Structural diversity and electronic properties of Cu$_2$Sn$_3$ (X = S, Se): A first-principles investigation

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The ternary semiconductors Cu$_2$Sn$_3$ (X = S, Se) are found frequently as secondary phases in synthesized Cu$_2$ZnSnS$_4$ and Cu$_2$ZnSnSe$_4$ samples, but previous reports on their crystal structures and electronic band gaps are conflicting. Here we report their structural and electronic properties as calculated using a first-principles approach. We find that (i) the diverse range of crystal structures such as the monoclinic, cubic, and tetragonal phases can all be derived from the zinc-blende structure with tetrahedral coordination. (ii) The energy stability of different structures is determined primarily by the local cation coordination around anions, which can be explained by a generalized valence octet rule. Structures with only Cu$_2$Sn and Cu$_2$Sn$_2$ clusters around the anions have low and nearly degenerate energies, which makes Cu and Sn partially disordered in the cation sublattice. (iii) The direct band gaps of the low-energy compounds Cu$_2$Sn$_3$ and Cu$_2$SnSe$_3$ should be in the range of 0.8−0.9 and 0.4 eV, respectively, and are weakly dependent on the long-range structural order. A direct analogy is drawn with the ordered vacancy compounds found in the Cu(In,Ga)Se$_2$ solar-cell absorbers.

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I. INTRODUCTION

As candidates for low-cost thin-film solar-cell absorbers, quaternary semiconductors Cu$_2$ZnSnS$_4$ (CZTS) and Cu$_2$ZnSnSe$_4$ (CZTSe) have been studied intensively in the past five years. Due to the increased number of elements in the materials, their synthesis is relatively more difficult than for binary and ternary semiconductors because more secondary phases such as ZnS, Cu$_2$SnS$_3$ (CTS), ZnSe, and Cu$_2$SnSe$_3$ (CTSe) may coexist in the samples. The coexistence of these secondary phase compounds will inevitably influence the electrical and optical properties of CZTS and CTSe, which have been observed experimentally and taken as the reason for the scattering of the measured properties.

Despite a long history of the experimental study of CTS and CTSe ternary compounds, their fundamental properties such as the crystal structure and band gap are still under debate. As listed in Table I, a diverse range of phases, such as monoclinic, cubic, tetragonal, and hexagonal with Cc, F43m, I42m, and P6$_3$/mmc symmetries, respectively, have been proposed by different groups, and so far it is not clear which structure is the ground state. For the measured band gap of CTS, different groups have also reported scattered values, from 1.35 to 0.95 eV, and to even zero (metallic) for hexagonal CTS. Once again, it is not clear what factors determine the significant differences. Without this knowledge, it is difficult to understand their influence on the properties of the synthetic CZTS and CTSe samples or whether the ternary compounds could be considered as candidates for solar cell absorbers.

In this paper, we investigate the structural and electronic properties of CTS and CTSe using first-principles total energy and band-structure calculations, and discuss the reasons for their structural diversity observed experimentally as well as the common character in the electronic and optical properties of different phases, which we find are determined primarily by local coordination environments, while being less sensitive to long-range order.

II. CALCULATION METHODS

The calculation is performed within the density functional formalism as implemented in the code VASP. The projector augmented-wave pseudopotentials are used with an energy cutoff of 400 eV for the plane-wave basis functions. The Brillouin zone integration is carried out using $8 \times 4 \times 8$ (for the monoclinic cell) or $9 \times 9 \times 3$ (for the orthorhombic cell) Monkhorst-Pack $k$-point meshes. Test calculations confirm that the total energy is converged to within 0.1 meV per atom. For the exchange-correlation functional, the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) is used to relax the structural parameters, while the hybrid nonlocal exchange-correlation functional (HSE) is used to calculate the electronic structure and optical properties since GGA underestimates the band gap for these compounds.

III. CRYSTAL STRUCTURES

In Fig. 1(a), we plot the experimentally observed monoclinic structure with Cc symmetry (mo-1 structure, the structural parameters are listed in Table II), which has 24 atoms in its primitive cell and is isomorphic to the structure of Cu$_2$SiS$_3$. One obvious characteristic of this structure is that all S anions are tetrahedrally bonded by four cations, as in zinc-blende structure, and the structure has clear atomic layers connected by perpendicular bonds, as the (111) layers in
the zinc-blende structure. Therefore, the monoclinic Cu2SnS3 structure with \( Cc \) symmetry is in fact a superstructure of zinc blende, and its primitive cell can be described as a zinc-blende supercell with the basis vectors

\[
\begin{pmatrix}
\bar{a} \\
\bar{b} \\
\bar{c}
\end{pmatrix} = \begin{pmatrix}
-0.5 & 0.5 & 1.0 \\
1.5 & 1.5 & 0.0 \\
0.5 & -0.5 & 1.0
\end{pmatrix} \begin{pmatrix}
\bar{a}' \\
\bar{b}' \\
\bar{c}'
\end{pmatrix},
\]

where \( \bar{a}' \), \( \bar{b}' \), and \( \bar{c}' \) are the basis vectors of the cubic zinc-blende conventional cell [Fig. 1(b)]. Since the kesterite structure of Cu2ZnSnS4 is also derived from a zinc-blende structure, the similarity of the complex Cu2SnS3 monoclinic structure to the simpler zinc-blende lattice is important: Cu2ZnSnS4 can be considered as a substitutional alloy of its two main secondary phases ZnS and Cu2SnS3, all having the same zinc-blende-derived lattice. Due to this similarity, the simulated x-ray diffraction (XRD) patterns for ZnS, monoclinic Cu2SnS3, and kesterite Cu2ZnSnS4 all have similar main diffractions lines,\(^{20}\) which makes the distinction between the ZnS and Cu2SnS3 secondary phases in Cu2ZnSnS4 samples using diffraction techniques difficult if the crystal quality is not good enough.

Besides the monoclinic structure, other structures have also been proposed by previous experiments, e.g., the cubic structure with \( F\bar{4}3m \) symmetry and tetragonal structure with \( I\bar{4}2m \) symmetry.\(^{17,19,21}\) As we know, the binary zinc-blende structure has \( F\bar{4}3m \) symmetry, and the quaternary stannite structure, which is also derived from zinc blende, has \( I\bar{4}2m \) symmetry, so the ternary Cu2SnS3 can have the symmetry (\( F\bar{4}3m \) or \( I\bar{4}2m \)) only if the cations are randomly occupied over the cation sublattice of the zinc-blende structure. In this case, the occupation of Cu or Sn cations on the atomic sites becomes fractional rather than integral. The partial occupation makes the construction of small primitive cell to model the real structure difficult. However, since all of these structures have the same underlying zinc-blende frame, and differ only in the cation arrangement, the study of their properties can be changed into the study of the influence of cation arrangement on the properties of Cu2SnS3.

To study the influence of cation arrangement, we have constructed six zinc-blende based superstructures, in which mo-1 is the monoclinic structure with \( Cc \) symmetry [Fig. 1(a)] that is proposed by experiment;\(^{12}\) mo-2, mo-3, and mo-4 have the same lattice vectors as mo-1 but different cation arrangements and symmetries. In fact, the mo-2 structure has an orthorhombic primitive cell with the basis vectors

\[
\begin{pmatrix}
\bar{a} \\
\bar{b} \\
\bar{c}
\end{pmatrix} = \begin{pmatrix}
1.5 & 1.5 & 0.0 \\
0.5 & -0.5 & 0.0 \\
0.0 & 0.0 & 1.0
\end{pmatrix} \begin{pmatrix}
\bar{a}' \\
\bar{b}' \\
\bar{c}'
\end{pmatrix},
\]

\[\text{TABLE I. Structural properties (cell shape, symmetry, lattice constants } a,b, \text{ and } c \text{ in } \text{Å} \text{ and band gaps (in eV) of CTS and CTSe reported in the literature.}}\]

<table>
<thead>
<tr>
<th>Cell shape</th>
<th>Symmetry</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( E_g )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTS</td>
<td>Monoclinic</td>
<td>( Cc )</td>
<td>6.65</td>
<td>11.54</td>
<td>6.67</td>
<td>12</td>
</tr>
<tr>
<td>CTS</td>
<td>Triclinic</td>
<td>6.66</td>
<td>11.48</td>
<td>20.03</td>
<td>0.95</td>
<td>13,14</td>
</tr>
<tr>
<td>CTS</td>
<td>Cubic</td>
<td>5.43</td>
<td>1.15</td>
<td>1.98</td>
<td>0.98</td>
<td>16</td>
</tr>
<tr>
<td>CTS</td>
<td>Cubic</td>
<td>( F\bar{4}3m )</td>
<td>5.43</td>
<td>10.82</td>
<td>1.35</td>
<td>17</td>
</tr>
<tr>
<td>CTS</td>
<td>Tetragonal</td>
<td>( I\bar{4}2m )</td>
<td>5.41</td>
<td>17.27</td>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>CTS</td>
<td>Hexagonal</td>
<td>( P6_3/mmc )</td>
<td>3.90</td>
<td>11.61</td>
<td>1.15</td>
<td>20</td>
</tr>
<tr>
<td>CTSe</td>
<td>Monoclinic</td>
<td>( Cc )</td>
<td>6.95</td>
<td>12.05</td>
<td>6.97</td>
<td>0.84</td>
</tr>
<tr>
<td>CTSe</td>
<td>Cubic</td>
<td>5.73</td>
<td></td>
<td></td>
<td></td>
<td>21</td>
</tr>
</tbody>
</table>

\[\text{FIG. 1. (Color online) The crystal structure of Cu2SnS3: (a) monoclinic structure with } Cc \text{ symmetry, (b) cubic structure with } F\bar{4}3m \text{ symmetry (equivalent to zinc-blende structure), in which Cu and Sn are mixed on the cation sites, and there are five possible cation coordination pattern around the S anion, Cu\(_4\), Cu3Sn, Cu2Sn, CuSn, and Sn4, as shown by the five insets.}\]
TABLE III. The symmetry, amount of each cluster in the 24-atom cells, calculated lattice constants $a$, $b$, and $c$ (in Å), angle $\beta$ (in degree), and relative energy difference (meV/atom) of different Cu$_3$SnS$_3$ structures.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Symmetry</th>
<th>Cu$_4$</th>
<th>Cu$_3$Sn</th>
<th>Cu$_2$Sn$_2$</th>
<th>CuSn$_3$</th>
<th>Sn$_4$</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$\beta$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mo-1</td>
<td>$C_c$</td>
<td>0</td>
<td>8</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>6.71</td>
<td>11.62</td>
<td>6.74</td>
<td>70.33</td>
<td>0.00</td>
</tr>
<tr>
<td>mo-2</td>
<td>$Imm2$</td>
<td>0</td>
<td>8</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>6.70</td>
<td>11.61</td>
<td>6.70</td>
<td>71.65</td>
<td>$-$0.42</td>
</tr>
<tr>
<td>mo-3</td>
<td>$C2$</td>
<td>1</td>
<td>6</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>6.73</td>
<td>11.63</td>
<td>6.73</td>
<td>70.43</td>
<td>31.46</td>
</tr>
<tr>
<td>mo-4</td>
<td>$Pm$</td>
<td>0</td>
<td>9</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>6.71</td>
<td>11.66</td>
<td>6.75</td>
<td>71.01</td>
<td>23.66</td>
</tr>
<tr>
<td>or-1</td>
<td>$C22_1$</td>
<td>0</td>
<td>8</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>5.47</td>
<td>5.49</td>
<td>16.49</td>
<td>90</td>
<td>2.56</td>
</tr>
<tr>
<td>or-2</td>
<td>$P4$</td>
<td>0</td>
<td>8</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>5.48</td>
<td>5.48</td>
<td>16.49</td>
<td>90</td>
<td>3.70</td>
</tr>
</tbody>
</table>

and the monoclinic cell in Eq. (1) is a supercell of mo-2 with the relationship

$$\begin{bmatrix}
    \alpha' \\
    \beta' \\
    \gamma'
\end{bmatrix} = \begin{bmatrix}
    0 & -1 & 1 \\
    1 & 0 & 0 \\
    0 & 1 & 1
\end{bmatrix} \begin{bmatrix}
    \alpha \\
    \beta \\
    \gamma
\end{bmatrix}. \quad (3)
$$

The structures or-1 and or-2 have an orthorhombic cell with $a = \sqrt{2} \alpha$, $b = \sqrt{2} \beta$, $c = 3 \sqrt{2} \gamma$, which are constructed manually to compare with the monoclinic structures proposed by experiment. As the cation arrangement is changed, the clusters around the S anions are also changed. There are five different clusters around S, Cu$_4$, Cu$_3$Sn, Cu$_2$Sn$_2$, CuSn$_3$, and Sn$_4$ [shown in Fig. 1(b)]. Different structures are characterized by the symmetry and numbers of different clusters, as shown in Table III. For example, the mo-1 structure only has Cu$_3$Sn and Cu$_2$Sn$_2$ clusters.

In previous studies of ternary CuInSe$_2$ and quaternary Cu$_2$ZnSnS$_4$ structures, the valence octet rule was found to play an important role in determining the energy stability of different structures. The octet rule states that if the sum of the valence electrons of the cations surrounding the anion atom divided by the coordination number (four for tetrahedral structure) plus the number of the anion valence electrons is equal to eight, then the structure has low energy because the anion is in an eight-electron closed-shell state. For tetrahedral Cu$_2$ZnSnS$_4$, this requires the sum of the cation valence electrons surrounding each anion is equal to eight since S has six valence electrons. Cu, Zn, Sn, and S have one, two, four, and six valence electrons, respectively, so when S is surrounded only by two Cu, one Zn, and one Sn cations, such as those in the kesterite Cu$_2$ZnSnS$_4$ structure, it satisfies the octet rule, and therefore can have the lowest energy.

For Cu$_2$SnS$_3$, the material stoichiometry forbids ideal coordination, i.e., all tetrahedral coordination environments of S formed from Sn and Cu will deviate from the octet rule. Therefore, while none of the five clusters shown in Fig. 1(b) satisfies the octet rule completely, we can apply a generalized octet rule in which the structures with the smallest deviation from the octet rule should be favored. Furthermore, to preserve local charge neutrality, electron-rich clusters that exceed the octet rule (e.g., Cu$_2$Sn$_2$) should be close to electron-deficient clusters (e.g., Cu$_3$Sn). For the five clusters Cu$_4$, Cu$_3$Sn, Cu$_2$Sn$_2$, CuSn$_3$, and Sn$_4$, the sum of the cation valence electrons are 4, 7, 10, 13, and 16, respectively, therefore, Cu$_3$Sn and Cu$_2$Sn$_2$ should be energetically favored over other clusters. In Table III, we list the abundance of these clusters for different structures. The four structures (mo-1, mo-2, or-1, and or-2) have a minimum deviation from the octet rule, i.e., they have eight Cu$_3$Sn and four Cu$_2$Sn$_2$ clusters, therefore, we expect these structures have lower total energies.

The above analysis can be supported by direct first-principles total energy calculation. As shown in Table III, mo-1, mo-2, or-1, and or-2 structures have significantly lower energy than mo-3 and mo-4, indicating that in the synthesized samples only the Cu$_3$Sn and Cu$_2$Sn$_2$ clusters surrounding the S anions should exist. Comparing the energy, mo-2 has slightly lower energy than mo-1 by 0.4 meV/atom. These two structures can be described by the same monoclinic cell and only have a slightly different cation occupation. The small energy difference suggests that at finite temperature the cations may be partially disordered in the cation sublattice, i.e., it has well-defined short-range order (the type of clusters around the anions) but lacking long-range order. This explains the experimentally observed structural diversity with different crystal symmetry. The situation is similar to the CuInSe$_2$-derived ordered vacancy compounds. Ordered vacancy compounds are formed by creating ordered (In$_{Cu4}$ + 2V$_{Cu}$) defect pairs in CuInSe$_2$, whereas Cu$_2$SnS$_3$ can be considered as formed by creating ordered (Sn$_{2Cu}$ + 2Cu$_{2S}$) defect pairs in Cu$_2$ZnSnS$_4$.

Our analysis above indicates that the stable Cu$_2$SnS$_3$ structures have the following properties: (i) The basic structure is a superstructure of the zinc-blende structure, (ii) the cations occupy the fcc sublattice of the zinc-blende structure with all S anions surrounded by only Cu$_3$Sn and Cu$_2$Sn$_2$ clusters, and (iii) the cation occupation may have long-range disorder at finite temperature. It should be noted that a hexagonal structure was reported previously, in which the S anions are not tetrahedrally coordinated, but our total energy calculation shows that its energy is ~500 meV/atom higher than that of the mo-1 structure, suggesting that it cannot be an energetically stable structure. Recently we have predicted wurtzite-derived (hexagonal) polytype structures (wurtzite-kesterite and wurtzite-stannite) of the quaternary CZTS, in which the S anions are tetrahedrally coordinated by two Cu, one Zn, and one Sn, and based on the similar derivation relation, we expect there may be wurtzite-derived CTS structures, but to our knowledge there have been no experimental reports about them.

Experimentally, XRD is commonly used for structural characterization, however, here we will show that it is difficult to distinguish the different cation occupations of Cu$_2$SnS$_3$ if the crystal quality is not good. We simulated the XRD spectrum for mo-1, mo-2, and or-1 structures (Fig. 2), in
which the positions of the main peaks all agree with the experimental measurement,\textsuperscript{14,16} because our calculated lattice constants and bond lengths agree with experimental values. The difference in the three structures exists only in the small superstructure peaks and the splitting of main peaks, which can only be detected when the synthesized sample has high quality.

**IV. ELECTRONIC AND OPTICAL PROPERTIES**

We will now study the influence of the structural diversity (cation occupations) on the electronic properties of Cu\textsubscript{2}SnS\textsubscript{3}. Because PBE exchange correlation severely underestimates the band gap, here we use the hybrid HSE functional to calculate the band structure. Figure 3 plots the calculated band structure of Cu\textsubscript{2}SnS\textsubscript{3} and Cu\textsubscript{2}SnSe\textsubscript{3}. We can see that for this structure a direct band gap exists at the Γ point. The calculated density of states (DOS) for mo-1 and or-1 structures is plotted in Fig. 4, where the black lines show the total DOS. Comparing the DOS of mo-1 and or-1 structures, we find that they are very similar, even in the band gaps which are 0.84 eV for mo-1 and 0.88 eV for or-1 structure. This similarity is also observed for the calculated DOS of other structures with only Cu\textsubscript{1}Sn and Cu\textsubscript{2}Sn\textsubscript{2} clusters around the S anions, indicating that the electronic structures of these compounds are insensitive to the cation distribution as long as they have the same local ordered structures.

Figure 4 also plots the partial density of states projected on Cu, Sn, and S atoms. As we can see, the valence-band maximum (VBM) is mainly the antibonding component of the hybridization between Cu d states and S p states, while the conduction-band minimum (CBM) is mainly the antibonding component of hybridization between the Sn s and S s states (this can be quantitatively seen in the component analysis of the conduction-band minimum state). This band component is similar to that of Cu\textsubscript{2}ZnSnS\textsubscript{4}, where Zn does not contribute significantly to the band edge states. Relative to Cu\textsubscript{2}ZnSnS\textsubscript{4}, which has a band gap of 1.5 eV, the creation of ordered (Sn\textsubscript{2n} + 2Cu\textsubscript{2n}) defect pairs in Cu\textsubscript{2}ZnSn\textsubscript{4} in forming Cu\textsubscript{2}SnS\textsubscript{3} shifts the VBM upward because the formation of Cu\textsubscript{2n} enhances the p-d repulsion, and shifts the CBM downward because the formation of Sn\textsubscript{2n} makes CBM localized more on the more electronegative Sn sites,\textsuperscript{8} therefore, decreasing the band gap of Cu\textsubscript{2}SnS\textsubscript{3} to \textasciitilde 0.8–0.9 eV. Considering different structures with the same amount of Cu\textsubscript{1}Sn and Cu\textsubscript{2}Sn\textsubscript{2} clusters, the hybridization strength between the cation and anion states is comparable, so their band gaps differ by only a small amount, and are influenced only weakly by the long-range cation arrangement.

Comparing the calculated band gaps of CTS with the measured values listed in Table I, we find that the calculated values 0.8–0.9 eV agrees reasonably well with experiment (0.95–1.35 eV), considering the calculation uncertainty and the fact that the absorption measurement often overestimates the band gap, especially for samples with poor quality.\textsuperscript{15,16} The zero band gap (metallic) observed in Ref. 18 may result from the nontetrahedral structure of the synthesized CTS sample, but as aforementioned, this structure is highly unstable; otherwise, a highly nonstoichiometric material may have been formed. Considering the scattered band gap values in previous experimental literature, further accurate experimental measurement is called for.
As CTS has a substantially smaller band gap than CZTS, and their structures and lattice constants are highly compatible, we expect that CTS may be used as a cheap bottom layer and CZTS as middle layer materials in low-cost multijunction solar cells.

Turning to the selenide material, Cu$_2$SnSe$_3$ can be a secondary phase in synthesized CZTSe samples. Our calculations have shown that it has a similar crystal structure and density of states as CTS, but its band gap is relatively smaller, with values of only 0.39 eV for the mo-1 structure and 0.40 eV for the or-1 structure. The smaller gap of CTS than CTS is similar to the situation between CZTSe (band gap 1.0 eV) and CZTS (band gap 1.5 eV), which can be understood considering two factors: (i) Se has a higher 4p level than the S 3p level, so the valence band of CTS is higher than CTS, and (ii) Sn-Se bond length is larger than the Sn-S bond, thus the s-s hybridization is weaker, shifting down the conduction band of CTS. Comparing with the experimental value 0.84 eV in Refs. 19 and 20, the calculated band gap is much smaller. This disagreement between calculations and experiments has also existed in CZTSe systems before, where earlier absorption spectrum measurements reported band gap sizes ~1.5 eV, much larger than our calculated value of 1.0 eV. However, our calculated value was confirmed by recent experimental measurements. The large uncertainty in the band-gap measurement for these compounds comes partially from the high defect density and poor crystal quality.

In Fig. 5, we plot the imaginary part of the calculated dielectric functions for CTS and CZTS, as well as for CTS and CZTSe, where all the diagonal elements are averaged. The calculated result for CZTS is in good agreement with that obtained in Ref. 26. The overall shape is similar for CTS (CZTSe) and CZTS (CZTSe), due to their similar band component near the gap, but the energy threshold from zero to nonzero dielectric function is redshifted for CTS than CZTS, which represents the band-gap sizes. As the imaginary part of the dielectric function is closely related to the absorption coefficient, the similar dielectric function of CTS and CZTS indicates their absorption of light is also comparable, differing only in the onset-to-absorption frequency. According to the calculated results, the alloying of CTS with CZTS should cause the change in the absorption spectrum with a redshift of the absorption curve, and this feature could be used for band-structure engineering for solar-cell designs if the synthesis can be controlled.

V. CONCLUSIONS

In conclusion, we have studied the structural and electronic properties of CTS and CTSe using a first-principles electronic structure approach. We have found that their stable structures are all derived from the zinc-blende structure with all anions tetrahedrally coordinated by Cu$_3$Sn and Cu$_2$Sn$_2$, but may contain long-range cation disorder at finite temperature. The structural preferences can be rationalized in terms of a generalized valence octet rule. Our calculations predict that CTS and CTSe have similar optical properties to those of CZTS and CZTSe, but their direct band gaps are smaller (0.9 and 0.4 eV, respectively), and are weakly influenced by the long-range cation ordering. These low band-gap materials may be suitable for extending the visible light absorption of low-cost thin-film solar cells based on CZTS.

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