

Theoretical Prediction of Thermodynamic Properties of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ ($0 \leq x \leq 1$) 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 $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ 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 $\text{Cd}_x\text{Zn}_{1-x}\text{S}$. 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 thermoelectric 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 wurtzite 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]:

$$G^*(V; P, T) = E(V) + PV + F_{\text{vib}}(\Theta_{\text{D}}, T). \quad (1)$$

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

$$F_{\text{vib}}(\Theta_{\text{D}}, T) = nk_{\text{B}}T \left[\frac{9}{8}x + 3 \ln(1 - e^{-x}) - D(x) \right].$$

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In the above equation $x = \frac{\Theta_D}{T}$ is a dimensionless parameter, whereas n is number of atoms per unit cell and $D(x) = \frac{3}{x^3} \int_0^x \frac{y^3 e^{-y}}{1 - e^{-y}} dy$ is the Debye integral.

The Θ_D of the materials is evaluated by

$$\Theta_D = \frac{\hbar}{k_B} \left(6\pi V^{1/2} n \right)^{1/3} f(\sigma) \sqrt{\frac{B}{M}}. \quad (2)$$

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 σ 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 α , etc. [18]:

$$C_v = 3nk_B \left[4D(x) - \frac{3x}{e^x - 1} \right], \quad (3)$$

$$S_{vib} = nk_B \left[4D(x) - 3 \ln(1 - e^{-x}) \right], \quad (4)$$

$$U_{vib} = 3nk_B \left[\frac{3}{8} \Theta_D + TD(x) \right], \quad (5)$$

$$\alpha = \frac{\gamma C_v}{BV} \text{ with } \gamma = -\frac{d(\ln \Theta_D(V))}{d(\ln V)}, \quad (6)$$

where γ is the Grüneisen parameter.

Slack's equation [21] can be used to determine the thermal conductivity κ of semiconductors i.e.

$$\kappa = A \frac{M \Theta_D^3 V}{\gamma^2 T n^{2/3}}. \quad (7)$$

The constant A is determined by Julian et al. [22] by using the Grüneisen parameter, i.e.:

$$A = \frac{2.43 \times 10^{-8} \gamma^2}{(\gamma^2 - 0.514\gamma + 0.228)}. \quad (8)$$

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 $Cd_xZn_{1-x}S$ (where $0 \leq x \leq 1$) which shows that compressibility of $Cd_xZn_{1-x}S$ 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 then these forces are weakened which in turn decrease the bulk modulus. The increase in pressure will

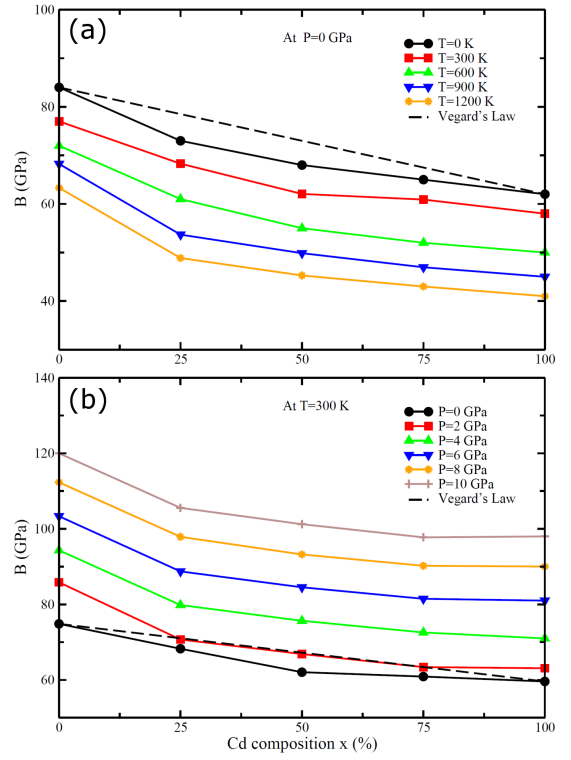


Fig. 1. Variation in bulk modulus of $Cd_xZn_{1-x}S$ as a function of Cd concentration. Effect of (a) temperature, (b) pressure on bulk modulus.

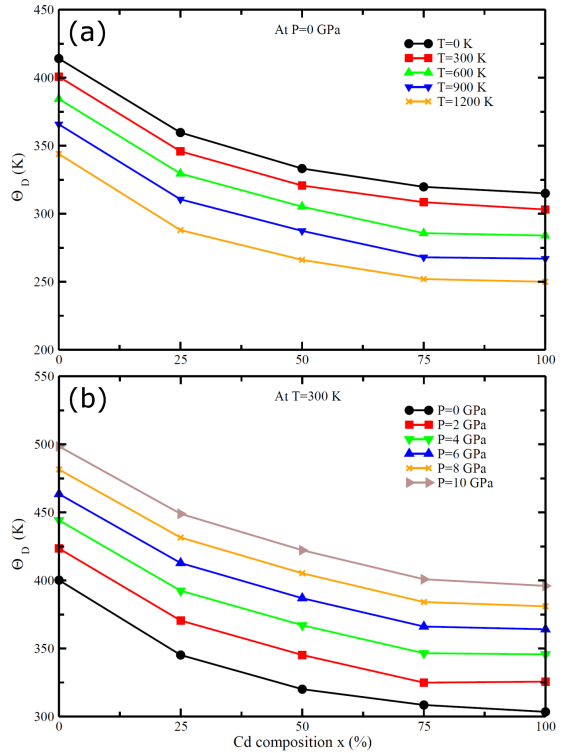


Fig. 2. Variation in the Debye temperature of $Cd_xZn_{1-x}S$ as a function of Cd concentration. Effect of (a) temperature, (b) pressure on Θ_D .

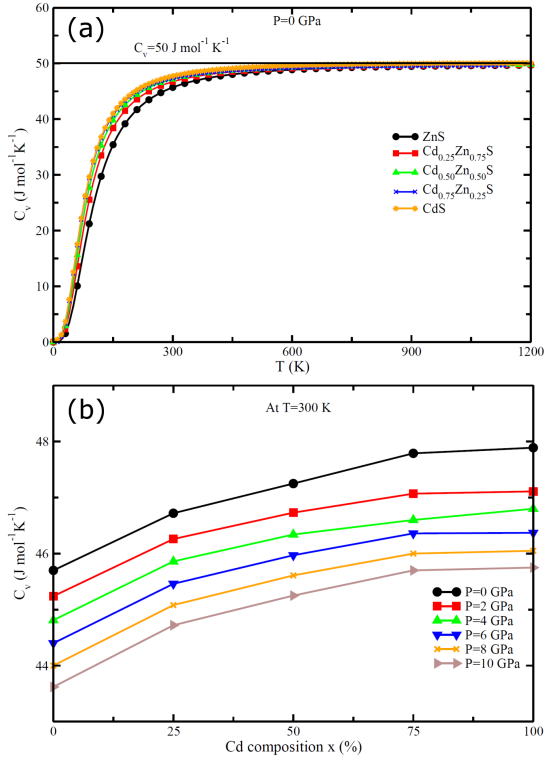


Fig. 3. Variation in C_v of $Cd_xZn_{1-x}S$ as a function of Cd concentration. Effect of (a) temperature, (b) pressure on C_v .

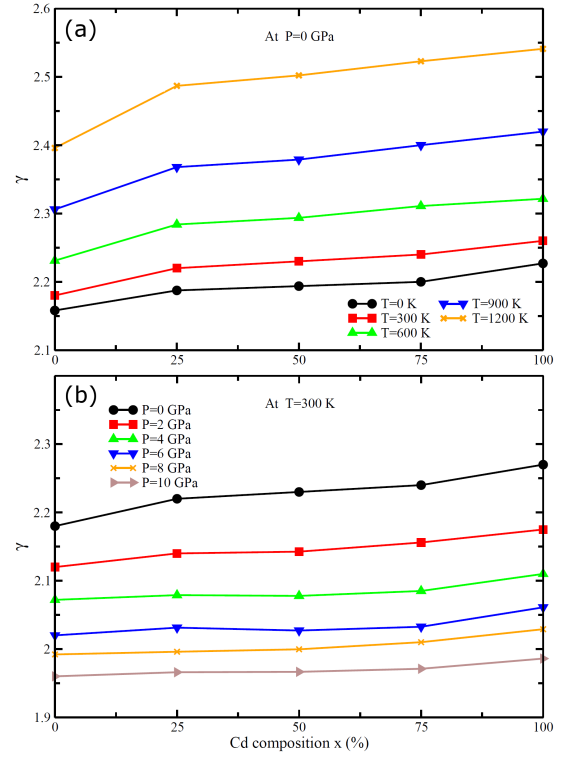


Fig. 5. Variation in Grüneisen parameter of $Cd_xZn_{1-x}S$ as a function of Cd concentration. Effect of (a) temperature, (b) pressure on γ .

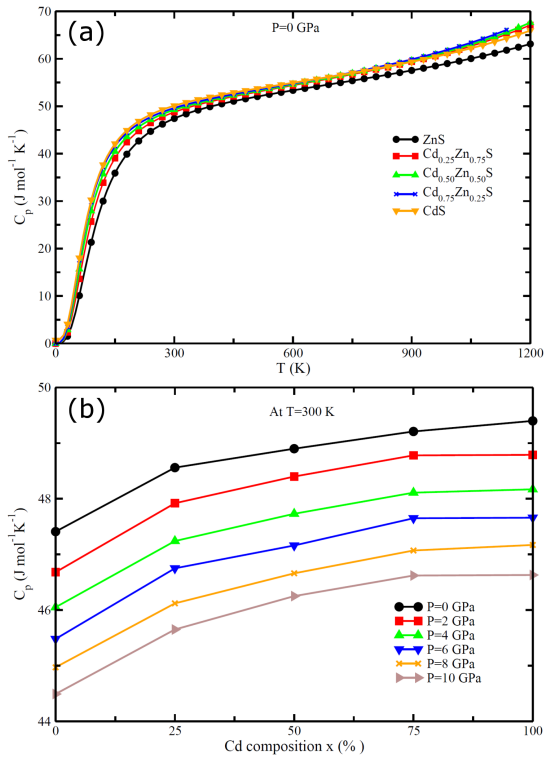


Fig. 4. Variation in C_p of $Cd_xZn_{1-x}S$ as a function of Cd concentration. Effect of (a) temperature, (b) pressure on C_p .

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 Θ_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 Θ_D and bulk modulus and therefore, variations of Θ_D is almost the same as that of bulk modulus of $Cd_xZn_{1-x}S$ as function of Cd concentration as shown in Fig. 2. The variation in Θ_D and bulk modulus is approximately constant between 75% and 100% Cd substitutions. The Θ_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

C_v due to anharmonic oscillations [9, 24]. Our calculated results of bulk modulus are 74.85 GPa and 59.60 GPa for ZnS and CdS which are in excellent agreement to experimental results of 76.9 GPa and 62 GPa [17] for ZnS and CdS, respectively. Most of our calculated results by employing GGA+U functional are in close agreement to available theoretical and experimental results taken from Refs. [10, 25–47] and compared in Table I.

A good semiconducting material for the fabrication of a thermoelectric device has high power factor with low value of κ . CdS has low value of the κ as compared to ZnS as inferred from this work. The acoustic phonons are considered to be decisive to determine the thermal conductivity [7] of semiconductors while the role of optical phonons is considered less due to their short life times and less group velocities [48]. A net decrease in thermal conductivity of $Cd_xZn_{1-x}S$ is found with increase in Cd substitutions. Our calculated values of thermal conductivities are close to experimental findings [37, 38].

The atoms in the semiconducting crystals deviate from their harmonic vibrations at some finite temperature and the material starts to expand. The thermal expansion of all materials is connected to anharmonicity which is measured by a dimensionless Grüneisen parameter. The

anharmonicity is related to many other factors like size of atoms, type of crystal structure, and nature of chemical bonds, etc. The anharmonicity of $Cd_xZn_{1-x}S$ increases with increase in Cd substitution. Thermal expansion coefficient is found to increase rapidly up to 25% Cd substitution and then approximately remain insensitive to Cd substitution from 25% to 100% of Cd substitutions. The substitution of Cd in ZnS may increase the ionicity of $Cd_xZn_{1-x}S$ (as the case of other zinc chalcogenides [49]) which may be the reason for less sensitivity of thermal expansion coefficient in 25% to 100% range of Cd substitutions. The Grüneisen parameter and thermal expansion coefficient are more sensitive to temperature as compared to pressure as shown in Fig. 5 and Fig. 6. A more pronounced increase is found in their values between 0% to 25% Cd substitutions at higher temperature. This may be due to the fact that Zn atom (lighter than Cd atom) is more oscillating at higher temperature.

Stability criterion for a structure is based on the Helmholtz free energy. A structure having more negative value of free energy is considered to be more stable. The Helmholtz free energy of a system at certain temperature T is $F(Z; T) = E(Z) + F_{el}(Z; T) + F_{vib}(Z; T)$ where Z represents the structural information of crystal.

Comparison of calculated thermodynamic properties of $Cd_xZn_{1-x}S$ at $P = 0$ GPa and $T = 300$ K with available experimental and theoretical data.

TABLE I

Property		ZnS	$Cd_{0.25}Zn_{0.75}S$	$Cd_{0.50}Zn_{0.50}S$	$Cd_{0.75}Zn_{0.25}S$	CdS
B [GPa]	this work	74.85	68.27	62.06	60.90	59.60
	exp. other calc.	76.9 ^a 73.97 ^b , 80.97 ^c , 79.9 ^d , 83.1 ^e	72.21 ^b	67.88 ^b	62.91 ^b , 55.8 ^f , 61.69 ^g	62 ^a 61.37 ^b , 50.8 ^h
γ (gamma)	this work	2.18	2.22	2.23	2.24	2.27
	other calc.	2.042 ⁱ				0.5 ^j , 2.15 ^k
κ [W m ⁻¹ K ⁻¹]	this work	22.91	27.39	25.12	22.78	16.75
	exp. other calc.	20 ^l , 27 ^m 11.33 ^k				16 ⁿ , 14 ⁿ , 20 ^o 3.59 ^k
S_{vib} [J mol ⁻¹ K ⁻¹]	this work	56.21	62.2	65.2	67.75	67.98
	exp. other calc.	57 ^p 88.4 ^q , 55 ^r				69.04 ^o , 72 ^o 95 ^s , 92 ^t
U_{vib} [kJ mol ⁻¹]	this work	16.32	16.02	15.98	15.75	15.72
	other calc.	17 ^u				16 ^s
C_v [J mol ⁻¹ K ⁻¹]	this work	45.70	46.72	47.25	47.89	47.99
	other calc.	46.29 ^v , 42.3 ^q				47 ^g , 48 ^s
C_p [J mol ⁻¹ K ⁻¹]	this work	47.41	48.56	48.90	49.21	49.40
	exp. other calc.	47 ^w 45 ^x				53.97 ^o , 48.67 ^o
Θ_D [K]	this work	400.21	345	320	308.51	303.45
	exp. other calc.	230 ^m , 349 ^y 370.17 ^v , 379 ^k				286 ^o , 265 ^o 375 ^g , 231 ^k
F_{vib} [kJ mol ⁻¹]	this work	0.0085	-2.5	-3.81	-4.59	-4.8
	other calc.	0.5 ^u				-5 ^s
α [$\times 10^{-5}$ K ⁻¹]	this work	5.71	6.51	6.65	6.74	7.12
	other calc.	6.8 ^x				8.5 ^g , 2.3 ^t

^a[25], ^b[10], ^c[26], ^d[27], ^e[28], ^f[29], ^g[30], ^h[31], ⁱ[32], ^j[33], ^k[34], ^l[35], ^m[36], ⁿ[37], ^o[38], ^p[39], ^q[40], ^r[41], ^s[42], ^t[43], ^u[24], ^v[44], ^w[45], ^x[46], ^y[47]

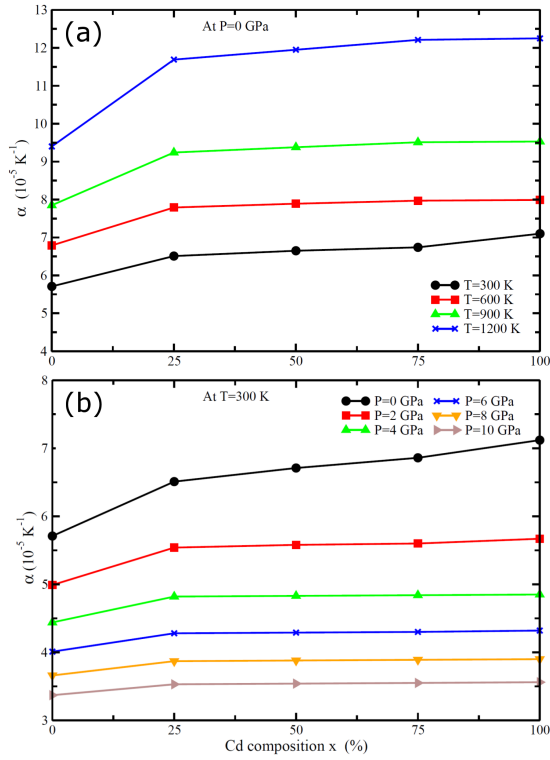


Fig. 6. Variation in thermal expansion coefficient of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ as a function of Cd concentration. Effect of (a) temperature, (b) pressure on α .

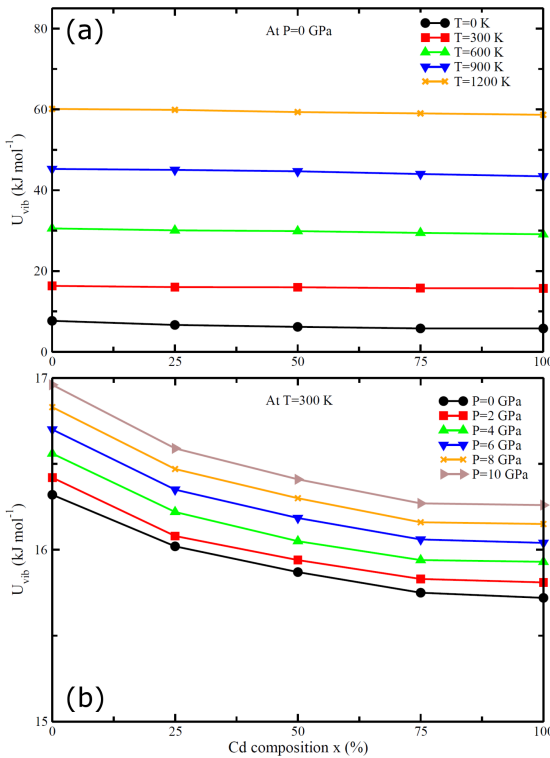


Fig. 7. Variation in internal energy of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ as a function of Cd concentration. Effect of (a) temperature, (b) pressure on U_{vib} .

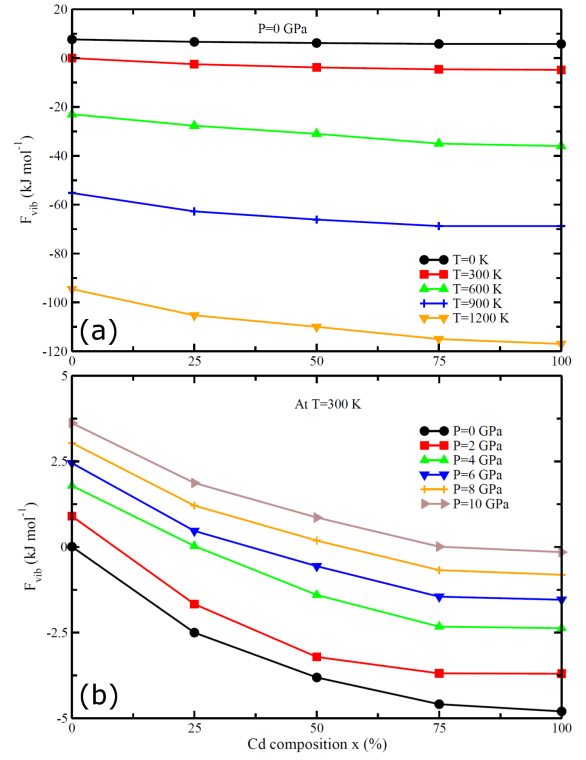


Fig. 8. Variation in Helmholtz free energy of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ as a function of Cd concentration. Effect of (a) temperature, (b) pressure on F_{vib} .

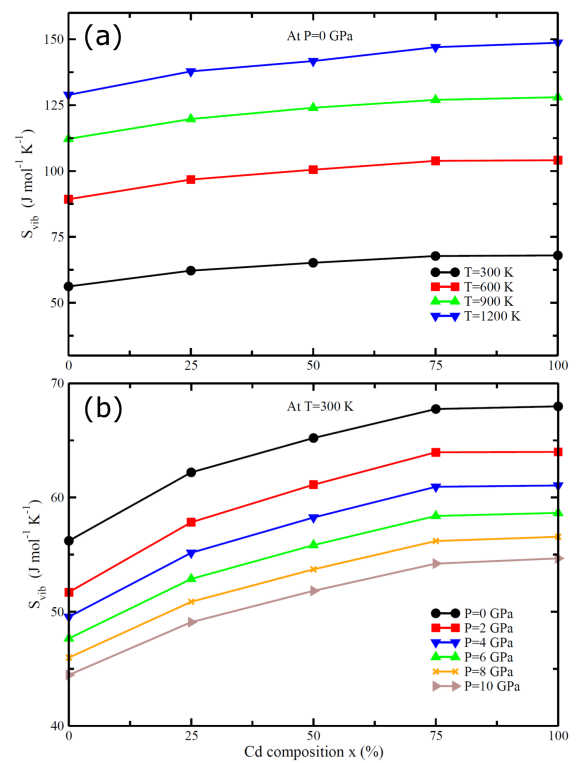


Fig. 9. Variation in entropy of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ as a function of Cd concentration. Effect of (a) temperature, (b) pressure on S_{vib} .

$E(Z)$ 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 $F_{vib} = U_{vib} - TS_{vib}$ where S_{vib} is vibrational contribution to entropy. Cd substituted ZnS has slightly less free energy than the pure ZnS which shows that Cd rich $Cd_xZn_{1-x}S$ 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 $Cd_xZn_{1-x}S$. 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.

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