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Stability and Electronic Structures of Cu_xS Solar Cell Absorbers

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Abstract — Cu_xS is one of the most promising solar cell absorber materials that has the potential to replace the leading thin-film solar cell material $\text{Cu}(\text{In,Ga})\text{Se}_2$ for high efficiency and low cost. In the past, solar cells based on Cu_xS have reached efficiency as high as 10%, but it also suffers serious stability issues. To further improve its efficiency and especially the stability, it is important to understand the stability and electronic structure of Cu_xS . However, due to the complexity of their crystal structures, no systematic theoretical studies have been carried out to understand the stability and electronic structure of the Cu_xS systems. In this work, using first-principles method, we have systematically studied the crystal and electronic band structures of Cu_xS ($1.25 < x \leq 2$). For Cu_2S , we find that all the three chalcocite phases, i.e., the low-chalcocite, the high-chalcocite, and the cubic-chalcocite phases, have direct bandgaps around 1.3–1.5 eV, with the low-chalcocite being the most stable one. However, Cu vacancies can form spontaneously in these compounds, causing instability of Cu_2S . We find that under Cu-rich condition, the anilite $\text{Cu}_{1.75}\text{S}$ is the most stable structure. It has a predicted bandgap of 1.4 eV and could be a promising solar cell absorber.

Index Terms — Cu_xS , stability, band structure, absorber, first-principles method, chalcocite, anilite, Cu vacancies.

I. INTRODUCTION

Thin-film solar cells have great potential to provide low-cost, high-efficiency renewable energies. Among all the thin-film solar cell materials, $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) is one of the most promising materials with high solar conversion efficiency (~20%) and long-term durability. However, wide deployment of CIGS-based photovoltaic devices may encounter material limitations related to scarcity of indium as well as gallium, which makes it an urgent issue to search for other low-cost light-absorbing materials that are abundant and nontoxic. Cu_2S , which is closely related to CIGS, is one of the promising solar cell absorber materials to replace CIGS. In the past, solar cells based on Cu_xS 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_xS . However, due to the complexity of their crystal structures, no systematic studies have been actually carried out to understand the stability and electronic structure of the Cu_xS systems.

There exist various mineral forms of Cu_xS ($1 \leq x \leq 2$), in which the location of Cu atoms in the close-packed S lattice are not well identified and their position changes as a function of x . In the copper-rich environment, the experimentally identified stable compounds of Cu_xS are chalcocite (Cu_2S), djurleite ($\text{Cu}_{1.94}\text{S}$), digenite ($\text{Cu}_{1.8}\text{S}$), and anilite ($\text{Cu}_{1.75}\text{S}$), all of which are p-type. The chalcocite Cu_2S has three different phases at different temperature. One is in monoclinic phase (low-chalcocite) formed at a temperature below 104°C. It changes to hexagonal phase (high-chalcocite) between 104°–436°C and transforms further to cubic phase (cubic-chalcocite) when the temperature is higher than 436°C. Fig. 1 shows the crystal structures of these compounds. Although the experimentally observed bandgaps of Cu_xS fall in the range of 1.1–1.2 eV, it is not clear what are the natures of these measured bandgaps.

II. THEORETICAL APPROACH

In this work [1], we employ the first-principles methods to systematically search for the most energetically favorable Cu_xS structures in a wide range of $1.2 < x \leq 2.0$. To find the most stable structures of Cu_xS , we calculate the heat of formation $\Delta H(x)$ of Cu_xS using the definition

$$\Delta H(x) = E(\text{Cu}_x\text{S}) - xE(\text{Cu}) - E(\text{S}) \quad (1)$$

where $E(\text{Cu}_x\text{S})$ is the total energy of the lowest-energy configuration at the Cu composition x . $E(\text{Cu})$ and $E(\text{S})$ are total energies of Cu and S in their bulk structures.

III. RESULTS AND DISCUSSIONS

We first calculate the three chalcocite Cu_2S phases at the stoichiometric composition $x = 2$. The low-chalcocite phase has a monoclinic crystal structure with space group C_{2h}^5 (shown in Fig. 1a). All the 36 crystallographically distinct Wyckoff sites are fully occupied, with 24 of them occupied by Cu atoms and 12 by S atoms. Because every Wyckoff site represents 4 equivalent atomic positions, there are a total 96 Cu and 48 S atoms in each unit cell. In high- and cubic-chalcocite structures, however, the Wyckoff sites are not fully occupied; only statistical distributions of atoms among the equivalent positions

were reported experimentally. We use $2 \times 2 \times 2$ supercells to reproduce the experimentally observed ratios of partially occupied Wyckoff sites. In the high-chalcocite structure, 32 Cu atoms are at $2b$, $4f$, and $6g$ Wyckoff sites and 16 S atoms are at $2c$ Wyckoff sites. In the cubic-chalcocite structure, 64 atoms are at $8c$, $4b$, and $192l$ Wyckoff sites and 32 S atoms are at $4a$ Wyckoff sites. We use the Monte Carlo method to search the possible structures within the two configurations, and only the structures with lowest total energy are considered as the most plausible high-chalcocite and cubic-chalcocite structures. For the three chalcocite Cu_2S phases, the monoclinic phase has the lowest heat of formation per formula unit at 0 K, which is consistent with experimental observations. We find that all three chalcocites have direct bandgaps at Γ with values around 1.3 to 1.5 eV.

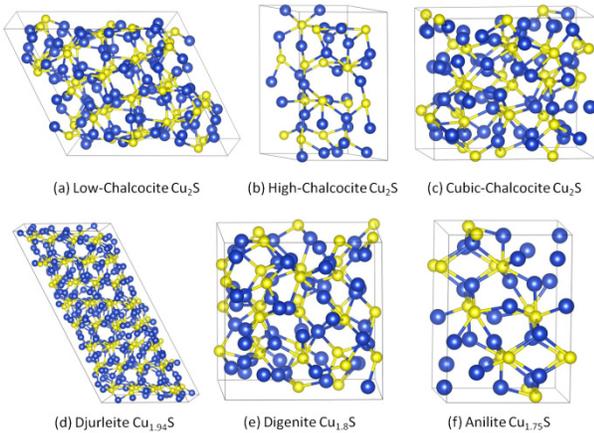


Fig. 1. Crystal structures for: (a) low-chalcocite (monoclinic), (b) high-chalcocite (hexagonal), (c) cubic-chalcocite (cubic), (d) djurleite, (e) digenite, and (f) anilite.

The djurleite $\text{Cu}_{1.94}\text{S}$ (Fig. 1d) belongs to the monoclinic crystal system, similar to the low-chalcocite Cu_2S . The unit cell of this $\text{Cu}_{1.94}\text{S}$ structure can be derived from a supercell of the low-chalcocite Cu_2S , in which 62 of the 96 distinct Wyckoff sites are occupied by 248 Cu atoms, and 32 Wyckoff sites are occupied by 128 S atoms. Two Wyckoff sites are unoccupied or can be considered as having 8 Cu vacancies. Because there are Cu vacancies in the djurleite unit cell, holes are created in the valence band. The calculated heat of formation is -0.41 eV per formula unit, indicating that it is more stable than low-chalcocite Cu_2S even at the Cu-rich limit and Cu vacancies can form spontaneously in Cu_2S .

For the digenite $\text{Cu}_{1.8}\text{S}$ (Fig. 1e), the cell can be constructed by having a $2 \times 2 \times 2$ cubic chalcocite Cu_2S supercell with 6 Cu vacancies. In this supercell, 58 Cu atoms occupy the $8c$, $4b$ and $192l$ Wyckoff sites, and 32 S

atoms occupy the $4b$ Wyckoff sites. Again, due to the Cu vacancy, holes are created inside the valence band. The heat of formation of digenite is lower than that of the cubic-chalcocite and the high-chalcocite Cu_2S , but is higher than the low-chalcocite Cu_2S and the djurleite $\text{Cu}_{1.94}\text{S}$. Consequently, it is not a stable structure at 0 K.

The anilite $\text{Cu}_{1.75}\text{S}$ shown (Fig. 1f) belongs to an orthorhombic crystal system with space group D_{2h}^{16} . In the unit cell, 28 Cu atoms occupy the $4c$ and $8d$ Wyckoff sites and 16 S atoms occupy the $4c$ Wyckoff sites. We note that at 0 K, anilite at $x = 1.75$ has the lowest heat of formation of -0.44 eV per formula unit among all Cu_xS , indicating that it is more stable than the low-chalcocite and djurleite at $x = 2$ and 1.94 , respectively. It has a nominal predicted bandgap of 1.39 eV and is heavily doped with holes.

The above results indicate that Cu_2S is not stable against formation of Cu vacancies. To understand the general stability of Cu_xS as a function of x (Cu/S ratio), we calculate the heat of formation $\Delta H(x)$ of Cu_xS derived from the three chalcocite phases to find out the most stable Cu_xS structures. The results are plotted in Fig. 2.

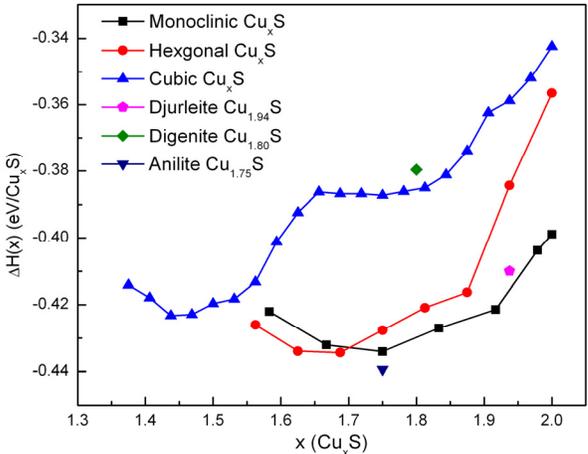


Fig. 2. Calculated heat of formation of Cu_xS as a function of x . The initial structures, i.e., $x = 2$, are based on the three chalcocite Cu_2S structures as shown in Figs. 1 (a), (b), and (c).

We find that the global minimum of the $\Delta H(x)$ occurs at $x_1 = 1.69$ and $x_2 = 1.75$ for, respectively, the hexagonal and monoclinic phases, with nearly the same $\Delta H = -0.43$ eV per formula unit. A phase transition from the monoclinic to the hexagonal phase can occur at $x_c \approx 1.70$. For $x < x_c$, the hexagonal structure of Cu_xS is more stable than that of the monoclinic phase, whereas the opposite is true for $x > x_c$. For the cubic Cu_xS , the heat of formation decreases when the density of Cu vacancy increases. It reaches a value of $\Delta H(x) = -0.42$ eV per formula unit when x decreases to 1.44, but is still higher than the other

two phases of Cu_xS . For the hexagonal structures, the stability is enhanced with increased x up to $x_1 = 1.69$. However, as the Cu concentration increases further, the formation energy goes up, which will destabilize the structures of Cu_xS ($x > 1.69$) and may result in phase separation into $\text{Cu}_{1.69}\text{S}$ and metallic Cu. For the monoclinic structures of Cu_xS , the energy lowers as x increases up to $x_2 = 1.75$, and further increase in the Cu concentration again destabilizes the structures. Therefore, the most energetically favorable Cu_xS compounds may have a Cu/S ratio in the range of $1.69 < x < 1.75$.

We noticed, however, that the heat of formation of the low-chalcocite (monoclinic) and high-chalcocite (hexagonal) $\text{Cu}_{1.75}\text{S}$ is 20 meV higher than that of the anilite $\text{Cu}_{1.75}\text{S}$, which is the most stable structure among all Cu_xS at the Cu-rich limit. The calculated band structure of anilite $\text{Cu}_{1.75}\text{S}$ shows that it has a nominal bandgap of 1.39 eV and is a naturally hole-doped semiconductor. Therefore, it is ideal for photovoltaic applications. The hole carrier concentration can be controlled, in principle, by doping anilite with donors such as Sn or In. The large curvature at the band edge indicate that it should have good electron, as well as hole, conductivities. Therefore, we suggest that anilite-based Cu_xS could be a promising material for photovoltaic absorbers.

IV. CONCLUSION

In summary, using first-principle calculations, we have systematically studied the stability and electronic structure of the Cu_xS system in a wide range of $1.2 < x \leq 2.0$. We find that Cu_2S 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 bandgap around 1.39 eV and could be a promising solar cell absorber.

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REFERENCES

- [1] Qiang Xu, Bing Huang, Yufeng Zhao, Yanfa Yan, Rommel Noufi, and Su-Huai Wei, "Crystal and electronic structures of Cu_xS solar cell absorbers," *Appl. Phys. Lett.* **100**, 061906 (2012).