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Searching Stable Cu_xS Structures for Photovoltaic Application

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Introduction

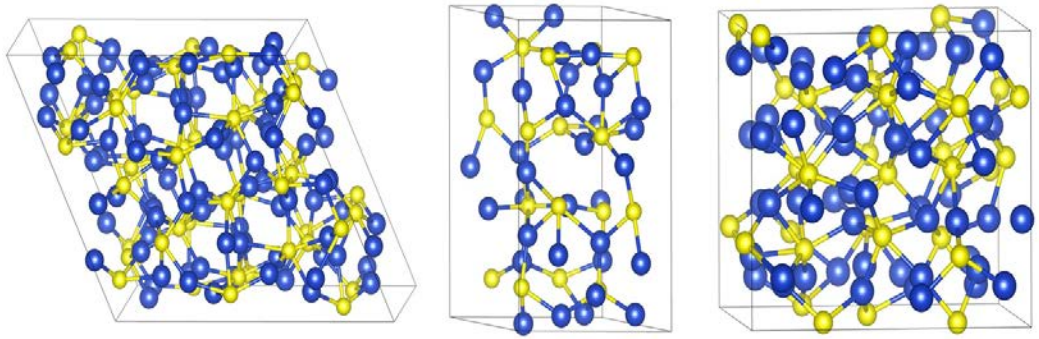
- Cu_xS is one of the promising solar cell absorber materials to replace CIGS.
- Solar cells based on Cu_xS have reached an efficiency as high as 10%.
- To further improve its efficiency and especially the stability, it is important to understand the stability and electronic structure of Cu_xS.

However, due to the complexity of their crystal structures, no systematic studies have been carried out to understand the stability and electronic structure of the Cu_xS systems.

Cu_xS Crystal Structure

The experimentally identified stable compounds of Cu_xS ($1<x\leq2$):

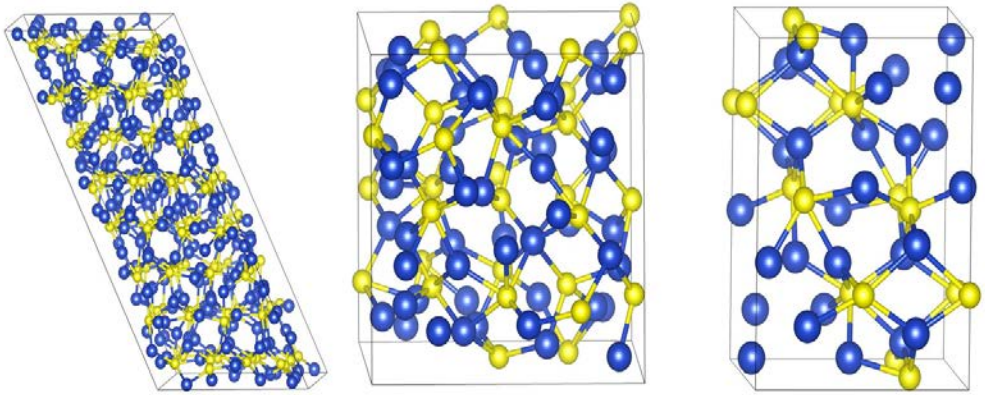
- Chalcocite (Cu_2S)
- Djurleite ($Cu_{1.94}S$)
- Digenite ($Cu_{1.8}S$)
- Anilite ($Cu_{1.75}S$)



(a) Low-Chalcocite Cu_2S (b) High-Chalcocite Cu_2S (c) Cubic-Chalcocite Cu_2S

Three different structures of chalcocite Cu_2S :

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



(d) Djurleite $Cu_{1.94}S$ (e) Digenite $Cu_{1.8}S$ (f) Anilite $Cu_{1.75}S$

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.

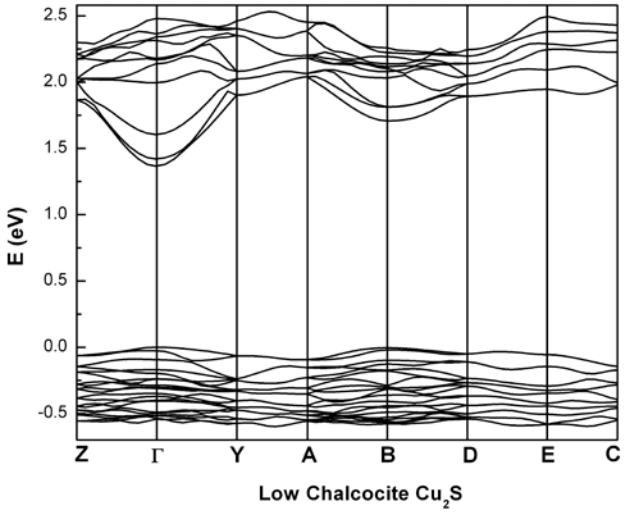
x	Crystal system	a_0 (Å)	b_0(Å)	c_0 (Å)	α	β	γ	V (Å^3)	E_g (eV)	ΔH (eV)
2	Monoclinic	15.27	11.93	13.45	90.0°	115.6°	90.0°	46.04	1.39	−0.40
2	Hexagonal	7.87	8.19	13.36	90.7°	90.0°	118.5°	47.28	1.49	−0.36
2	Cubic	12.04	12.26	10.47	90.3°	90.3°	87.0°	48.20	1.34	−0.34
1.94	Monoclinic	13.53	15.95	29.95	90.0°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

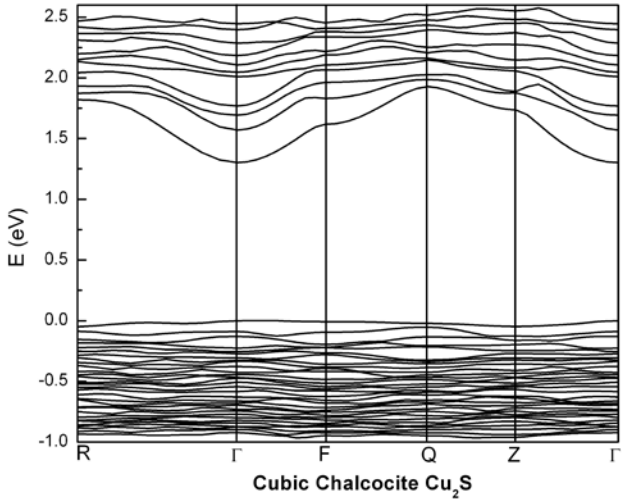
The heat of formation ΔH(x) of Cu_xS

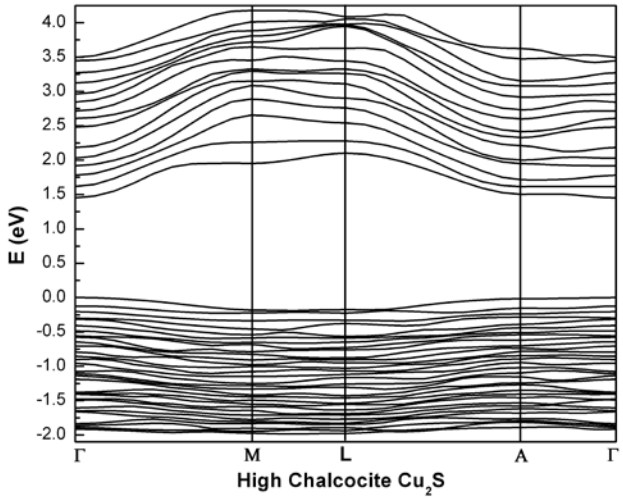
$$\Delta H(x) = E(\mathrm{Cu}_x\mathrm{S}) - xE(\mathrm{Cu}) - E(\mathrm{S})$$

- 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

The Band Structures of Chalcocite Cu_2S



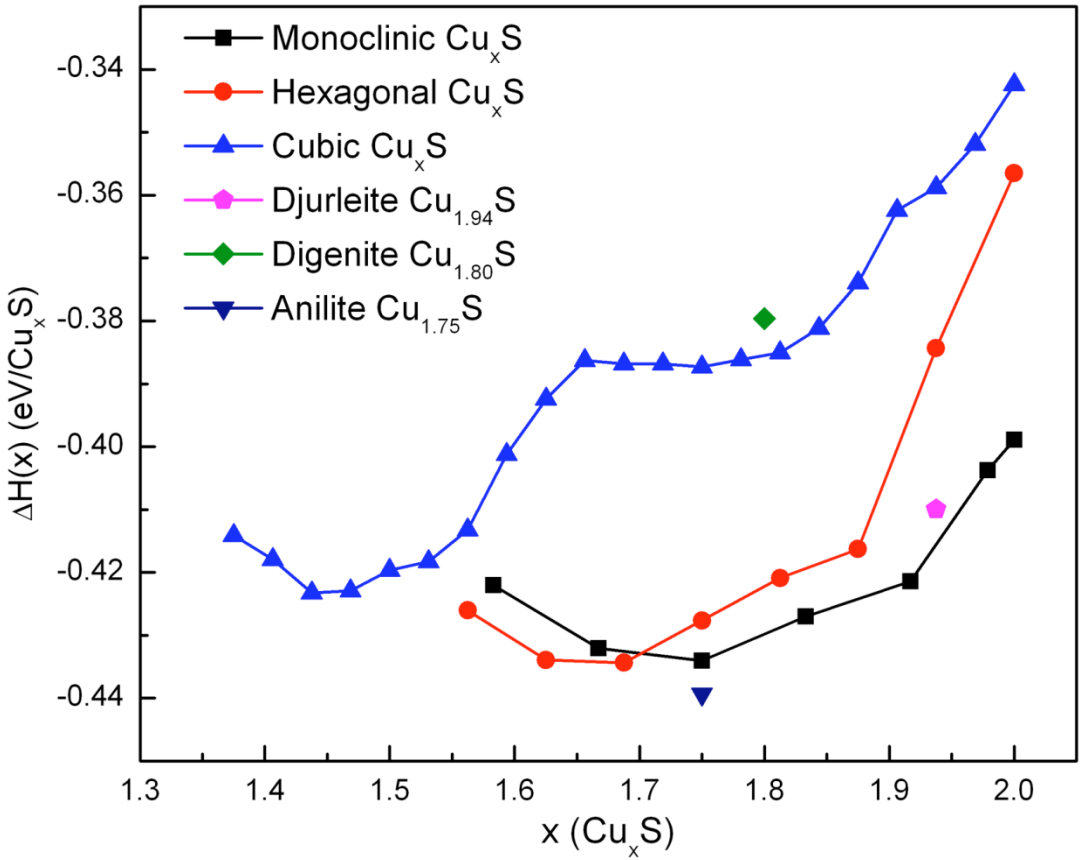




All three chalcocites have direct band gaps at Γ with values around 1.3–1.5 eV (HSE results).

Calculated Heat of Formation of Cu_xS as a Function of x

- The global minimum of the ΔH(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 $Cu_{1.75}S$ is 20meV higher than that of the anilite $Cu_{1.75}S$.

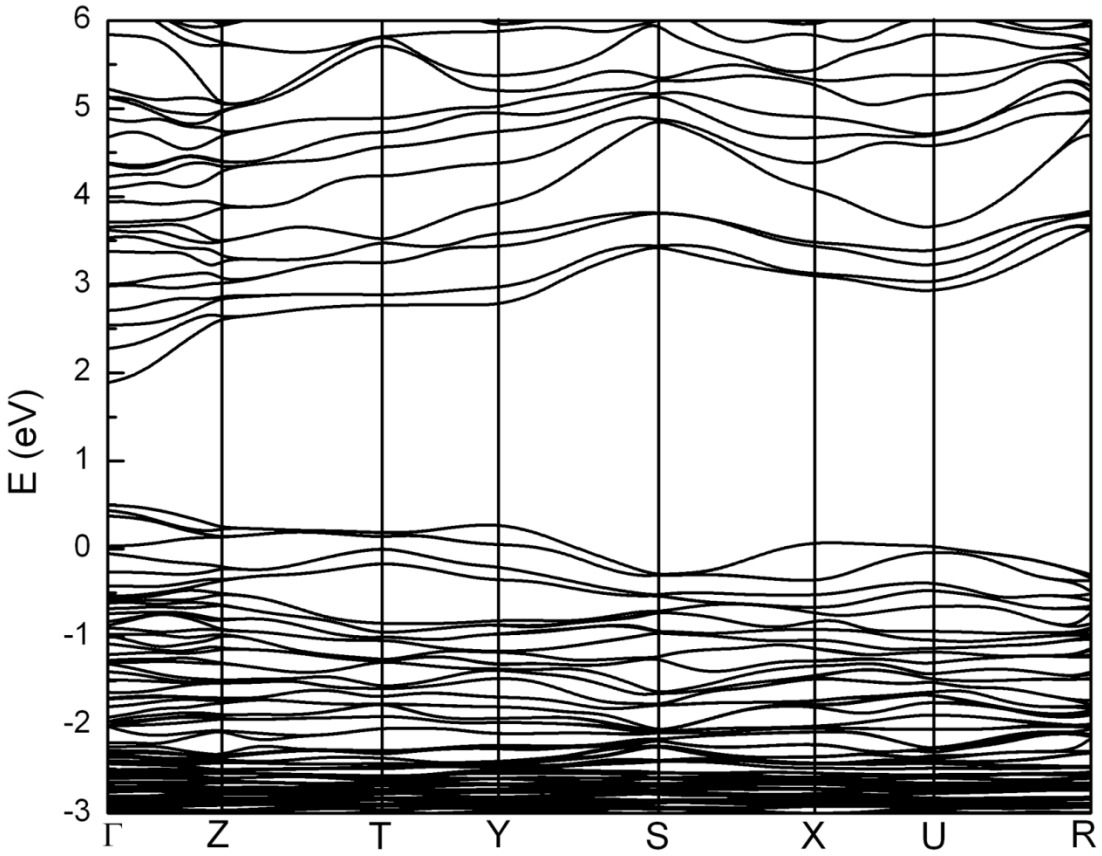


The initial structures, i.e., x=2, are based on the three chalcocite Cu_2S structures.

The anilite structure is indeed the most stable structure among all Cu_xS at the Cu-rich limit.

The HSE Band Structure of Anilite $Cu_{1.75}S$

- It has a band gap of 1.39 eV at the Γ 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 Cu_xS could be promising materials for photovoltaic absorbers.

Conclusion

- 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 $Cu_{1.75}S$ 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 !