PAS is clearly a form of optical spectroscopy.

Usual temperature sensors such as thermistors and thermopiles have inherent disadvantages for being used in PAS in terms of sensitivity, detector rise time and the speed at which measurements can be made. A more appropriate method is the measurement of heat production through volume and pressure changes produced in the sample or in an appropriate transducing material in contact with the sample. In this aspect piezoelectric transducers are employed in many cases for the detection of ultrasonic pulses in liquid and solid samples. Quartz crystals, piezoelectric ceramics such as lead zirconate titanate (PZT), lead metaniobate, and lithium niobate as well as piezoelectric polymer films can be applied
to the detection of laser-induced shock pulses.[49,56-58]

4.3.1 Calibration of PA cell

Experimental set up for the calibration of PA cell by finding velocity of sound in aluminum sheet as shown below. A Q-switched Nd-YAG laser with second harmonic frequency of 532 nm and output power of one joule has been used as the laser source. PA signal amplitude at different locations of the aluminum sheet is taken for the input pulse. Distance vs. time delay of the samples are measured and the average velocity of the PA signal was calculated. It is observed from the experiment that velocity of sound in Aluminum sheet is \( \sim 2600 \text{ m/s} \) whereas it can change from 2000 m/s to 2600 m/s theoretically. The experimental set up is shown in figure 4.17.

![Experimental set up for the calibration of PA cell by finding velocity of sound in aluminum sheet.](image)

Figure 4.17: Experimental set up for the calibration of PA cell by finding velocity of sound in aluminum sheet.

Typical photographs of the selected output signals are given in figure 4.18.
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4.3.2 Measurement of Photo acoustic signal by pulsed Nd: YAG laser

For the generation of efficient PA signals, laser pulse durations in the range of tens to hundreds of nanoseconds are required. To obtain adequate penetration depth, it is also desirable to use a wavelength suitable to the samples. These requirements can be met, in part, by using the second harmonic frequency from the Q-switched Nd: YAG laser operating at 532nm, at a pulse repetition frequency of 10 Hz, with one joule pulse energy.

Measurements of PA signal amplitude with different input laser intensity

We have observed PA signal variation at different input power levels for samples using pulsed Nd-YAG laser with 532 nm wavelength. Experimental set up for the study of variation of PA signal amplitude with different input power for CdSe QDs based samples is described in the 2nd chapter (figure 2.5). The synthesis of the metal NPs and CdSe QDs for the study were carried out by microwave rapid-heating method. Absorption spectra of the prepared CdSe QDs were recorded using UV-Visible spectrophotometer. The samples are labelled as $S_1$, $S_2$ and $S_3$ where $S_1$ is CdSe nanofluid incorporated with Rh-6G dye solution of $10^{-4}$ M and $S_2$ is a mixture of sample $S_1$ with Au nanofluid in volume ratio 1:0.5 and $S_3$ is sample $S_1$ with Ag nanofluid mixture in volume ratio...
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1.0.5. CdSe QDs based nanofluid with Rh-6G dye is taken as the reference sample ($S_1$) and sample $S_2$ shows maximum PA signal output where Au NPs are incorporated to $S_1$. It is observed from figure 4.19 that as power increases, amplitude of the PA signal also increases and an abrupt change occurs at a threshold. It is also observed that the output of the PA signal varies differently for samples and it is higher in the case of samples incorporated with Au metal NPs. Generation of PA signal, on introducing metal NPs is a nonlinear function of pump beam intensity as clearly seen in the figure 4.19. This enhancement can be attributed to Brownian motion, nano convection, and heat diffusion on addition of Au metal NPs to the fluid. The Variation of PA signal amplitude of CdSe QDs based samples with different input energies are tabulated in Table 4.3. The introduction of metal NPs in CdSe enhance thermal diffusivity which reduce the depletion of pump in the coupling medium thereby enhancing the PA signal amplitude with pump power. It can be seen that in CdSe sample ($S_1$) the PA signal propagation is linear with pump power while it is nonlinear in samples with metal NPs ($S_2$ and $S_3$) added. The observation is also supported by the enhanced

![Figure 4.19: Variation of PA signal amplitude at different input power for $S_1$, $S_2$ and $S_3$ samples](image)
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thermal diffusivity of metal incorporated CdSe samples. Typical images of the PA signal output from DSO for different samples ($S_1$, $S_2$ and $S_3$) are shown in figure 4.20.

![Typical images of the PA signal output from DSO for different samples ($S_1$, $S_2$ and $S_3$)](image)

Figure 4.20: Typical images of the PA signal of samples ($S_1$, $S_2$ and $S_3$)

4.3.3 Measurement of photo acoustic spectrum using continuous wave light source

PA signal generation has also been done with modulated chopped light from the continuous wave using a Xenon lamp. The synthesis of the samples were carried out by microwave rapid-heating method. The products were collected for size characterizations after being cooled down to room temperature. Absorption spectra of the prepared CdSe QDs were recorded using UV-Visible Spectrophotometer. The samples are labeled as $S_1$, $S_2$ and $S_3$ where $S_1$ is CdSe nanofluid incorporated with Rh-6G

<table>
<thead>
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<th>Energy (m J)</th>
<th>PA signal voltage (mV)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_1$</td>
<td>$S_2$</td>
</tr>
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</tr>
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<td>84.8</td>
<td>74</td>
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<tr>
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<td>848</td>
</tr>
<tr>
<td>238</td>
<td>480</td>
<td>1120</td>
</tr>
</tbody>
</table>

Table 4.3: Variation of PA signal amplitude with different power in CdSe QDs based samples
dye solution of $10^{-4}$ M and $S_1$ is mixture of sample $S_1$ with Au nanofluid in volume ratio 1:0.5 and $S_3$ is a mixture of sample $S_1$ with Ag nanofluid in volume ratio 1:0.5.

In the experimental section, the sample is taken in the PA cell which is firmly held on a holder, and properly aligned with the laser beam axis. The modulated chopped light from the Xenon lamp is focused and passed through the sample in the PA cell. The acoustic signals generated are detected by the PZT, and recorded using a lock in amplifier. When readings are taken for one sample, it is pipetted out and the next sample is filled, without moving the PA cell. The experiment is repeated for different samples by varying wavelengths using filters. The experimental arrangement of the PA study is shown in 2nd chapter(figure 2.4). It consists of a light beam from a standard solar irradiation of 1000W Xe lamp (Oriel 6269). A water column kept after the Xenon lamp will effectively filter out the infrared portion of the spectrum. Light coming out of the Xe lamp is intensity modulated using a mechanical chopper(Ithaco HMS 230) and is focused to the PA cell. The acoustic signal is processed using a lock-in-amplifier (Stanford Research Systems SR 510).

PA cell contains the samples, and a fabricated piezoelectric transducer chamber to detect the acoustic signals [58]. The cell is of stainless steel body with an inner diameter of 2 cm and length 5 cm. Glass windows are fixed with flanges and O-rings to the cell for the entry and exit of the laser beam. One side of the cell has an opening in which the transducer chamber is fixed. A Lead Zirconate-Titanate (PZT) disc of 4 mm thickness and 15 mm diameter is the piezoelectric transducer that is contained in this chamber. The PZT disc is spring-loaded against the thin front diaphragm as shown, with a thin layer of silicon grease applied between them to ensure good acoustic coupling. The PA signal is taken out through the BNC connector. Due to its high sensitivity a few $\mu$V of electrical signal could directly be obtained from the transducer with absorbing sample in the cell [55].

Absorption spectra and the corresponding PA spectra of the samples $S_1$, $S_2$ and $S_3$ are shown below in figure 4.21.
4. Thermo-optic studies on CdSe quantum dots based materials

Figure 4.21: (a) Absorption spectra, (b) PA spectra and (c) Emission spectra of the CdSe based samples, S₁, S₂ and S₃.

It is observed that the output PA spectrum is similar to the absorption spectrum and can be used to identify the absorbing energy levels of the samples. We observed that the change from optics signal to PA signal indicates the transformation of transverse wave to longitudinal wave where direct measurement of absorbed energy is observed. We also observed from the spectrum that there is a transfer of energy due to the exciton-plasmon interactions especially in the case of CdSe QDs based nanofluid incorporated with Ag NPs. This enhancement can be attributed to Brownian motion, nano convection, and heat diffusion on addition of Ag metal NPs to the fluid. Depending on the sample and the pump flux at different wavelengths nonlinear and/or excited state absorption can occur in a typical nanofluid medium. Various non-radiative relaxation channels are active in a highly excited large molecule, which
will lead to the generation of photo acoustic signals. Analysis of these PA signals can yield valuable information about the nature of absorption and the distribution of various energy levels of the molecule. Using the same experimental setup in figure 2.4 a relation ship between the amplitude and modulation frequency of samples $S_1$, $S_2$ and $S_3$ are studied and the results are shown in figure 2.4. The linear nature for plot of

![Figure 4.22: Log frequency versus log amplitude of $S_1$ and $S_2$ and $S_3$ samples.](image)

samples $S_1$ and $S_2$ and $S_3$ indicates that, due to the relatively high thermal diffusivity, the heat generated at the sample interface is transmitted instantaneously to other side without leaving any temperature gradient inside the sample. But for materials of very low thermal diffusivity, this cannot be applied [59-62].

### 4.4 Conclusion

- CdSe QDs prepared by reflux method shows variation of energy band gap of the NPs from 2.56 eV to 2.35 eV as the particle size increased during the reflux period.
4. *Thermo-optic studies on CdSe quantum dots based materials*

- Studies on size dependent variation of thermal diffusivity of CdSe QDs based nanofluid using laser induced mode matched thermal lens technique shows a decrease in thermal diffusivity with particle size. This trend is theoretically supported by Brownian motion of NPs and liquid layering around NPs, where rapid heat transports in smaller particles cause high thermal diffusivity.

- Influence of pH on thermo optic properties of MSA capped CdSe QDs prepared by microwave irradiation method shows a significant increase in thermal diffusivity with optimum pH.

- At this optimum value of pH, increase in surface charge of NPs increases repulsive forces thus resulting in reduced agglomeration of QDs which enhances mobility and heat transport. The major advantages of such material is that they can be used as both coolant and insulator by adjusting the corresponding pH values.

- A study on charge and heat energy transfer dynamics of directly coupled mixtures of CdSe QDs with metal NPs using TL and photoluminescence techniques shows an effective increase of the absorption cross section of the semiconductor nanostructure and modified emission properties due to the exciton-plasmon interactions.

- Quenching of emission and shortening of exciton lifetime in the QD-NP superstructures can be explained using a typical model, based on the exciton-plasmon resonance occurring due to the overlap of the emission peak of excitons in QDs and absorption peak of the plasmons in NPs.

- In our study the heat and charge transport mechanism of QD with metal NPs can be optimized with properties of QDs and metal. The emission properties of the QD with metal nanofluid can be tuned and it’s potential to be used as a coolant is also discussed.

- Calibration of PA cell by finding the velocity of sound in aluminium sheet using pulsed Nd-YAG laser with 532 nm wavelength laser source shows that velocity of sound in aluminum sheet is ~2600 m/s in experiment whereas it can vary from 2000m/s to 2600m/s theoretically.
4. Thermo-optic studies on CdSe quantum dots based materials

- Variation of PA signal amplitude with different input energies are studied. Output of the PA signal varies differently for samples and it is higher in the case of samples incorporated with metal NPs.

- Enhancement of PA signal with CdSe QDs based nanofluid sample incorporated with Au NP can be attributed to Brownian motion, nano convection, and heat diffusion on the addition of metal NPs to the fluid.

- Measurement of Photo acoustic spectrum using chopped optical radiation at different wavelength from a Xenon lamp gives information about the absorption regions of the CdSe QDs based nanofluids.

- The linear nature of the log frequency vs. log amplitude curve indicates that at relatively high thermal diffusivity value of the sample, the heat generated at the sample interface is transmitted instantaneously to other side without leaving any temperature gradient inside the sample.

4.5 References


4. Thermo-optic studies on CdSe quantum dots based materials


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