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INVESTIGATION OF STRUCTURAL, ELASTIC AND THERMAL PROPERTIES OF $CuGaSe_2$: FIRST PRINCIPLES METHOD

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The structural and elastic properties of $CuGaSe_2$ have been systematically reported by using the first-principles method. The calculated lattice constants *a* and *c*, bulk modulus *B* and its first derivative B' are in agreement with the available experimental data and other theoretical values. We have also computed the six independent components(C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, C_{66}). The mechanical stability of $CuGaSe_2$ is confirmed by using the above independent components. Moreover the pressure and temperature dependences of the Debye temperature Θ, thermal expansion coefficient α and heat capacities C_V and C_P were predicted by using the quasi-harmonic Debye model.

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Keyword: $CuGaSe_2$, elastic properties, thermal properties

1. Introduction

Chalcopyrite structure crystals are under development for optoelectronic applications such as solar cells and nonlinear optical devices [1-4]. With wide band gap and a high optical absorption coefficient, $CuGaSe_2$ belongs to these promising chalcopyrite structure crystals. Recently, there are some theoretical and experimental studies on $CuGaSe_2$. In experimental studies, heterojunctions based on $CuGaSe_2$ single crystals [5] or polycrystalline [6] have been prepared with power conversion. The vibrational spectra of the $CuInSe_2$ and $CuGaSe_2$ have been used by Raman microspectrometry [7]. In theoretical studies, Maeda *et al* have been performed the formation energies in chalcopyrite-type $CuInSe_2$, $CuGaSe_2$ and $CuAlSe_2$ [8]. Xue *et al* have been carried out the $CuGaSe_2$ up to 100 GPa based on density functional theory [9]. Rare theoretical studies were reported on the elastic for $CuGaSe_2$ and thermal properties. In this work, we investigated the structural and elastic in $CuGaSe_2$ by using first-principles calculation based on the density functional theory (DFT). DFT has been successlfully used in studying structures and elastic properties of materials and has been widely used in theoretical studies of similar materials such as $AgGaS_2$ [10] and $AgGaSe_2$ [11] .

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2.Calculations method

In this paper, the structural and elastic properties of $CuGaSe_2$ crystal are performed by using the pseudopotential plane-wave within the framework of the density function theory and implemented through the Cambridge Serial Total Energy (CASTEP) program [12-13]. The exchange-correlation energy is described in the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional [14]. Vanderbilt-type ultrasoft pseudopotentials are employed to describe the electron-ion interactions [15]. In the structure calculation, a plane-wave basis set with energy cut-off 750.00 eV is used. For the Brillouin-zone sampling, the 8× 8 ×7 Monkhorst-Pack mesh is adopted.

3. Result and discussion

3.1. Structural properties

At ambient condition, the initial crystal structure of $CuGaSe_2$ is shown in figure 1. The structural properties are very important for studying the solid material. At the first step, a set of total energy calculation versus total volume, $E(V)$, for $CuGaSe_2$ was carried out in order to determine the structural parameters. The calculated total energies as a function of volumes for $CuGaSe_2$ are shown in figure 2. Then, we fitted the calculated $E(V)$ points to the Birch-Murnaghan equation of state (EOS) [16].

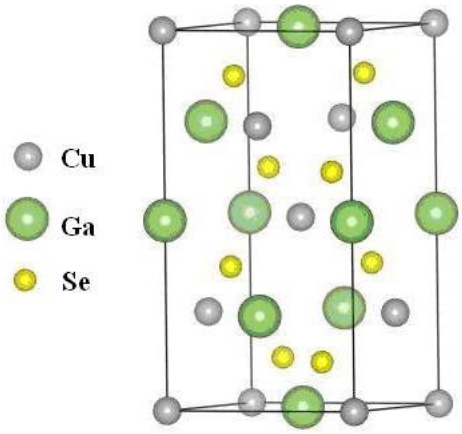

Fig. 1. Crystal structure of $CuGaSe_2$

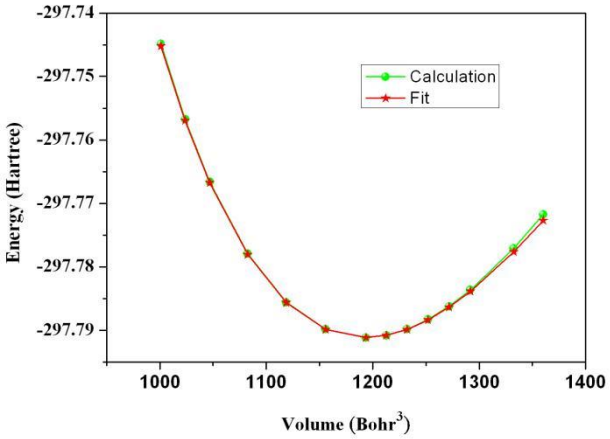

Fig. 2. Total energy vs. volume of $CuGaSe_2$ crystal

The optimized and fitted lattice constants, bulk modulus *B* and its pressure derivative B ' are listed in table 1 along with the other available results. In our GGA-PBE calculations, lattice constants *a* and *c* are 5.6169 Å and 11.2122 Å, and fitted lattice constants *a* and *c* are 5.6239 Å and 11.2262 Å respectively, which are very close to the experimental works [19, 20], and they are more consistent than previous theoretical results[8, 9, 17, 18]. The bulk modulus *B* and its pressure derivative B ' (table 1) have also been obtained by fitting EOS. The calculated values are also in good agreement with the other works [9, 21, 22] in table 1. This excellent agreement indicates that our calculation method is feasible to study elastic properties further.

Table 1 The lattice constants a (Å), c (Å), the bulk modulus B(GPa) and its first derivative of $CuGaSe_2$ compared to experimental and theoretical values

	This work		Theor.				Expt.	
a	5.6169[a]	5.6239[b]	5.681[c]	5.685[d]	5.609[e]	5.665[f]	5.596[g]	5.61[h]
c	11.2122[a]	11.2262[b]	11.209[c]	11.22[d]	11.147[e]	11.232[f]	11.003[g]	11[h]
B	61.64[a]	61.16[b]	57.7[c]	57.84[i]			71[j]	
B'		5.25[b]	4.75[c]					

[a]optimized lattice constants [b]Fitted lattice constants [c] From Ref. [9]. [d]From Ref.[17]
[e]From Ref. [8] [f]From Ref. [18]. [g]From Ref[19] [h]From Ref. [20] [i]From Ref. [21]
[j]From Ref. [22]

Table 2 The calculated elastic constants $C_{11}, C_{12}, C_{13}, C_{33}, C_{44}$ *and* C_{66} *(GPa) together with other theoretical values of* $CuGaSe_2$

$CuGaSe_2$	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
Present	86.84	47.88	49.47	87.56	42.50	43.62
Theor.[23]	87.3	54.6	63.8	100.8	37	33.6

The elastic constants of chalcopyrite structure have C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66} independent components. If the chalcopyrite structure is mechanically stable, the above six components must obey the Born stability criteria [24]. In this paper, our calculated values obey the mechanical stability criteria. Therefore, we can conclude the $CuGaSe_2$ is mechanically stable. The elastic constants obtained from our GGA-PBE method and evaluated with the other theoretical data are listed in table 2. Our results are consistent with the available theoretical data [23].

In order to study their elastic nature systematically, we further calculated the other interesting elastic quantities for $CuGaSe_2$ such as the bulk modulus *B*, the shear modulus *G* and the Young's modulus *E* .

Based the above C_{ij} values, the bulk modulus *B* can be given by the Voigt approximation (B_V) [25] and the Reuss approximation (B_R) [26]

$$B_V = \frac{1}{9}(2C_{11} + C_{33} + 2C_{12} + 4C_{13}) = 61.65GPa$$

$$B_R = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}} = 61.64GPa$$

the shear modulus *G* can be given by the Voigt approximation (G_V)[25] and the Reuss approximation (G_R) [26]

$$G_V = \frac{1}{15}(2C_{11} + C_{33} - C_{12} - 2C_{13} + 6C_{44} + 3C_{66}) = 33.35GPa$$

$$G_R = 15\left\{18B_V / C^2 + 6/(C_{11} - C_{12}) + 6/C_{44} + 3/C_{66}\right\}^{-1} = 28.58GPa$$

Where $C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2$

Finally, the Voigt and Reuss approximation can be averaged, to obtain the bulk modulus(*B*) and the shear modulus(*G*) of $CuGaSe_2$: 61.65 and 30.97 GPa, respectively, as proposed by Hill [27]. The Young's modulus(*E*) of the material would be $E = 9BG/(3B + G) = 79.58GPa$.

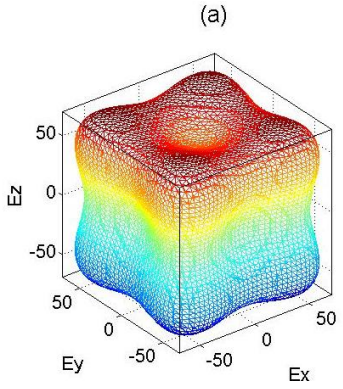

Fig. 3. Direction dependence of Young's modulus E(GPa)

The three dimensional(3D) surface constructions of the directional dependences of reciprocals of *E* are very useful. The expressions of the reciprocals of *E* for the $CuGaSe_2$ can be obtained from Ref.[28]. In figure 3, we show the plotted figure for the mechanical stable structure of $CuGaSe_2$. The surface in each graph represents the magnitude of *E* along different orientations. Overall, along z axis, the anisotropy of *E* seems to strengthen much significantly than x and y axis.

3.2 Thermal properties

In order to obtain the thermal properties of $CuGaSe_2$, the quasi-harmonic Debye model is used[29]. The ranges of the pressure (*P*) and temperature(*T*) are from 0 to 15 GPa and from 0 to 1000 K.

Fig. 4 plots relationships of the ratio V/V_0-*T* and V/V_0-*P*, respectively. In figure 4(a), the ratio V/V_0 varies monotonically with the increaseing of the temperature from 0 to 1000 K at different pressure *P* = 3, 6, 9,12 and 15 GPa, respectively. In figure 4(b), it can be found that the ratio V/V_0 decreases as the pressure changes from 0 to 15 GPa at different temperatures *T* = 0, 500, and 1000 K, respectively. At low pressure, the discrepancy of V/V_0 among different temperatures is small. As the pressure increases, the discrepancy of V/V_0 increases. In a word, the influences of the pressure on the V/V_0 are much more significant than that of the temperature.

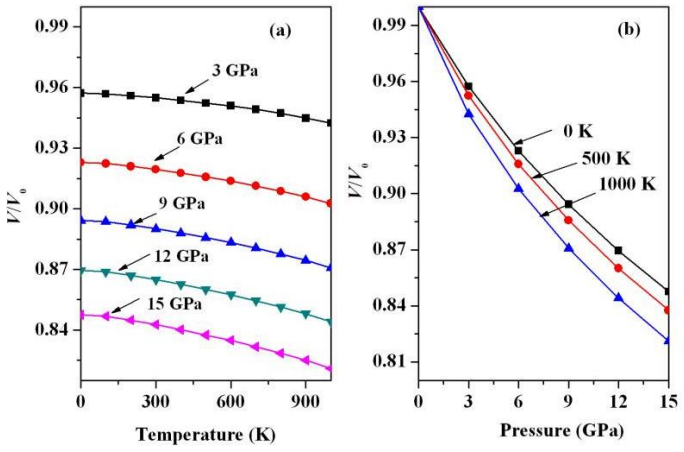

Fig. 4. The ratio V/V_0-T and V/V_0-P diagram of $CuGaSe_2$

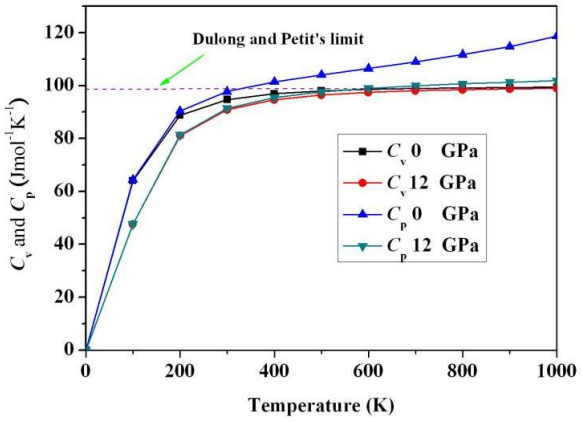

Fig. 5. Heat capacity of $CuGaSe_2$ at various pressures and temperatures

The C_V and constant pressure C_P as a function of temperature T at different pressures(0 and 12 GPa) are plotted in figure 5. At first C_V and C_P increases steeply, while with the increase of temperature T, C_P takes on the linear increase, C_V is close to a constant at sufficient high temperatures, 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 94.75 J mol^{-1} K^{-1} and 97.79 J mol^{-1} K^{-1}, respectively.

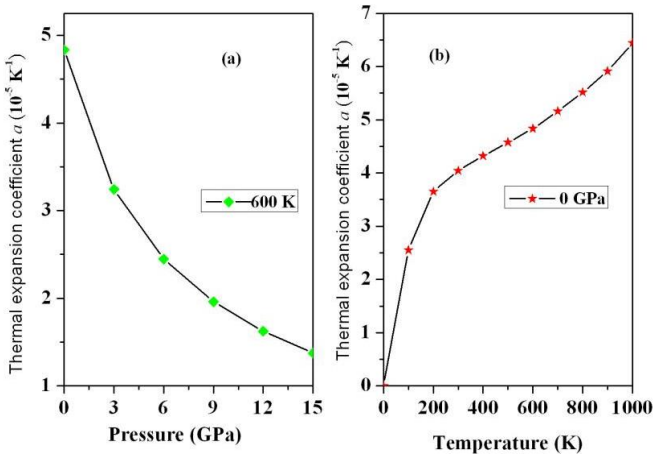

Fig. 6. The pressure dependence of thermal expansion coefficient α of $CuGaSe_2$ at 600 K (a) and the temperature dependence of thermal expansion coefficient α of $CuGaSe_2$ under 0GPa (b)

The thermal expansion coefficient α dependence on pressure and temperature is given in figure 6. From figure 6, we can see that the α at T = 600 K, it changes linearly with pressure following a gently decreasing trend. Whereas the α increases quickly with temperature at T < 200 K at P = 0 GPa.The α of $CuGaSe_2$ is 5.19×10^{-5} K^{-1} at 0 GPa and 300 K.

In table 3, we obtained the Θ, C_V and C_P and α at different temperatures (300, 600 and 900 K) and different pressures (0, 3, 6, 9, 12 and 15 GPa). At zero pressure and zero temperature, We obtained Θ = 313.2 K, which agrees excellently with the result 274.51 K of Kumar *et al* [30]. It indicates that our thermal calculations for $CuGaSe_2$ are reliable. These data provide reference values for crystal growth.

Table 3 The calculated Debye temperature Θ (K), heat capacity C_V and C_P (J mol^{-1} K^{-1}) and thermal expansion coefficient α ($\times 10^{-5}$ K^{-1}) of the $CuGaSe_2$ at temperatures T (K) and pressures P (GPa)

T	*P*	0	3	6	9	12	15
300	Θ	306.7	343.3	372.2	395.9	416.0	433.3
	C_V	94.7	93.5	92.5	91.6	90.8	90.1
	C_P	97.8	95.3	93.7	92.5	91.5	90.6
	α	4.04	2.83	2.17	1.75	1.45	1.23
600	Θ	295.8	336.2	366.9	391.8	412.8	430.7
	C_V	98.6	98.2	97.9	97.7	97.5	97.3
	C_P	106.5	102.7	100.9	99.8	99.0	98.5
	α	4.83	3.24	2.45	1.96	1.62	1.37
900	Θ	282.5	328.5	361.1	387.4	409.2	427.8
	C_V	99.3	99.1	99.0	98.9	98.8	98.7
	C_P	114.8	106.9	103.9	102.3	101.3	100.6
	α	5.91	3.61	2.65	2.09	1.71	1.44

4. Conclusions

We have calculated the structural, elastic and thermal properties of $CuGaSe_2$ crystal in this paper. The structural properties such as lattice constants *a* and *c*, bulk modulus *B* and its first derivative B ' obtained from our calculation consistent with the available experimental and theoretical values. The calculated elastic constants of $CuGaSe_2$ obey the Bron criteria, so the $CuGaSe_2$ is a mechanically stable structure. The thermal properties of the $CuGaSe_2$ crystal are predicted by the quasi-harmonic Debye model. We have reported the Debye temperature Θ, the heat capacity C_V and C_P, the thermal expansion coefficient α in dependence on the temperature *T* and pressure *P* as these are very useful for crystal growth.

Acknowledgments

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