First-principles calculation of electronic structure and optical properties of Cu$_2$ZnSnO$_2$S$_2$

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Abstract. With the application of PBE plane wave ultra-soft pseudo-potential technology under the generalized gradient approximation (GGA) based upon the density function theory (DFT), the EV curve, enthalpy-pressure diagram, elasticity coefficient, energy band, state density, absorption coefficient, complex dielectric function, complex refractive index, reflectance, complex conductivity and energy loss function as a function of photon energy of the following four material structures, Cu$_2$ZnSnO$_2$S$_2$WKS (Wurtzite-Kesterite), W-ST (Wurtzite-Stannite) and KS (Kesterite), ST (Stannite) are calculated and generated respectively, and these factors of each strictures are systematically compared. The results show that Cu$_2$ZnSnO$_2$S$_2$WKS is a direct bandgap semiconductor material. From the EV curve and the enthalpy-pressure diagram, it is known that the KS structure is more stable than the other three structures.

Key words: First-principles; Energy density; Optical properties.

1. Introduction
The energy crisis has prompted people to find a renewable and clean energy source. Solar energy is a very ideal renewable energy source; solar cells can convert solar energy into electricity. Energy and environmental issues are two major issues that humans are concerned about today. Therefore, new energy, new materials, and environmental protection have become the focus of discussion in recent years. The ideal materials of the solar cell absorber layer should be a direct bandgap semiconductor material with a band gap of 1.4 to 1.6 eV and the raw materials, which are producing the layers, should be rich in reserves, easy to access, low in price, non-toxic and non-polluting [1]. Cu$_2$ZnSnS$_4$ (CZTS) thin-film solar cells are rich in content, cheap, and non-toxic, and are hot topic in the field of solar cells. The optical band gap of CZTS is about 1.5eV and its absorption coefficient is greater than 104cm$^{-1}$. The theoretical conversion efficiency of CZTS solar cells is as high as 32.4%, which is very promising [2]; the current maximum conversion efficiency is only about 12% [3].

In terms of a excellent performance of Cu$_2$ZnSnS$_4$, many researchers in China have conducted research to seek materials with higher conversion efficiency. As a solution to this issue, a doping was
done, because Cu, Zn, Sn, S and O elements are abundant in the crust, and are non-toxic and non-polluting. In the paper, the quantum chemistry program CASTEP (first-principle plane wave super soft pseudo-potential method based on density functional theory) is applied to generate the EV curve, enthalpy-pressure diagram, energy band, state density, complex refractive index, reflectivity, complex conductivity and energy loss function for Cu$_2$ZnSnO$_2$S$_2$ in its four structures.

![Figure 1](image1.png)

**Fig. 1.** The total energy of KS, ST, W-KS and W-ST as a function of the volume

2. **Computation method and Physical Description**

2.1. **Computation Methods**

The computations of this study use CASTEP package in the Material Studio software, which is an ab initio quantum calculation program based on density functional theory combined with the plane wave pseudo-potential method. [4] In the calculation, the generalized gradient approximation (GGA) PBE is used to process the exchange-associated energy between electrons.

![Figure 2](image2.png)

**Fig. 2.** Enthalpy of KS, ST, W-KS and W-ST as a function of pressure.

The functional relationship between volume and energy (EV curve) are drawn; It can be seen from the figure that the curve of the KS structures is much lower than that of the other three structures. It can also be said the KS structure is relatively stable. As shown in the Fig. 1 for the EV curve, the enthalpy pressure curve from 0 to 80 GPa is carried out in Fig. 2. There is no obvious phase change, therefore the curve of KS structure is slightly lower than the that of other three structures.
3. Results and Discussion

3.1. Energy Band and State Density

The band structures was displayed in Fig. 3. The four structures are direct bandgap semiconductors. The energy band of are KS. The band diagrams of the KS and ST structure show that the valence band tops and the conduction band bottoms at F, Q, and Z are direct band gaps, and their bandgap widths are approximately 1.4 to 1.6 eV, therefore it can be applicable for the ideal absorbent layer material. W-KS structure band diagram and W-ST structure energy band diagram show band bottom at F, Q, and Z are direct band gaps, and the bandgap width does not belong between 1.4 and 1.6 eV, therefore it is inapplicable for absorbent layer material. The Fig. 4 below shows the density of states for each of the four structures. The main factor affecting the physical solids properties is the electronic structure near the Fermi level, so the calculated electron density range is -28 to that the valence band top and the conduction 3 eV. From the state density distribution curve in the figure, it can figure out that the valence band of Cu$_2$ZnSnO$_2$S$_2$ is divided into four regions, that is, the lowest valence band region of -28 to -26 eV, and the lower valence region of -26 to -21 eV, the median valence band of -18 to -16 eV, the upper valence band of -16 to -11 eV, and the conduction band of -10 to 5 eV. The upper band region of the four structures is mainly composed of S-3P states, and there is also an O 2P state contribution; the conduction band region is mainly composed of Cu 3p state and Zn 3s state.

![Fig. 3. The band structure for KS ST, W-KS and W-ST structure](image)
3.2. Theoretical description of optical properties

In the linear response range, the solid macroscopic optical response function can usually be described by the complex permittivity \( \varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2(\omega) \) or the complex refractive index \( n(\omega) + ik(\omega) \), among them: \( \varepsilon_2 = n^2 - k^2, \omega_2 = 2nk \).

According to the definition of the direct transition probability and the Kramers-Kronig dispersion relationship, the imaginary and real part of the crystal dielectric function, absorption coefficient, reflectivity, complex photoconductivity, and energy loss function can be deduced. Etc. The specific derivation process is not depicted here. The following are the theoretical formulas on which the calculations are based:

\[
\begin{align*}
\varepsilon_2 &= \frac{C_1}{\omega^2} \sum_{\nu} \int_{BZ} d^3 K \frac{2}{2\pi} |e \cdot M_{\nu K}(K)|^2 \cdot \delta[E_{\nu}(K) - E_{\nu}(K - \hbar\omega)] \\
\varepsilon_1 &= 1 + C_2 \sum_{\nu} \int_{BZ} d^3 K \frac{2}{2\pi} \frac{|e \cdot M_{\nu K}(K)|^2}{[E_{\nu}(K) - E_{\nu}(K)] \cdot [E_{\nu}(K) - E_{\nu}(K)]^2 - \hbar^2 \omega^2} \\
n(\omega) &= \frac{1}{\sqrt{2}} \left[ (\varepsilon_1^2 + \varepsilon_2^2)^{1/2} + \varepsilon_1 \right]^{1/2} \\
\alpha(\omega) &= \frac{2\omega k(\omega)}{c} = \frac{4\pi k(\omega)}{\lambda_0} \\
k(\omega) &= \frac{1}{\sqrt{2}} \left[ (\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1 \right]^{1/2} \\
R(\omega) &= \frac{(n-1)^2 + k^2}{n + k^2 + k^2}
\end{align*}
\]
\[
\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega) = -i\frac{\omega}{4\pi}[\varepsilon(\omega) - 1] + i\frac{\omega}{4\pi}\varepsilon_2 + i\left(\frac{\omega}{4\pi} - \frac{\omega}{4\pi}\varepsilon_1\right)
\]

Where: C and V represent the conduction band and valence band, respectively, BZ is the first Brillouin zone, K is the inverted lattice vector, h is Planck's constant, |e \cdot M_\mathbb{CV}(K)|^2 is the momentum transition matrix element, \( \omega \) is the angular frequency, and \( C_1 \) and \( C_2 \) are constants, \( E_\mathbb{C}(K) \) and \( E_\mathbb{V}(K) \) are the energy level of the conduction band and the valence band respectively, \( n \) is the refractive index, \( k \) is the extinction coefficient, \( C \) is the propagation speed of light in vacuum, \( \lambda_0 \) is the wavelength of light in vacuum, \( R \) is the reflection, the \( \sigma \) is the photoconductivity, and L is the energy loss function. These relationships are the theoretical basis for analyzing the energy band structure and optical properties of crystals, which reflect the luminescence mechanism of the spectra generated by electronic transitions between energy levels. And in a sense, the complex mediation function \( \varepsilon(\omega) \) can better characterize the physical properties of the material than the macroscopic optical constants, and is easier to relate to the microscopic model of the physical process and the microscopic electronic structure of the solid.

### 3.3. Optical Properties

#### 3.3.1. Absorption coefficient

As shown in the Fig. 5, there are four absorption spectrum curves for the structures. The absorption spectrum is divided roughly into 3 parts, the visible light absorption area of 0 to 3eV for KS, W-KS, and W-ST structures, the ultraviolet light absorption area of 3 to 10eV, and the high energy absorption area of more than 10eV; the are of visible light absorption region(0-8 eV) and ultraviolet light intensity absorption region(8-12 eV) of ST structure are greater than the area of high-energy absorption region(more than 12 eV) of ST structure. With the increase of photon energy, the absorption coefficient gradually increases. When the photon energy is to 4.5 eV, the maximum absorption peak reaches 2.4×10^5 cm^{-1}. However, in the visible light region, the absorption coefficient of the W-ST structure is slightly higher than that of the KS, ST, and W-KS structures, and the high absorption coefficient is one of the advantages of the most promising absorption layer materials.

#### 3.3.2. Complex dielectric function

The complex dielectric function was shown in Fig. 6. The complex dielectric function serves as a bridge between the transitional microscopic physical processes and the solid electronic structure, which reflects the solid energy band structure and other various spectral...
Information [5]. As a direct bandgap semiconductor material, its spectrum is generated by the electronic transitions between the energy levels, and each dielectric peak can be explained by the energy band and the density of states. The graph above shows the plot of the real and imaginary parts of the dielectric function of Cu$_2$ZnSnO$_2$S$_2$ as a function of photon energy. As can be seen from the figure, when the frequency is very low, the dielectric function changes slowly with energy. At this time, the imaginary part of the dielectric function is 0, and there are 3 peaks. The three structures of KS, W-KS, and W-ST reaches the maximum value and is 4.5 eV. The basic uniform dielectric function of the ST structure varies evenly and slowly from 25 to -2.5 eV, and it is concluded that the ST structure cannot bridge the transition between the micro physical process and the solid electronic structure. The dielectric peak pair at the photon energy of 0.5 eV is related to the direct transition threshold and the top of the valence band to the bottom of the conduction band, the value is relatively large. The optical band gaps of KS, W-KS and W-ST structures are all large, and the real part and the imaginary part curve of the dielectric function move toward the high energy direction.

3.3.3. Complex refractive index. The Fig. 7 shows the complex refractive index refractive index plots for the four structures.

![Complex refractive index plot](image)

**Fig. 7** The complex refractive index for the four structures.

The complex refractive index can be obtained from the relation between the complex refractive index(3) and the complex dielectric function(4), the refractive index n and the extinction coefficient k shown in the figure. In the high-energy region (photon energy greater than 16.5 eV), the imaginary part is close to 0, and the real part has a small change, which indicates that the absorption is weak at high frequencies, and their refractive index is almost constant at high frequencies. Comparing the four structures, only the ST structure differs significantly from the other three, and the three are basically the same. The ST structure has a slightly smaller refractive index of 0 to 3 eV, which facilitates the absorption of light. With the increase of energy, the refractive index of the four structures generally decreases.

3.3.4. Reflectivity. The reflectance spectra of the four structures are shown in the Fig.8. Light is directly incident from air into a medium with complex refractive index, i.e., n$_1$=1, n$_2$=n+ik, and the relationship between reflectance and complex refractive index (6) can be obtained. It can be seen from the figure that the transitions between the reflection bands mainly occur in two areas, in the energy region of 8 to 11 eV and in the energy region of 15 to 17 eV respectively, in both area the reflectivity averages 80%; the peak of the W-ST structure at 10 eV reaches the maximum of 92%, the W-KS structure reflection peak reached a maximum of 90% at 10eV, and the KS and ST reflection peaks reach a maximum of 88% at 10eV. Therefore, the high-energy reflectances of the four structures are mainly concentrated in the visible light region, while in the ultraviolet and high-energy regions, the reflectivity averages 50%. The
relatively low reflectance also provides favorable conditions for them to become good absorber materials. Besides, the four structures have a good absorption effect.

![Reflectance Spectra](image)

**Fig. 8** The reflectance spectra of the four structures.

3.3.5. Complex conductivity

![Photo-conductive](image)

**Fig. 9** photo-conductive for the four structures

The photo-conductive for the four structures was shown in the Fig. 9. The photoconductivity of semiconductors refers to the phenomenon that the electrical conductivity of semiconductors changes due to illumination. The change may be the increase of electrical conductivity or the decrease of electrical conductivity. The first basic physical process that leads to electro-optic phenomena is that light excitation generates free carriers in the semiconductor. In the simplest case, absorption of photons causes the electrons to excite electrons from the valence band to the conduction band, thereby generating electrons that can move freely in the conduction band and holes that can move freely in the valence band, thereby causing photoelectric signals. Therefore, photoconductivity is an important parameter for optoelectronic materials. It can be seen from the figure that the real part of the photoconductivity of the four structures is 0 at energy 0, where the real part of the photoconductivity of each system Re is 0 in the range of energy greater than 16 eV.

4. Conclusion

1) The four structures of Cu$_2$ZnSnO$_4$S$_2$ belong to direct bandgap semiconductor materials.

2) The optical band gaps of the KS, W-KS and W-ST structures are all large, and the real and imaginary parts of the dielectric function curve move towards the high energy direction.

3) The photoconductivity can rise rapidly and a good performance has been achieved. The photoconductivity reaches the maximum at 0.9eV, which is the result of the inter-band excitation transition.
4) In the UV and high energy regions, the reflectivity averages 50%, and the lower reflectance also provides favorable conditions for the four structures to become good absorber materials.

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