The theoretical study on formation energy of zinc-blende and wurtzite ZnO$_{1-x}$S$_x$ alloys

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Abstract. A theoretical study on formation energy of zinc-blende (ZB) and wurtzite (WZ) ZnO$_{1-x}$S$_x$ has been carried out with the first-principles methods and the Alloy Theoretic Automated Toolkit (ATAT). The cluster expansion approach was used to describe the disordered alloys, for $x = 1/6$, $1/3$, $1/2$, $2/3$, and $5/6$. With the analysis of the formation energy, the WZ structure is thermodynamically more stable than ZB structure at all temperatures and alloy compositions, which is in agreement with experiments.

1. Introduction

Zinc Oxide alloys have attracted extensive attention in the last few years. So they have many applications such as solar cells[1, 2], catalysts[2], gas sensors[3], short wavelength light emitters[4, 5]. For band gap engineering, a lot of theoretical and experimental works focused on cations-substituted alloys, such as Be$_x$Zn$_{1-x}$O, Mg$_x$Zn$_{1-x}$O and Cd$_x$Zn$_{1-x}$O has been carried out[6-8], while less attention has been paid to anion doping. With anion doping, the alloy ZnO$_{1-x}$S$_x$ can be a candidate for the flexible adjustment of the band gap energies[9]. However, the significant difference between the stability of ZnS and ZnO at film growth temperature[10-12] initiates a problem in the process of alloying ZnO$_{1-x}$S$_x$.

In this work, we examine the thermodynamic properties of the ZB and WZ ZnO$_{1-x}$S$_x$ alloys by a first-principles theoretical method. The main focus of this work is to obtain the formation energy of zinc-blende (ZB) and wurtzite (WZ) ZnO$_{1-x}$S$_x$ alloys.

2. Method of calculation

The cluster expansion (CE) approach[13-15] is implemented in the Alloy Theoretic Automated Toolkit (ATAT)[16, 17] code, which has successfully been applied to the study of thermodynamic properties. Our calculations have been made using the Alloy Theoretic Automated Toolkit (ATAT) within the framework of the Density Functional Theory (DFT) under the generalized gradient approximation (GGA) along with the ultrasoft pseudopotentials[18] as implemented in the Quantum ESPRESSO package[19]. ATAT is a suite of software tools[20]. It relies upon the cluster expansion formalism[13, 21, 22].

In this work, an ATAT with changing atoms is employed for modeling the thermodynamics properties of ZB- and WZ- ZnO$_{1-x}$S$_x$ alloys. The total energy is converged at the $10^{-3}$ eV cation$^{-1}$ level and the total force is converged at the $10^{-3}$ eV/Å cation$^{-1}$ level. The kinetic energy cutoff of 1088 eV is found to be sufficient.
3. Results and discussions

3.1. The ordered phases:
In order to study the stability of ZnOS in the ordered form, we calculated the formation energies of the seven (n = 0, 1, 2, 3, 4, 5, 6) structures using the following relation

\[
E_{\text{form}}(n) = E_{ZnO_{\frac{1-n}{6}}S_{\frac{n}{6}}} - \frac{n}{6}E_{ZnO} - \frac{1-n}{6}E_{ZnS},
\]

where \( E_{ZnO_{\frac{1-n}{6}}S_{\frac{n}{6}}} \) is the total energy of the \( n \)th ordered alloy, \( E_{ZnO} \) and \( E_{ZnS} \) are total energies of ZnO and ZnS binaries, respectively. The formation energy of ZB and WZ structure can give a measurement of the stability of a material which is shown in Figure 1 (a) and (b) (hollow inverted triangles). When the concentration of S are 1/6, 1/3, 1/2, 2/3 and 5/6, the formation energy of WZ structure are generally lower than those of ZB structure, which indicates that the WZ structure has a more stability.

![Figure 1](image)

Figure 1. Calculated energy of formation for the ordered and the disordered ZnO\(_{1-x}\)S\(_x\) alloys of (a) zinc-blende (ZB) and (b) wurtzite (WZ) structure.

3.2. The disordered phases:
There are several sources of substitutional disorder in oxides[22]. Given there is some disturbance of atomic components, we will consider the disordered phases. Following the idea of Connolly and Williams[23], the formation energy of the disordered solid solutions can be written as
\[ E_{\text{form}}^\text{dis}(x) = \sum_{n=0}^{6} P_n(x) E_n^\text{form} \]  
\[ P_n(x) = \binom{6}{n} x^n (1-x)^{6-n} \],

where \( E_n^\text{form} \) is the energy of formation of each of the seven ordered structures. \( P_n(x) \) is a statistical weight, representing the probability that the \( n \)th short-range ordered structure occurs in the alloy. In Figure 1 (a) and (b), the calculated formation energies for both ordered and disordered phases are positive and yield to a miscibility gap. Then it is clear that the disordered alloys have relatively lower formation energy. While the formation energy of WZ structure is smaller than that of ZB structure which shows that the WZ structure is easier to form.

4. Conclusion
In summary, we have performed first-principles density-functional calculations to investigate the thermodynamical properties of semiconductor alloy \( \text{ZnO}_{1-x}\text{S}_x \) with the ordered and disordered forms. With the analysis of the formation energy, the WZ structure is thermodynamically more stable than ZB structure at all temperatures and alloy compositions, which is in agreement with experiments.

Acknowledgments
This work was supported by the Scientific Research Foundation of Suzhou University (Grant No. 2019jb04).

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