



Theoretical Insights into Size and Shape-Dependent Thermophysical properties of $(\text{Cd}_x\text{Zn}_{1-x})\text{S}$ semiconductor nanomaterial

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Abstract

The surface effect and the crystal structure led to the formation of theoretical models to study the effects of shape and size on thermodynamic properties, such as cohesive energy, melting temperature, Debye temperature, specific heat capacity and band gap energy of nanomaterials and semiconductor nanomaterials. In the present study, Qi and Wang model which was capable of producing thermophysical behaviors of nanomaterial in agreement with the experimental observations is used to predict shape and size dependent prominent thermophysical properties characterizing the nanostructured materials. The theoretical findings of the present study indicate that the fundamental physical quantities such as, cohesive energy, melting temperature and Debye temperature increase rapidly with increase in particle size for $(\text{Cd}_x\text{Zn}_{1-x})\text{S}$. The specific heat capacity and energy band gap of $(\text{Cd}_x\text{Zn}_{1-x})\text{S}$ has shoot up increase with decrease in size. This behavior is prominent within 5nm to 1.5nm and 7nm to 1.5nm respectively. This change in behavior is due to the effect of surface to volume ratio over the bulk materials. The findings reinforce the reliability of Qi and Wang Model for producing the thermodynamic properties of similar nanostructured materials paving way for potential applications in technological advancements.

Keywords: Nanostructured materials, Debye temperature, Melting temperature, Energy band gap, etc.



Introduction

As the size of low-dimensional materials decreases to the nanometer size range the electronic, magnetic, optic, catalytic, and thermodynamic properties of materials are significantly altered from those of either the bulk or a single molecule. Mixed Semiconductor compound nanomaterial possess fascinating physical and chemical properties in comparison to the counterpart bulk material [1–6]. It is well-known that nanocrystals are intrinsically characterized by a large ratio of the number of surface-to volume atoms, which modifies some of the basic material properties. Physical properties like melting temperature, cohesive energy, specific heat capacity and Debye temperature and energy band gap of nanomaterials are found to vary from bulk materials because of the large number of atoms on their surface in comparison to the bulk material. The physical parameters [7-12] remain constant for bulk material at normal conditions. However, these parameters are found to change with the reduction in size of material to nano level. The physical properties of MSNs have been widely investigated because of their industrial and scientific applications.

Over the years, numerous theoretical simulations and experimental studies have been conducted to explore the size-dependent thermophysical properties of semiconductor nanomaterials, which are critical for the fabrication of mechanical and electronic nanodevices [13-17]. Several models or theoretical approaches, have been attempted to explain the size-dependent properties of nanomaterials. However, these models fail to account for the properties of non-spherical nanoparticles and limited semiconductor nanomaterial. To address this limitation, Qi introduced a theoretical framework to study cohesive energy at the nanoscale. However, practical implementation of this model faced challenges due to the complexity of estimating required parameters. Subsequently, the Qi and Wang model [18-20] was developed to extend this approach, incorporating particle shape and size into calculations of cohesive energy, melting temperature, Debye temperature, specific heat capacity, and band gap energy in mixed semiconductor nanomaterials.

This study applies the Qi and Wang model to examine the thermophysical properties of $(\text{Cd}_x\text{Zn}_{1-x})\text{S}$ nanomaterials. By incorporating surface-to-volume atom ratios, shape factors, and particle size, the model determines cohesive energy, which directly influences melting temperature and band gap energy. The findings indicate that as particle size decreases, cohesive energy and melting temperature decline, while the band gap increases due to quantum

confinement, significantly altering the optical and electronic properties of semiconductor nanomaterials. The study explores these variations in $(\text{Cd}_x\text{Zn}_{1-x})\text{S}$ nanocrystal of different shapes spherical nanosolids, tetrahedral, hexahedral, and octahedral highlighting the tunability of mixed semiconductor nanomaterials (MSCNs). This adaptability makes them promising for optoelectronic applications, overcoming limitations of bulk semiconductors [20-22] with narrow band gaps. The theoretical framework is detailed in Section 2, results and discussions in Section 3, and conclusions in Section 4.

Formalism

The Qi and Wang model provides a theoretical framework to study the influence of nanoscale effects on the properties of mixed semiconductor compound nanomaterials. This model particularly focuses on size- and shape-dependent parameters, including cohesive energy, melting temperature, Debye temperature, specific heat capacity and energy band gap. These properties are critical for understanding and designing nanomaterials for advanced technological applications.

Cohesive energy (E_{cn}): It is a measure of the energy required to disassemble a solid into its constituent atoms. For mixed nanomaterials, the cohesive energy depends significantly on the surface-to-volume ratio.

From the Qi and Wang model, the cohesive energy, E_{cn} can be expressed as follows:

$$E_{cn} = E_0 \left(1 - \frac{3N}{4n} \right) \quad (1)$$

Where, E_0 is cohesive energy of the bulk material per atom, n is the total number of atoms and N is the number of surface atoms. $\frac{N}{n}$ depends on the shape and size of the semiconductor nanomaterials. Considering the atoms of the nanosolids as spherical with atomic radius r and R is the radius of the nanosolid, then the expression for $\frac{N}{n}$ is given as

$$\frac{N}{n} = \frac{\text{Surface area of nanoparticle} / \text{Surface area of an atom}}{\text{Volume of nanoparticle} / \text{Volume of an atom}}$$

$$\text{or} \quad \frac{N}{n} = \frac{4\pi R^2}{\pi r^2} \frac{\frac{4}{3}\pi r^3}{\frac{4}{3}\pi R^3} = \alpha \frac{4r}{R} = \alpha \frac{4d}{D} \quad (2)$$

Where, D is diameter of spherical nanosolid, d is the diameter of an atom of nanosolid and α is the shape parameter of the nanomaterial [3,4,23-25].

In accordance with Qi and Wang Model, the cohesive energy of the nanomaterial in terms of shape and size parameter is given

$$E_{cn} = E_0 \left(1 - \frac{3N}{4n}\right) = E_0 \left(1 - 3\alpha \frac{d}{D}\right) \quad (3)$$

The cohesive energy is responsible for the atomic structure, thermal stability, atomic diffusion, crystal growth and many other properties.

Melting Temperature (T_{mN}): The melting temperature for various nanomaterials is significantly smaller than for the bulk materials. Various thermodynamic models have been used for investigating T_{mN} . The cohesive energy of the solids and the melting temperature are linearly related. Hence it is related to melting temperature.

Therefore, the relation for the melting temperature of nanomaterials is given as

$$T_{mN} = T_{mB} \left(1 - \frac{3N}{4n}\right) \quad (4)$$

$\frac{N}{n}$ when expressed in terms of shape and size parameter then, the melting temperature T_{mN} assumes the form

$$T_{mN} = T_{mB} \left(1 - \frac{3N}{4n}\right) = T_{mB} \left(1 - 3\alpha \frac{d}{D}\right) \quad (5)$$

Debye Temperature (θ_{DN}): It is an important thermodynamic property which is mentioned in Debye theory [26] of specific heat capacity of solids. For nanostructured materials, the amplitude of vibration of the surface atoms is higher than that of the bulk atoms and their frequency of vibration is smaller with respect to the bulk material. This temperature can be used to characterize the properties of many materials, such as thermal vibration and phase transition.

The computational expression for Debye temperature for mixed nanomaterial is written as

$$\theta_{DN} = \theta_{DB} \left(1 - \frac{3N}{4n}\right)^{1/2} = \theta_{DB} \left(1 - 3\alpha \frac{d}{D}\right)^{1/2} \quad (6)$$

where θ_{DN} and θ_{DB} are Debye temperatures in nanosolid and its counterpart bulk material respectively.

Specific heat capacity (C_{PN}): It is an important thermodynamic quantity. It is expected to change under the effect of changing size of nanomaterials.

The expression for specific heat capacity for mixed nanomaterial in terms of shape and size parameter used in the study is given below

$$C_{pN} = C_{pB} \left(1 - \frac{3N}{4n}\right)^{-1} = C_{pB} \left(1 - 3\alpha \frac{d}{D}\right)^{-1} \quad (7)$$

Energy Band Gap (E_{gN}): The energy band gap (E_{gN}) determines the electronic and optical properties of semiconductors. For nanomaterials, the band gap widens as the size decreases due to the quantum confinement effect. If E_{gN} and E_{gB} are energy bandgap in nanomaterial and its corresponding bulk material, the relative change in energy bandgap of nanomaterial [27-34] is expressed as

$$\frac{\Delta E_{gN}}{E_{gB}} = 1 - \frac{E_a(N)}{E_a(B)} = 1 - \frac{T_{mN}}{T_{mB}} \quad (8)$$

Where, T_{mN} is melting temperature of nanomaterial and its corresponding bulk form is

$$T_{mB}$$

$$E_{gN} = E_{gB} \left(1 + 3\alpha \frac{d}{D}\right) \quad (9)$$

Results and Discussion

The Qi and Wang model theory used in the present work explains the effect of shape and size on cohesive energy, melting temperature, Debye temperature, specific heat capacity and energy band gap for $(\text{Cd}_x\text{Zn}_{1-x})\text{S}$. The model theory used in the present work requires shape parameter and atomic diameter as input parameter. The shape parameter for spherical nanocrystal is found to be 1, however, if the shape of the nanomaterial is different from the spherical, shape parameter is found greater than one. The shape parameter for nanomaterials of various geometries is listed in Table 1.

Table 1: The shape parameter for nanomaterials of various geometries.

Shape	Shape parameter, α
Spherical nanosolids	1
Regular Hexahedral	1.24
Regular Octahedral	1.18
Regular Tetrahedral	1.49

Using the atomic diameter value $d=0.2379$ nm at concentration(x) = 0.3 and the shape parameter E_{cn} , T_{mN} , θ_{DN} , C_{pN} and E_{gN} for $(\text{Cd}_x\text{Zn}_{1-x})\text{S}$ of different shape and size are

calculated using the equations (3), (5), (6), (7) and (9) respectively. The results obtained are depicted through graphical representations marked from figures 1 to 5 at concentration $x=0.3$.

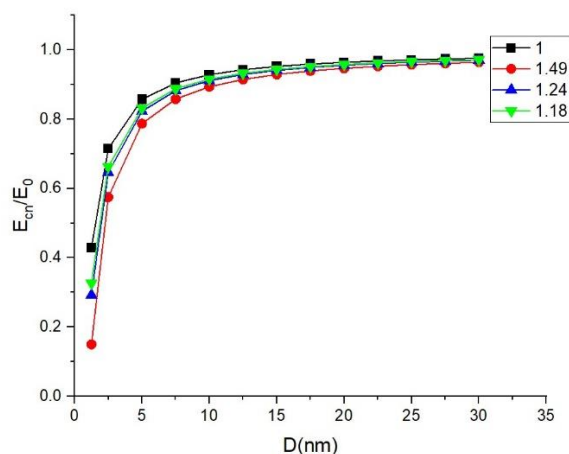


Figure 1: Ratio variation of cohesive energy with the size and different geometrics. Grey square represents $\alpha = 1$ for spherical nanosolid, red circle denotes $\alpha = 1.49$ for regular tetrahedral shape, blue up and green down triangle stand for regular hexahedral and regular octahedral respectively.

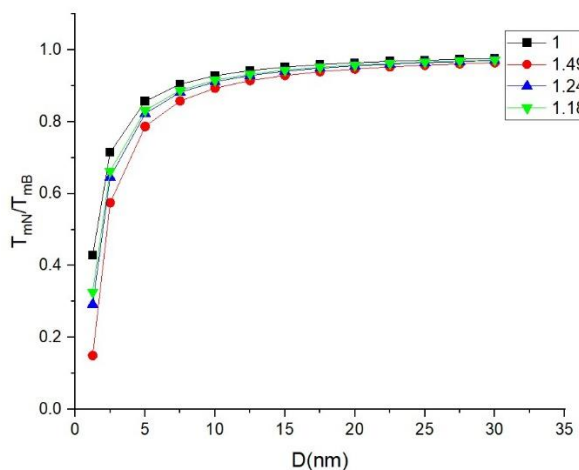


Figure 2: Ratio variation of melting temperature with the size and different geometrics. Grey square represents $\alpha = 1$ for spherical nanosolid, red circle denotes $\alpha = 1.49$ for regular tetrahedral shape, blue up and green down triangle stand for regular hexahedral and regular octahedral respectively.

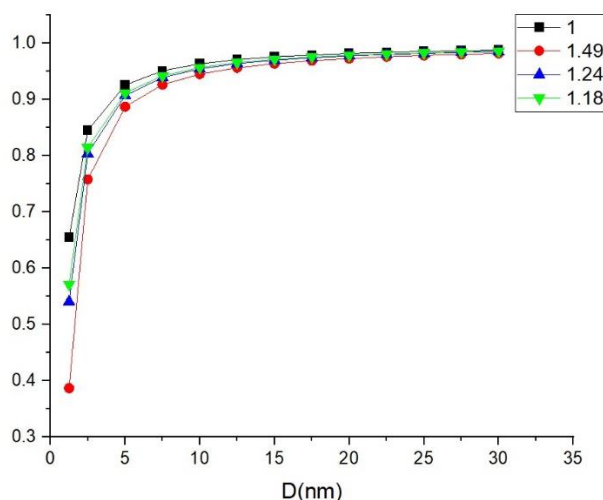


Figure 3: Ratio variation of Debye temperature with the size and different geometrics. Grey square represents $\alpha = 1$ for spherical nanosolid, red circle denotes $\alpha = 1.49$ for regular tetrahedral shape, blue up and green down triangle stand for regular hexahedral and regular octahedral respectively.

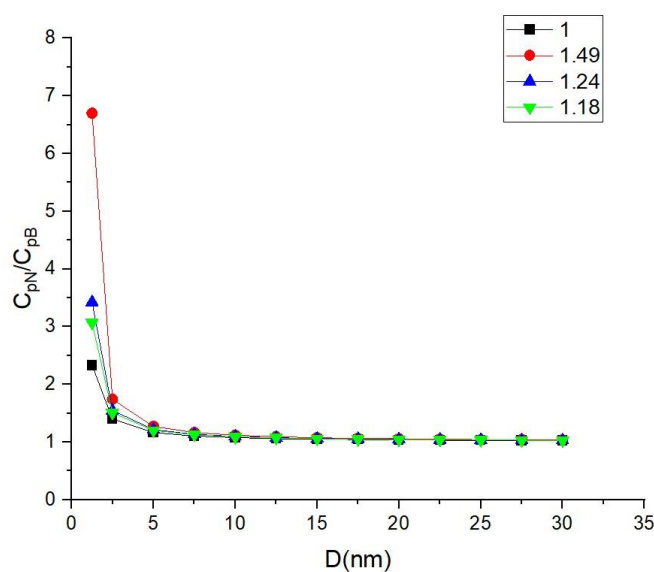


Figure 4: Ratio variation of specific heat capacity with the size and different geometrics. Grey square represents $\alpha = 1$ for spherical nanosolid, red circle denotes $\alpha = 1.49$ for regular tetrahedral shape, blue up and green down triangle stand for regular hexahedral and regular octahedral respectively.

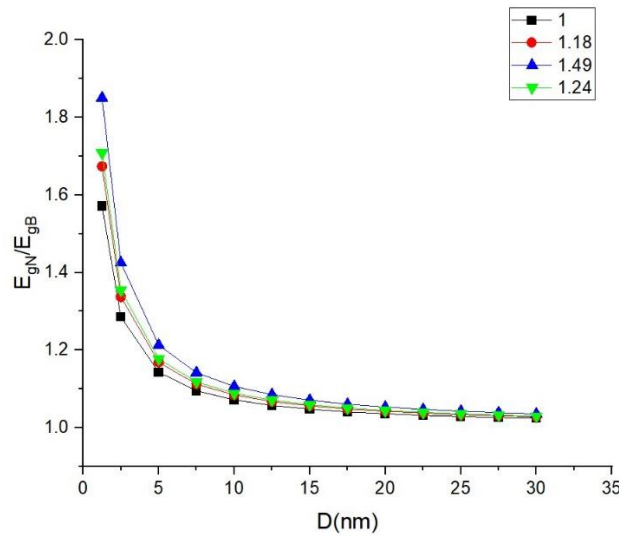


Figure 5: Ratio variation of energy band gap with the size and different geometrics. Grey square represents $\alpha = 1$ for spherical nanosolid, red circle denotes $\alpha = 1.49$ for regular tetrahedral shape, blue up and green down triangle stand for regular hexahedral and regular octahedral respectively.

The variation in cohesive energy and melting temperature [35] for $(\text{Cd}_x\text{Zn}_{1-x})\text{S}$ nanomaterials with different shapes spherical nanosolid, regular tetrahedral, regular hexahedral, and regular octahedral calculated using equations (3) and (5) are illustrated in Figures 1 and 2. The analysis reveals that the effect of shape on cohesive energy and melting temperature are profound nanomaterials with sizes smaller than 30 nm. Cohesive energy and melting temperature increase exponentially approximately up to 15 nm, beyond which the changes become negligible and stabilize.

Figure 3 illustrates that the variation of Debye temperature (θ_{DN}) obtained using equation (6) as a function of particle size and shape for $(\text{Cd}_x\text{Zn}_{1-x})\text{S}$ nanomaterials. The analysis considers nanosolids spherical, tetrahedral, hexahedral, and octahedral morphologies. The results indicate that θ_{DN} exhibits an inverse exponential dependence on grain size, with a pronounced reduction as the particle size decreases attributed to enhanced surface effects and reduced phonon confinement. However, beyond 15 nm, the variation becomes negligible. The calculated values of θ_{DN} align well with previously reported theoretical and experimental results, validating the reliability and accuracy of the Qi and Wang model used in predicting the thermophysical behavior of semiconductor nanomaterials.

Figures 4 and 5 represent the variations in specific heat capacity and energy band gap [36] with particle size and shape for $(\text{Cd}_x\text{Zn}_{1-x})\text{S}$ nanomaterials. The variations in C_{PN} and E_{gN} are calculated using equations (7) and (9) respectively. The results are presented for different nanoparticle shapes, including spherical, tetrahedral, hexahedral, and octahedral structures. The graphs indicate that as grain size decreases, specific heat capacity and energy band gap increase exponentially.

Conclusion

The Qi and Wang model was applied to investigate the thermophysical properties of $(\text{Cd}_x\text{Zn}_{1-x})\text{S}$. The calculated values of cohesive energy E_{cn} , melting temperature T_{mN} , and Debye temperature θ_{DN} , specific heat capacity, C_{PN} and energy band gap E_{gN} showed good agreement with experimental results. Cohesive energy, melting temperature and Debye temperature increase with particle size up to 15 nm but decrease significantly at smaller sizes due to increased mean bond length and a higher surface atom ratio. The variation trends of specific heat capacity and band gap energy with grain size align well with theoretical predictions and previous studies. These properties exhibit an inverse exponential relationship with decreasing grain size.

Beyond 15 nm, the effect of shape becomes negligible, and thermophysical parameters stabilize. Given the significance of melting temperature, this model holds potential for studying temperature-related phenomena in nanoparticles. Overall, the model effectively explains the thermodynamic and optical properties of nanomaterials, making it valuable for researchers exploring electronic, thermal, and optical characteristics of mixed nanomaterials.

Key findings of the study are:

- This behavior is due to the quantum confinement effect.
- The shape of the nanomaterials influences the band gap.
- One possible reason is surface atoms of the nanomaterial induce additional energy levels that may impact the band gap.

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