

Structural, mechanical and thermodynamic properties of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) studied by a density functional theory method

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In the paper, we will investigate the basic physical properties of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) by using the density functional theory approach. The calculated lattice parameters are in good correspondence with the theoretical data, and the chosen theoretical method is proved to be reliable. In the first part, the Mulliken population analysis indicates the bonds between S atoms and other three atoms in Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) exhibit the feature of covalent bond. And then, the calculated elastic constants prove the mechanical stability of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) in I $\bar{4}2m$ structure. Results are given for B/G and A^U reveal Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) can behave as a ductile and elastic material. Finally, the pressure and temperature dependence of heat capacity, thermal expansion, entropy and Debye temperature in the rang from 0 to 1000 K and from 0 GPa to 50 GPa are also reported in this study.

1. Introduction

In the past few years, the earth abundant quaternary chalcopyrites [1–7] as $\text{Cu}_2\text{CoSnS}_4$ (CCTS) and related compounds ($\text{Cu}_2\text{CoSiS}_4$ (CCSiS), $\text{Cu}_2\text{CoGeS}_4$ (CCGeS)) are receiving much interest. The reason is that these compounds contain the earth abundant, environmental friendly, low cost, non-toxic elements, which is beneficial to the massive development of solar technology. Recently, the thin film solar cells with $\text{Cu}_2\text{CoSnS}_4$ (CCTS) and photoactive layers exhibited power conversion efficiency (PCE) value of 3.23%, which is bigger than $\text{Cu}_2\text{FeSnS}_4$ (2.73%) and $\text{Cu}_2\text{NiSnS}_4$ (2.71%) [8].

Similar to the $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), the quaternary materials Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) have the characteristic of high absorption coefficient ($\sim 10^4 \text{ cm}^{-1}$) and suitable band gap [9,10]. Cui et al. [11] and have been successfully synthesized $\text{Cu}_2\text{FeSnS}_4$ and $\text{Cu}_2\text{CoSnS}_4$ nanoparticles and indicated both of them are great potential in low-cost thin film. Zhang et al [12] had synthesized $\text{Cu}_2\text{CoSnS}_4$ and reported the stannite (ST) structure is stable. As has been reported [13], Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) compounds showed the tetrahedral stannite (I $\bar{4}2m$) structure. These three crystals structures are very similar with only cations in different positions. This makes caused great difficulty in the experiment among these three structures. In other side, there are no reports have described and compared about the structural parameters, elastic, and thermal parameters of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) so far.

In this framework, we employed the density function theory to report a systematic studies of the lattice parameters, Mulliken population analysis, elastic constants, and the thermal properties under high temperature and high pressure of stannite Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$). The structure of this paper is as follows: the calculation method and parameters setting have been given in Section 2; Section 3 focuses on the results and discussions, including the structural, elastic and thermal properties. The last section is the conclusion.

2. Computational details

In this paper, the calculation work of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) crystal were carried out by using first-principles method. The norm conserving ultra-soft pseudo-potentials with GGA-PBE functional [14–17] were performed for exchange-correlation energy calculations and the interaction between nuclei and the electrons. The valence electron configuration of Cu, Co, Si, Ge, Sn and S atoms

are $3d^{10}4s^1$, $3d^74s^2$, $3s^23p^2$, $3d^{10}4s^24p^2$, $4d^{10}5s^25p^2$, $3s^23p^4$ respectively. During the optimization, changing of the maximum force is taken as 0.01 eV/\AA . In order to ensure the accuracy and convergence of the calculation results, the cut off energy was at 500 eV . Brillouin zone integration was carried out using $5 \times 5 \times 5$ k -points mesh. In addition, the pressure and temperature dependence of thermodynamic quantity such as: specific heats, entropy and Debye temperature are obtained by using the Gibbs program [18–20].

3. Results and discussion

3.1. Structural properties

The crystal structures of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) compounds belong to the $I \bar{4}2m$ space group have been shown in Fig. 1. The crystal structure of these three materials is very similar, with eight atoms in each primitive cell, belonging to the body centered tetragonal symmetry. In the crystal structure, the coordinates of the atoms are: $\text{Co}:2a (0,0,0)$, $\text{Cu}:4d (0,1/2,1/4)$, $\text{S}:8i (x, y, z)$, and other three atoms ($\text{Si, Ge, Sn}:2b (0,0,1/2)$). Both crystal structures are tetragonal type, while the difference between them is the site position of their S atom.

The curve (Fig. 2) of total energy versus the volume for Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) can be obtained by fitting to Birch Murnaghan (BM) equation of state (EOS) [21–23]. The calculated equilibrium energies are -382.464 hartree for $\text{Cu}_2\text{CoSnS}_4$, -383.339 hartree for $\text{Cu}_2\text{CoGeS}_4$ and -383.388 hartree for $\text{Cu}_2\text{CoSiS}_4$, respectively. Grounded on these calculated values, we conclude that the ground energy is increasing with the atomic number (Sn, Ge and Si) increased.

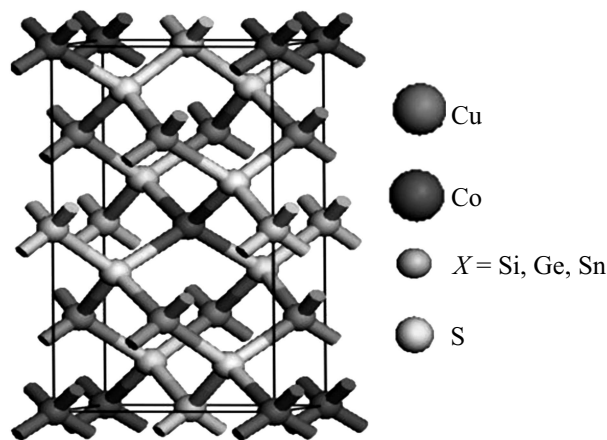


Figure 1. Crystalline structures of stannite Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$).

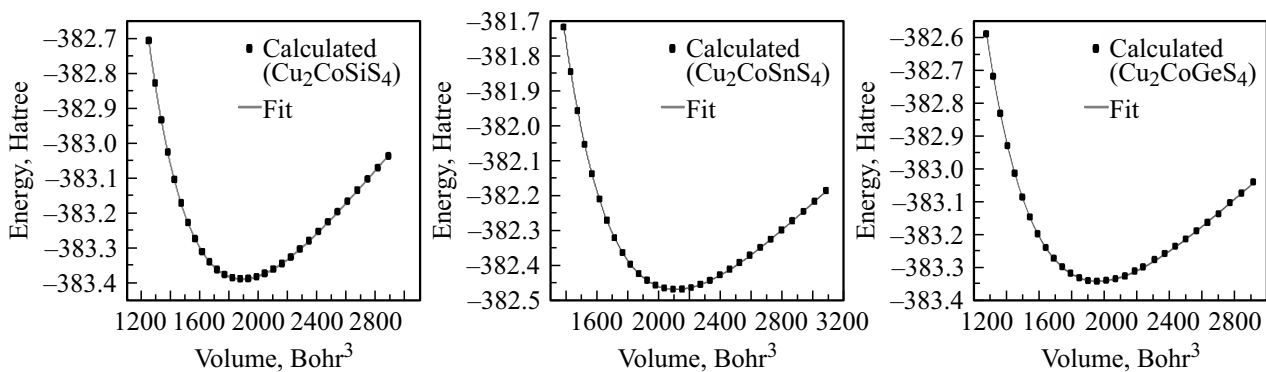


Figure 2. Computed total energy (Hartree) versus volume (Bohr^3) for Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$).

Table 1. Equilibrium structural parameters a , c , equilibrium volume and atomic positions, the pressure derivative (B) of bulk modulus, bond length and Mulliken population analysis

Compound	a (Å)	c (Å)	V_0 (Å ³)	B'	Mulliken population analysis		
					Bond	Population	Bond length / Å
$\text{Cu}_2\text{CoSnS}_4$	5.405	10.601	309.669	4.837	S–Cu	0.42	2.300
	5.399 [13]	10.818 [13]	315.36 [13]		S–Co	0.56	2.173
					S–Sn	0.16	2.566
$\text{Cu}_2\text{CoGeS}_4$	5.266	10.400	288.447	4.701	S–Cu	0.45	2.286
	5.296 [13]	10.474 [13]	293.74 [13]		S–Co	0.55	2.185
					S–Ge	0.13	2.331
$\text{Cu}_2\text{CoSiS}_4$	5.2249	10.2493	279.806	4.622	S–Cu	0.34	2.299
	5.2683 [13]	10.3350 [13]	286.85 [13]		S–Co	0.42	2.223
					S–Si	0.57	2.176

The equilibrium structural parameters (a , c), equilibrium volume and atomic positions, the pressure derivative (B) of bulk modulus, bond length and Mulliken population analysis are listed in Table 1. The calculated data in Table 1 reveals that the lattice parameters well agree in the theoretical values. In order to get more information about the chemical bonds, the mulliken population analysis of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) crystals are also shown in Table 1. By mulliken population analysis, the interaction between S atoms and Sn atoms is stronger than the other two interactions (S–Ge and S–Si). The bond lengths increase with the rising of atomic number, the situation is similar to that of ternary semiconductors [24]. In the case of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$), the bonds between S atoms and other three atoms exhibit the feature of covalent bond.

4. Elastic properties

The elastic constants are usually used to describe the hardness and stability of the materials. There are six independent components for Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) with the tetragonal phase, namely C_{ij} (C_{11} , C_{12} , C_{13} , C_{33} , C_{44} and C_{66}). Unfortunately, there are no reports about these parameters in previous work. Based on the results of C_{ij} , we can get more important mechanical parameters, such as the bulk modulus B , Poisson ratio ν , Lamé constants λ , and shear modulus G . All of these parameters of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) are summarized in Table 2. The calculated six elastic constants satisfy the Born stability criteria [25,26]: $C_{11} > |C_{12}|$, $(C_{11} + C_{12})C_{33} > 2C_{13}^2$, $C_{44} > 0$, and $C_{66} > 0$. All the structures of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) can be found to satisfy mechanical stability.

In order to get more information of the mechanical properties of the materials, B and G are calculated on the basis of elastic constants. The B and G can be calculated from elastic stiffness tensor in Voigt approximations and Reuss approximations [27]. For tetragonal structure, the Voigt approximations and Reuss approximations of G and B can be expressed as:

$$G_V = \frac{1}{15}(2C_{11} + C_{33} - C_{12} - 2C_{13} + 6C_{44} + 3C_{66}),$$

$$G_R = 15 \left\{ \frac{18B_V}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} + \frac{6}{C_{11} - C_{12}} + \frac{6}{C_{44}} + \frac{3}{C_{66}} \right\}^{-1},$$

$$B_V = \frac{1}{9}(2C_{11} + C_{33}2C_{12} + 4C_{13}), \quad B_R = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}}.$$

Table 2. Calculated elastic parameters for Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) compounds: elastic constants (C_{ij} , in GPa), bulk moduli (B_V , B_R , B , in GPa), shear moduli (G_V , G_R , G , in GPa), Pugh's indicator (B/G), Young's moduli (E , in GPa), Poisson's ratio (ν), Lamé's constant (λ , in GPa) and the elastic anisotropy indices (A^U)

C_{ij}	$\text{Cu}_2\text{CoSnS}_4$	$\text{Cu}_2\text{CoGeS}_4$	$\text{Cu}_2\text{CoSiS}_4$
C_{11}	91.680	108.201	270.224
C_{12}	70.231	81.459	99.181
C_{13}	68.453	73.992	79.882
C_{33}	97.858	91.747 107.199	
C_{44}	35.900	26.660	25.126
C_{66}	53.397	51.914	55.125
B_V, B_R	77.277, 77.226	85.226, 83.579	129.505, 101.552
B	77.251	84.402	115.528
G_V, G_R	29.978, 20.893	26.294, 20.134	46.989, 36.131
G	25.435	23.214	41.560
λ	60.294	68.926	87.822
E	34.921	37.170	159.707
σ	0.425	0.429	0.3364
A^U	2.174	1.549	1.778

As you can see in the Table 2 that the difference of B and G among $\text{Cu}_2\text{CoSiS}_4$, $\text{Cu}_2\text{CoGeS}_4$ and $\text{Cu}_2\text{CoSnS}_4$ is significant, and the value of $\text{Cu}_2\text{CoSiS}_4$ is the largest among them. The Hill approximation should be expressed as the mathematical mean of the two limits: $B = \frac{B_V + B_R}{2}$, $G = \frac{G_V + G_R}{2}$. In general, the bulk modulus and shear modulus of CCSiS is the largest among the three crystal structures. The B/G and ν . (Poisson rate) are associated with roughness and durability of the material. Pugh [28] suggested that the results of B/G can predict the brittle or ductile character of materials. If the value of B/G is bigger than 1.75, the material has a tendency for ductility, otherwise the material reveals a brittle manner. It's shown in our calculations, the B/G ratio for the Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) is larger than 2 (3.037 for CCTS , 3.636 for CCGeS , and 2.780 for CCSiS), which indicated that Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) should behave as a ductile material.

Poisson rate is also a measurement of compressibility which is obtained as [29] $\nu = \frac{3B - 2G}{2(3B + G)}$. Poisson rate of the material can behave elastic for $\nu > 1/3$, fragile for $\nu < 1/3$ [30]. The results indicates the Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) can behave elastic. Finally, the universal elastic anisotropy index have been investigated by the following formula [31,32]: $A^U \frac{5G_V}{G_R} + \frac{B_V}{B_R} - 6$. $A^U = 0$ and $A^U > 0$ represents the crystal is an anisotropy materials. The obtained results in Table 2 show that Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) have a certain degree of elastic anisotropy.

4.1. Thermodynamic properties

The thermal properties are studied by using Gibbs program [33,34] in this section for the first time. All the thermal parameter are calculated in at temperature range of 0–1000 K and pressure range of 0–50 GPa.

Fig. 3 presents the relationship between temperature and specific heat capacities (C_p , C_v) of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) alloys at 0 GPa. It can be found that C_p and C_v have the same trend at temperature range 0–1000 K for the three materials. In the low temperature limit, the heat capacities are proportional to T^3 . The constant volume C_v of $\text{Cu}_2\text{CoGeS}_4$ and $\text{Cu}_2\text{CoSnS}_4$ approaches the classical Dulong-petit limit 99.6 J/mol · K, while the C_v of $\text{Cu}_2\text{CoSiS}_4$ approaches the limit 99.2 J/mol · K at high temperature ($T > 300$ K). There is very slight difference between C_p and C_v , and the limit values of C_p of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) are 99.01 J/mol · K, 100.02 J/mol · K and 100.02 J/mol · K.

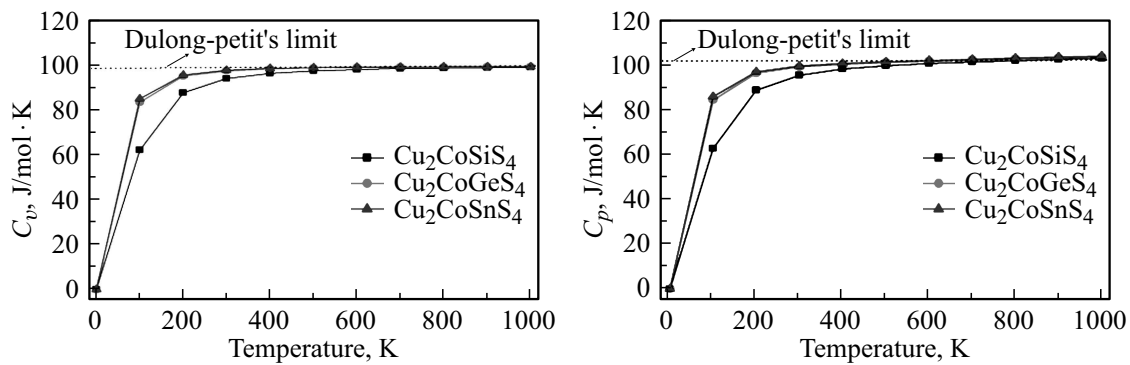


Figure 3. The value of heat capacity of C_v (left) and C_p (right) at different temperature of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$).

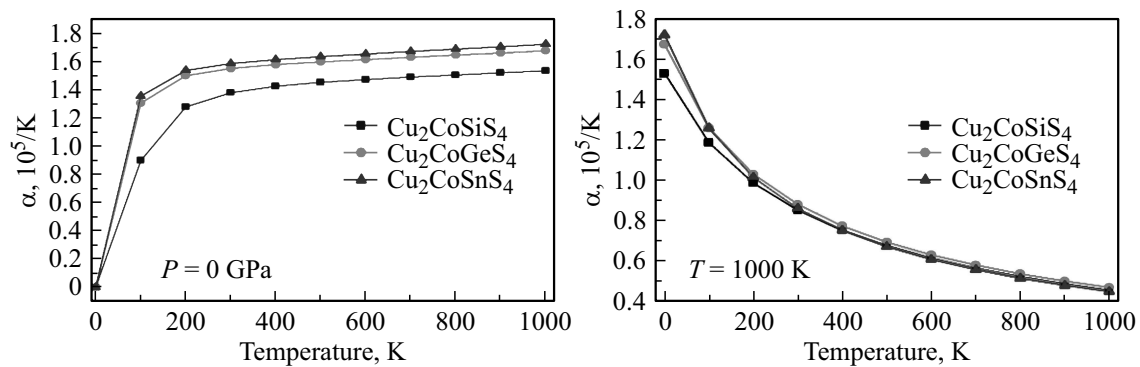


Figure 4. Variations α with (left) temperature and (right) pressure of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$).

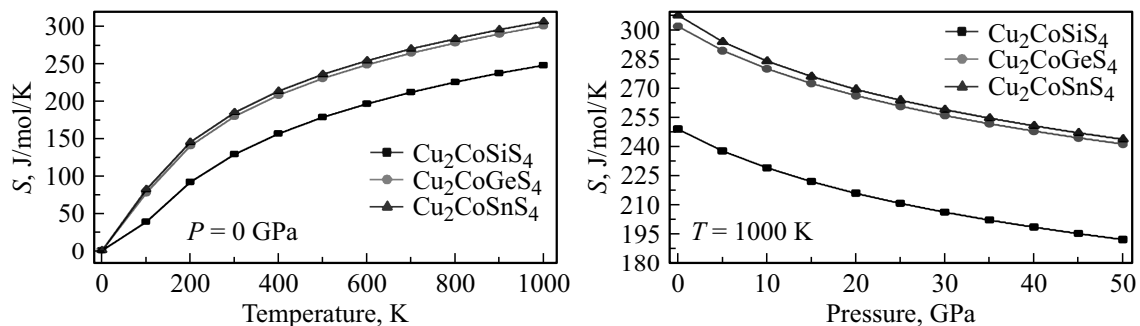


Figure 5. Variations S with (left) temperature and (right) pressure of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$).

The variations of the thermal expansion coefficient α under different temperature and pressure for Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) compounds are plotted in Fig. 4. The temperature dependence of α at $P = 0$ GPa are depicted in Fig. 4 (left). The coefficient α increases quickly as the temperature increasing below 300 K and then begin to change slowly with temperature rising. The relationship curves between α and pressure at a given temperature of 1000 K is shown in Fig. 4 (right). The coefficient decreases drastically with the pressure increasing at a given temperature. With increasing the temperature and pressure, the α would close to $0.46 \cdot 10^5$, $0.47 \cdot 10^5$, and $0.45 \cdot 10^5 \text{ K}^{-1}$ for $\text{Cu}_2\text{CoSiS}_4$, $\text{Cu}_2\text{CoGeS}_4$, and $\text{Cu}_2\text{CoSnS}_4$ alloys. Unfortunately, there have been no experimental and theoretical studies for the thermal properties of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$), and our study can be used as a guide for future research.

The calculated entropy (S) of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) dependence on temperature (left) and pressure (right) are plotted in Fig. 5. It can be clearly found that entropy S increased with increasing

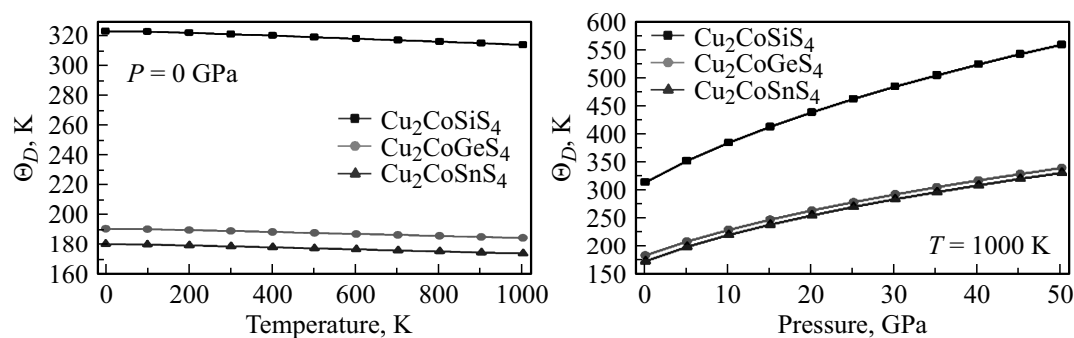


Figure 6. Variations Debye temperature with (left) temperature and (right) pressure of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$).

of temperature at a given pressure of 0 GPa and decreased with increasing of pressure at a given temperature of 1000 K. As can be seen from the figures, the variation trends of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) are almost same under the different temperature and pressure. The calculated entropies of $\text{Cu}_2\text{CoGeS}_4$ and $\text{Cu}_2\text{CoSnS}_4$ are very close, which are much bigger than $\text{Cu}_2\text{CoSiS}_4$.

Fig. 6(left) depicts the temperature dependence of Θ_D of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) at 0 GPa. Our calculated values of Θ_D are 322.94, 190.93, and 180.69 K, respectively for Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) alloys at 0GPa and 1000 K. The Debye temperatures is almost a constant in the range of (0–1000) K, but it decrease slowly with increasing temperature for Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$). Debye temperatures are increasing with the increasing pressure which are shown in Fig. 6 (right). The calculated Θ_D of $\text{Cu}_2\text{CoSiS}_4$ is biggest among these three materials.

5. Conclusions

The detailed studies and comparison of the basic properties of Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) alloys by using the density function theory and the quasi-harmonic Debye model. The obtained lattice parameters from our calculations for the stannite structure agree well with the theoretical results. Based on the mulliken population's analysis, we found that the bonds between S atoms and other three atoms exhibit the feature of covalent bond. The calculated elastic constants for the Cu_2CoXS_4 ($X = \text{Si, Ge, Sn}$) proved these materials are mechanically stable. Following Pugh's empirical relationship, the universal elastic anisotropy index indicates that they could be shown ductility. Finally, the temperature and pressure dependence of the thermal parameters such as: volume expansion coefficient α , heat capacities C_v , C_p , entropy S and Debye temperature Θ are calculated successfully.

Acknowledgments

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