First-principles calculation on thermodynamic properties of ZnO\(_{1-x}\)S\(_x\) alloys with considering lattice vibrations

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Abstract. Thermodynamic properties of zinc-blende (ZB) and wurtzite (WZ) ZnO\(_{1-x}\)S\(_x\) have been studied with the first-principles methods. The critical temperature for separation is 1981 K for the ZB structures and 1563 K for the WZ structures with the inclusion of lattice vibrations which leads to a large reduction with 20.7 % and 16.7 % for the ZB and WZ structures, respectively. And with the analysis of the phase diagram, The lower critical temperature and the more symmetric phase diagram of WZ structure indicate it has better thermodynamic stability, which is in agreement with experiments.

1. Introduction
Zinc Oxide alloys in further developments of optoelectronics have attracted extensive attention in last few years. Yoo et al[1] reported, the range of concentration is 0 < x < 0.15 for the ZnO\(_x\)S\(_{1-x}\) films by pulsed laser deposition. Meyer et al[2] extend a wider range of the alloy concentration to 0 ≤ x ≤ 1 in the temperature ∼620 K by RF reactive sputtering. A zinc-blende (ZB) phase was expected to the thermodynamically stable phase of ZnS structure and theoretical studies mainly focused on the phase stability of ZB-ZnO\(_x\)S\(_{1-x}\) alloy[3, 4]. For example, Ito et al studied ZB-ZnO\(_x\)S\(_{1-x}\) alloy with the valence force field (VFF) method[3]. Moon et al have made some theoretical studies about ZB-ZnO\(_x\)S\(_{1-x}\) alloy using special quasi-random structures (SQSs)[5]. While a wurtzite (WZ) phase was expected to the thermodynamically stable phase of ZnO structure and the thermodynamically stable phase of ZnOS alloy needs to a comparative study of these two structures. To our knowledge, X. F. Fan et al have made some theoretical studies about the ZB and WZ phase stability of ZnOS alloy. However, they didn’t consider the effect of lattice vibrations which makes the critical temperatures for ZB and WZ phase is too high to mix randomly ZnO and ZnS[6]. In this work, we obtain the composition-temperature (x-T) phase diagrams of the solid solution of ZB and WZ ZnO\(_x\)S\(_{1-x}\) alloys from the spinodal and binodal curves. Since the understanding of phase diagrams can provide an insight into the growth process of ZnO\(_x\)S\(_{1-x}\). The main focus of this work is to obtain the composition-temperature (x-T) phase diagrams of ZB and WZ ZnO\(_x\)S\(_{1-x}\) alloys by taking into consideration the effect of lattice vibrations.

2. Method of calculation
Our calculations have been made using Density Functional Theory (DFT) under the generalized gradient approximation (GGA) along with the ultrasoft pseudopotentials[7] as implemented in the Quantum ESPRESSO package[8]. The Alloy Theoretic Automated Toolkit (ATAT) is a suite of
software tools which encourage users to contribute[9]. It relies upon the cluster expansion formalism[10, 11, 12] that can be used to calculate thermodynamic properties of alloys.

In this work, the total force is converged at the $10^{-3}$ eV/Å cation$^{-1}$ level and the total energy is converged at the $10^{-4}$ eV cation$^{-1}$ level. The kinetic energy cutoff is 1088 eV. The total energies are obtained after the energy minimization is finished.

3. Results and discussions

3.1 Thermodynamic properties without lattice vibrations

Thermodynamic properties of ZB and WZ ZnO$_{1-x}$S$_x$ alloys are calculated by estimating the solubility limit. The effects of lattice vibrations were not previously included. The thermal stability of alloys without the consideration of lattice vibrations is determined by the Helmholtz free energy[13]:

$$\Delta F(x, T) = \Delta H(x, T) - T\Delta S(x, T),$$

(1)

Within the Bragg-Williams mean-field approximation, the entropy is given by

$$\Delta S(x) = -k_B[x \ln x + (1 - x) \ln(1 - x)],$$

(2)

Figure 1 shows a comparison of the ZB and WZ ZnO$_{1-x}$S$_x$ composition-temperature ($x$-T) phase diagrams. The critical temperatures (Tc) are 2499 K and 1876 K respectively for ZB and WZ phases, respectively, which are much lower than the Tc (4018 K and 3831 K) calculated using the SQS[6]. It is because we choose the bigger supercells in CE than those of SQS which are only supercell for the ZB structure and or supercells for the WZ structure. The wide range between spinodal and binodal curves may exist as metastable phase, where the phase separation may occur. And on the S-rich side, the ranges of the metastable region are relatively larger for ZB phase than for WZ phase. On the O-rich side, the reverse situation occurs. The WZ ZnO$_{1-x}$S$_x$ phase diagram is more symmetric with a peak at $x = 0.488$, as compared to $x = 0.449$ in the ZB ZnO$_{1-x}$S$_x$ phase diagram. The concentration is less than 7% in the O-rich region for WZ phase and the limit of phase separation is about 10% in the S-rich region for ZB phase at the growth temperature of 1000 K. The values are consistent with the previous experimental results where the author achieved the ZB structure ZnO$_{1-x}$S$_x$ for and the WZ structure for in the bulk crystal[14].

3.2 Thermodynamic properties with lattice vibrations

The vibrational effect may have an important contribution to the stability of alloy phase in In$_2$Ga$_{1-x}$N alloy[15]. The phonon contribution to the free energy was determined within the harmonic approximation using the stiffness-vs.-length scheme[16]. The effective springs of a Born-von Karman model are often transferable from one structure to another after controlling bond length[17-19], or

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Figure 1. The x-T phase diagram for zinc-blende (ZB) and wurtzite (WZ) ZnO$_{1-x}$S$_x$. Dashed lines and the red solid line represent the spinodal and binodal curves for ZB structures. Dashed lines and the black solid line represent the spinodal and binodal curves for WZ structures.
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composition[20]. The vibrational free energy $G_v$ with the corresponding temperature was given out. We calculate the vibrational free energy difference $\Delta G_v$ as

$$\Delta G_v = G_v(ZnO_{1-x}S_x) - xG_v(ZnS) - (1-x)G_v(ZnO),$$

(3)

The free energy of formation $\Delta G$ of the ZnO$_{1-x}$S$_x$ alloy is given by

$$\Delta G = \Delta H - T\Delta S + \Delta G_v,$$

(4)

Figure 2 shows a comparison of the ZB and WZ ZnO$_{1-x}$S$_x$ phase diagrams with the effects of lattice vibrations. As shown in Figure 1 and Figure 2, inclusion of the lattice vibrational effect reduces the critical temperature $T_c$ 20.7% for the ZB ZnO$_{1-x}$S$_x$ from 2499 K to 1981 K. For the WZ structure, $T_c$ is reduced by about 16.7% from 1876 K to 1563 K. The WZ structure has a lower $T_c$ and is more symmetric than the ZB structure. The lower critical temperature and the more symmetric phase diagram of WZ structure indicate it has better thermodynamic stability, which is in agreement with experiments by He et al[21].

![Figure 2](image)

**Figure 2.** The $x$-$T$ phase diagram for zinc-blende (ZB) and wurtzite (WZ) ZnO$_{1-x}$S$_x$ (including the effects of lattice vibrations). The red solid line and dashed lines represent the binodal and spinodal curves for ZB structures. The black solid line and dashed lines represent the binodal and spinodal curves for WZ structures.

### 4. Conclusion

In summary, thermodynamic properties of zinc-blende (ZB) and wurtzite (WZ) ZnO$_{1-x}$S$_x$ has been studied with the first-principles methods. The thermodynamic $x$-$T$ phase diagrams are calculated and the critical temperatures of $T_c = 1981$ K for ZB structures and $T_c = 1563$ K for WZ are found with the inclusion of the lattice vibrational effects. With the analysis of the $x$-$T$ phase diagram, the lower critical temperature and the more symmetric phase diagram of WZ structure indicate it has better thermodynamic stability, which is in agreement with experiments.

### Acknowledgments

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

[1] Yoo, Y.Z., Jin, Z.-W., Chikyow, T., Fukumura, T., Kawasaki, M., Koinuma, H. (2002) S doping in ZnO film by supplying ZnS species with pulsed-laser-deposition method. Appl. Phys. Lett., 81: 3798-3800

[2] Meyer, B.K., Polity, A., Farangis, B., He, Y., Hasselkamp, D., Kra¨mer, T., Wang, C. (2004) Structural properties and bandgap bowing of ZnO_{1-x}S_{x} thin films deposited by reactive sputtering. Appl. Phys. Lett., 85: 4929-4931

[3] Ito, Y., Nabetani, Y., Kato, T., Matsumoto, T. (2003) Theoretical analysis of microscopic strain distribution and phase stability of Zn chalcogenide alloys using Valence force field model. Mat. Sci. Semicon. Proc., 6: 409-412

[4] Janetzko, F., Jug, K. (2004) Miscibility of zinc chalcogenides. J. Phys. Chem. A, 108: 5449-5453

[5] Moon, C.-Y., Wei, S.-H., Zhu, Y., Chen, G. (2006) Band-gap bowing coefficients in large size-mismatched II-VI alloys: first-principles calculations. Phys. Rev. B, 74: 233202

[6] Fan, X.F., Shen, Z.X., Lu, Y.M., Kuo, J.-L. (2009) A theoretical study of thermal stability and electronic properties of wurtzite and zincblende ZnO,S_{1-x}. New J. Phys., 11: 093008-1-16

[7] Vanderbilt, D. (1990) Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. Phys. Rev. B, 41: 7892-7895

[8] Giannozzi, P., Baroni, S., Bonini, N., Calandra, M. (2009) QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J. Phys.: Condens. Matter, 21: 395502-1-19

[9] Powell, A.C., Arroyave, R. (2008) Open source software for materials and process modelling. JOM 60: 32-39

[10] Fontaine, D.D. (1994) Cluster approach to order-disorder transformations in alloys. Solid State Phys., 47: 33-176

[11] Wolverton, C., Ozolins, V., Zunger, A. (2000) Short-range-order types in binary alloys: a reflection of coherent phase stability. J. Phys.: Condens. Matter, 12: 2749-2768

[12] Ceder, G., van de Walle, A., Marianetti, C., Morgan, D. (2000) First-principles alloy theory in oxides. Modelling Simul. Mater. Sci. Eng., 8: 311-321

[13] Chen, A.B., Sher, A. (1995) Semiconductor Alloys: Physics and Material Engineering. Plenum Press, New York.

[14] Locmelis, S., Br¨unig, C., Binnewies, M., B¨orger, A., Becker, K.D., Homann, T., Bredow, T. (2007) Optical band gap in the system ZnO_{1-x}S_{x}. An experimental and quantum chemical study. J. Mater. Sci., 42: 1965-1971

[15] Gan, C., Feng, Y., Srolovitz, D. (2006) First-principles calculation of the thermodynamics of In_{x}Ga_{1-x}N alloys: Effect of lattice vibrations. Phys. Rev. B, 73: 235214

[16] van de Walle, A., Ceder, G. (2002) The Effect of Lattice Vibrations on Substitutional Alloy Thermodynamics. Rev. Mod. Phys., 74: 11-45

[17] van de Walle, A., Ceder, G. (2000) First-Principles Computation of the Vibrational Entropy of Ordered and Disordered Pd3V. Phys. Rev. B, 61: 5972-5978

[18] Morgan, D., van de Walle, A., Ceder, G., Althoff, J.D., Fontaine, D.D. (2000) Vibrational thermodynamics: coupling of chemical order and size effects. Mater. Sci. Eng., 8: 295

[19] Wu, E.J., Ceder, G., van de Walle, A., Asta, M. (2003) Using bond-length dependent transferable force constants to predict vibrational entropies in Au-Cu, Au-Pd, and Cu-Pd alloys. Phys. Rev. B 67: 134103-1-7

[20] Liu, J., Ghosh, G., van de Walle, A., Asta, M. (2007) Transferable force-constant modeling of vibrational thermodynamic properties in fcc-based Al-TM (TM = Ti, Zr, Hf) alloys. Phys. Rev. B 75: 104117

[21] He, Y., Wang, L., Zhang, L., Li, M., Shang, X., Fang, Y., Chen, C. (2012) Solubility limits and phase structures in epitaxial ZnO/S alloy films grown by pulsed laser deposition. J. Alloy. Compd. 534: 81-85