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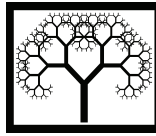
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Temperature-Dependent Phase Stability of CdS Quantum Dots from First-Principle Molecular Dynamic Calculations

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Abstract

Because of their applications in optoelectronics and applications for quantum dots and other low-dimensions nanostructures, the cadmium sulfide compounds have attracted much attention in recent years. Their optoelectronic and bio-related applications, have led to a situation where the analysis of thermal stability of CdS quantum dots becomes one of the most important avenues of research in this field. In this work, first principle molecular dynamic simulations are performed for wurtzite, graphitic and rocksalt phases of the $Cd_{48}S_{48}$ nanostructure, and a relative stability of this nanostructure is studied in different phases at various temperatures. Our results indicate that the phase stability sequence is rocksalt, wurtzite and graphitic phase for the $Cd_{48}S_{48}$ nanostructure in the temperature range from 300 K to 450 K. The same situation holds for bulk CdS crystals under high pressure and 0 K. Our work also demonstrates that although the temperature can affect the total energy of the CdS nanostructure, it can not change the phase stability sequence of CdS nanostructures in the temperature range studied in this work.

Keywords: quantum dots, temperature-dependent phase stability, CdS, first-principle molecular dynamic calculations.

1 Introduction

Due to their unique optoelectronic properties and a wide range of current and potential applications, nano-sized semiconductors have attracted much attention in recent years [1, 2]. Among these semiconductors, cadmium sulfide (CdS), being one of the most important wide-gap semiconductors, is stable and exhibits high luminescence [3, 4, 5]. CdS nanostructures have found many applications in photovoltaic cells, photonic switches and optoelectronic devices [2]. In recent years, CdS quantum dots

have also been used in biolabeling, bioimaging, drug delivery and other biotechnological areas [3, 6, 7]. It is due to these optoelectronic and bio-related applications, the analysis of thermal stability of CdS quantum dots becomes one of the most important avenues of research in this field. Additionally, CdS quantum dots represent an intermediate state of matter between molecular species and bulk materials [3]. Therefore, a better understanding of their temperature dependent phase stability and phase transformations will ultimately enable us to tailor their electrical and optical properties from molecular level to bulk crystals.

It has been known for a long time that the bulk CdS is highly stable and it exists in the hexagonal wurtzite phase in a wide range of temperatures, from room temperature to its melting point 1750 °C [8, 9, 10]. Recently it has been shown that due to the large surface to volume ratio and reconstruction of surface crystal structure, the thermodynamic properties of the CdS nanostructure can differ significantly from bulk CdS [11]. For example, under appropriate conditions some wurtzite structure semiconductor materials can transform into a graphitic structure when they are in the form of thin nanoplates [12]. Since the internal pressure deduced from surface stress is very large for nanostructures, at ambient conditions, the stability phase in nanosize structures is always a high pressure stability phase structure in bulk [13]. Nevertheless, the temperature-dependent phase stability of the CdS quantum dots remains poorly understood to date. In particular, systematic calculations and comprehensive comparisons of their thermodynamic stability, as well as mechanical, electronic, and optical properties under different temperature conditions are still lacking. To fill this gap, in this work we carry out first-principle molecular dynamic (MD) calculations for CdS quantum dots of various phase structures and study temperature-dependent phase stability of these nanostructures. Based on our calculations, we analyze the relative stability of different CdS phases under different temperature conditions.

The remainder of this paper is organized as follows. In section 2, we provide technical details of the calculations performed in this work. In section 3, we present and discuss our first-principle MD results for wurtzite, graphitic and rocksalt phase nanostructures. Finally, in section 4, we present our summary and conclusions.

2 Computational Methods

In what follows, we focus on the temperature dependent phase stability of CdS nanostructures. The initial structures are directly cut out from CdS wurtzite, graphitic and rocksalt crystals, respectively. In particular, the structure in Figure 1a-c is the wurtzite CdS nanostructure with hexagonal prism structures, containing 96 atoms of eight layers (four Cd-S double layers). The structure in Figure 1d-f is the graphitic CdS nanostructure with hexagonal prism structures, containing 96 atoms of four layers. Finally, the structure in Figure 1g-i is the rocksalt CdS nanostructure, containing 96 atoms also. We denote them as 96A-WZ, 96A-GR and 96A-RS, respectively.

The calculations described in this work are performed by using two density func-

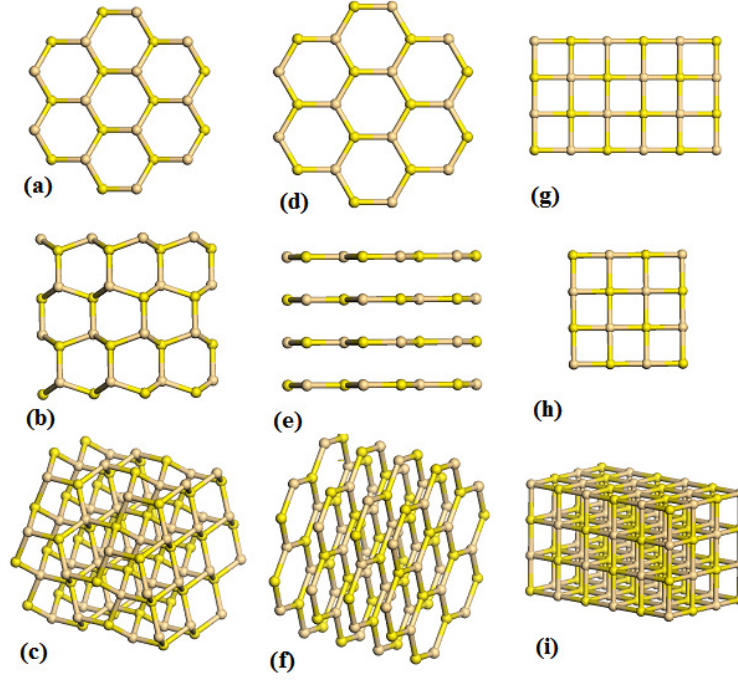


Figure 1: Side and top views of initial CdS nanostructures: (a) top view of 96A-WZ, (b) side view of 96A-WZ, (c) 3d view of 96A-WZ, (d) top view of 4L-96A-GR, (e) side view of 96A-GR, (f) 3d view of 96A-GR, (g) top view of 96A-RS, (h) side view of 96A-RS, (i) 3d view of 96A-RS

tional theory (DFT) packages: one is the CASTEP package [14], and the other one is the Car-Parrinello molecular dynamics package (CPMD) [15]. The CASTEP package is used to calculate the enthalpy of CdS under different pressures, and the CPMD code is used to calculate the total energy of CdS nanostructure under different temperatures. For the CASTEP computational scheme, the interactions between the valence electrons and the ion-cores were modeled by ultrasoft pseudopotentials [16], and the generalized gradient approximation (GGA) with the PBE exchange-correlation functional were adopted [17]. The k point separation in the Brillouin zone of the reciprocal space was taken to be $0.04nm^{-1}$, which corresponds to an $8 \times 8 \times 8$ k point mesh. A high cutoff energy of 500 eV was selected for the plane wave basis in this work. For the CPMD computational scheme, the interactions between the valence electrons and the ion-cores were modeled by the HSC (Hamann, Schluter and Chiang) norm-conserving methodology [18] and by SGS pseudopotentials [19] for Cd and S elements, respectively. In details, the Cd pseudopotentials are generated from a $5s^1 5p^{0.25} 5d^{0.25}$ reference configuration, and core radii r_c with values of 1.6, 1.6, and 2.4 a.u. are used for s , p , and d orbitals, respectively. The exchange-correlation effects are treated with local density approximation (LDA) [20]. The CPMD calculations are performed in a cubic box of 20 Å side with periodic boundary conditions, and one point ($k=0$) in the Brillouin zone. The kinetic energy cutoff of the plane wave basis set is 20 Ry. In this work, the time step for Born-Oppenheimer molecular dynamics is

0.12 fs in the NTP ensemble, and the simulation time is 12 ps. Our simulation results indicated that simulation time of 12 fs is sufficient to equilibrate the nanostructure.

Based on the above two calculational schemes, trial calculations were performed for stress-free wurtzite CdS crystal. The lattice parameters are listed in Table 1. The calculated lattice parameters a and c are 4.13 Å, 6.78 Å and 4.21 Å, 6.85 Å for CPMD and CASTEP, respectively. As can be seen, the calculated lattice parameters from both calculational schemes agree well with experimental values of 4.12 Å and 6.68 Å [21], as well as with previous theoretical values of 4.11 Å and 6.63 Å. The $c : a$ ratios of 1.64 and 1.63 are also close to the ideal value of 1.63 for the hcp structure.

	code	a	c	c/a
This work	CPMD	4.13	6.78	1.64
	CASTEP	4.21	6.85	1.63
Experimental [21]		4.12	6.68	1.62
Theoretical [11]	VASP	4.11	6.63	1.61

Table 1: Comparison between the present CPMD and CASTEP computations and previous theoretical and experimental results for bulk CdS in wurtzite structure (lattice parameters are given in Å)

3 Results and discussions

Since the atom numbers are the same for different phases of the CdS nanostructure studied in this work, the relative stability of various phases of the CdS nanostructure under different temperature conditions can be determined by comparing the total energy. By performing first principle MD simulations, the total energy is calculated for these nanostructures under different temperatures. The temperature range studied in this work is from 300 K to 450 K. The relationships between the total energy and temperature for various phases of the CdS nanostructure are plotted in Figure 2. From our calculations, the total energy E_t increases almost linearly with temperature T for all nanostructures studied in this work. This implies that the stability is decreasing with increase in temperature for all CdS nanostructures studied here. For the rocksalt phase CdS nanostructure, with increasing temperature T (in K), the total energy E_t^{rocksalt} (in Ha) increases approximately according to a linear relationship: $E_t^{\text{rocksalt}} = -512.01952 + 0.00386T$. For the wurtzite phase CdS nanostructure, this relationship can be expressed as: $E_t^{\text{wurtzite}} = -511.27856 + 0.00234T$. For the graphitic phase CdS nanostructure, this relationship can be expressed as: $E_t^{\text{graphitic}} = -511.36445 + 0.00347T$. As can be seen from Figure 2, there are no cross points for the total energy curves, which indicates that the stability sequence for the CdS nanostructures remains the same in the temperature range studied in this work. Furthermore, the stability sequence of these CdS nanostructures is rocksalt, wurtzite and graphitic phase.

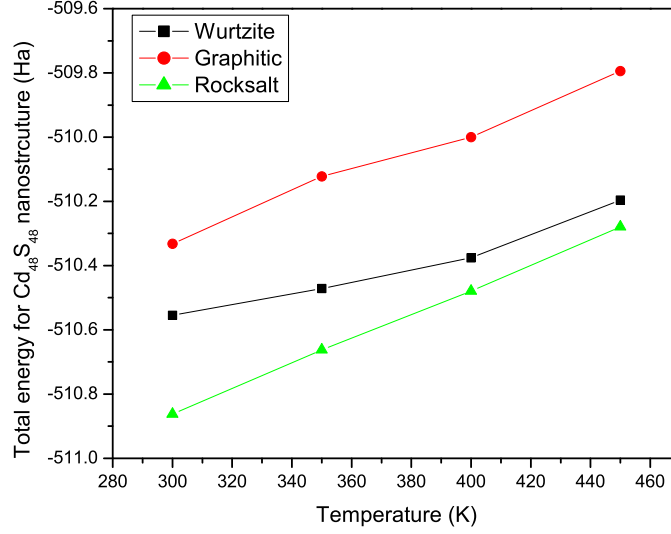


Figure 2: The relationship between total energy and temperature for various phase structure nanosized $Cd_{48}S_{48}$

In order to understand the stability sequence of these nanostructures, their snapshots after relaxation at different temperatures and the corresponding bond distributions are shown in Figures 3 and 4, respectively. With increase in temperature, the number of broken bonds is increasing for all CdS nanostructures. At the temperature of 300 K, only the rocksalt phase CdS nanostructure can maintain the initial input structure, while the wurtzite and graphitic phase CdS nanostructures can not maintain the initial input crystal structure due to larger numbers of broken bonds. For the rocksalt CdS nanostructure, its crystal structure is maintained until the temperature of 400 K is reached, but the crystal structure is corrupted when the temperature increases further to 450 K. Since the number of broken bonds increases with increasing temperature, the total energy is also increasing with increase in temperature. For the rocksalt CdS nanostructure, it can maintain its crystal structure under higher temperature than the wurtzite and graphitic phase CdS nanostructures. Therefore, it is a stable nanostructure in the temperature range from 300 K to 450 K, in contrast to the other two CdS nanostructures.

It is well known that the wurtzite phase is stable for the bulk CdS at ambient conditions. However, as our calculation show for nanosized CdS structures, the rocksalt, a high pressure phase, is the most stable in the above temperature range. For a spherical or quasi-isotropic nanocrystal with diameter x , the internal pressure P_{in} , induced by the curvature, can be expressed as $P_{in} = 4f/x$ using the Laplace-Yong equation, where f denotes the surface stress [22]. Thus, the total pressure is $P_{tot} = P_{in} + P$. If $P \approx 0$, $P_{tot} = P_{in} = 4f/x$. For the nanosized materials, because the x value is very small, the value of P_{in} is very large and cannot be neglected. Therefore, the smaller the diameter x is, the bigger the value of the total pressure P_{tot} . In this work, the

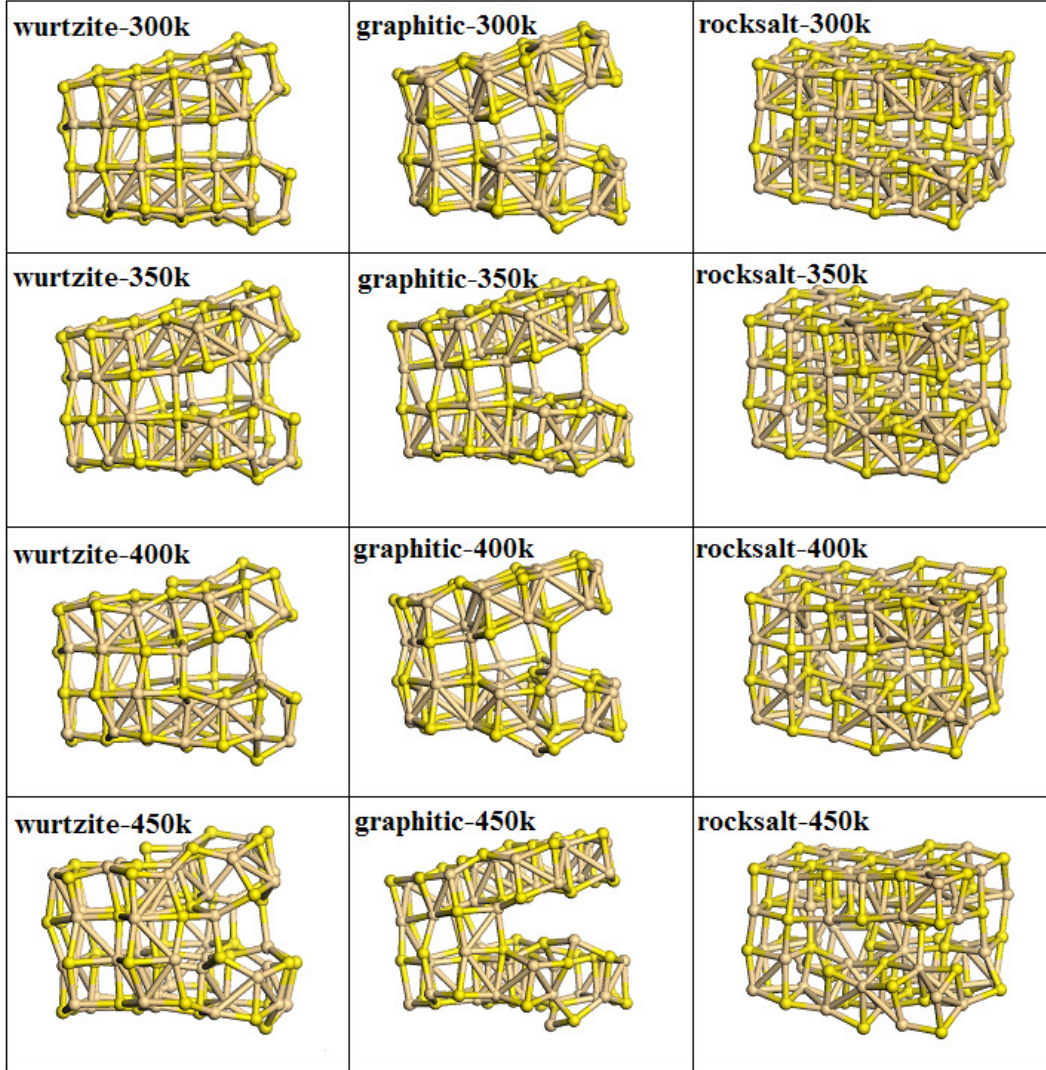


Figure 3: Snapshots of nanosized $Cd_{48}S_{48}$ after relaxation at different temperatures

relationship between enthalpy and pressure for wurtzite, graphitic and rocksalt CdS bulk crystals is also calculated, and it is shown in Figure 5. It can be seen that with increase in pressure, the stability sequence for wurtzite, graphitic and rocksalt phases is changing. At the pressure range from 0 to 4.3 GPa, wurtzite is the stability phase. When the pressure is above 4.3 GPa, the rocksalt phase becomes the most stable, and the stability sequence is rocksalt, wurtzite and graphitic phase. The stability sequence for bulk CdS materials under high pressure is the same as that of CdS nanostructures at ambient conditions. These results imply that the curvature induced internal pressure is the main reason for the phase stability of CdS nanostructures. Although the temperature can affect the total energy of the CdS nanostructure, it can not change its phase stability sequence in the temperature range studied in this work.

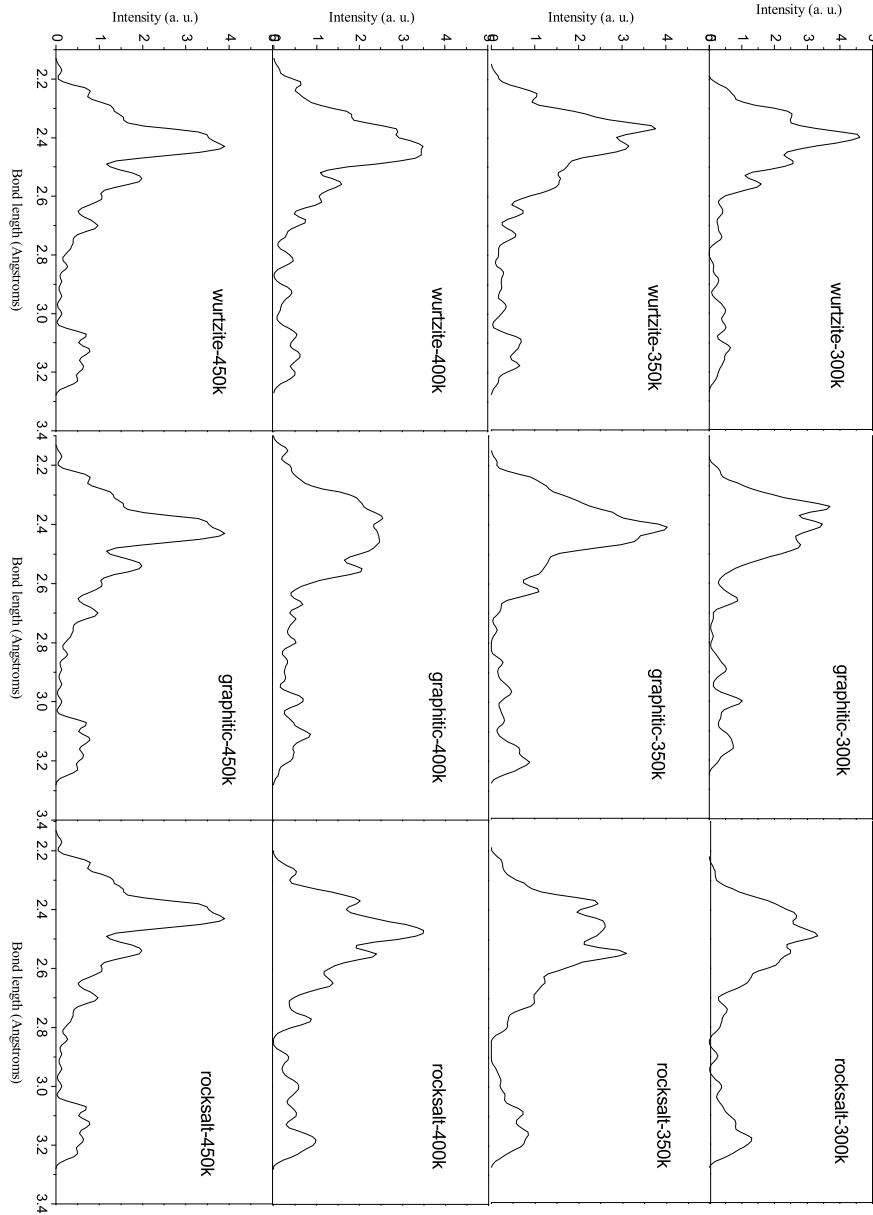


Figure 4: The bond lengths distribution for various phase structures of nanosized $Cd_{48}S_{48}$ at different temperatures

4 Conclusion

In order to understand the relative stability of the $Cd_{48}S_{48}$ nanostructure in different phases at various temperatures, first principle MD simulations were carried out for wurtzite, graphitic and rocksalt phases of the $Cd_{48}S_{48}$ nanostructure, and a relation-

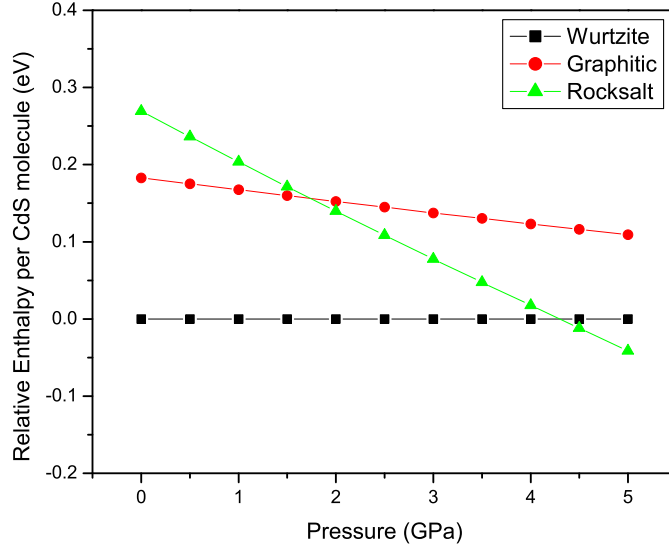


Figure 5: The relative enthalpy for wurtzite, graphitic and rocksalt CdS crystal at pressure

ship between the total energy and temperature for different CdS nanostructures were deduced. We conclude that at the temperature range studied in this work, the phase stability sequence for the $Cd_{48}S_{48}$ nanostructure is rocksalt, wurtzite and graphitic phase, which is the same as that of bulk CdS crystals under high pressure. Although the temperature can affect the total energy of the CdS nanostructure, it can not change the phase stability sequence of CdS nanostructures in the temperature range studied in this work. The next step is to analyze the size dependence of the phase stability sequence. The results of this analysis will be reported in a separate publication.

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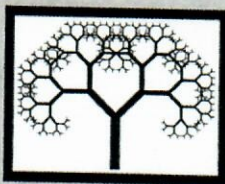
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