

FIRST-PRINCIPLES STUDY OF THE ELASTIC AND THERMODYNAMIC PROPERTIES OF CuBiS_2 PHOTOVOLTAIC ABSORBER MATERIAL

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The ground state parameters such as the lattice constants (a , b , and c), bulk modulus (B_0) and pressure derivative of bulk modulus (B_0') are calculated for CuBiS_2 crystal using density functional theory. Detailed comparisons are made with published experimental and theoretical data and show generally good agreement. The nine independent elastic constants (c_{11} , c_{22} , c_{33} , c_{44} , c_{55} , c_{66} , c_{12} , c_{13} , and c_{23}) were evaluated. Based on the quasi-harmonic Debye model, we have obtained successfully the bulk modulus B , Debye temperature Θ and Grüneisen parameter γ , heat capacities C_v , entropy S , as well as thermal expansion coefficient α as a function of the pressure and temperature of CuBiS_2 in the ranges of 0-10 GPa and 0-600 K for the first time.

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1. Introduction

In the field of thin-film photovoltaic technologies, the cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) solar cell possessing a dominant position [1, 2]. However, due to the limited availability and toxicity of the elements in these compounds, their terawatt scale application is restrained. Therefore, the research interests of scientists are attracted to find the alternative inexpensive and earth abundant materials for efficient thin-film solar cells.

Ternary chalcogenide semiconductor CuBiS_2 , which possesses some excellent properties such as the proper band gap and high optical absorption, shows considerable technological potential for solar cell [3-6]. The available experimental results on the geometry and electronic structure of CuBiS_2 show it crystallizes in an orthorhombic, layer structure with the $pnma$ space group and possesses a direct band gap of 1.65 eV [3, 4]. There are several theoretical works on this material concerning electronic band structure, optical properties were reported recently [5, 6]. However, there are no reported theoretical nor experimental studies on the elastic and thermodynamic properties of CuBiS_2 up to now.

In this work, we present a detailed and systematic study on the structure, elastic properties, and thermodynamic properties of CuBiS_2 compound by using first-principles calculation based on density functional theory.

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2. Calculated details

2.1. Geometry optimization

The calculated results have been obtained using the plane-wave pseudopotential method within the frame work of the density functional theory implanted in the CASTEP code[7, 8]. We adopt the non-local Vanderbilt-type ultrasoft pseudopotentials (USPP) [9] for the interactions of the electrons with the ion cores, together with the generalized gradient approximation (GGA) for exchange-correlation function in the scheme of Perdew–Burke–Ernzerhof (PBE) [10]. The electronic states were $3d^{10}4s^1$ for Cu, $6s^26p^3$ for Bi, and $3s^23p^4$ for S. We set the plane-wave cutoff energy to be 400.00 eV and employed a $8 \times 12 \times 4$ Monkhorst–Pack mesh grid for the special points sampling integration over the irreducible Brillouin-zone (IBZ). The calculations assured a very high level convergence with respect to the total energy difference within 1.0×10^{-6} eV/atom.

2.2. Elastic properties

To calculate the isothermal elastic constants, the internal energy $E(\eta_{ij})$ for the strained CuBiS_2 crystal, instead of the Helmholtz free energy A , was used to perform the first-principles calculations. The elastic constants are extracted as proportional to the second order coefficient in a polynomial fit of the total energy as a function of Lagrangian strains η_{ij} [11-13], which can be present as follows:

$$c_{ijkl} = \rho_0 \left. \frac{\partial^2 E}{\partial \eta_{ij} \partial \eta_{kl}} \right|_{\eta=0} \quad (i, j, k, l = x, y, z) \quad (1)$$

For the orthorhombic CuBiS_2 , there are nine independent elastic constants. By choosing the applied deformation, the energy associated with these distortions can be obtained and all the elastic constants, bulk modulus, shear modulus, Young's modulus and Poisson ratio can then be determined.

2.3. Thermodynamic properties

The thermal properties of a material determine the suitable conditions for initiating and maintaining the quality of device fabrication. In order to investigate the thermal properties of CuBiS_2 under high pressure and high temperature we have used the Gibbs program [14]. This program is based on the quasi-harmonic Debye model, in which the non-equilibrium Gibbs function $G^*(V; P, T)$ takes the form of

$$G^*(V; P, T) = E(V) + PV + A_{vib}(\Theta(V); T) \quad (2)$$

where $E(V)$ is the total energy per unit cell, PV corresponds to the constant hydrostatic pressure condition, $\Theta(V)$ is the Debye temperature, and A_{vib} is the vibrational Helmholtz free energy, which can be written as [15, 16]

$$A_{vib}(\Theta; T) = nkT \left[\frac{9}{8} \frac{\Theta}{T} + 3 \ln(1 - e^{-\Theta/T}) - D(\Theta/T) \right] \quad (3)$$

where n is the number of atoms per formula unit, $D(\Theta/T)$ represents the Debye integral, and for an isotropic solid, Θ is expressed as [15]

$$\Theta = \frac{\hbar}{k} [6\pi^2 V^{1/2} n]^{1/3} f(\sigma) \sqrt{\frac{B_s}{M}} \quad (4)$$

where M is the molecular mass per unit cell, B_s is the adiabatic bulk modulus, which is approximated by the static compressibility [14]

$$B_s \cong B(V) = V \left\{ \frac{d^2 E(V)}{dV^2} \right\} \quad (5)$$

$f(\sigma)$ is given by Refs.[17,18], σ is the Poisson ratio.

Therefore, the non-equilibrium Gibbs function $G^*(V;P,T)$ as a function of $(V;P,T)$ can be minimized with respect to volume V

$$\left(\frac{\partial G^*(V;P,T)}{\partial V} \right)_{P,T} = 0 \quad (6)$$

By solving Eq. (6), one can get the thermal equation of state $V(P, T)$. The heat capacity C_v , the entropy S , and the thermal expansion coefficient α are taken as:

$$C_v = 3nk \left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right] \quad (7)$$

$$S = nk \left[4D(\Theta/T) - 3 \ln(1 - e^{-\Theta/T}) \right] \quad (8)$$

$$\alpha = - \frac{\gamma C_v}{B_s V} \quad (9)$$

where γ is the Grüneisen parameter, which is defined as:

$$\gamma = - \frac{d \ln \Theta(V)}{d \ln V} \quad (10)$$

Through the quasi-harmonic Debye model, one could calculate the thermodynamic quantities of CuBiS₂ at any pressures and temperatures from the calculated E - V data at $T=0$ and $P=0$.

3. Result and discussion

3.1. Structure properties

The structural properties are very important for understanding the solid properties from the microscopic viewpoint. We calculated the total energy as a function of the unit-cell volume around the equilibrium cell volume V_0 . The calculated energies as a function of the primitive-cell volume for CuBiS₂ are shown in Fig.1. Then, we fitted the calculated E - V points to the Birch-Murnaghan equation of state (EOS) to calculate derived structural properties,

$$E(V) = E_0 + \frac{B_0 V}{B_0} \left(\frac{V_0/V}{B_0 - 1} + 1 \right) \frac{B_0 V_0}{B_0 - 1} \quad (11)$$

where E_0 is the equilibrium energy, B_0 is the bulk modulus, B_0' is the first derivative of B_0 with pressure P . The calculated lattice constants a , b , and c , bulk modulus B_0 and its pressure derivative B_0' are presented in Table 1, together with the available experimental and theoretical results. It can be seen that the obtained lattice constants a , b , and c are 6.283, 3.907, and 14.214 Å respectively, with 2.31%, 0.1%, and 2.13% deviation from the experimental values [4]. The bulk modulus B_0 and the pressure derivative of bulk modulus B_0' of CuBiS₂ are the first report. Up to now, the experimental and other theoretical bulk modulus values about this promising material have not been reported, our result can provide useful reference for experimental researchers.

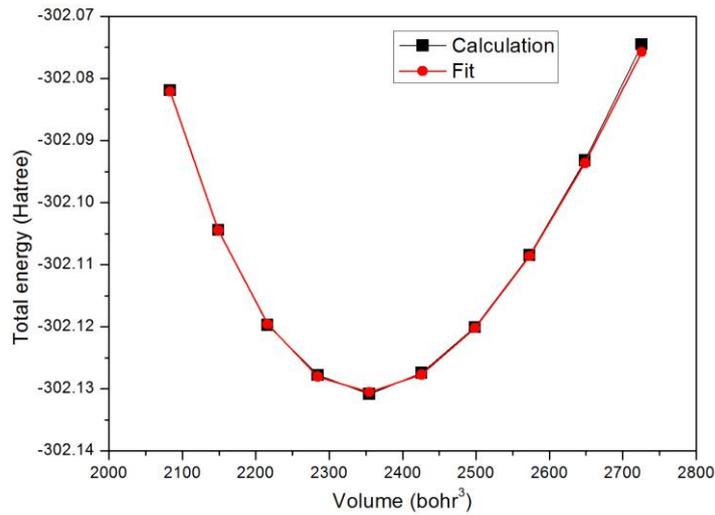


Fig. 1. Calculated total energy as a function of volume of CuBiS₂ crystal

Table 1. Lattice constants (a , b , and c), bulk modulus (B_0), pressure derivative of bulk modulus (B_0') of CuBiS₂.

	a (Å)	b (Å)	c (Å)	B_0 (GPa)	B_0' (GPa)
This work	6.283	3.907	14.214	73.52	5.06
Theor. (HSE06)	6.18 ^a	3.925 ^a	14.643 ^a	---	---
	6.045 ^b	3.807 ^b	14.545 ^b	---	---
Exp.	6.1414 ^c	3.9191 ^c	14.524 ^c	---	---

a Ref. [5]; b Ref. [6]; c Ref. [4]

3.3. Elastic properties

The elastic constants of solids are important parameters because they can provide useful information about the mechanical and dynamic characteristics, especially the stability and stiffness of materials. Thus, it is necessary to study the elastic constants to understand the mechanical properties of CuBiS₂. The elastic stiffness tensor of orthorhombic compounds have nine independent components because of the symmetry properties of the D_{2h} space group, namely c_{11} , c_{22} , c_{33} , c_{44} , c_{55} , c_{66} , c_{12} , c_{13} and c_{23} in Young's notation, respectively. In this work, the calculated single crystal elastic constants of CuBiS₂ at zero pressure are displayed in the Table 2.

Table 2. Elastic constants c_{ij} of orthorhombic CuBiS_2 , calculated from them: bulk (B_{VRH}) and shear modulus (G_{VRH}) in the Voigt-Reuss-Hill approximation, and the Young modulus. All values are given in gigapascal.

c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{12}	c_{13}	c_{23}
97.65	117.05	153.89	36.92	25.95	24.49	29.44	36.77	63.08
B_V	B_R	B_H	G_V	G_R	G_H	σ	E	B/G
69.69	64.64	67.16	33.42	31.42	32.42	0.292	83.795	2.07

Unfortunately, to our knowledge, there are no experimental values about the elastic stiffness coefficients have been reported for CuBiS_2 . So, to check the suitability and reliability of our calculated values, we tested firstly the obtained constants have or not met the Born stability criteria [19], which for the orthorhombic CuBiS_2 lattice requires that

$$\left. \begin{aligned} (c_{11} + c_{22} - 2c_{12}) > 0, (c_{11} + c_{33} - 2c_{13}) > 0, \\ (c_{22} + c_{33} - 2c_{23}) > 0, c_{11} > 0, c_{22} > 0, c_{33} > 0, \\ c_{44} > 0, c_{55} > 0, c_{66} > 0 \\ (c_{11} + c_{22} + c_{33} + 2c_{12} + 2c_{13} + 2c_{23}) > 0 \end{aligned} \right\} \quad (12)$$

One can find that our calculated elastic constants satisfy all these conditions, implying that CuBiS_2 crystal is mechanically stable.

The Voigt [20] and Reuss [21] limits for the bulk modulus (B) and shear modulus (G) are:

$$B_V = (1/9)(c_{11} + c_{22} + c_{33}) + (2/9)(c_{12} + c_{13} + c_{23}) \quad (13)$$

$$B_R = 1/\{(s_{11} + s_{22} + s_{33}) + 2(s_{12} + s_{23} + s_{13})\} \quad (14)$$

$$G_R = 15/\{4(s_{11} + s_{22} + s_{33} - s_{12} - s_{23} - s_{13}) + 3(s_{44} + s_{55} + s_{66})\} \quad (15)$$

$$G_V = (1/15)(c_{11} + c_{22} + c_{33} - c_{12} - c_{23} - c_{13}) + (1/5)(c_{44} + c_{55} + c_{66}) \quad (16)$$

In the Voigt-Reuss-Hill (VRH) approximation [22], the B and G of the polycrystalline material are approximated as the arithmetic mean of the Voigt and Reuss limits:

$$B_{\text{VRH}} = \frac{1}{2}(B_V + B_R), \quad G_{\text{VRH}} = \frac{1}{2}(G_V + G_R) \quad (17)$$

It can be noted that the bulk modulus values B_{VRH} is an equivalent combination of elastic constants c_{ij} . It can be found that the difference between the B_{VRH} and the fitted bulk modulus B_0 is little. Therefore, we would say that our calculated elastic constants are suitable and reasonable. It is certainly that these theoretical values of elastic constants of CuBiS_2 still waiting for experimental proofs.

One of the most important parameters for estimating mechanical properties of compounds is elastic anisotropy of crystal. The elastic anisotropy behavior of a orthorhombic crystal can be measured by the shear anisotropic factors[23]:

$$A_1 = \frac{4c_{44}}{c_{11} + c_{33} - 2c_{13}}, \quad (18)$$

$$A_2 = \frac{4c_{55}}{c_{22} + c_{33} - 2c_{23}}, \quad (19)$$

$$A_3 = \frac{4c_{66}}{c_{11} + c_{22} - 2c_{12}}. \quad (20)$$

For an isotropic crystal the factors A_1 , A_2 , and A_3 must be 1, while any value smaller or greater than 1 indicates anisotropy. The magnitude of a deviation from 1 is a measure of the degree of elastic anisotropy possessed by the crystal. These calculated independent elastic shear anisotropy factors $A_1 = 0.83$, $A_2 = 0.71$, and $A_3 = 0.63$, respectively, obviously deviate from 1, indicating a strong elastic anisotropy of the orthorhombic CuBiS_2 .

Two other parameters are important for technological and engineering applications: Young's modulus E and Poisson's ratio σ . E and σ can be calculated using Hill's bulk and the shear modulus (B_H and G_H), and they are given as: $E = (9B_H G_H) / (3B_H + G_H)$, $\sigma = (3B_H - 2G_H) / (6B_H + 2G_H)$. Young's modulus is often used to provide a measure of stiffness of a solid, i.e., the larger is the value of Young's modulus, the stiffer is the material. The value of Poisson's ratio σ provides the information about the characteristics of the bonding forces. The $\sigma = 0.25$ and 0.5 are the lower and upper limit for the central forces in solids, respectively. Our calculated value of σ is equal to 0.292 at 0 GPa, lying in the typical range of values of ionic rather than covalent materials [24].

The ratio of shear modulus to bulk modulus B/G has been proposed by Pugh to roughly estimate brittle or ductile behavior of materials[25], a high (low) B/G values is associated with ductility (brittleness). The critical value which separates ductile and brittle materials is 1.75. Our result shows that the B/G ratio is 2.07 for CuBiS_2 , which means the crystal is ductile. The calculated bulk and shear modulus, Young's modulus and Poisson's ratio, along with the ratio of B/G are all listed in the Table 2.

3.4 Thermal properties

Based on the quasi-harmonic Debye model, we have investigated the thermodynamic properties of the CuBiS_2 over a range of pressures from 0 to 10 GPa. The temperature and pressure dependences of the bulk modulus B for CuBiS_2 are plotted in Fig. 2. It can be seen from the Fig. 2(a) that B decreases with T increasing at a given pressure, while it increases with P increasing at a given temperature. It also shows that the effect of increasing pressure on CuBiS_2 is the same as that of decreasing temperature. However, the effect of the pressure on the bulk modulus is more important than that of the temperature. From Fig. 2(b), we find that, at zero pressure, the bulk modulus B is nearly a constant at low temperature, whereas B decreases dramatically with the increase of temperature.

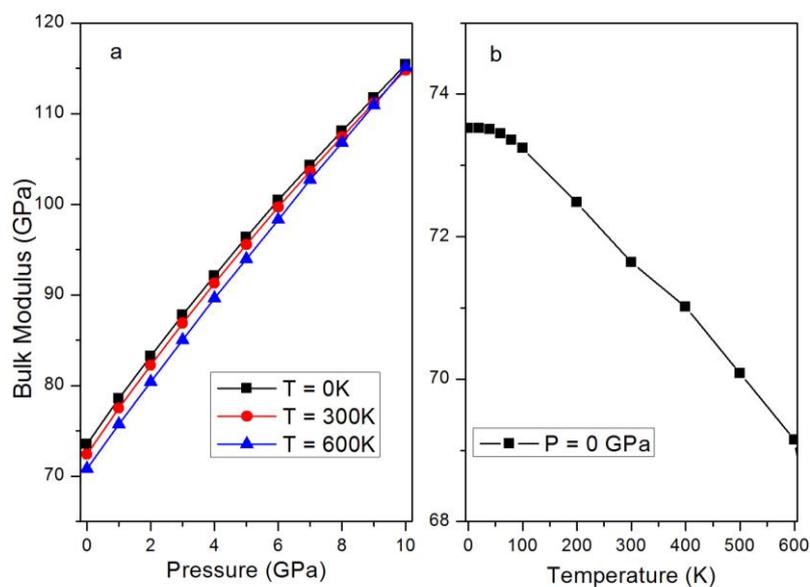


Fig. 2. Pressure and temperature dependence of the bulk modulus of CuBiS_2 .

The values of the Debye temperature Θ as a function of pressure and temperature are listed in Table 3. It can be noticed that, with the applied pressure increasing, the Debye temperatures are almost linearly increasing. While the Debye temperature Θ decreases with the increasing temperature at a given pressure. The temperature and pressure dependence of Θ reveal that the thermal vibration frequency of atoms in CuBiS_2 changes with temperature and pressure. The Grüneisen parameter γ , which describes the anharmonic effects in the vibrating lattice and gives the volume dependence of Debye temperature Θ , can correctly predict the anharmonic properties of a material. In Table 3, we also list the values of Grüneisen parameter γ at different temperatures and different pressures. It shows the value γ increases as the temperature increases at a given pressure, while it decreases as the pressure increases at a given temperature.

Table 3 Debye temperature Θ (K) and Grüneisen constant γ of the CuBiS_2 at temperatures T (K) and pressures P (GPa)

T	P	0	2	4	6	8	10
0	Θ	352.70	373.76	391.88	407.79	421.69	434.29
	γ	2.387	2.166	1.985	1.829	1.693	1.565
300	Θ	350.23	371.87	390.38	406.54	420.67	433.41
	γ	2.414	2.185	2.000	1.842	1.703	1.574
600	Θ	346.22	368.77	388.12	404.45	418.95	431.91
	γ	2.458	2.217	2.022	1.862	1.720	1.590

As very important parameters, the heat capacities of a substance not only provide essential insight into the vibrational properties but also mandatory for many applications. The variations of the heat capacities C_v versus temperature at various pressures are shown in Fig. 3. It can be found that the constant volume C_v increase with T^3 at lower temperature T , while with the increase of temperature T , C_v follows the Debye model and approaches the Dulong–Petit limit indicating the thermal energy at high temperature excites all phonon modes, which is common to all solids at high temperature. Fig. 3 also indicate that temperature and pressure have opposite influences on the heat capacity and the effect of temperature on the heat capacity is more significant than that of pressure. It is worth mentioning that, in our work, the value of C_v is $93.29 \text{ J mol}^{-1} \text{ K}^{-1}$ at 300 K and zero pressure. The relationship between entropy S and temperature T is displayed in Fig. 4. It is found that at given pressure P , the entropy S increases mostly exponentially with the temperature T . It can also be noticed that the effects of temperature on entropy S are more important at high temperature than those at low temperature. At 300 K and zero pressure, the obtained value of entropy is $120.9 \text{ J mol}^{-1} \text{ K}^{-1}$ for CuBiS_2 .

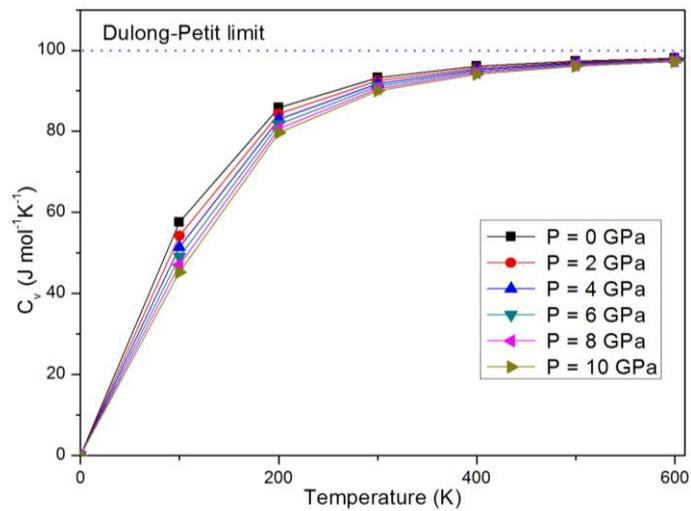


Fig. 3. variation of the heat capacity C_v with temperature under different pressure.

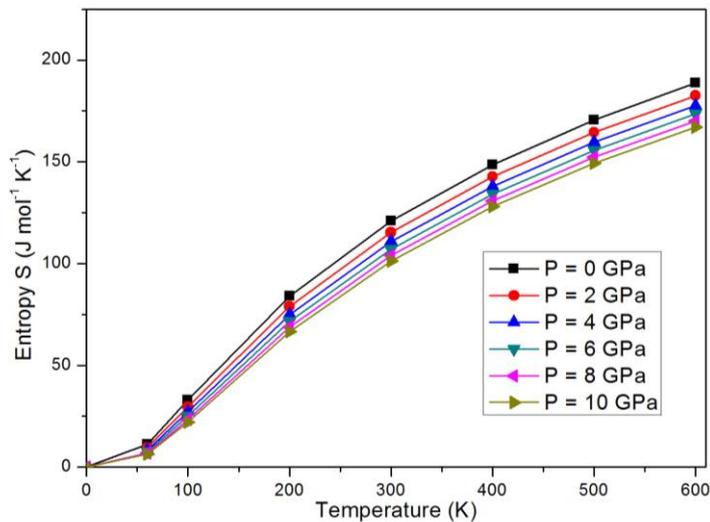


Fig.4. Variation of entropy S with temperature T at various pressures.

Within the quasi-harmonic approximation, the anharmonicity is restricted to the thermal expansion. Fig. 5 shows the volume thermal expansion coefficient dependence on pressure and temperature. It can be seen that at a given temperature, the volume thermal expansion coefficient increases quickly especially at zero pressure below the temperature 300 K, and it gradually tends to a linear increase at higher temperature region, it is due to the electronic contribution. However, it is noted from Fig. 5 (b) that, as the pressure increases, the volume thermal expansion coefficient decreases strongly at 300 K. These results indicating the anharmonic effects are important at low temperatures and high pressures for CuBiS_2 . Meanwhile, at 300 K and zero pressure, the volume thermal expansion coefficient $\alpha = 1.491 \times 10^{-5} \text{ K}^{-1}$ and rapidly decreases by 19.11%, 32.39%, 42.18%, 49.83%, 56.13% with pressure increasing to 2, 4, 6, 8, 10 GPa, respectively.

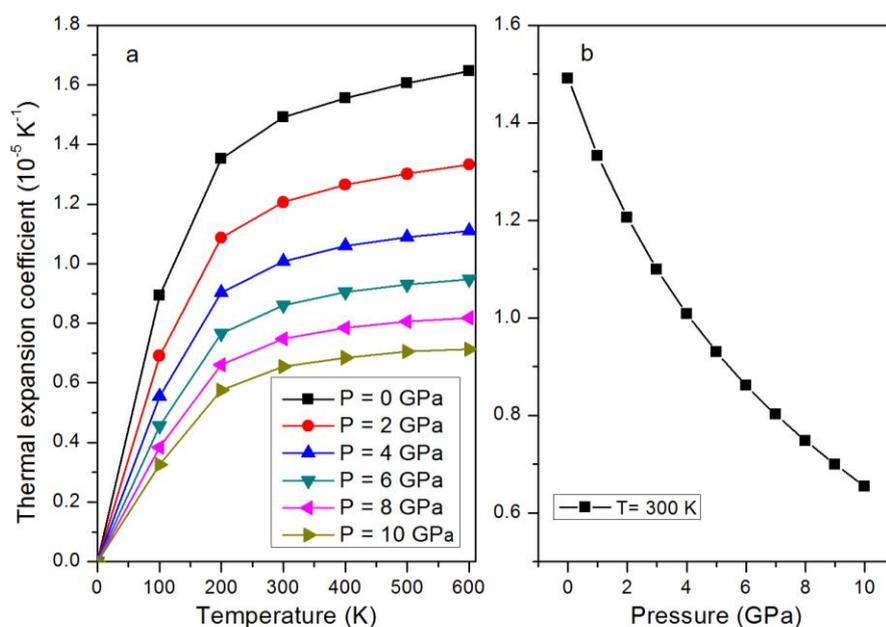


Fig.5. Pressure and temperature dependence of the thermal expansion coefficient α .

4. Conclusions

In summary, the geometry structure and elastic properties of CuBiS_2 crystal were investigated from first-principles calculations. The ground state properties such as equilibrium lattice constants (a , b , and c), bulk modulus B_0 and its first derivative B'_0 obtained from our calculation agree well with the available experimental and theoretical values. According to the calculated elastic constants, the structure of CuBiS_2 is mechanically stable. The three shear anisotropic factors ($A_1 = 0.83$, $A_2 = 0.71$, and $A_3 = 0.63$) implied the strong elastic anisotropy of CuBiS_2 crystal. Our calculated value of Poisson's ratio σ is equal to 0.292 at 0 GPa, indicating that CuBiS_2 is a ionic material. Meanwhile, the calculated ratio B/G is 2.07, suggesting a ductile deformation failure for CuBiS_2 .

Through the quasi-harmonic Debye model, we have successfully obtained the pressure and temperature dependence of the bulk modulus B , Debye temperature Θ , the Grüneisen parameter γ , the heat capacity C_v , the entropy S , and the thermal expansion coefficient α of CuBiS_2 crystal as these are essential for thin film growth. To the best of our knowledge, most of the investigated properties are reported for the first time and hoped to stimulate the succeeding studies.

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