Searching Stable Cu$_x$S Structures for Photovoltaic Application

Qiang Xu
Bing Huang
Yufeng Zhao
Yanfa Yan
Rommel Noufi
Su-Huai Wei

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Introduction

- Cu$_x$S is one of the promising solar cell absorber materials to replace CIGS.

- Solar cells based on Cu$_x$S have reached an efficiency as high as 10%.

- To further improve its efficiency and especially the stability, it is important to understand the stability and electronic structure of Cu$_x$S.

However, due to the complexity of their crystal structures, no systematic studies have been carried out to understand the stability and electronic structure of the Cu$_x$S systems.
The experimentally identified stable compounds of Cu$_x$S (1<$x$≤2):

- Chalcocite (Cu$_2$S)
- Djurleite (Cu$_{1.94}$S)
- Digenite (Cu$_{1.8}$S)
- Anilite (Cu$_{1.75}$S)

Three different structures of chalcocite Cu$_2$S:

- monoclinic phase (low-chalcocite) (t<104 °C).
- hexagonal phase (high-chalcocite) (104 °C<t<436 °C)
- cubic phase (cubic-chalcocite) (t>436 °C).
Methods of Calculations

- Using Vienna Ab-initio Simulation Package (VASP)
- All-electron-like projector augmented wave (PAW) potential
- The Perdew-Burke-Ernserhof (PBE) exchange correlation potential
- For more accurate calculation of band gaps, we also use hybrid functional (HSE) potentials
- Plane wave expansion up to 500eV
- The calculated cell are fully relaxed, which maximum force converges below 0.01eV/Å
The Optimized Structure Parameters and Band Gaps

The calculated lattice parameters, volume (V), band gap (E_g), and heat of formation per formula unit (ΔH) of Cu_xS.

<table>
<thead>
<tr>
<th>x</th>
<th>Crystal system</th>
<th>a_0 (Å)</th>
<th>b_0 (Å)</th>
<th>c_0 (Å)</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>V (Å^3)</th>
<th>E_e (eV)</th>
<th>ΔH (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Monoclinic</td>
<td>15.27</td>
<td>11.93</td>
<td>13.45</td>
<td>90.0°</td>
<td>115.6°</td>
<td>90.0°</td>
<td>46.04</td>
<td>1.39</td>
<td>-0.40</td>
</tr>
<tr>
<td>2</td>
<td>Hexagonal</td>
<td>7.87</td>
<td>8.19</td>
<td>13.36</td>
<td>90.7°</td>
<td>90.0°</td>
<td>118.5°</td>
<td>47.28</td>
<td>1.49</td>
<td>-0.36</td>
</tr>
<tr>
<td>2</td>
<td>Cubic</td>
<td>12.04</td>
<td>12.26</td>
<td>10.47</td>
<td>90.3°</td>
<td>90.3°</td>
<td>87.0°</td>
<td>48.20</td>
<td>1.34</td>
<td>-0.34</td>
</tr>
<tr>
<td>1.94</td>
<td>Monoclinic</td>
<td>13.53</td>
<td>15.95</td>
<td>29.95</td>
<td>90.0°</td>
<td>116.7°</td>
<td>90.0°</td>
<td>45.13</td>
<td>1.12</td>
<td>-0.41</td>
</tr>
<tr>
<td>1.80</td>
<td>Cubic</td>
<td>11.36</td>
<td>11.15</td>
<td>11.27</td>
<td>90.6°</td>
<td>89.1°</td>
<td>91.4°</td>
<td>44.61</td>
<td>1.20</td>
<td>-0.38</td>
</tr>
<tr>
<td>1.75</td>
<td>Orthorhombic</td>
<td>7.91</td>
<td>7.98</td>
<td>10.92</td>
<td>90.0°</td>
<td>90.0°</td>
<td>90.0°</td>
<td>43.06</td>
<td>1.39</td>
<td>-0.44</td>
</tr>
</tbody>
</table>

The heat of formation ΔH(x) of Cu_xS

\[
ΔH(x) = E(Cu_xS) - xE(Cu) - E(S)
\]

- Monoclinic Cu_2S is the most stable structure at x=2
- Anilite Cu_{1.75}S has lowest formation energy among the calculated Cu_xS compound
All three chalcocites have direct band gaps at Γ with values around 1.3–1.5 eV (HSE results).
The global minimum of the $\Delta H(x)$ occurs at about $x=1.7$ for the hexagonal and the monoclinic phases.

A phase transition from the monoclinic to the hexagonal phase can occur at $x_c \approx 1.70$.

However, the heat of formation of the low chalcocite and high chalcocite $\text{Cu}_{1.75}\text{S}$ is 20meV higher than that of the anilite $\text{Cu}_{1.75}\text{S}$.

The anilite structure is indeed the most stable structure among all $\text{Cu}_x\text{S}$ at the Cu-rich limit.
It has a band gap of 1.39 eV at the $\Gamma$ point and is heavily hole-doped.

The hole carrier concentration can be controlled by doping anilite with donors such as Sn.

The large curvature at the band edge indicates that it should have good electron as well as hole conductivities.

We suggest that anilite based $\text{Cu}_x\text{S}$ could be promising materials for photovoltaic absorbers.
Conclusion

- $\text{Cu}_2\text{S}$ is more stable in the low-chalcocite structure, in agreement with experimental observations. However, it is not stable against the formation of Cu vacancies.

- We identified that at the Cu-rich limit, the most stable crystal structure is $\text{Cu}_{1.75}\text{S}$ in the anilite structure, which has a band gap around 1.39 eV and could be a promising solar cell absorbers.
Thanks for Your Attention!