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Original Article

Optical Properties of PbSe, PbS, and PbTe Semiconductor Quantum Dots and their Applications

H. I. Ikeri[1], S. T. Harry[2], E. I. Achuka[3], C N. Eze[4], O. K. Asielue[5], N. D. Ndubueze[6]

[1]*Department of Physics, Kingsley Ozumba Mbadiwe University Ogboko Ideato Imo.*
[2]*Department of Physics, Ignatius Ajuru University of Education, Rumuolumeni Port Harcourt.*
[3]*Department of Physics, Kingsley Ozumba Mbadiwe University Ogboko Ideato Imo.*
[3]*Department of Physics and Astronomy, University of Nigeria Nsukka, Enugu.*
[4]*Department of Physics, Federal University Mina.*
[4]*Department of Physics, Enugu State University of Science and Technology.*
[4]*Department of Physics and Astronomy, University of Nigeria Nsukka, Enugu.*
[5]*Department of Science Laboratory Technology Delta State Polytechnic Ogwashi.*
[6]*Department of Physics, Kingsley Ozumba Mbadiwe University Ogboko Ideato Imo.*

[5]*Corresponding Author : asieluekingsley@gmail.com*

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Abstract *- Optical properties of PbSe, PbS, and PbTe semiconductors in confinement regimes have been studied using the Brus equation. The results indicate that QDs exhibit size-dependent optical behavior and, hence, tunable bandgaps and emission wavelengths as a consequence of quantum confinement. As the QD size decreases, the absorption edge and emission peak are blue-shifted for all three materials. It is found that PbSe QDs display significant quantum confinement even at larger sizes. Due to its relatively large exciton Bohr radius (~46 nm), as the size decreases from 10 nm to 2 nm, the bandgap increases from 0.27 eV to over 1 eV, shifting absorption and emission into the near-infrared (NIR), leading to applications into NIR photodetectors, solar cells, and biomedical imaging. Also, PbS QDs exhibit significant quantum confinement effects at smaller sizes due to their smaller exciton Bohr radius (~20 nm) compared to PbSe. The bandgap increases from 0.41 eV to around 1.5 eV as the size decreases from 10 nm to 2 nm, shifting absorption and emission from the NIR into the visible range. This is utilized in solar cells, visible to NIR photodetectors and LEDs. Furthermore, PbTe QDs also exhibit pronounced quantum confinement effects because of their relatively large exciton Bohr radius (~46 nm). The bandgap increases from 0.32 eV to around 1 eV as the size decreases from 10 nm to 2 nm, shifting absorption and emission into the NIR and Mid-Infrared (MIR) regions, making them excellent materials for infrared detectors, thermoelectric and MIR applications. Among the semiconductor materials studied, PbS QD typically exhibits the largest increase in bandgap with decreasing size, making them suitable for applications requiring larger bandgap tunability, followed by PbSe and PbTe. These different optical characteristics are due to their unique electronic properties and exciton Bohr radii.*

Keywords *- Quantum dot, Quantum confinement, Charge carrier, Brus equation, Optical properties, Bandgap.*

1. Introduction

PbSe, PbS, and PbTe semiconductor Quantum Dots (QDs) have enticed both researchers and industries due to their unconventional and exotic optical and electronic characteristics, intrigue with quantum confinement effect such as the splitting of the continuum conduction band into discrete levels, increased and tunable band gap, contributing potentially for several applications such as optoelectronics, biomedical imaging, sensors, and solar cell technology. An interesting phenomenon which characterizes semiconductors in the nanoscale regime (QDs) is the ability to control their absorption and emission spectra by controlling their sizes, known as the quantization effect.

Nanosized semiconductors are quantum structures in which the motion of the charge carriers is confined in one or more directions by potential barriers, in contrast to bulk semiconductors that have their charge carriers free to move within their respective bands in all the 3D directions [1][2]. The semiconductor nanomaterials exhibit fascinating properties when reducing their dimensionality from 2D to 1D or 1D to 0D [3]. In a 2D quantum well, the charge carriers are confined in one direction, and the energy is only continuous in the two-dimensional space. In 1D quantum wire, the carriers are confined in two directions, and the energy is continuous in one dimension. In 0D quantum dots, the charge carriers are confined in all three spatial directions, and there is a zero-

dimensional degree of freedom, as shown in Figure 1[4]. A QD is a miniscule spot of matter that is typically concentrated into a single point and, hence the name dot.

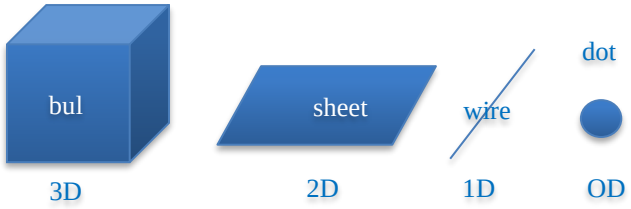

Fig. 1 Schematic representation of quantum confinement in different directions

QDs are semiconductor nanostructures with a diameter ranging between 1 nm and a few tens of nanometres, grown from semiconductor materials. The ultra-small size of QDs results in quantum confinement, which occurs when the physical dimension of a material is comparable to bulk exciton Bohr radius (A measure of the size of an exciton, which is a bound state excited electron in the conduction band and the hole it leaves behind in the valence band) as illustrated in Figure 2[5].

The confinement of carriers in QDs dramatically modulates the charge carrier states such that the energy levels that the carriers inhabit become discrete, with a finite separation between them, thereby enabling the development of new materials with significant milestones [6][7].

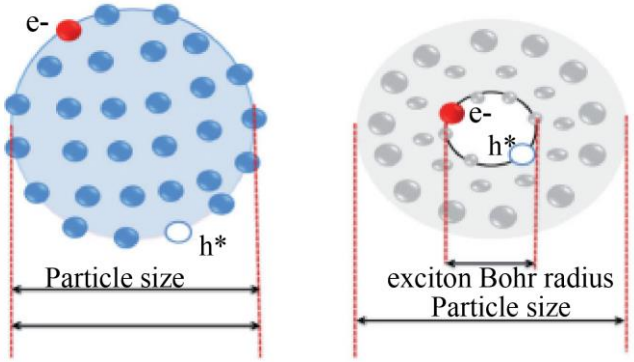

Fig. 2 (A) Formation of excitons. (B) Comparison of exciton radius and QD size

The bandgap energy of quantum dots is the energy difference between the valence band maximum and the conduction band minimum of the material, which can be tuned by changing the size of the QDs [8]. In bulk materials, the bandgap energy is a fixed property.

However, in QDs, due to the confinement of charge carriers, they exhibit discontinuous energy levels of the conduction band and valence band, accompanied by a bigger bandgap energy that increases as the size of the QDs decreases, as depicted in Figure 3[9]. This is because the electron and hole are squeezed in a smaller volume, leading to higher energy levels [10].

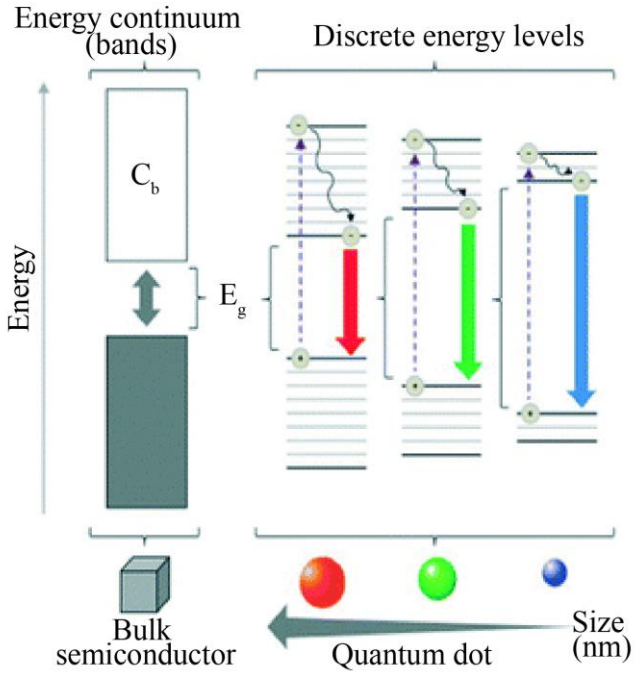

Fig. 3 The colour and size of the QD based on the energy level properties

This indicates that big dots make red light and small dots make blue light, with intermediate-sized dots producing green light (and the familiar spectrum of other colours, too). As a result, changing the size of a QD controls how it absorbs and emits energy [11]. This behaviour makes them appealing to a wide range of applications. In this paper, the optical properties of pbse, pbs and pbte semiconductor QDs have been studied using the Brus equation.

2. Theoretical Framework

The relationship between the bandgap Eg and the QDs size (R) can be explained by the Brus equation, which for spherical QDs is given by [12]:

$$E_{gap}(R) = E_{gap}^{bulk} + \frac{h^2\pi^2}{2R^2}\left(\frac{1}{m_r^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_r R} \quad (2.1)$$

The energy (E) of a photon is related to its wavelength (λ) by the equation:

$$\lambda = \frac{hc}{E} \quad (2.2)$$

Where:

$E_{gap}(R)$ is the size-dependent energy gap of the QDs., E_{gap}^{bulk} is the bulk energy gap of the material, $\hbar$ is the reduced Planck's constant, R is the radius of the QDs, m_e^* is the effective mass of the electron, m_h^* the effective mass of the hole, e is the elementary charge, ϵ_0 is the permittivity of free

space, ϵ_r is the relative permittivity (dielectric constant) of the material.

3. Materials and Methods

In this paper, the Brus equations described in equations 2.1 and 2.2 are respectively used for the computation of bandgap energy and emission wavelength of different sizes of PbSe, PbS, and PbTe (QDs). Bandgap and wavelength are plotted against various sizes in order to investigate their optical properties. The experimental parameters used for the computation are effective masses of electron M_e^* and hole, M_h^* expressed in units of the rest mass of the electron m_o, band gap of bulk semiconductors $E_{g(bulk)}$, specifically for group IV-VI (PbSe, PbS and PbTe) QDs as shown in Table 1.

Table 1. The Group IV-VI QDs experimental parameters used for the study

Quantum dots	M_e^x	M_h^x	$E_{g(bulk)}$ at 300k
PbSe	$0.05m_o$	$0.04m_o$	0.27eV
PbS	$0.25m_o$	$0.25m_o$	0.37eV
PbTe	$0.17m_o$	$0.20m_o$	0.32eV

4. Results and Discussion

The plot of the emission wavelength of PbSe, PbS, and PbTe QDs against their sizes is shown in Figure 4. The result shows that as the diameter of QD decreases, the optical wavelength shifts to shorter values (higher energy). This is due to the increase in the energy difference between the conduction and valence bands from the quantum confinement effect.

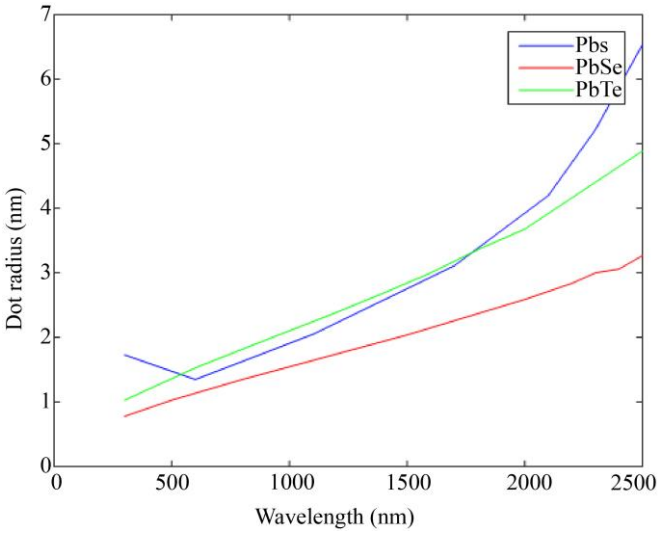

Fig. 4 Dot radius (size) versus wavelength

As the size of PbSe decreases from 8 nm to 2 nm, the optical wavelength shifts from the mid-infrared (~2000 nm) to the near-infrared (~1000 nm). Also, as the size of PbS decreases from 8 nm to 2 nm, the optical wavelength shifts from the NIR (~1600 nm) to the visible region (~800 nm).

In addition, as the size of PbTe decreases from 8 nm to 2 nm, the optical wavelength shifts from the MIR (~2000 nm) to the NIR (~1000 nm).

The plot of the optical bandgap of PbSe, PbS, and PbTe (QDs) against their sizes is shown in Figure 5.

The results show an increase in bandgap energy as the size of the QDs decreases, leading to blueshift.in absorption edge and emission peak, as depicted in Figure 6.

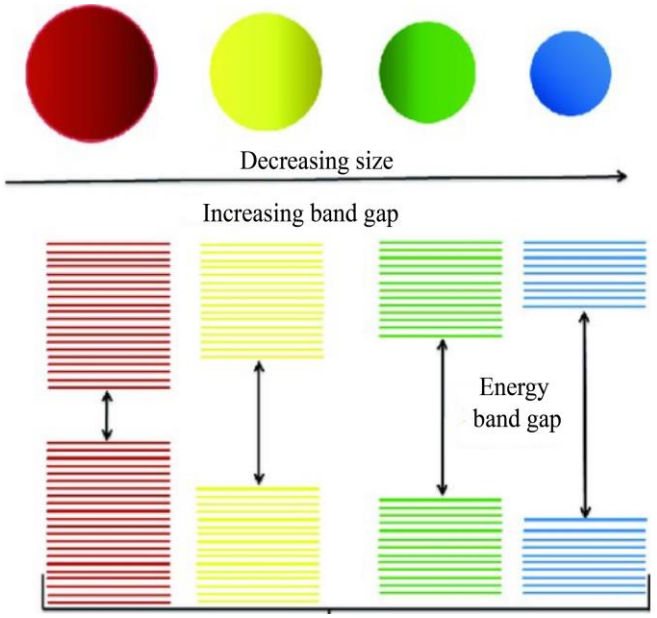

Fig. 5 Increased bandgap with decreasing size

The increase in bandgap with decreasing size is due to the quantum confinement effect, which confines the motion of charge carriers (electrons and holes) within the QDs.

This results in discrete energy levels and a wider bandgap, which illustrates the potential of QDs in various applications, especially where precise control over the bandgap is crucial for device performance.

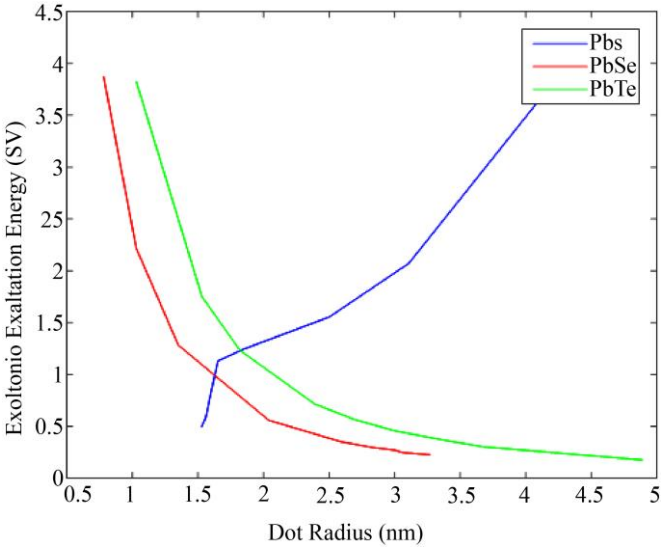

Fig. 6 Excitonic Kinetic Energy (bandgap) versus Dot Radius

The graph indicates that the PbSe bandgap increases from ~0.27 eV (bulk) to over 1 eV as size decreases from 8 nm to 2 nm. This tunability spans near-infrared (NIR) to the mid-infrared (MIR) regions. Similar to PbSe, PbS bandgap increases from ~0.41 eV (bulk) to around 1.5 eV as size decreases from 8 nm to 2 nm, which ranges from the visible to the NIR region. PbTe bandgap increases from ~0.32 eV (bulk) to around 1 eV as size decreases from 8 nm to 2 nm, primarily in the NIR to MIR regions. Among the QDs materials PbS QDs typically exhibit a more significant increase in bandgap with decreasing size compared to PbSe and PbTe QDs due to their specific electronic properties. The tunable bandgap of PbS, PbSe and PbTe QDs makes them ideal for use in optoelectronics, solar cells, biological imaging and thermoelectric applications.

5. Conclusion

In conclusion, charge carrier confinement in QDs gives rise to the modification of optical absorption and emission spectra and transition probabilities, such as discrete electronic state and size-dependent bandgap energy, contrary to the bulk materials. As the size of the QDs decreases, the energy required to excite an electron from the valence band to the conduction band increases, resulting in a wider bandgap. These trends illustrate the potential of QDs in various optoelectronic and sensing applications, where precise control over the bandgap is required. PbS QDs typically show the highest bandgap increase with size reduction, making them suitable for applications requiring larger bandgap tenability. At the same time, PbSe and PbTe QDs are more suitable for applications in the NIR and MIR regions due to their relatively smaller bandgap changes.

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