OPTICAL ATTENUATION MODELLING OF PbSe$_x$S$_{1-x}$ QUANTUM DOTS WITH VEGARD'S LAW AND BRUS EQUATION USE

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Lead Selenide Sulphide (PbSeS) nanomaterial, a chalcogenide semiconductor which has maximum radiation attenuation can be tuned for required wavelength in the range from ultraviolet to infrared. Hence it has received much interest among researchers. Further, the electronical and optical properties of PbSeS Quantum Dots were modeled by Brus Equation, Vegard's law and Interpolation principle calculations. Therefore, in this paper, we have studied the progress and structural parameters of PbSeS at different energy band gap and wavelength. The obtained results confirms that the attenuation of radiation versus wavelength is inversely proportional to the bandgap and also the mole fraction of lead increases with decrease in energy band gap. These findings confirm the quantum effects of the material and which can be utilized in solar cell and optoelectronics applications. The results are compared with available experimental data that supports the validity of the model reported.

1. Introduction

Generally, nano-sized materials are considered as promising candidates for recent research applications in various fields. Specifically, quantized semiconducting nano crystallites are called as Quantum Dots (QDs) or Nano Dots and a typical QDs composed by a few hundreds of atoms. One of the most important property of functional QDs is controlled attenuation of radiation and high photo-stability at required wavelength. These properties can be applied in various optoelectronics and solar cell applications. The nonlinear and linear optical properties of QDs and its quantum confinement effects can be analyzed by invoking quantum confinement phenomena [1-3]. The Density of States (DOS) highlights the features of Quantum confinement effects in zero dimensional Quantum Dots system. The DOS of QDs system describes the density of available energy states per unit energy [4]. For QDs systems the confinement produces series of discrete energy levels which explain the atomic effects of QDs relating to electrical and optical properties.

In semiconductor nanomaterials, the electron-hole pair created by absorption of photon is called as exciton. The energy required for an exciton creation is slightly lower than energy band gap of the material due to Columbic interaction between hole and electron. After this process the exciton ends as the electron-hole pair combines [5]. The quantum confinement effect occurs when nanomaterial's radius is smaller than the exciton Bohr radius, in such case the quantization of energy levels occurs as in Fig. 1. The optical spectroscopy result of quantum confinement confirms the changes in absorption of light with different energy levels of the material. The larger QDs exhibits red shifted with small energy band gap and smaller QDs exhibits blue shifted with large energy band gap.

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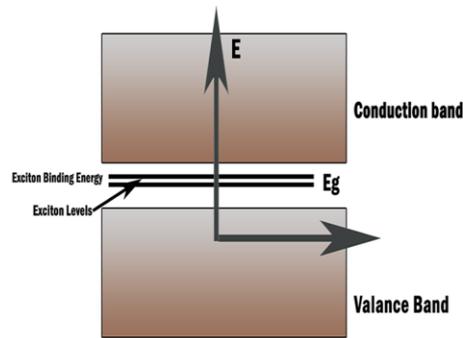
Fig. 1. Energy level of an exciton in semiconductor with conduction and valence band.

In semiconducting nanomaterials, quantum confinement effects are mostly studied for cadmium based compounds such as CdSe, CdS, CdS_xSe_{1-x}, etc. Due to very small exciton Bohr radius, these materials cannot strongly confined hence called as wide band gap semiconductors. Quantum confinement effects are likely to be strong in narrow band gap semiconductors for which exciton Bohr radius and dielectric constant are large [6]. QD's are highly influenced size which impacts the energy band gap cause change on emission and absorption spectra. Tuning the energy band gap of QDs is an important task to design new devices. This can be done by varying the mole fraction of the main constituent element of ternary alloy. Larger QDs possess smaller value of band gap energy which results in absorption of light with longer wavelengths, similarly smaller quantum dots has larger band gap energy with shorter wavelengths [7].

Attenuation is reduction of the intensity of light waves as they propagate through a medium. In depth, attenuation in optics is the reduction in intensity of the light beam (or signal) with respect to distance traveled through a transmission medium and therefore well-defined at specified wavelength. Therefore, from technology point of view the energy bands diagram is significantly defines the major parameters of the device's threshold of absorbed radiation, photoelectric threshold wavelength. When we consider solid state device as light emitting devices (LED's and laser diodes) two major parameters of consideration are: photoelectric threshold wavelength (that precise threshold wavelength of detection) and attenuation spectra (that precise depth of radiation penetration and therefore spectral characteristic of detection).

Lead chalcogenides occupy a unique place in group IV-VI semiconductors. Narrow band gap is one of the most fascinating properties of lead chalcogenides. Further, size dependent properties can be achieved by blending of lead chalcogenide with indium and cadmium. It also has large exciton Bohr radius [8] compared to cadmium. Moreover they possess large dielectric constant [9] and small effective mass of electron and hole [10]. Due to small electron and hole effective masses of lead chalcogenides it exhibits strong size quantization which provides an exceptional wide wavelength range viz., UV to infrared (400-3000nm). Therefore these properties can improve significantly the devices in the range of infrared such as [11, 12] Quantum dot switches [13, 14] and solar cells [15, 16]. Further, group IV-VI semiconductors and heterostructures could form quaternary and ternary alloys with direct band gap. Most of alloy composition with high absorption coefficients can be used as a perfect material for solar cell fabrication. Amongst different semiconducting materials, the elements such as PbSe and PbS have direct band gap at the L point of the Brillouin zone [17].

Ternary semiconductor such as PbSeS from the group of IV-VI semiconductors are most commonly used in infrared optoelectronics. It offers potential uses for intermediate wavelength detector and produces unique response to cover wavelength ranging from 3000-5000 nm [18]. Hence, this draws wider attention on these materials to design quantum dot solar cells and to improve the conversion efficiency.

This research work could help further studies for researchers who are experimentally involved in preparing ternary alloys and supports in certain change in amount of additives in alloy. The electronic properties of $PbSe_xS_{1-x}$ will change as 'x' function varies [0-1] which directly influences many applications on Pb based devices under different conditions. The electronic

properties of this alloy was studied by using Vegard's law [19-21] and optical properties of the alloy was studied by Brus equation [22]. In this research, an attempt has been made to observe how Brus equation and Vegard's law can be used to analyze attenuation of radiation versus wavelength and energy band gap of this ternary alloy.

2. Theoretical modeling of QDs

The energy band gap of QDs depends on dimension and effective mass of excited electrons and holes of the material. In $PbSe_xS_{1-x}$ QDs, mole fraction of Pb acts as a main constituent element to vary energy bandgap. Absorption of wavelength can be determined by corelating wavelength and energy band gap.

2.1. Energy band gap variation of PbSeS by Vegard's Law analysis

In ternary compounds, energy band gap changes by varying two solid materials. Therefore, in PbSeS QDs, Pb and Se have been varied with respect to doping concentration and temperature. To analyze, Let 'X' be the % fraction of Pb doping relative to selenide and then $E_g(PbS)$ represents the energy band gap of lead sulphide, $E_g(PbSe)$ represents the energy band gap of lead selenide and 'b' represents bowing parameter of the $PbSe_xS_{1-x}$ alloy. Hence, the energy band gap of alloy represented by equation (1).

$$E_{g,PbSeS}(X) = X\, E_{g,PbSe} + (1-X)\, E_{g,PbS} - bX(1-X) \tag{1}$$

The role of bowing parameter 'b' is more important to investigating the energy band gap of ternary and quaternary alloys [23]. The bowing parameter in semiconductor nanomaterial can be described by quadratic interpolation principle as given in equation (2), $E_g(PbS)$ and $E_g(PbSe)$ are intrinsic energy band gap of semiconductors. The degree to which the curve aberrate from the linear fit is described by the bowing parameter.

$$b(X) = \frac{X\, E_{g,PbSe} + (1-X)E_{g,PbS} - E_{g,PbSeS}(X)}{X(1-X)} \tag{2}$$

2.2. Wavelength analysis of Brus Equation

L. E. Brus demonstrated first theoretical calculation for semiconductor nanocrystal through Effective Mass Approximation (EMA) technique. In this technique an exciton is confined to spherical volume of crystallite and mass of holes and electrons is compensated with effective mass of hole (mh^*) and effective mass of electron (me^*) which is used to describe the wave function [23].

$$E_g(PbSe_xS_{1-x}\,QDs) = E_g(bulk) + h^2/8R^2\left(\frac{1}{me^*} + \frac{1}{mh^*}\right) - \frac{1.786e^2}{4\pi\varepsilon_o\varepsilon_r R^2} \tag{3}$$

where, E_g (bulk) is the energy band gap of bulk semiconductor.
E_g (QD) is the energy band gap of QDs.
me^* is represented as effective mass of excited electrons.
mh^* is represented as effective mass of excited holes.
R is represented as radius of the QD.
ε_o is represented as permittivity of vaccum
ε_r is represented as permittivity of concerned semiconductor material.
h is Planck's constant.
e is charge of electron.
E*Ry is Rydberg energy

Later Kayanuma resolved the electron - hole spatial correlation effect and modified the Brus equation. The size dependence on energy band gap of quantum dots can be computed as given in equation (4) [24].

$$E_g(PbSe_xS_{1-x}\ QDs) = E_g(bulk) + h^2/8R^2\left(\frac{1}{me^*}+\frac{1}{mh^*}\right) - \frac{1.786e^2}{4\pi\varepsilon_0\varepsilon_rR^2} - 0.248\ (E^*Ry) \qquad (4)$$

From equation (4), the first term represents energy band gap of bulk semiconductor material, which is the physical characteristics of the materials, the second additive term of the equation (4) is dependent on the inverse of square of the radius of QDs, which accounts for the additional energy due to quantum confinement. The third term on right side of equation (4) is high dielectric constants due to Columbic interaction of energy which are negligible for some materials, the last term represents spatial correlation effect and is substantial for low dielectric constant of semiconductor materials [25, 26]. So the Brus equation was rearranged and used in this research is given in equation (5).

$$E_g(PbSe_xS_{1-x}\ QDs) = E_g(bulk) + h^2/8R^2\left(\frac{1}{me^*}+\frac{1}{mh^*}\right) \qquad (5)$$

The important aspects of Brus equation is used to determine the wavelength of semiconductor QDs. The radius of QDs changes the wavelength of emitted light due to quantum confinement effect. By varying the parameter 'R' from 1-10nm from equation (5), the wavelength of QDs can also be varied. It is to be noted that, QD confinement region is much lesser than the exciton Bohr radius or comparable to the De Broglie wavelength.

2.2.1. Calculation of effective mass of hole and electron
The effective mass of hole and electron can be calculated by interpolation principle as given in equation (6) and (7); it is very important parameter to determine energy band gap [27].

$$m_{e^*}\ PbSe_xS_{1-x} = m_e\ PbS + X\ (m_e\ PbS - m_e\ PbSe) \qquad (6)$$

$$m_{h^*}\ PbSe_xS_{1-x} = m_h\ PbS + X\ (m_h\ PbS - m_h\ PbSe) \qquad (7)$$

2.3. Exciton Bohr radius variation
The exciton Bohr radius could define the extension of exciton in semiconductors QDs ranging from 1nm - 10nm. By analogy to the hydrogen atom the most possible distance between electron and hole in an exciton which is supposed to be known as exciton Bohr radius (r_B) [28, 29]. The exciton Bohr radius can be calculated from equation (8).

$$r_{B=}\ \frac{\varepsilon\hbar^2}{e^2}\left(\frac{1}{me^*}+\frac{1}{mh^*}\right) \qquad (8)$$

$\hbar$– Reduced Planck's constant
e – Charge of carrier
ε- Dielectric constant of material

If the exciton Bohr radius is smaller than QD radius, the quantum confinement effect will no longer hold. Therefore, the energy band gap of the material will not practically same as derived from the Brus equation.

3. Theoretical parameters details

The following parameters have been taken into account for analysis, which are adapted from the following references.

Table 1. Parameters of different elements.

Parameters	Value	Reference
Energy gap value of $(PbSe_xS_{1-x})$	(0.6-1.0)eV	30
Effective mass of electron (PbS)	0.12mo	31
Effective mass of hole (PbS)	0.11mo	31
Effective mass of electron (PbSe)	0.084mo	31
Effective mass of hole (PbSe)	0.070mo	31
Energy gap value of (PbSe)	0.278eV	32
Energy gap value of (PbS)	0.41eV	32
High frequency dielectric constant $(PbSe_xS_{1-x})$	~12.1	33

mo-Mass of electron at rest

4. Results and discussion

The results for bowing parameter 'b' can be calculated from equation 2 by varying the parameter 'X' (0.1 to 1.0). The calculated value of bowing parameter is -0.185 and there is good accord between proposed model and experimental verdicts [34].
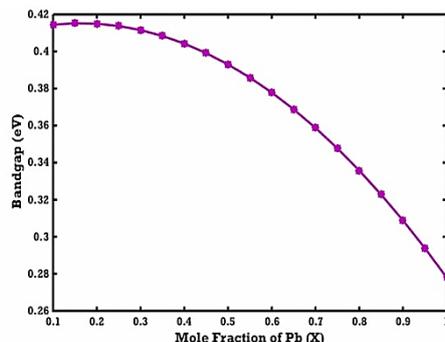
Fig. 2. Energy band gap variation of $PbSe_xS_{1-x}$ QDs with mole fraction of Pb.

At first, by varying the mole fraction of Pb, the possible energy bandgap of PbSeS QDs are calculated. It varies from 0.41eV to 0.27eV for X= 0.1 to 1.0. As the mole fraction of Pb increases, the energy bandgap of $PbSe_xS_{1-x}$ decreases to lower level as shown in Fig. 2. $PbSe_xS_{1-x}$ QDs finds an excellent energy band gap by creating more electron-hole pairs

The exciton Bohr radius of $PbSe_xS_{1-x}$ was calculated by varying the mole fraction of Pb and the results shows that the mole fraction of Pb increases with decrease in exciton Bohr radius due to effect of doping. From Fig. 3, it is observed that the calculated value of exciton Bohr radius is 10.5 nm for X=0.1. Similarly the obtained value is 1.04 nm for X = 1. The exciton Bohr radius is higher than the diameter of QDs; thus material is under strong confinement region. On varying the mole fraction of Pb from 0.1 to 1.0.The obtained radius range of QDs (i.e 1.04 to 10.5 nm)

indicates that the larger exciton Bohr radius would provide wide range of tunability and which can cover UV, visible and infrared range of electromagnetic spectrum.

The optimum energy band gap can be varied by varying the size of QDs and which has the ability to find various absorption range. From equation (5), the radius 'R' values ranging from 1 nm to 10 nm and the absorption wavelength ranges from 149 nm to 1832 nm which covers UV and infrared ranges.
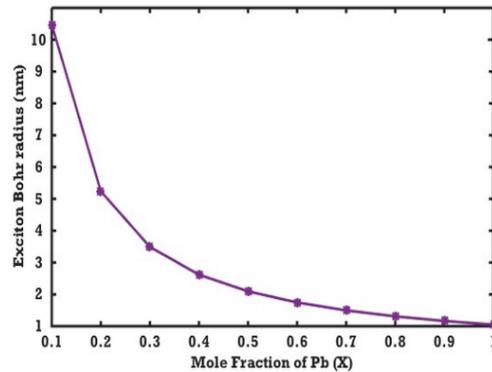
Fig. 3. Exciton Bohr radius Vs Mole fraction of Pb.

Fig. 4 shows that the QDs radius of 1 nm and the corresponding absorption wavelength of 202 nm lie in UV range. When the size of the QDs is slightly increased from 1.5 to 2.5 nm the absorption frequencies will be in visible range (405-834 nm). For solar cell, the energy of sunlight is predominant source for converting light energy to electrical energy. The sunlight reaches ground surface at the wavelength range of around 4 % of UV, 43 % of visible and remaining 53 % in near infrared and infrared ranges. The visible range is dominant source for solar cell which converts maximum amount of light energy in to electrical energy. Hence the perfect wavelength to absorb more sun rays to generate more electron–hole pairs for producing maximum amount of current generation. In $PbSe_xS_{1-x}$ QDs we can easily achieve this wavelength and also it is observed that it can be tunable to achieve near infrared range and infrared ranges.

QDs radius is tuned from 2.5-10 nm and the corresponding absorbed wavelengths are 834-1893 nm, respectively. Usually, in conventional solar cell materials, the near infrared and infrared ranges of sunlight are mostly dissipated in terms of heat. Hence, the conversion efficiency was not good enough. Whereas, $PbSe_xS_{1-x}$ QDs solar cell would have the ability to utilize the near infrared and infrared ranges and thus we can improve the efficiency of solar cell by generating more electron-hole pairs.

Further it is observed that $PbSe_xS_{1-x}$ QDs is tuned to achieve 1310 nm wavelength at 4 nm radius and 1550 nm wavelength at 5 nm radius. This is highly compactible for fabrication of Light Emitting Diodes (LEDs) and Laser Diodes (LDs) for fiber optic communication sources working under the band ranging between 1310 nm and 1675 nm and in accordance with experimental results [35-37]. For smaller QDs absorb small wavelengths and larger QDs absorb higher wavelengths.
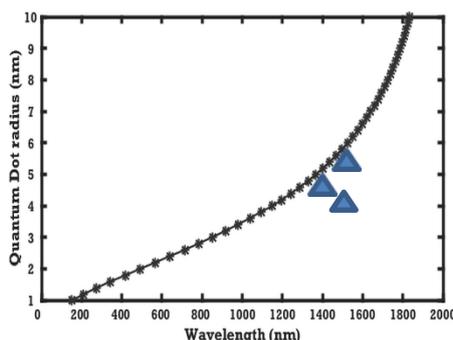
*Fig. 4. QDs radius Vs. Attenuation of radiation at Wavelength of PbSe$_x$S$_{1-x}$ QDs
and experimental results shown by solid triangle*

Hence, considering the observed results, it is confirmed that the wavelength is inversely proportional to energy band gap of QDs materials. Also, smaller QDs are red shifted and larger dots are blue shifted. The energy band gap has decreased on increasing the concentration of Pb which confirms the quantum confinement effect. Whereas, the Pb concentration need to be reduced to achieve high quality red shifted QDs which can absorb more energy from sun rays and produce high conversion efficiency.

5. Conclusions

For the successful performance of PbSe$_x$S$_{1-x}$ QDs in solar cell and optoelectronics devices, it requires three important parameters viz., tunable energy bandgap, attenuation of radiation versus wavelength and mole fraction variation of Pb. In this study we examined the tunable energy bandgap and attenuation of radiation versus wavelength of PbSe$_x$S$_{1-x}$ QDs from UV to infrared ranges for solar cell and optoelectronic devices applications. The obtained results suggests that PbSe$_x$S$_{1-x}$ QDs is a favorable semiconductor material for the fabrication of optoelectronic devices with good stability. This observation can also be used in single or multi-layer solar cells, LEDs and laser diodes in future.

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