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THEORETICAL STUDY OF THE STRUCTURAL AND THERMAL PROPERTIES OF CHALCOPYRITE STRUCTURE $AgInTe_2$

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The structural parameters and elastic constants of $AgInTe_2$ crystal are calculated by using the first-principle calculations within local density approximation. The calculated structural parameters and elastic constants are in agreement with other theoretical or experimental results. Based on the quasi-harmonic Debye method, the pressure and temperature dependencies of the equilibrium volume, the bulk modulus, the Debye temperature, the Grüneisen parameter, the thermal expansion coefficient and so on are obtained.

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1. Introduction

The I-III-VI_2 ternary chalcopyrite compounds have attracted attention for practical applications. Such ternary compounds have been studied because of their applications to photovoltaic solar cells and nonlinear optical devices [**1-5**]. $AgInX_2$ (X = S, Se and Te) are one of the I-III-VI_2 ternary chalcopyrite compounds. In recent years, there are many experimental and theoretical studies on the $AgInS_2$ and $AgInSe_2$. In experimental studies, bulk $AgInS_2$ and $AgInSe_2$ single crystal have been grown by Bridgeman method [**6-7**]. Structural, electrical and optical properties of $AgInS_2$ thin films grown has been investigated by the single source thermal evaporation method [**8**]. The optical properties of $AgInSe_2$ have been studied using various techniques, such as far infrared reflectivity and optical absorption [**9**]. In theoretical studies, Sharma et al. [**10**] have been reported the structural, electronic, optical, elastic and thermal properties of the $AgInS_2$ and $AgInSe_2$ using the full potential linearized augmented plane wave method. Compared to the $AgInS_2$ and $AgInSe_2$, the $AgInTe_2$ crystal has not been investigated adequately. There are some theoretical researches have been done on $AgInTe_2$, however, most of them are focused on elastic constants and specific heat [**11**]. Few pay attention to the thermal properties under high temperature and pressure, which are important to extend our knowledge to $AgInTe_2$ performance. Therefore, it is necessary to study temperature and pressure influences on thermal properties of $AgInTe_2$.

2. Calculations method

The calculations have been performed based on the plane wave pseudopotential density function theory (DFT) and implemented through the CASTEP code [**12**]. Vanderbilt-type ultrasoft pseudopotentials(USPP) [**13**] are used to describe the electron on interactions. The effects of exchange-correlation interaction are treated with the local density approximation(LDA) of the

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Ceperley-Alder data as parameterized by Perdew-Zunger(CA-PZ) [**14-15**]. In the structure calculation, a plane-wave basis set with an energy cut-off of 600 eV is used. For the Brillouin-zone sampling, 7 × 7 × 7 Monkhorst-Pack mesh is adopted.

In order to study the thermal properties of the chalcopyrite structure $AgInTe_2$, we apply the quasi-harmonic Debye method in this paper [**16**].

3. Result and discussion

3.1. Structural properties

The $AgInTe_2$ crystallizes in the chalcopyrite structure with a space group $I\bar{4}2d$. The Ag atom is located at (0, 0, 0), (0, 0.5, 0.25), the In atom at (0, 0, 0.5), (0, 0.5, 0.75) and Te atoms at (x, 0.25, 0.125), (-x, 0.75, 0.125), (0.75, x, 0.875), (0.25, -x, 0.875), where x = 0.26 for $AgInTe_2$. At the first step, a set of total energy calculation versus volume, for $AgInTe_2$ were carried out in order to obtain the structural parameters. Once the minimum total energies of the $AgInTe_2$ were obtained at different volumes, they were fitted to the Murnaghan equation of state [**17**].

Fig. 1. shows the calculated total energies versus volume for $AgInTe_2$. The calculated structural parameters and the experimental [**18-19**] and theoretical [**20**] results are listed in Table 1. It is shown that our calculations agreement with the experimental values. The calculated equilibrium values of the structural parameters *a* and *c*, for $AgInTe_2$ are 6.3546 Å and 12.6531 Å. The bulk modulus is close to the calculated value using the ab initio pseudopotential method [11]. Unfortunately, there are no other theoretical and experimental results for comparison with the B'.

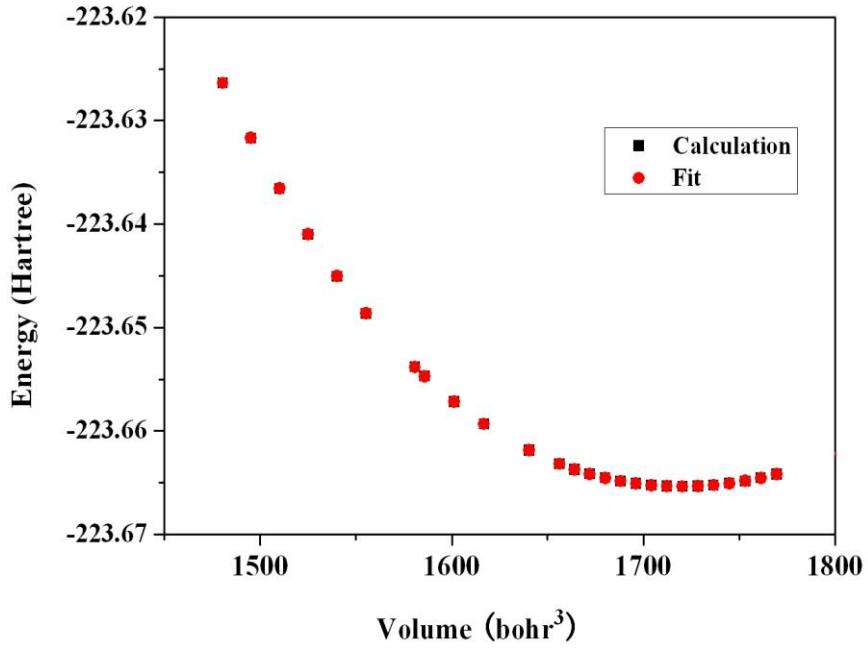

Fig. 1. Total energy as a function of the primitive unit cell volume for $AgInTe_2$

Table 1 The structural parameters a(Å) and c(Å), the bulk modulus B (GPa) and its first derivative B' of $AgInTe_2$ compared to other theoretical and experiment values

	a	*c*	*B*	B'
This work	6.3546	12.6531	50.35	5.4561
Expt.[18]	6.4672	12.6331		
Expt.[19]	6.262	12.897		
Theor.[20]	6.361	12.567		
Theor.[11]			50.1	

The elastic stiffness tensor of chalcopyrite material has six independent components because of the symmetry properties of the $I\bar{4}2d$ space group, namely $C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, C_{66}$ in Young notation. For the mechanical stable chalcopyrite structure, these elastic stiffness tensor components must satisfy certain relations, known as Born stability criteria [**21**]. The elastic constants obtained from our calculations and calculated with the other theoretical results [**11, 22**] are listed in Table 2. It can be seen that our calculated elastic constants satisfied Born stability criteria and the values in agreement with previous theoretical works.

Table 2 The calculated elastic constants C_{ij} (in GPa) and bulk modulus B (GPa) together with other theoretical values of $AgInTe_2$

$AgInTe_2$	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	*B*
Present	64.28	44.15	44.04	64.07	24.08	23.57	50.79
Theor.[22]	78.3	49.0	57.3	90.4	33.2	30.1	
Theor.[11]	63.4	43.6	54.2	71.4	22.4	23.0	50.1

3.2. Thermal properties

In this work, the thermal properties are obtained in the temperature range from 0 to 700 K and pressure range from 0 to 5 GPa.

Fig. 2 shows the relations of the equilibrium volume *V* and temperature at *P* = 0, 1, 2, 3, 4, 5 GPa, respectively. The equilibrium volume *V* increases as the temperature increases, whereas the *V* decreases dramatically as the pressure *P* increases at a given temperature. This suggests that the $AgInTe_2$, under loads turns to be more compressible with increasing pressure than with decreasing temperature.

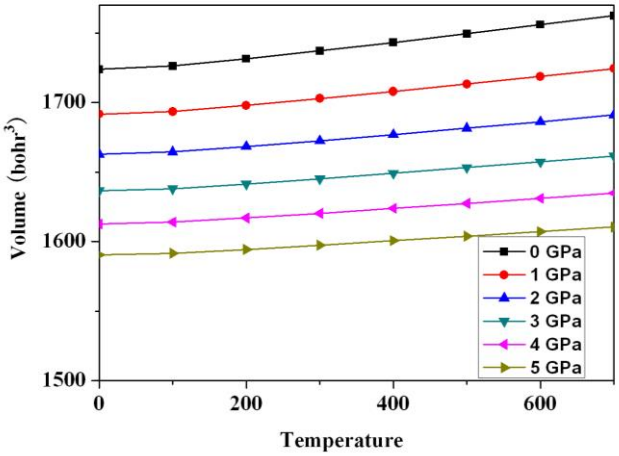

Fig. 2. Volume and temperature at various pressures for $AgInTe_2$

Bulk modulus of $AgInTe_2$ as a function of pressure at T = 0 K, 200 K, 400 K, 600 K is shown in Fig. 3. It is shown that Bulk modulus B linearly increases with increase of pressure at a given temperature, indicating the same effect on $AgInTe_2$ by increasing the P and decreasing the T.

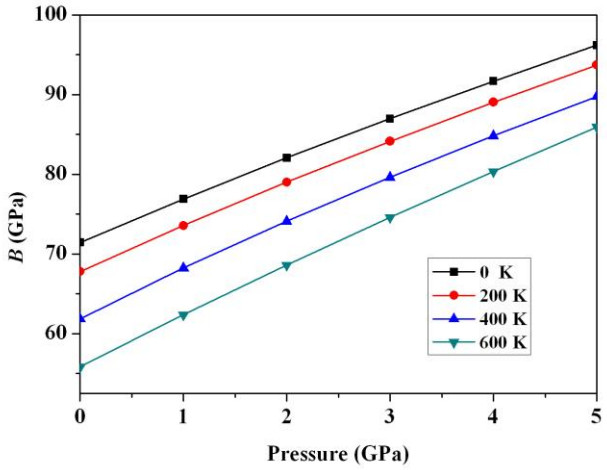

Fig. 3. Bulk modulus and pressure at various temperatures for $AgInTe_2$

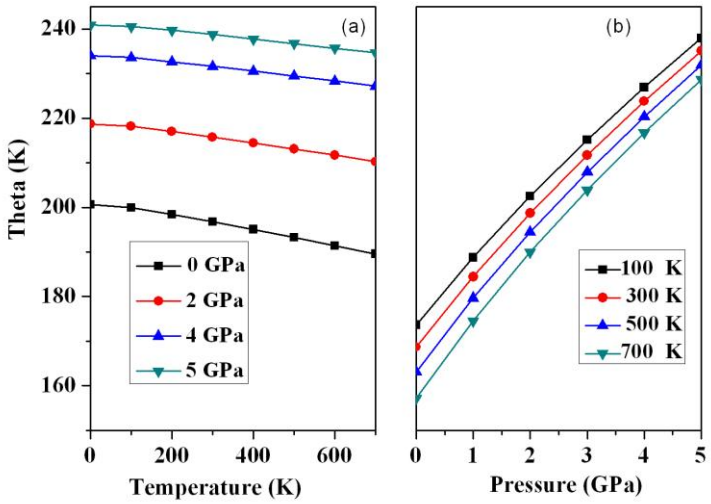

Fig. 4. Debye temperature of the $AgInTe_2$ at various pressures and temperatures

Fig. 4 and 5 shows the Debye temperature Θ versus temperature and pressure. It can be seen from Fig. 4(a) that Θ is nearly constant at low temperature and decreases linearly with increasing temperature. When at a given temperature (T = 100, 300, 500, 700 K), Debye temperature Θ increases almost linearly with applied pressure as shown in Fig. 4(b). The present calculated Debye temperature Θ = 200.65 K (P = 0 GPa, T = 0 K) and Θ = 196.8 K (P = 0 GPa, T = 300 K). The value at T = 0 K is in agreement with the value 168.86 K computed in terms of the simple relations [**23**]. This suggests that the Θ calculated from the quasi-harmonic Debye method is correct.

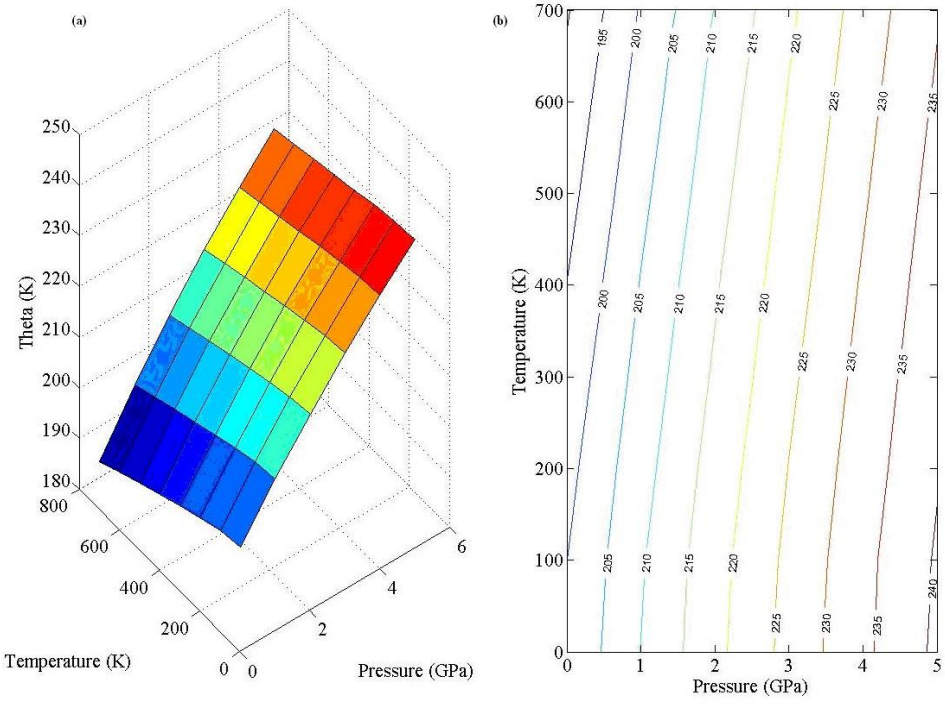

Fig. 5. Debye temperature Θ versus temperature and pressure for $AgInTe_2$ (a) three-dimensional plot (b) contours

In addition, we have also calculated the Internal energy *U*, Heat capacity at constant pressure C_P, Helmholtz free energy *A*, Grüneisen parameter γ and thermal expansion α of $AgInTe_2$ at 0 GPa under different temperature. The calculated results are listed in Table 3.

Table 3. The calculated Internal energy U (kJ/ mol), heat capacity of constant Heat capacity at constant pressure C_P (J /mol K), Helmholtz free energy A (kJ/ mol), Grüneisen parameter γ and thermal expansion α ($10^{-5}K^{-1}$) for $AgInTe_2$ at 0 GPa under different temperature*

T/K	*U*	*C*p	*A*	γ	α
0	7.51	0	7.51	2.492	0
100	11.88	82.92	4.56	2.501	2.69
200	20.93	96.56	-6.32	2.520	3.20
300	30.57	100.17	-22.28	2.541	3.37
400	40.38	102.16	-41.73	2.564	3.52
500	50.26	103.72	-63.86	2.588	3.65
600	60.17	105.17	-88.21	2.614	3.79
700	70.10	106.55	-114.39	2.640	3.89

4. Conclusions

In summary, the structural and elastic constants of $AgInTe_2$ were investigated using the pseudopotential plane wave method within the LDA. The calculated structural parameters and elastic constants are in agreement with experimental or previous theoretical works. Through the quasi-harmonic Debye method, the pressure and temperature dependences of the equilibrium volume, the bulk modulus, the Debye temperature, the Grüneisen parameter, the thermal expansion coefficient and so on are obtained. The results show that pressure and temperature have significant effects on these thermal properties. To the best of our knowledge, the thermal properties of of $AgInTe_2$ are reported for the first time.

Acknowledgments

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