Elastic and Thermo-physical Properties of Stannite-type $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ from First-principles Calculations

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[Manuscript received 10 December 2012, in revised form 26 February 2013]

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$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) with optimum band gaps about 1.5 eV are important absorbers for solar cells. The elastic constants and the thermo-physical properties of the stannite-type CZTS and CZTSe are calculated by using density-functional theory (DFT) and the quasi-harmonic Debye model. The bonding strength along the [100] and [010] directions is the same to that along the [001] direction and the shear elastic properties of the {001} plane are anisotropic for CZTS and CZTSe. Both compounds exhibit ductile behavior due to their high ratio of bulk modulus to shear modulus (K/G). The values of thermal capacity are close to 200 J/(mol·K) at above 300 K, and the thermal expansion coefficients decrease with increasing pressure at same temperature. The entropy is variable by power-exponent, and the internal energy is almost linear with increasing temperature for CZTS and CZTSe. The Gibbs energy of CZTS is lower than that of CZTSe under same temperature and pressure. The Debye temperatures are 297 and 232 K, and Grüneisen parameters are 2.36 and 2.37 for CZTS and CZTSe at 300 K, respectively.

KEY WORDS: Elastic property; Thermo-physical property; First-principles; $\text{Cu}_2\text{ZnSnS}_4$; $\text{Cu}_2\text{ZnSnSe}_4$

1. Introduction

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) are highly promising absorbers for thin-film solar cell due to cheap and abundant copper, zinc, tin, sulfur and selenium, and the reported optimum band gaps about 1.5 eV for both CZTS and CZTSe^[1,2]. Recently, $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) has been applied to solar cells by some research groups. Katagiri *et al.*^[3] reported CZTS-based solar cells with an efficiency of 6.7% fabricated by the sputtering and sulfurization method under Cu-poor and Zn-rich condition in the CuS–ZnS–SnS system. Barkhouse *et al.*^[4] further fabricated CZTSSe solar cells with an efficiency of 10.1% by hydrazine-based solution processing.

The CZTS (Se) has three crystal structures: kesterite (KS), stannite (ST), and Wurtz-stannite (Wurtz-ST) types. The phase stability of the KS-, ST-, and Wurtz-ST-type CZTSe has been investigated

by first-principles calculations^[5]. The formation enthalpy of KS-type CZTSe is slightly smaller than those of ST- and Wurtz-ST-type CZTSe. The electric band structure, mechanical and thermo-physical properties of KS-type $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ have been studied by many researchers^[6–9]. The elastic properties of ST-type CZTS and CZTSe have also been reported by Gürel *et al.*^[9]. However, the thermo-physical properties of ST-type CZTS and CZTSe are never reported in literature. It is very important and essential to learn some thermo-physical properties of ST-type CZTS and CZTSe. Therefore, the elastic and thermo-physical properties of ST-type $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ are studied using density functional theory (DFT)^[10] and the quasi-harmonic Debye model^[11,12] in this work.

2. Computational Procedure

Using the scalar relativistic all-electron Blöchl's projector augmented-wave (PAW) method, first-principles calculations were performed^[13,14], as applied in the highly-efficient Vienna Ab initio Simulation Package (VASP)^[15,16]. The exchange correlation

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energy was computed using the generalized gradient approximation (GGA)^[17] and local density approximation (LDA)^[18]. Here we adopted the standard version of the PAW potentials for Cu, Zn, Sn, S and Se atoms. A plane-wave energy cutoff of 500 eV was held constant for all the calculations. Brillouin zone integrations were performed using Monkhorst-Pack k -point meshes^[19] with a k -point sampling of $11 \times 11 \times 11$ for the ST-type CZTS and CZTSe. The Methfessel-Paxton technique^[20] with a smearing parameter of 0.2 eV was also used. The total energy per unit was converged numerically to less than 1×10^{-6} eV. After structural optimization, calculated forces were converged to less than 0.1 eV/nm.

A Vinet^[21] equation of state (EOS) was used to obtain the equilibrium volume (V_0), the total energy (U_{tot}), the bulk modulus (K) and the pressure derivative of the bulk modulus ($\partial K / \partial P$). The elastic constants can be obtained by calculating the total energy as a function of the strains. For a small strain (ε') on a solid, the elastic energy ΔU_e is a quadratic function of strains:

$$\Delta U_e = V \sum_{i,j} \frac{1}{2} C_{i,j} \cdot e_i e_j \quad (1)$$

where $C_{i,j}$ are the elastic constants, V is the total volume of the unit cell and e_i are the components of the strain matrix^[22]:

$$\varepsilon' = \begin{pmatrix} e_1 & e_6 & e_5 \\ e_6 & e_2 & e_4 \\ e_5 & e_4 & e_3 \end{pmatrix} \quad (2)$$

By applying a strain, the original lattice vectors a could be transformed into the strained ones a' as $a' = (I + \varepsilon')a$, where I is the identity matrix.

For a tetragonal material, there are 6 independent single-crystal elastic constants, that are C_{11} , C_{12} , C_{33} , C_{13} , C_{44} and C_{66} . The K , shear modulus (G) and Young's modulus (E) of polycrystalline can be obtained from the single crystal elastic constants^[23] as following expressions:

$$K_{\text{Vogit}} = (1/9)[2(C_{11} + C_{12}) + C_{33} + 4C_{13}] \quad (3)$$

$$G_{\text{Vogit}} = (1/30)(E + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66}) \quad (4)$$

$$K_{\text{Ruess}} = C^2 / E \quad (5)$$

$$G_{\text{Ruess}} = 15\{ (18K_{\text{Vogit}}/C^2) + [6/(C_{11} - C_{12})] + (6/C_{44}) + 3(3/C_{66}) \}^{-1} \quad (6)$$

$$E = C_{11} + C_{12} + 2C_{33} - 4C_{13} \quad (7)$$

$$C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2 \quad (8)$$

Finally, the mean values from Vogit Ruess Hill methods (VRH) are obtained by following equations:

$$K_{\text{VRH}} = \frac{1}{2}(K_{\text{Vogit}} + K_{\text{Ruess}}) \quad (9)$$

$$G_{\text{VRH}} = \frac{1}{2}(G_{\text{Vogit}} + G_{\text{Ruess}}) \quad (10)$$

The E and Poisson's ratio (ν) can be obtained from K and G ^[23]

$$E = \frac{9KG}{3K + G} \quad (11)$$

$$\nu = \frac{3K - 2G}{2(3K + G)} \quad (12)$$

The mechanical stability criteria^[24] are given by the following equations:

$$C_{11} > 0, C_{33} > 0, C_{44} > 0, C_{66} > 0 \quad (13)$$

$$(C_{11} - C_{12}) > 0, (C_{11} + C_{33} - 2C_{13}) > 0 \quad (14)$$

$$[2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0 \quad (15)$$

To investigate the thermo-physical properties of ST-type CZTS and CZTSe, the non-equilibrium Gibbs function (U_G^*) of the quasi-harmonic Debye model was applied here as following^[11]:

$$U_G^*(V, P, T) = U_{\text{unit}} + PV + A_{\text{vib}}(\Theta, T) \quad (16)$$

where U_{unit} is the total energy per unit, $P \cdot V$ corresponds to the constant hydrostatic condition, Θ is the Debye temperature, T is the thermodynamic temperature, and the vibration term ($A_{\text{vib}}(\Theta, T)$) can be expressed as^[25,26]:

$$A_{\text{vib}}(\Theta, T) = nk_B T \left[\frac{8}{9} \frac{\Theta}{T} + 3 \ln(1 - \exp(-\Theta/T)) - D(\Theta/T) \right] \quad (17)$$

where $D(\Theta/T)$ represents the Debye integral, n is the number of atoms per formula unit, k_B is Boltzmann constant.

The Debye temperature can be estimated from the average sound velocity using the following equation:

$$\Theta = \frac{\hbar}{k_B} \left(\frac{3}{4\pi V_{\text{at}}} \right)^{1/3} v_m \quad (18)$$

where $\hbar$ is the Planck's constant and V_{at} is the atomic volume. The average sound velocity in a polycrystalline system (v_m) is evaluated by

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (19)$$

where v_t and v_l mean transverse and longitudinal sound velocities, respectively, which can be related to G and K by the Navier's equations

$$v_t = \left(\frac{3K + 4G}{3\rho} \right)^{1/2} \text{ and } v_l = \left(\frac{G}{\rho} \right)^{1/2} \quad (20)$$

Finally, Θ is expressed as^[25]

$$\Theta = \frac{\hbar}{k_B} [6\pi^2 V^{1/2} n]^{1/3} f(v) \sqrt{\frac{K_s}{M}} \quad (21)$$

Table 1 Theoretical and experimental lattice parameters a , c , and c/a of ST-type CZTS and CZTSe

parameters	a (nm)	c (nm)	c/a	Ref./method
ST-type CZTS	0.5467	1.0967	1.99	This work/GGA
	0.5322	1.0667	2.00	This work/LDA
	0.5325	1.0629	2.00	Ref. [9]/LDA
	0.5436	1.1020	2.00	Ref. [29] /experiment
	0.5770	1.1540	2.00	This work/GGA
ST-type CZTSe	0.5605	1.1207	2.00	This work/LDA
	0.5604	1.1208	2.00	Ref. [9]/LDA
	0.5692	1.1340	1.99	Ref. [30]/experiment

where M is the molecular mass per unit cell, K_s is the adiabatic bulk modulus, which can be approximated by the static compressibility^[11]

$$K_s \approx K_{\text{vogit}} = V \left(\frac{d^2 U_{\text{unit}}}{dV^2} \right) \quad (22)$$

The Poisson's ratio is taken from Eq. (11), $f(v)$ is given by Ref. [26] and Ref. [27]. Therefore, the non-equilibrium Gibbs function can be minimized with respect to the volume V :

$$\left(\frac{\partial U_G^*(V, P, T)}{\partial V} \right)_{P, T} = 0 \quad (23)$$

Thermal equation of state can be obtained by solving Eq. (23). The isothermal bulk modulus K_T and the heat capacity C_V and the thermal expansion coefficient α are given by Ref. [28] as the following:

$$K_T(P, T) = V \left(\frac{\partial^2 U_G^*(V, P, T)}{\partial V^2} \right)_{P, T} \quad (24)$$

$$C_V = 3nk_B \left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right] \quad (25)$$

$$\alpha = \frac{\gamma C_V}{K_T V} \quad (26)$$

where γ is defined as an harmonic effect of the vibrating lattice which can be described in terms of a Grüneisen parameter are usually defined as:

$$\gamma = \frac{\partial \ln \Theta_D}{\partial \ln V} \quad (27)$$

3. Results and Discussion

3.1 Elastic properties

Relationships between total energy and volume of the ST-type CZTS and CZTSe are calculated to obtain lattice parameters, as shown in Fig. 1. Minimum total energies of ST-type CZTS and CZTSe are -32.73 eV/cell and -29.67 eV/cell, respectively, the total energy of CZTS is smaller than that of CZTSe at the same volume in the ST-type structure. The calculated values are both in agreement with Vinet EOS^[21]. Lattice parameters a and c are optimized through the minimization of total energy by means

Fig. 1 Relationships between total energy and volume of the ST-type CZTS and CZTSe using GGA

of the equilibrium volume. The results are listed in Table 1. The obtained lattice parameters well meet the experimental^[29,30] and reported values^[9].

Elastic properties of materials are usually characterized by Young's modulus, shear modulus, bulk modulus and Poisson's ratio obtained from the elastic constants. The elastic constants of the CZTS and CZTSe with ST-type phase were calculated by using the GGA and the LDA in this work, respectively, and are listed in Table 2. The calculated elastic constants of the CZTS and CZTSe with ST-type phase by using LDA in this work are in good agreement with the reported data using LDA^[9]. The calculated elastic constants of the CZTS and CZTSe with ST-type phase by using GGA in this work are all smaller than those by using LDA in this work and the reported data^[9]. Usually, the value of energy is underestimated and the volume is overestimated using GGA, and the result is on the contrary using LDA. However, the GGA is modified on the basis of the LDA, therefore, the GGA method is selected to calculate elastic constants in this work. We hope that the experimental data can be found for comparison. The elastic constants of the ST-type CZTS and CZTSe obtained from calculation meet their stability conditions. $C_{11} \approx C_{33}$, which indicates that the bonding strength along the [100] and [010] direction is the same to that along the [001] direction in the present calculations. The fact that $C_{11} + C_{12}$ is larger than C_{33} indicates that the elastic modulus is higher in the (001) plane than that along the c -axis. In addition, the fact that $C_{66} \approx C_{44}$ indi-

Table 2 Elastic constants (C_{ij}), bulk modulus (K), shear modulus (G), Young's modulus (E) and Poisson's ratio (ν) for the ST-type CZTS and CZTSe obtained from calculations

Parameter	ST-type CZTS			ST-type CZTSe		
	This work/GGA	This work/LDA	Ref. [9]/LDA	This work/GGA	This work/LDA	Ref. [9]/LDA
C_{11} (GPa)	91.61	114.69	117.06	75.71	95.19	91.15
C_{12} (GPa)	57.40	76.67	77.45	46.28	62.52	60.46
C_{13} (GPa)	55.40	74.75	76.06	45.48	62.31	60.44
C_{33} (GPa)	91.54	116.46	122.95	74.44	96.56	92.84
C_{44} (GPa)	40.32	45.71	47.22	33.02	38.33	37.86
C_{66} (GPa)	42.18	48.79	49.14	33.56	38.85	38.25
K_V (GPa)	67.91	88.69	88.69	55.59	73.47	70.90
K_R (GPa)	67.90	90.07	90.07	55.58	73.46	70.90
K_{VRH} (GPa)	67.90	88.69		55.59	73.47	
G_V (GPa)	31.67	36.02		25.83	29.75	
G_R (GPa)	26.87	30.35		22.14	25.23	
G_{VRH} (GPa)	29.27	33.18		23.99	27.49	
E (GPa)	76.78	88.51		62.91	73.33	
ν	0.312	0.33		0.311	0.334	
K/G	2.32	2.67		2.32	2.67

Fig. 2 Volume *vs.* temperature at various pressures: (a) ST-type CZTS; (b) ST-type CZTSe

cates that the $[100](001)$ shear is as easy as the $[100](010)$ shear for the two ST-type phases. The shear elastic anisotropy factor^[31] can be estimated as $A=2C_{66}/(C_{11}-C_{12})$. If $A=1$, no anisotropy exists. $A=2.47$ for the ST-type CZTS and $A=2.28$ for the ST-type CZTSe indicate that the shear elastic properties of the $\{001\}$ plane are anisotropic for both materials.

From the equation of state, the bulk modulus for the ST-type CZTS is 67.91 GPa which is close to 68.69 GPa obtained from the single crystal elastic constants, and the bulk modulus for the ST-type CZTSe is 55.59 GPa which is close to 56.7 GPa obtained from the single crystal elastic constants. The ratio between the bulk and the shear modulus, K/G is proposed by Pugh^[32] to predict brittle or ductile behavior of both materials. According to the Pugh criterion, a high K/G value indicates a tendency for ductility. If $K/G>1.75$, then ductile behavior exists, otherwise the material behaves in a brittle manner. The ratio

for the ST-type CZTS is 2.32 and that for the ST-type CZTSe is 2.318, which indicates that the ST-type CZTS and CZTSe are both more prone to ductile.

3.2 Thermo-physical properties

Through the quasi-harmonic Debye model, the thermo-physical properties of the ST-type CZTS and CZTSe can both be calculated at any temperature and pressure. In this work, the thermo-physical properties were determined from 0 to 1200 K, and the pressure effect was studied in 0–20 GPa. The temperature effects on the volume of the ST-type CZTS and CZTSe are shown in Fig. 2. As expected, the volume increases with increasing temperature and the volume decreases with increasing pressures. The volume of the ST-type CZTS is smaller than that of the ST-type CZTSe at the same temperature and pressure because the volume difference could be from the

Fig. 3 Heat capacity *vs.* temperature at various pressures: (a) ST-type CZTS; (b) ST-type CZTSe

Fig. 4 Bulk thermal expansion coefficient *vs.* temperature at various pressures: (a) ST-type CZTS; (b) ST-type CZTSe

Fig. 5 Entropy (S) and internal energy (U_{in}) *vs.* temperature: (a, c) ST-type CZTS; (b, d) ST-type CZTSe

different size of Se and S. However, it can be seen that the increasing tendency of the calculated data is similar at different pressures with increasing temperature for these two materials.

Heat capacity and thermal expansion coefficient of ST-type CZTS and CZTSe are very essential information for many applications. Fig. 3 and Fig. 4 represent the heat capacity $C_V(T)$ and bulk thermal expansion coefficients $\alpha(T)$ as a function of temperature at different pressures, respectively. The curves of C_V in Fig. 3 show a sharp increase up to 150 K, and that is close to a constant at above 300 K, which is the so-called Dulong-Petit limit^[22]. It can also be seen that the bulk thermal expansion coefficients of ST-type CZTS and CZTSe both decrease with increasing pressure at same temperature in Fig. 4. However, the heat capacity and bulk thermal expansion coefficient of the ST-type CZTS are the same to these of the ST-type CZTSe at a high temperature and a same pressure except for 0 GPa.

Fig. 5 shows that entropy (S) and internal energy (U_{in}) as a function of temperature at different pressures, respectively. The entropy is variable by power-exponent with increasing temperature, and the internal energy is independent of pressures and almost linear at different temperature for the ST-type CZTS and CZTSe. The entropies and internal energies are basically similar for the ST-type CZTS and CZTSe at the same temperature and pressure because of the closed physical properties of both components. A proper grasp of the interrelationship existed between thermal and elastic properties. It is of considerable helping in cementing the internal consistency of the understanding on many thermal physics related issues. It emerges from basic thermodynamic considerations that isothermal bulk modulus (K_T) has two separable components that derive, respectively, from the response of internal energy and entropy to changes in volume at constant temperature^[33]. The expression is as follow:

$$B_T = V \left(\frac{\partial^2 U}{\partial V^2} \right)_T - VT \left(\frac{\partial^2 S}{\partial V^2} \right)_T \quad (28)$$

The relationships between the bulk modulus and temperature for the ST-type CZTS and CZTSe are shown in Fig. 6. The bulk modulus slightly decreases with increasing temperature at a given pressure and increases with increasing pressure at a given temperature. However, the bulk modulus of the ST-type CZTSe is little smaller than that of the ST-type CZTS at the same temperature and pressure, because the entropy based contribution to negative bulk modulus for ST-type CZTS is lower than that for ST-type CZTSe, but both internal energies are presumably the same.

In order to know the phase stabilities of ST-type CZTS and CZTSe, Gibbs energy (U_G) and vibration energy (U_v) are treated as mandatory parameters for these materials. After the equilibrium states for a given (P , T) have been obtained, these thermodynamic properties can also be evaluated by using the corresponding equilibrium volume in the appropriate thermodynamic expressions. Fig. 7 shows the relationship among the calculated vibration energy, Gibbs energy and temperature at various pressures for the ST-type CZTS and CZTSe. The vibrational energy slightly decreases at below 300 K, and yet decreases linearly with increasing temperature at above 300 K. In general, Gibbs energy involves total energy, $P \cdot V$ and vibration energy. The Gibbs energy is nearly invariable with increasing temperature at same pressure, and the Gibbs energy of ST-type CZTS is lower than that of ST-type CZTSe at same condition.

The Debye temperatures of the ST-type CZTS and CZTSe are obtained as 297 K and 232 K at 300 K, respectively. Grüneisen parameters are also obtained as 2.36 and 2.37 at 300 K, respectively. As far as we know, there are no experimental values available for the ST-type CZTS and CZTSe and we are not aware of other theoretical data for these quantities. Therefore, our calculations should be taken as predictions.

Fig. 6 Bulk modulus *vs.* temperature at various pressures: (a) ST-type CZTS; (b) ST-type CZTSe

Fig. 7 Vibration energy and Gibbs energy *vs.* temperature: (a, c) ST-type CZTS; (b, d) ST-type CZTSe

4. Conclusion

The elastic properties of ST-type CZTS and CZTSe are obtained by using density-functional theory (DFT). The bonding strength along the [100] and [010] direction is the same to that along the [001] direction and the shear elastic properties of the {001} plane are anisotropic for ST-type CZTS and CZTSe. The high K/G ratio shows that the two compounds have both ductile behaviors. Using the Debye model, relationships among volumes, the heat capacity, thermal expansion coefficients, entropy, vibration energy, internal energy, Gibbs energy and temperature at various pressures are also predicated in this work. The present results give helps for the design of novel materials based on ST-type CZTS and CZTSe compounds, and these could be used to stimulate future experimental and theoretical work.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (No. 51075197).

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