THE STRUCTURAL, MECHANICAL AND THERMODYNAMICAL PROPERTIES OF Cu$_2$MnSnS$_4$: A FIRST-PRINCIPLES STUDY

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First-principle calculations of structural, elastic and thermal properties of Cu$_2$MnSnS$_4$ compound is performed in the framework of the Density Functional Theory. The lattice constant, Mulliken population analysis and ground state energy are calculated. Based on the calculated results, it is found that the bonds between S atoms and other three atoms (Cu, Mn, Sn) exhibit the feature of covalent bond. Also, elastic properties of the compound including bulk modulus B, shear modulus G, Young’s modulus E and Poisson’s ratio $\nu$ are calculated. The results reveal that Cu$_2$MnSnS$_4$ is mechanically a ductile and anisotropic. The thermodynamical properties such as heat capacity, Debye temperature and entropy were calculated employing the quasi-harmonic Debye model at different temperatures (0-1000K) and pressures (0-40GPa) using the quasi-harmonic Debye model for the first-time.

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1. Introduction

In recent years, in order to deal with the increasing serious energy crisis and environmental pollution, research on new materials is of pressing need and of great significance. Quaternary semiconducting compounds of the I$_2$-II-IV-VI$_4$ type, where I = Cu, Ag, II = Zn, Cd, Hg, Mn, Fe or Co, IV = Si, Ge, Sn or Pb and VI = S, Se or Te, have been investigated by different groups [1-3] because of their attractive semiconducting properties and potential applications in thin film solar cells. Cu$_2$MnSnS$_4$ (CMTS) belonging to Cu-based quaternary chalcogenide semiconductor, has direct band gap energy of between 1.0 eV and 1.4 eV, a large absorption coefficient of over $10^4$ cm$^{-1}$, which is regarded as one of the promising absorber materials [4-6].

The crystallographic parameter values of the Cu$_2$MnSnS$_4$ have been reported by using the melt and anneal technique and X-ray powder diffraction measurements [7, 8], respectively. The magnetic behavior of various I$_2$-(Mn,Fe,Co)-IV-VI$_4$ have been measured[9-11]. The crystallography structure of Cu$_2$MnSnS$_4$ was a stannite with space group I 42m (No. 121) [12, 13] As reported by several authors, the CMTS compound has a suitable band gap. Liang et al. reported a value close to 1.1 eV for CMTS [6], but Cui et al also reported the value around 1.3 eV [14]. The band gap of the Cu$_2$MnSnS$_4$ thin film is about 1.29 eV determined by the UV-vis-NIR absorption spectra measurement, which indicates it has potential applications in solar cells [15]. However, the available information related to structural, mechanical and thermal properties for the Cu$_2$MnSnS$_4$ compound is very scarce. The knowledge of the crystallographic parameters as well as Mulliken population

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analysis are important to study their basic crystal properties.

In this work, we have investigated the structural, elastic and thermodynamical properties of \( \text{Cu}_2\text{MnSnS}_4 \) compound using density function theory. The present work helps in further understanding of the basic properties, compensate the lack of theoretical data for \( \text{Cu}_2\text{MnSnS}_4 \) compound and also provides reference data for the future experimental and theoretical work on these intermetallic compounds.

2. Calculations method

In this paper, all the results of \( \text{Cu}_2\text{MnSnS}_4 \) crystal were obtained by using a plane-wave basis set for the electronic wave functions and periodic boundary conditions, as implemented in the CASTEP package. The exchange-correlation energy is evaluated in the generalized gradient approximation (GGA) Perdew-Burke-Ernnerhof (PBE) functional [16-19]. The calculations were performed following the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization technique. The interaction between the valence electrons and the core-electrons is described by ultra-soft pseudo-potentials. In order to meet the calculation accuracy and ensure the calculation speed, the plane wave cut off energy is 440eV, and the whole Brillouin zone is calculated by the K point grid of \( 5 \times 5 \times 5 \). Convergence shows that the brillouin zone sampling and the kinetic energy cut-off are sufficient for crystal optimization.

The thermodynamic properties are studied within the quasi-harmonic Debye model implemented in the Gibbs program [20-23]. We use the density function theory to calculate the total energy (E) of crystal for a grid of volume of the unit cell(V) at \( T = 0 \text{ K}, \text{ P} = 0 \text{ GPa} \). The final optimal curve of total energy is obtained by minimizing the energy verses volume by Birch–Murnaghan equation of state [24]. Using this, the thermodynamic properties such as the bulk modulus, specific heats, and Debye temperature at non-zero temperature and pressure are calculated.

3. Result and discussion

3.1. structure and elastic properties

The structure was solved in the space group I \( \bar{4} \text{2}m \) (No.121), which describes the structure of the compound \( \text{Cu}_2\text{MnSnS}_4 \) (Fig.1). The Fig.1 shows the unit cell of the studied phase. This structure is based on a stannite-type arrangement of sulfur and metal atoms, in which each cation is tetrahedrally coordinated to four atoms of sulfur. In order to investigate the ground-state properties of \( \text{Cu}_2\text{MnSnS}_4 \) alloy, the geometry optimizations are performed first with full relaxation of the cell shape and atomic positions. The results of first-principles calculations of the structural properties of the compound are presents in Table 1, together with the available experimental values [8, 25-27]. The comparison shows that our results are in reasonable agreement with experimental values. Pseudo-atomic valence states had been set as \( \text{Cu}-3d^{10}4s^1, \text{Mn}-3d^54s^2, \text{Sn}-5p^2, \text{S}-3p^4 \).

To analyze the chemical bonding information, the Mulliken population analysis of \( \text{Cu}_2\text{MnSnS}_4 \) crystal is shown in Table 1. One can see from Table 1, the Cu atom and S atom got the charges, the Mn atom and Sn atom lost the charges at the same time when the structure was in the process of optimization. By Mulliken population analysis’s interaction between S atoms and Mn atoms is stronger than the other two interactions(S-Cu and S-Sn). In the case of \( \text{Cu}_2\text{MnSnS}_4 \) the bonds between S atoms and other three atoms exhibit the feature of covalent bond. The bond length increases with the rising of atomic number, the situation is similar to that of ternary semiconductors [28].
Fig. 1. Unit cell of the Cu$_2$MnSnS$_4$ phase.

Table 1. Lattice constants and Mulliken population analysis of Cu$_2$MnSnS$_4$ crystal.

<table>
<thead>
<tr>
<th>Lattice constants/Å</th>
<th>Calculated value</th>
<th>Experimental value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5.627</td>
<td>5.518 [8], 5.458 [25], 5.49 [26], 5.514 [27].</td>
</tr>
<tr>
<td>c</td>
<td>10.659</td>
<td>10.807 [8], 10.827 [25], 10.82 [26], 10.789 [27].</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>Total</th>
<th>Charge/e</th>
<th>bond</th>
<th>Population</th>
<th>Bond length/ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.64</td>
<td>0.65</td>
<td>9.76</td>
<td>11.05</td>
<td>-0.05</td>
<td>S-Cu</td>
<td>0.41</td>
<td>2.328</td>
</tr>
<tr>
<td>Mn</td>
<td>0.38</td>
<td>0.5</td>
<td>6.03</td>
<td>6.91</td>
<td>0.09</td>
<td>S-Mn</td>
<td>0.63</td>
<td>2.169</td>
</tr>
<tr>
<td>Sn</td>
<td>1.44</td>
<td>1.55</td>
<td>0.00</td>
<td>2.99</td>
<td>0.99</td>
<td>S-Sn</td>
<td>0.02</td>
<td>2.676</td>
</tr>
<tr>
<td>S</td>
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<td>4.42</td>
<td>0.00</td>
<td>6.25</td>
<td>-0.25</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

3.2. Mechanical properties

The Poisson ratio ($\nu$), elastic constants $C_{ij}$ (GPa), bulk modulus ($B$) and other mechanical parameters have been calculated and simulated by using GGA-PBE method are listed in Table 2. The elastic constants of stannite structure have $C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, $C_{44}$ and $C_{66}$ six independent components. If the stannite structure is mechanically stable, the above six components must obey the Born stability criteria\cite{28-31}: $C_{11}>0$, $C_{33}>0$, $C_{44}>0$, $C_{66}>0$, $(C_{11}+C_{12})>0$, $(C_{11}C_{33}-C_{13}^2)>0$, and $[(C_{11}+C_{12})C_{33}-2C_{13}^2]>0$. As shown in Table 2, all of the elastic constants for the compound satisfies these criteria mentioned above, indicating that these compounds are mechanically stable.

All these stannites studied are more resistive to volume compression than to shear due to $B_H > G_H$. Considering that a solid with a larger $B_H/G_H$ (> 1.75) and $\nu$ (> 0.26) values is ductile, otherwise it is brittle\cite{30,32}. As seen from the results, the values of $B_H/G_H$ ratio for Cu$_2$MnSnS$_4$ compounds are larger than the critical value (1.75), thus indicating this semiconductor is ductile. In addition, Zener’s anisotropy index $A = 2C_{44}/(C_{11} - C_{12})=1.77$\cite{30} is studied. For isotropic case $A = 1$, while the deviations from unity measure the degree of elastic anisotropy. Our results show that the compound under consideration is highly anisotropic.
Table 2. Calculated mechanical parameters of Cu$_2$MnSnS$_4$ compound

| Elastic stiffness constants $C_{ij}$ (GPa) | $C_{11}$ | 89.557 | Young modulus (GPa) | $X$ | 42.545 |
| $C_{12}$ | 59.523 | $Y$ | 42.545 |
| $C_{13}$ | 54.289 | $Z$ | 37.856 |
| $C_{22}$ | 77.396 | Poisson ratios | $E_{xy}$ | 0.4165 |
| $C_{33}$ | 26.643 | | $E_{xz}$ | 0.4093 |
| $C_{44}$ | 34.743 | | $E_{yx}$ | 0.4165 |

Bulk modulus (GPa)

| Voigt | 65.856 | $E_{yz}$ | 0.4093 |
| Reuss | 65.081 | $E_{zx}$ | 0.3642 |
| Hill | 65.469 | $E_{zy}$ | 0.3642 |

Shear modulus (GPa)

| Voigt | 23.500 | Lame lambda (GPa) | Voigt | 50.190 |
| Reuss | 20.794 | Reuss | 51.219 |
| Hill | 22.147 | Hill | 50.704 |

Universal anisotropy index | 0.663 | Compressibility (GPa$^{-1}$) | 0.015 |

3.3. Thermodynamic properties

The thermal properties of a crystal determine the suitable conditions for initiating and maintaining the quality of crystal growth. Through the quasi-harmonic Debye model, we have investigated the thermal properties of the Cu$_2$MnSnS$_4$ over a range of pressures from 0GPa to 40GPa and a range of temperatures from 0K to 1000K.

As very important parameters, the heat capacities of a substance not only provide essential insight into the vibrational properties but are also mandatory for many applications. Our calculation of the heat capacities $C_p$ and $C_v$ of Cu$_2$MnSnS$_4$ versus temperature at different pressures (0GPa and 40GPa) are shown in the following Fig. 2. The heat capacity $C_v$ [33] can be written in the form of

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

where $n$ is the number of atoms per unit, $D(\theta/T)$ represents the Debye integral. From the figure, the heat capacities increase with increasing temperature, because phonon thermal softening occurs when the temperature increases. The constant volume heat capacity $C_v$ and the constant pressure capacity $C_p$ are very similar in appearance and both of them are proportional to $T^3$ at low temperatures. At high temperatures, the heat capacity tends to the Petit and Dulong limit, which is a common feature for all solids at high temperature. This results show that the interactions between ions in the nano-laminates have great effect on heat capacities especially at low temperature. From Fig. 2 it is clear that when $T < 400$ K, the heat capacity ($C_v$) depends on both temperature and pressure, whereas at high temperatures, $C_v$ approaches approximately 99.55 J mol$^{-1}$ K$^{-1}$. 
Fig. 2. Heat capacity of Cu$_2$MnSnS$_4$ versus temperature under different pressure

The entropy(S) of Cu$_2$MnSnS$_4$ versus temperature and pressure are shown in Fig.3 (a). The entropies are variable by power exponent with increasing temperature. The $\theta_D(k)$ is related to heat capacity, melting temperature and the thermal vibration frequency of a solid. The variation of the Debye temperature $\theta_D(k)$ as a function of pressure and temperature illustrated by our results is displayed in Fig. 3 (b). We observe that $\theta_D(k)$ decreases non-linearly with increasing temperature for Cu$_2$MnSnS$_4$. The variation of $\theta_D(k)$ with temperature and pressure reflects the fact that the thermal vibration frequency of the atoms in Cu$_2$MnSnS$_4$ changes slowly with temperature but changes rapidly with pressure.

![Fig.3 The entropy (a) and Debye temperature (b) versus temperature and pressure](image)

4. Conclusions

Owing to the lack of reported values of the elastic and thermal properties of Cu$_2$MnSnS$_4$. The parameters of the basic properties of Cu$_2$MnSnS$_4$ crystal have been calculated by using the plane wave pseudo-potential density functional theory as well as quasi-harmonic Debye model. The calculated lattice constants ($a$, $c$) have been discussed which are in good agreement with the experimental data. Furthermore, the Zener’s anisotropy index A and $B_H/G_H$ are studied, which indicate Cu$_2$MnSnS$_4$ is a anisotropic and ductile material.

The first-time results on temperature and pressure dependence Debye temperature, entropy and heat capacities are obtained and discussed. The results indicated: the heat capacity ($C_v$) decreased
with the pressure increasing at same temperature, while increase with temperature increasing under the same pressure. In addition, the thermal expansion coefficient increases exponentially with the temperature up to 400K.

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**References**