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Electronic-structure and thermodynamic properties of $ZnS_{1-x}Se_x$ ternary alloys from the first-principles calculations

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ABSTRACT

In this paper, the composition-dependent electronic-structure and thermodynamic properties for hexagonal wurtzite (WZ) and face-centered cubic zincblende (ZB) $ZnS_{1-x}Se_x$ ternary alloys have been studied utilizing first-principles pseudopotential plane-wave self-consistent field calculations. Special quasi-random structure method was applied to generate disordered structures of 16-atom supercell for $x = 0.25$, 0.5 and 0.75. We obtained a direct band-gap at Γ point and a shrinking tendency of the band-gap with increasing Se content in both phases. The reasons for the band-gap shrinkage have been discussed based on the analysis of electronic density of states and band offsets. Δ-sol method was applied to correct the band gaps calculated by density functional theory. The Δ-sol corrected band-gaps are in good agreement with experimental band-gaps. The thermodynamic properties were calculated by the cluster expansion method. It turns out that, the stretching forces decrease considerably and linearly with the bond length, while the bending forces are dependent insignificantly on the bond length. The phase diagrams reveal that the lattice vibration effects can influence the critical temperature T_c and the solubility of S- and Se-rich $ZnS_{1-x}Se_x$ alloys, but the influence is not obvious for ZB-$ZnS_{1-x}Se_x$. Based on the calculated phase diagrams without lattice vibration effects, the T_c for WZ- and ZB-$ZnS_{1-x}Se_x$ are 559 K and 421 K, respectively. When the vibration enthalpy is included, the T_c values of both phases are lowered to 543 K and 418 K, respectively. And if the vibration entropy is also taken into account, the T_c values of both phases are further lowered to 529 K and 415 K, respectively. With inclusion of lattice vibration effects, the $ZnS_{1-x}Se_x$ alloy starts a phase transition from ZB to WZ at a temperature of 1600 K, and the solid solubility of Se increases with the temperature rise.

1. Introduction

Recently, II-VI semiconductor binaries and their alloys have attracted considerable attention for their potential applications in photonic, optoelectronic, and spintronic devices [1–3]. Among this group, ZnS and ZnSe are promising candidates with wide direct band gaps. ZnS and ZnSe have been reported to crystallize in the hexagonal wurtzite (WZ) and face-centered cubic zincblende (ZB) phases. ZnS has a band-gap of 3.50 eV [4] and 3.82 eV [5] for WZ and ZB structures, respectively, while ZnSe has a band-gap of 2.66 eV [4] and 2.87 eV [5] for WZ and ZB structures, respectively. They are suitable for short-wavelength optoelectronic device applications, such as ultraviolet light-emitting diodes (LEDs), highly efficient optical detectors and memories, blue-green laser diodes, solar cells and tunable mid-IR laser sources for remote sensing [6–10]. It is more interesting to create a $ZnS_{1-x}Se_x$ solid solution by introducing Se^{2-} ions into a ZnS crystal lattice. It enables easy tuning of the band gap (ranging from 2.66 eV to 3.50 eV for the WZ phase and 2.87 eV to 3.82 eV for the ZB phase) and lattice parameters of the alloy due to the efficient miscibility of ZnS and ZnSe in the whole composition range [11]. $ZnS_{1-x}Se_x$ alloys are excellent candidates for window and/or buffer layers in thin-film hetero-junction solar cells [12,13], and are promising materials in the fabrication of lenses, output couplers, biomedical labels and optically controlled switches due to their small exciton binding energy and low absorption at infrared wavelength. Thus $ZnS_{1-x}Se_x$ alloys have attracted significant interest in recent years from both experimental and theoretical points of view. Park et al. [14] studied structure and photoluminescence properties of $ZnSe_{1-x}S_x$ alloy nanorods and found a strong blue-green emission band. The intensity of the emission band enhances with increasing S concentration due to the increase of structural defects such as dislocations and stacking faults in the nanorods. Fridjine et al. [15] demonstrated the tunable band-gap of $ZnS_{1-x}Se_x$ thin films from 3.5 to 3.1 eV with increasing composition x ($0 \le x \le 0.45$). Density functional theory (DFT) calculations indicate that $ZnS_{1-x}Se_x$ alloys have a

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reducing band-gap with increasing Se content and a strong absorption ability for visible up to ultraviolet light, which provides potential applications in solar cells and optoelectronic devices [6]. Although DFT [16] within the generalized gradient approximation (GGA) [17] has been used to investigate the electronic properties of alloys successfully, it fails to correctly predict their band gaps. It usually underestimates the band gap by 30% − 100% with respect to the experimental one [18]. Several methods such as GW approximations [19], Heyd-Scuseria-Ernzerhof (HSE) screened-hybrid functionals [20], and modified Becke-Johnson (MBJ) potentials [21] have been used to correct the DFT-derived band gaps. However, there are few reports regarding corrections to the band gaps of $ZnS_{1-x}Se_x$ alloys in WZ and ZB phases. In addition, the band offset is a vital parameter with regard to device modeling and the determination of doping abilities of semiconductor compounds. The theoretical valence band maximum (VBM) and conduction band minimum (CBM) offsets between ZnS and ZnSe are 0.50 eV and 0.52 eV, respectively [22]. These quantities can be used to further evaluate the charge transport and quantum confinement properties when designing a ZnS/ZnSe quantum well. To better apply this technology to photoelectric device applications, it is necessary to know the band offsets among $ZnS_{1-x}Se_x$ alloys.

Besides the electronic-structure information, thermodynamic properties are quite important for the synthesis and growth of alloy crystals. The first-principles phase diagram of $ZnSe_{1-x}S_x$ alloys was carried out by Li et al. [23] based on Monte Carlo techniques and cluster expansion method. All positive formation energies imply that a miscibility gap exists and the alloy system tends to phase separation. The calculated consolute temperature is 327 K and the effect of lattice vibration can reduce it to 281 K. However, in Li's work, they only investigated the ZB structure, and ignored the WZ phase. Although the stable structures of both ZnS and ZnSe are ZB at room temperature, the ZnS can present WZ structure at high temperatures. Therefore, the existence of WZ-$ZnS_{1-x}Se_x$ alloys and the occurrence of phase transition between WZ and ZB structures deserve consideration.

In this study, we investigated the composition-dependent electronic-structure and thermodynamic properties of both WZ- and ZB-$ZnS_{1-x}Se_x$ alloys based on DFT calculations. We carefully analyzed the cause for the changes of electronic-structure and thermodynamic properties. Furthermore, the role of phonon vibration played in the phase diagram was also discussed. The paper is organized as follows: A detailed description of the computational methods is given in Section 2. The results and discussion are presented in Section 3, and the conclusions of our research are described in the final section.

2. Computational details

2.1. DFT calculations

In this work, calculations of electronic band structure and total energy of $ZnS_{1-x}Se_x$ alloys in both phases were performed by using first-principles plane wave basis set based on DFT, as implemented in the QUANTUM ESPRESSO package [24], with ultrasoft pseudopotentials (USPPs) [25] from Garrity-Bennett-Rabe-Vanderbilt (GBRV) pseudopotential library [26]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [27] was applied for the exchange-correlation potential. The convergence thresholds on the pressure and the self-consistent field energy tolerance for variable cell relaxation were set to less than 0.05 GPa and 1.4×10^{-5} eV, respectively. The valence electron configurations of the pseudopotentials were set to $3d^{10}4s^2$ for Zn, $3s^23p^4$ for S, and $4s^24p^4$ for Se. Plane wave energy cutoff for the convergence of energy eigenvalues was 600 eV. A Monkhorst-Pack k-points mesh [28] was used for the Brillouin zone integrations. Monkhorst-Pack grids were determined automatically for different alloy configurations and the parameter called *KPPRA* was set to 1000. The k-points of the entire reciprocal space were determined by the *KPPRA* parameter and the number of atoms. In each basis vector direction of the reciprocal space, the k-points were equally distributed.

2.2. Δ-sol method

To investigate electronic-structure properties, the 16-atom (8 cations and 8 anions) special quasirandom structures (SQSs) [29,30] of WZ- and ZB-$ZnS_{1-x}Se_x$ alloys for $x = 0.25$, 0.5 and 0.75 were constructed by the Alloy Theoretical Automated Toolkit (ATAT) [31]. The calculated band-gaps from DFT with the generalized gradient approximation (GGA) [17] are far less than the experimental data. That is due to the DFT in GGA can't correctly calculate energy gaps between occupied and unoccupied states [32]. It often underestimates the experimental band-gaps by 30% − 100% [18]. To solve the DFT band-gaps problem and reduce the energy gap errors, we applied a viable method: Δ-sol [32] to correct alloy band-gaps. In the research of efficient band gap prediction for solids, Chan et al. [32] have demonstrated that at computational costs similar to typical DFT calculations, the Δ-sol method reduces Kohn-Sham gaps errors by an average of 70% on over 100 compounds with experimental gaps of 0.5–4 eV. The Δ-sol method has been applied to evaluate the band-gap in $In_xGa_{1-x}N$ and satisfactory results have been obtained by Scharoch et al. [33] in the study of an efficient method of DFT/LDA band-gap correction.

The Δ-sol method was used to correct $ZnS_{1-x}Se_x$ alloy Kohn-Sham energy gap errors, as it can reduce them markedly. Furthermore, the Δ-sol method is easier and quicker than applying the GW approximation, HSE screened-hybrid functional, and MBJ potential. In fact, the Δ-sol method fits experimental data from pure binary compounds. It can determine the band gaps of $ZnS_{1-x}Se_x$ alloys quickly, avoiding complex calculations and reducing computation cost. Relevant expressions of this method can be defined as an evaluation of the fundamental gap E_{FG} of a system performed by calculating the energies of systems with N, $N+1$, and $N-1$ electrons.

$$E_{FG} = E(N+1) + E(N{-}1){-}2E(N) \tag{1}$$

where N denotes the number of electrons in the systems. For atoms and molecules, the Δ-sol method can generate reasonable and credible results [34,35]. If the Eq. (1) is applied to a solid solution system, the crucial problem is how to determine the N value. In order to use the Eq. (1) to correct band-gaps in the $ZnS_{1-x}Se_x$ solid solution system, we firstly calculated the E_{FG} of ZnS and ZnSe by adding and removing n charges to N_0 valence electrons of elements per unit cell.

$$E_{FG} = [E(N_0+n) + E(N_0{-}n){-}2E(N_0)]/n \tag{2}$$

where N_0 is the number of valence electrons in the system. The n values of two end points (ZnS and ZnSe) must be attempted until the calculated E_{FG} is equivalent to the experimental band gap. In most cases, n is not an integer. Here, $n = N_0/N$. For $N = N*$, the $N*$ parameters at other Se concentrations can be obtained via linear interpolation. This method can be used to calculate the E_{FG} values of $ZnS_{1-x}Se_x$ alloys with $x = 0.25$, 0.5, and 0.75 using Eq. (2).

2.3. Band offsets

The band offset can intuitively reflect the relative changes in the VBM and CBM values of $ZnS_{1-x}Se_x$ alloys with different compositions. It is an indispensable quantity used to directly assess charge transport, quantum confinement, and conversion efficiency in almost all electronic and photoelectric devices involving heterostructures such as light emitting diodes, laser diodes, and solar cells [36,37]. So for the practical application of $ZnS_{1-x}Se_x$ alloys in electronic and optoelectronic devices as heterojunctions, we investigated the natural valence band and conduction band offsets for interfaces between different Se concentrations of $ZnS_{1-x}Se_x$ alloys. The branch-point energy (BPE) E_{BP} can be regarded as an energy reference level to align the energy bands for different semiconductors [38]. Hence the natural band offsets can be obtained by calculating E_{BP} for every involved semiconductor. The

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