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DENSITY FUNCTION THEORY OF ELASTIC AND THERMAL PROPERTIES FOR $CuTlS_2$ CRYSTAL

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In this paper, we focus on the study of the structural, elastic and thermal properties of chalcopyrite structure $CuTlS_2$ crystal using the first principle theory. The lattice parameters a and c are obtained which are excellent consistent with the earlier values. We have also computed the six independent components (C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66}). The relation of bulk modulus (B) and Temperature and Pressure have been calculated and analysed for the first time. The thermal properties of the $CuTlS_2$ crystal such as Debye temperature, the thermal expansion coefficient, the heat capacity C_v and C_p are also worked out by the quasi-harmonic Debye model.

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1. Introduction

Chalcopyrite crystal structure have been reported to be interesting materials which exhibit promising and it has been widely used in solar cells, photovoltaic applications, nonlinear optical devices, etc.[1-4]. More and more scholars began to study the properties of this kind of chalcopyrite materials by theoretical and experimental research. The ternary compound $CuTlS_2$ belongs to these promising chalcopyrite structure crystals. Recently, there are some theoretical and experimental studies on $CuTlS_2$ and the band gap energy and lattice parameters of $CuTlS_2$ have been predicted [5-6]. In this work, we investigated the structural, elastic and thermal properties for $CuTlS_2$ by using first-principles calculation based on the density functional theory (DFT).The results agree well with the experimental results.

The density functional theory (DFT) method has been established almost 40 years and successfully applied to the calculation of physical, chemical, biological and other aspects of materials. DFT has been successfully used in studying structures and elastic properties of materials and has been widely used in theoretical studies of similar materials such as $CuTlSe_2$[7]， $AgGaS_2$[8] and $AgGaSe_2$[9] .

2. Calculations method

In this paper, all the results of $CuTlS_2$ crystal are performed by using the pseudopotential plane-wave within the framework of the density function theory[10-11]. The exchange correlation energy is evaluated in the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional [12-15]. The electron-ion interactions is described by Vanderbilt-type ultra-soft pseudopotentials [16]. In the structure calculation, a plane-wave basis set with energy cut-off 350.00 eV is used， and the Brillouin-zone sampling is adopted by the K point grid of 4 ×4×4.

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3. Result and discussion

3.1. Structural properties

The ternary compound $CuTlS_2$ belongs to chalcopyrite family of compounds. These materials crystals have the chalcopyrite structure (space group: $I\bar{4}2d$), with four atoms in a unit cell, each sulfur ion is coordinated by two "Cu" and two "Tl" ions, each "Cu" and each "Tl" ion are coordinated by four sulfur ions [17], so there are two different interactions that lead to two different bond lengths, R_{Cu-S} and R_{Tl-S} .Each atom in this structure is four-fold coordinated, like in the diamond or zinc blend crystal structures. The crystal structure of $CuTlS_2$ has been shown in Fig. 1.

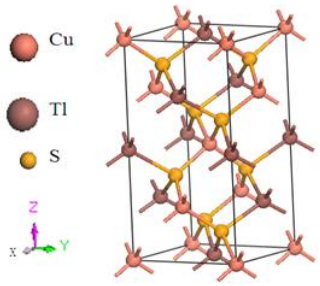


Fig . 1. Crystal structure of $CuTlS_2$

For solid materials it is important to study the structure properties. At the first step, we set up a series of lattice parameters and calculate the corresponding volume of cell energy. Next step ,We calculated the total energies as a function of volumes for $CuTlS_2$ and fitted the calculated E(V) points to the Birch-Murnaghan equation of state (EOS) , as showed in Fig. 2 [18].

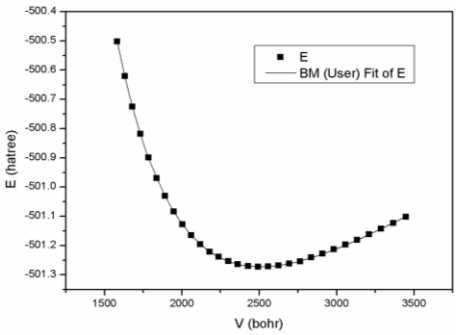


Fig. 2. E-V curves of different lattice constant values

The lattice parameters have been calculated and simulated by using GGA-PBE method. The fitted lattice parameters a and c are listed in table 1, which are close to the experimental works. This results give us more confidence to study elastic properties and thermal properties further.

Table 1. Calculated lattice parameters a (Å), c (Å)of $CuTlS_2$ compared to other theoretical data.

	This work	Reference	
a (Å)	5.5911	5.580[a]	5.80[b]
c(Å)	11.1922	11.166[a]	11.166[b]

a From Ref.[19], b From Ref.[20]

The bulk-modulus (B) as a function of temperature (T), we studied their relationship at zero-pressure, is plotted in Fig3(left). The relationship between them can be obtained by solving equation[21] :

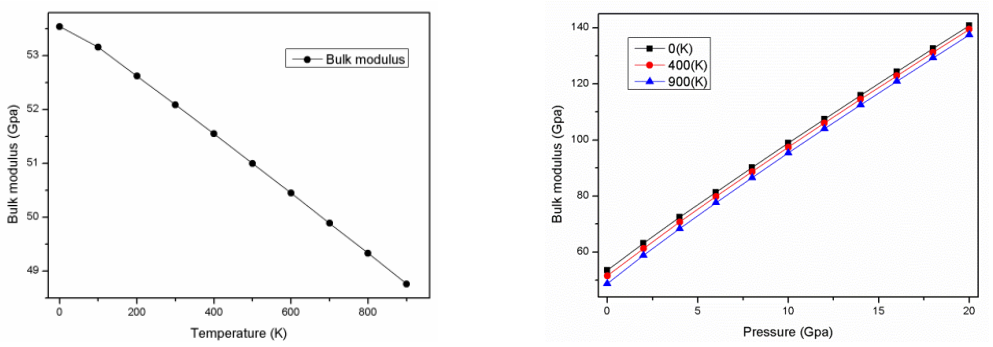
$$\left(\frac{\partial G^{*}(V;p,T)}{\partial V}\right)_{p,T} = 0$$

The bulk modulus B can be expressed as:

$$B_T(p,T) = -V\left(\frac{\partial p}{\partial T}\right)_T = V\left(\frac{\partial^2 G^{*}(V;p,T)}{\partial V^2}\right)_{p,T}$$

In the above formula G * is Gibbs function，V represents the volume. According to Fig. 3(left) we can see that the bulk modulus (B) falls sharply with increasing temperature in the range of 0K ~ 900K. The result means a dramatic change in cell volume.

Fig. 3(right) shows the relationship between bulk modulus (B) and pressure (P) at different temperatures (T = 0K, 400K, 900K). As the pressure gets higher, the bulk modulus (B) has the same tendency to change at different temperatures.



a) *b)*

Fig. 3 The bulk modulus versus temperature(a) and pressure(b)

3.2 Mechanical properties

We use the GGA-PBE method to calculate and simulate the elastic constant Cij (GPa), the values shown in Table 2. Chalcopyrite structure has six independent elastic parameters: C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66}. If the chalcopyrite structure is mechanically stable, the above six values must comply with the Born Stability Criteria [22-25]:$C_{11}>0$, $C_{33}>0$, $C_{44}>0$, $C_{66}>0$, $(C_{11}-C_{12})>0$, $(C_{11}C_{33}-C_{13}^2)>0$, and $[(C_{11}+C_{12})C_{33}- 2C_{13}^2]>0$. As shown in Table 2, all of the elastic constants for $CuTlS_2$ satisfies these criteria mentioned above, indicating that the $CuTlS_2$ is mechanically stable.

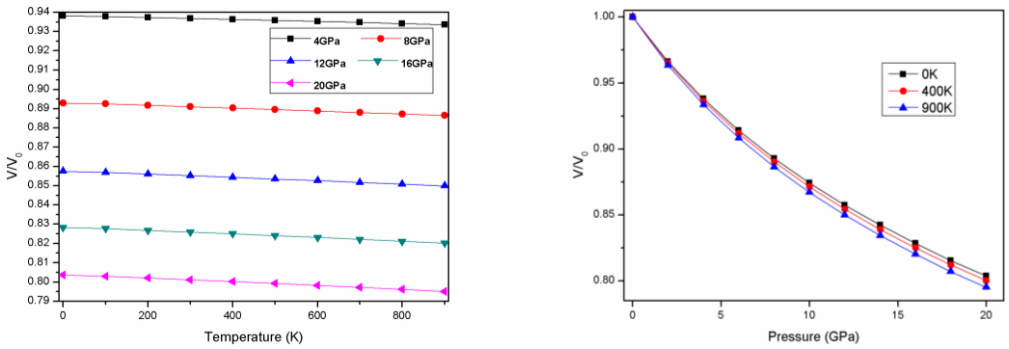
In order to systematically study their elastic properties, we further calculated other elastic parameters for $CuTlS_2$ such as the bulk modulus, the shear modulus, the universal anisotropy index, the young modulus, poisson ratios, lame lambda, and compressibility. These data are shown in Table2.

Table2. Calculated mechanical parameters of $CuTlS_2$ compound.

Elastic stiffness constants Cij(GPa)	C_{11}	96.36600	Young modulus (GPa)	X	28.45738
	C_{12}	77.07231		Y	28.45738
	C_{13}	75.29107		Z	29.71373
	C_{33}	95.08274	Poisson ratios	E_{xy}	0.4750
	C_{44}	24.97995		E_{xz}	0.4158
	C_{66}	30.03979		E_{yx}	0.4750
Bulk modulus (GPa)	Voigt	82.56929		E_{yz}	0.4158
	Reuss	82.53587		E_{zx}	0.4341
	Hill	82.55258		E_{zy}	0.4341
Shear modulus(GPa)	Voigt	20.01062	Lame lambda(GPa)	Voigt	69.22888
	Reuss	15.96699		Reuss	71.89121
	Hill	17.98880		Hill	70.56005
Universal anisotropy index		1.26665	Compressibility(GPa^{-1})		0.01212

3.3 Thermal properties

In order to study more information about the thermal properties of $CuTlS_2$, We used the quasi-harmonic Debye model [26-27]. The ranges of the temperature (T) and pressure (P) are from 0K to 900 K and from 0 GPa to 20 GPa.



a) *b)*

Fig. 4. The ratio V/V_0-T (a)and V/V_0-P(b) diagram of $CuTlS_2$

Fig. 4 plots the relationships of the V/V_0 -T and V/V_0 -P (relative volume ratio V/V_0 with temperature and pressure), respectively. In Fig.4 (left), the ratio V/V_0 no significant changes with the increasing of the temperature from 0K to 900 K at different pressure(P=4 GPa, 8 GPa,12 GPa,16 GPa and 20GPa), respectively. In Fig. 4 (right), it can be found that the ratio V/V_0 significantly reduced as the pressure changes from 0GPa to 20GPa at different temperatures (T = 0K, 400K, and 900K), respectively. At low pressure, their curves almost coincide, with the pressure increasing their curves have been significantly changed. In summary, pressure have more significant influences on the V/V_0 and temperature have less influences on the V/V_0.

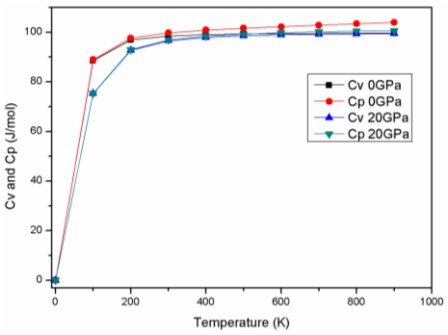
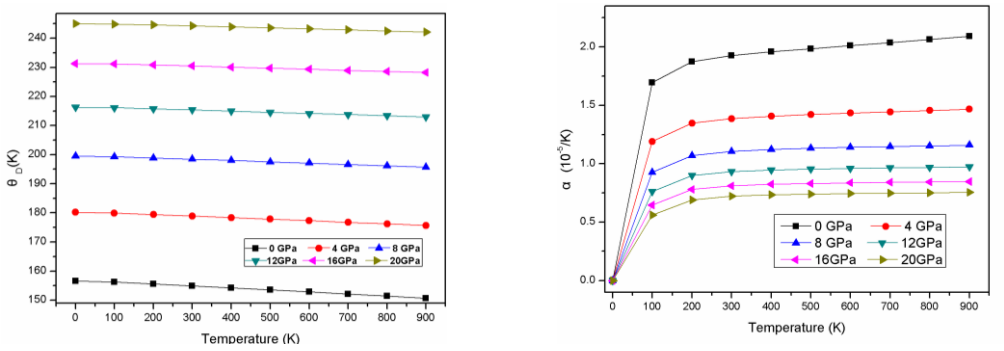


Fig. 5 Heat capacity of $CuTlS_2$ versus tempertures under different pressures

Fig. 5 shows the relationship between the heat capacity C_v and C_p as a function of temperature under different pressures (0 GPa and 20 GPa). In Fig.5, it can be found that when the pressure is constant, the heat capacity (C_v and C_p) increases with the increase of temperature, in 0K-300K of heat capacity with temperature increased significantly. When the temperature is higher than 400K, the heat capacity C_v and C_p approaches constant, obeying Dulong and Petit's Rule and approaching the Dulong-Petit limit. At 0 GPa and 300 K, the C_V and C_P are 98.45637 J mol^{-1} K^{-1} and 99.76047 J mol^{-1} K^{-1}, respectively.



a) *b)*

Fig .6. The Debye temperature (left)and the thermal expansion coefficient(right) of $CuTlS_2$ under different pressure

Fig.6 shows the temperature dependence of the Debye temperature θ_D (k) and the thermal expansion coefficient $\alpha(10^{-5}/k)$ at different pressures. Meanwhile, when the pressure is constant, α increases with the increase of temperature, the most obvious is the temperature is lower than 200K, the various of expansion coefficient $\alpha(10^{-5}/k)$ as a function of pressure and temperature illustrated by our results is displayed in Fig.6 (right). As the pressure goes higher, the effect of change of the temperature on the Debye temperature values is not significant, in Fig. 6 (left).

4. Conclusions

In conclusions, we have calculated the structural, elastic and thermal properties of $CuTlS_2$ crystal in this paper. The lattice constants a and c, bulk modulus (B) and elastic constants are also

obtained, which are consistent with the available theoretical results. The elastic constants, bulk modulus, shear modulus, Young's modulus of $CuTlS_2$ are successfully obtained. The calculated elastic constants of $CuTlS_2$ obey the Bron criteria, so the $CuTlS_2$ is a mechanically stable structure. The thermal properties of the $CuTlS_2$ crystal are predicted by the quasi-harmonic Debye model. We have reported the relative volume ratio V/V_0 ,the Debye temperature θ_D (k), the heat capacity C_v and C_p, and the thermal expansion coefficient $\alpha(10^{-5}/k)$ in dependence on the temperature (T) and pressure (P).

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