Theoretical Prediction of Thermodynamic Properties of Cd\(_x\)Zn\(_{1-x}\)S (0 ≤ \(x\) ≤ 1) under the Effects of Pressure (0–10 GPa) and Temperature (0–1200 K)

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A comprehensive study of thermodynamic properties of Cd-substituted zinc sulphide (zinc blende phase) has been performed by using quasi harmonic Debye model in a wide range of temperature (0–1200 K) and pressure(0–10 GPa). The Cd substitutions can effectively tailor the thermodynamic properties of various materials to get desirable properties. Cd rich Cd\(_x\)Zn\(_{1-x}\)S have least thermal conductivity, bulk modulus, and the Debye temperature whereas the molar heat capacities, the Grüneisen parameter, and entropy are found to be relatively high. The anharmonicity of the semiconducting system changes in response of variation in temperature and pressure which in turn control the thermal expansion of the Cd\(_x\)Zn\(_{1-x}\)S. Internal energy, free energy, and entropy are more temperature sensitive as compared to the pressure.

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1. Introduction

The search of new materials with improved thermal, electrical, and optical properties have increased the interest of technologists in the semiconductors. The II–VI semiconductors have been used for various technologically important applications like solar cells [1, 2], light emitting diodes [3, 4], and displays of luminescent biological tags [5, 6], etc. The working of all these devices is based upon the motion of the electrons and thermal vibrations of the atoms. Thermal vibrations lead to the phonon contribution to the efficiency of devices which in turn control the heat dissipation in the devices. The knowledge of different thermodynamic properties of the materials like thermal conductivity, free energy, and molar heat capacities is essential for the fabrication of all optoelectronic and thermoelctrical devices. The technologists are more interested in a semiconductor which has reduced values of thermal conductivity and free energy. These thermal properties can be tailored by the formation of solid solutions, substitution of impurities, and reduction of the grain size [7].

The most of the members of II–VI group crystallize either in zinc blende or wurzite structure and some can crystallize in both phases [8, 9] like ZnS. Cd substituted ZnS in zinc blende phase has been extensively studied theoretically as well as experimentally for their electronic and optical properties [10–16]. But there is no comprehensive study found in the literature for thermodynamic properties of Cd-substituted zinc sulphide in zinc blende phase. In the present work, a systematic first principles study has been carried on Cd-substituted zinc sulphide for the measurement of various thermodynamic properties over a wide range of temperature (0–1200 K) and pressure(0–10 GPa).

2. Theory and computational details

WIEN2k code [17] has been used to implement the density functional theory (DFT) for structural optimization of the materials with the help of full potential linearized augmented plane wave plus local orbital (FP-LAPW+lo) method. The generalized gradient approximation is used as exchange and correlational functional whereas the Hubbard parameter is included to enhance the accuracy of results. The core and valence states are separated by −9.5 Ry energy for all the materials under consideration. The self consistency is obtained by 2000 k-points in full Brillouin zone. The iteration process is repeated until the total calculated energy, charge, and force approach to 10\(^{-5}\) Ry, 10\(^{-4}\) e, and 1 mRy/bohr, respectively. The Hubbard parameters (U) employed in this study are 5.0 eV and 3.44 eV for ZnS and CdZnS, respectively, which are optimized by the method proposed by Gunnarsson et al. [18].

The thermodynamic properties have been modeled by help of quasi harmonic Debye model embedded in GIBBS2 code [19]. The Gibbs function in the scope of this model can be represented as [20]:

\[
G^*(V; P, T) = E(V) + PV + F_{\text{vib}}(\Theta_D, T). 
\]

(1)

\(E(V)\) represents the total energy per unit volume of the cell, \(P\) is hydrostatic pressure, and \(\Theta_D\) is the Debye temperature. \(F_{\text{vib}}(\Theta_D, T)\) is lattice contribution to the Helmholtz free energy which is mathematically stated as [18]:

\[
F_{\text{vib}}(\Theta_D, T) = n k_B T \left[ \frac{9}{8} x + 3 \ln (1 - e^{-x}) - D(x) \right]. 
\]
In the above equation \( x = \frac{\Theta_D}{\Theta_D^0} \) is a dimensionless parameter, whereas \( n \) is number of atoms per unit cell and 
\[ D(x) = \frac{1}{3} \int_0^1 \frac{y^3}{e^y - 1} \, dy \]
is the Debye integral.

The \( \Theta_D \) of the materials is evaluated by
\[ \Theta_D = \frac{\hbar}{k_B} \left( 6\pi V^{1/2} \right)^{1/3} f(\sigma) \sqrt{\frac{B}{M}}, \tag{2} \]

Here \( B \) is bulk modulus and \( M \) is molecular mass of unit cell. The explicit function \( f(\sigma) \) is given as
\[ f(\sigma) = \left\{ \frac{1}{3} \left[ 2 \left( \frac{2(1+\sigma)}{3(1-2\sigma)} \right)^{3/2} + \left( \frac{1+\sigma}{3(1-\sigma)} \right)^{3/2} \right] \right\}^{-1/3}. \]

Here \( \sigma \) is the Poisson ratio.

The following relations can be used to determine the specific heat \( C_v \), entropy \( S_{vib} \), internal energy \( U_{vib} \), and thermal expansion coefficient \( \alpha \), etc. [18]:
\[ C_v = 3nk_B \left[ 4D(x) - \frac{3x}{e^x - 1} \right], \tag{3} \]
\[ S_{vib} = nk_B \left[ 4D(x) - 3\ln \left( 1 - e^{-x} \right) \right], \tag{4} \]
\[ U_{vib} = 3nk_B \left[ \frac{3}{8} \Theta_D + TD(x) \right], \tag{5} \]
\[ \alpha = \frac{\gamma C_v}{BV} \text{ with } \gamma = -\frac{d(\ln \Theta_D(V))}{d(\ln V)}, \tag{6} \]

where \( \gamma \) is the Grüneisen parameter.

Slack’s equation [21] can be used to determine the thermal conductivity \( \kappa \) of semiconductors i.e.
\[ \kappa = A \frac{M \Theta_D^0 V}{\gamma^2 T_n^{2/3}}. \tag{7} \]

The constant \( A \) is determined by Julian et al. [22] by using the Grüneisen parameter, i.e.:
\[ A = \frac{2.43 \times 10^{-8} \gamma^2}{(\gamma^2 - 0.514\gamma + 0.228)}. \tag{8} \]

3. Results and discussions

Bulk modulus is an important parameter to determine the mechanical strength of a material. The composition dependent variation of the bulk modulus is displayed in Fig. 1 and compared with Vegard’s law. The results show a slight deviation from Vegard’s law which may be due to mismatch of the lattice constants of ZnS and CdS. Furthermore, the bulk modulus is found to decrease with increase in Cd concentration in Cd\textsubscript{x}Zn\textsubscript{1−x}S (where 0 ≤ \( x \) ≤ 1) which shows that compressibility of Cd\textsubscript{x}Zn\textsubscript{1−x}S increases with increase in Cd concentration (\( x \)).

The effect of temperature on bulk modulus can be understood by studying its relationship with anharmonic interatomic potential [23]. These interatomic potentials can be used to measure the strength of interatomic forces which hold a solid together. When temperature is increased these forces are weakened which in turn decrease the bulk modulus. The increase in pressure will
increase the packing fraction of the solid and as a result, the bulk modulus will increase. The bulk modulus can be used to determine the $\Theta_D$ by using Eq. (2). The Debye temperature relates the elastic properties with thermodynamic properties and can be stated as the temperature of highest normal mode of vibration. The hard materials have high values of $\Theta_D$ and bulk modulus and therefore, variations of $\Theta_D$ is almost the same as that of bulk modulus of Cd$_x$Zn$_{1-x}$S as function of Cd concentration as shown in Fig. 2. The variation in $\Theta_D$ and bulk modulus is approximately constant between 75% and 100% Cd substitutions. The $\Theta_D$ and heat capacities are strongly dependent on phonon frequencies in a solid [7]. Cd substitutions may significantly change the phonon frequencies of ZnS which in turn increase the molar heat capacities $C_v$ and $C_p$. The effect of Cd concentration to $C_v$ and $C_p$ between 75% and 100% is negligible whereas they show a slight dependence to Cd concentration when Cd concentration is less than Zn concentration. The effect of pressure on molar heat capacities have been displayed in Fig. 3 and Fig. 4 which show that their values are decreased for increasing pressure. Molar heat capacities follow $T^3$ law at low temperature limit whereas they are found independent of temperature in high temperature limit. $C_v$ approaches to classical limit and converges to same value of 50 J/(mol K) at high temperature but $C_p$ does not converge to same value at high temperature due to thermal expansion. The values of $C_p$ are different than
Comparison of calculated thermodynamic properties of Cd$_x$Zn$_{1-x}$S at $P = 0$ GPa and $T = 300$ K with available experimental and theoretical data.

<table>
<thead>
<tr>
<th>Property</th>
<th>ZnS</th>
<th>Cd$<em>{0.25}$Zn$</em>{0.75}$S</th>
<th>Cd$<em>{0.50}$Zn$</em>{0.50}$S</th>
<th>Cd$<em>{0.75}$Zn$</em>{0.25}$S</th>
<th>CdS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$ [GPa]</td>
<td>this work exp.</td>
<td>74.85, 76.9°</td>
<td>68.27</td>
<td>62.06</td>
<td>60.90</td>
</tr>
<tr>
<td></td>
<td>other calc.</td>
<td>73.97°, 80.97°, 79.9°, 83.1°</td>
<td>72.21°</td>
<td>67.88°</td>
<td>62.91°, 55.8°, 61.69°</td>
</tr>
<tr>
<td></td>
<td>2.18</td>
<td>2.042°</td>
<td>2.22</td>
<td>2.23</td>
<td>2.24</td>
</tr>
<tr>
<td></td>
<td>0.5°, 2.15°</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma$ (gamma)</td>
<td>this work exp.</td>
<td>22.91°</td>
<td>20°, 27°</td>
<td>11.33°</td>
<td>27.39</td>
</tr>
<tr>
<td></td>
<td>other calc.</td>
<td></td>
<td></td>
<td></td>
<td>25.12°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>22.78</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.75</td>
</tr>
<tr>
<td>$S_{vib}$ [J mol$^{-1}$ K$^{-1}$]</td>
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<td>56.21°</td>
<td>57°</td>
<td>62.2°</td>
<td>65.2°</td>
</tr>
<tr>
<td></td>
<td>other calc.</td>
<td>88.4°, 55°</td>
<td></td>
<td></td>
<td>67.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>67.98</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>69.04°, 72°</td>
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<td></td>
<td></td>
<td>95°, 92°</td>
</tr>
<tr>
<td>$U_{vib}$ [kJ mol$^{-1}$]</td>
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<td>17°</td>
<td>16.02°</td>
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<tr>
<td></td>
<td>other calc.</td>
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<td>15.75</td>
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<td>15.72</td>
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<td></td>
<td></td>
<td>16°</td>
</tr>
<tr>
<td>$C_v$ [J mol$^{-1}$ K$^{-1}$]</td>
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<td>46.72°</td>
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<td></td>
<td>47°, 48°</td>
</tr>
<tr>
<td>$C_p$ [J mol$^{-1}$ K$^{-1}$]</td>
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<td>47.41°</td>
<td>48.56°</td>
<td>48.90°</td>
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<td>other calc.</td>
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<td></td>
<td></td>
<td>49.40</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>53.97°, 48.6°</td>
</tr>
<tr>
<td>$\Theta_\text{D}$ [K]</td>
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<td>345</td>
<td>320</td>
<td>308.51</td>
</tr>
<tr>
<td></td>
<td>other calc.</td>
<td>230°, 349°</td>
<td></td>
<td></td>
<td>303.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>370°, 17°, 379°</td>
<td></td>
<td></td>
<td>286°, 265°</td>
</tr>
<tr>
<td>$F_{vib}$ [kJ mol$^{-1}$]</td>
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<td>0.0085°</td>
<td>−2.5</td>
<td>−3.81</td>
<td>−4.59</td>
</tr>
<tr>
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<td>other calc.</td>
<td>0.5°</td>
<td></td>
<td></td>
<td>−4.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−5°</td>
</tr>
<tr>
<td>$\alpha$ [$10^{-5}$ K$^{-1}$]</td>
<td>this work exp.</td>
<td>5.71°</td>
<td>6.51</td>
<td>6.65</td>
<td>6.74</td>
</tr>
<tr>
<td></td>
<td>other calc.</td>
<td>6.8°</td>
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<td></td>
<td>7.12</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>8.5°, 2.3°</td>
</tr>
</tbody>
</table>

References: [9, 24], [25], [26], [27], [28], [29], [30], [31], [32], [33], [34], [35], [36], [37], [38], [39], [40], [41], [42], [43], [24], [44], [45], [46], [47]
Fig. 6. Variation in thermal expansion coefficient of Cd$_x$Zn$_{1-x}$S as a function of Cd concentration. Effect of (a) temperature, (b) pressure on $\alpha$.

Fig. 7. Variation in internal energy of Cd$_x$Zn$_{1-x}$S as a function of Cd concentration. Effect of (a) temperature, (b) pressure on $U_{vib}$.

Fig. 8. Variation in Helmholtz free energy of Cd$_x$Zn$_{1-x}$S as a function of Cd concentration. Effect of (a) temperature, (b) pressure on $F_{vib}$.

Fig. 9. Variation in entropy of Cd$_x$Zn$_{1-x}$S as a function of Cd concentration. Effect of (a) temperature, (b) pressure on $S_{vib}$. 
$E(Z)$ and $F_{el}$ represent the static energy and electronic contribution to free energy, respectively. $F_{el}$ can be neglected in case of semiconductors and insulator at room and higher temperature due to relatively less contribution in comparison of lattice contribution. Free energy and internal energy are related by $F_{el} = U_{el} - TS_{el}$ where $S_{el}$ is vibrational contribution to entropy. Cd substituted ZnS has slightly less free energy than the pure ZnS which shows that Cd rich Cd$_x$Zn$_{1-x}$S is more thermally stable. The internal energy slightly decreases with increase in Cd concentration whereas Cd rich ZnS has more vibrational entropy as compared to pure ZnS. The internal energy and entropy are found to increase with rise of temperature due to enhanced vibrational frequencies. At high temperature free energy decreases due to increased value of entropic contribution of energy ($TS$). The internal energy, entropy, and free energy are found to be more temperature dependent as compared to their pressure dependence as represented in Figs. 7–9.

4. Conclusions

Quasi harmonic Debye model has been used to study the thermodynamic properties of Cd-substituted zinc sulphide which may be helpful to choose an appropriate material for device fabrication. Our study shows that Cd rich zinc sulphide has less bulk modulus, the Debye temperature, and thermal conductivity. More pronounced variations are found in bulk modulus, the Debye temperature, molar heat capacities, and thermal expansion coefficient when Cd concentrations are less than Zn concentrations in Cd$_x$Zn$_{1-x}$S. The molar heat capacity $C_v$ approaches to classical limit at high temperature irrespective of percentage compositions of Cd but $C_p$ does not converge to same value due to large anharmonic oscillations. Anharmonicity, thermal expansion coefficient, internal energy, and entropy are found to increase with rise of temperature whereas bulk modulus, the Debye temperature, and free energy have opposite temperature dependence. At higher temperature, a rapid increase in the Grüneisen parameter and thermal expansion coefficient is found when Cd concentration is less than Zn concentration which shows that Zn atom (being lighter element than Cd) is oscillating with larger amplitude. The various thermodynamic properties are more temperature dependent as compared to pressure. Most of the calculated thermodynamic properties are in good agreement to available theoretical and experimental data at ambient conditions as presented in Table I.

References