First principles simulations of $Cu_2ZnSnS_xO_{4-x}$ alloys

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Abstract

Crystalline Cu_2ZnSnS_4 (CZTS) has been well studied for its photovoltaic properties. This poster reports a systematic computational study of CZTS alloys with oxygen substituting for S in the form $Cu_2ZnSnS_xO_{4-x}$, in order to understand their stability and structural properties. The calculations find Cu_2ZnSnO_4 (CZTO) to have a well-defined meta-stable kesterite structure with a heat formation of 4.7 eV lower than that of CZTS. This result is consistent with the general observation that CZTS is very reactive when exposed to air. Interestingly, the results find that CZTS is stable with respect to its decomposition products; the calculated enthalpy for CZTS→Cu_2S + ZnS + SnS_2 is ΔH_{cal} = +0.6 eV. However, for CZTO the corresponding decomposition is predicted to be exothermic; the calculated enthalpy for CZTO→Cu_2O + ZnO + SnO_2 is ΔH_{cal} = -1.7 eV. The simulations of S/O alloys show that there are preferred structures for the O configurations. For example, for alloys with x = 2, the energy difference between the lowest and highest energy O arrangements is 0.25 eV/formula unit.

Results & Discussions

I Values of the heats of formation

From the heats of formation, it is possible to predict the synthesis and decomposition processes for the CZTSO family.

Table I: Summary of heat of formation results for CZTSO and related materials in units of eV per formula unit. * were used to fit the O_2 reference energy.

Formula Unit	ΔH_{cal}	ΔH_{exp}
CuO *	-1.645	-1.630,[a] -1.617, [b] -1.677 [c]
Cu_2O *	-1.756	-1.747, [a] -1.769, [b] -1.795 [c]
ZnO *	-3.410	-3.633 [a]
SnO *	-2.949	-2.909 [a]
SnO_2 *	-5.788	-5.987 [a]
CuS	-0.721	-0.550, [a] -0.542 [c]
Cu_2S	-0.931	-0.823, [a] -0.824 [c]
ZnS	-1.774	-1.996, [a] -2.127 [c]
SnS	-1.072	-1.036, [a] -1.118 [c]
SnS_2	-1.320	-1.592 [c]
Sn_2S_3	-2.353	-2.732 [c]
SO_3	-5.089	-4.711 [a]
$CuSO_4$ *	-7.894	-7.995, [a] -7.980 [b]
$ZnSO_4$ *	-10.207	-10.186, [a] –10.171 [c]
Cu_2SnO_3	-5.938	—
Cu_2SnS_3	-2.680	—
KS-CZTS	-4.596	—
KS-CZTO	-9.246	—

II Does oxidation occur naturally?

Possible oxidation and selenization reactions that relate the synthesis and decomposition processes for the CZTS family.

R1: $Cu_2ZnSnS_4+(4-x)\frac{1}{2}O_2 \rightarrow Cu_2ZnSnS_xO_{4-x}+(4-x)S_{solid}$

R2: $Cu_2ZnSnS_4+(4-x)\frac{3}{2}O_2 \rightarrow Cu_2ZnSnS_xO_{4-x}+(4-x)SO_{2\ (gas)}$

R3: $Cu_2ZnSnS_4+(4-x)Se_{solid} \rightarrow Cu_2ZnSnS_xSe_{4-x}+(4-x)S_{solid}$

R4: $Cu_2ZnSnS_4+(4-x)Se_{gas} \rightarrow Cu_2ZnSnS_xSe_{4-x}+(4-x)S_{gas}$

R5: $\frac{x}{4}(Cu_2S+ZnS+SnS_2)+(1-\frac{x}{4})(Cu_2O+ZnO+SnO_2) \rightarrow Cu_2ZnSnS_xO_{4-x}$

R6: $\frac{x}{4}(Cu_2S+ZnS+SnS_2)+(1-\frac{x}{4})(Cu_2Se+ZnSe+SnSe_2) \rightarrow Cu_2ZnSnS_xSe_{4-x}$

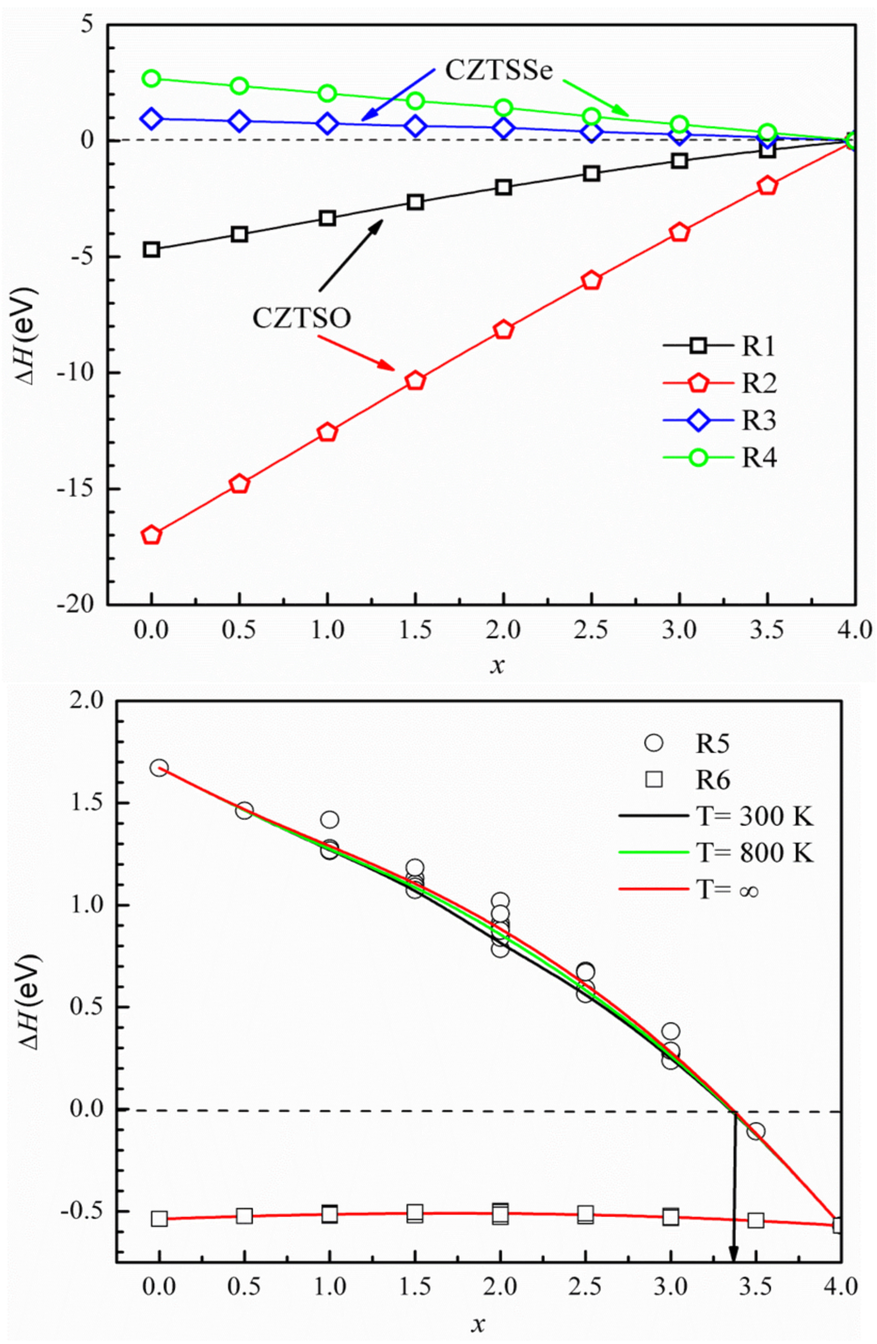

Fig. 1. Calculated reaction energies of *R*1, *R*2, *R*3, *R*4, *R*5 and *R*6 averaged over all alloy configurations and plotted as a function of *x* (the concentration of sulfur).

III Where does the oxygen go?

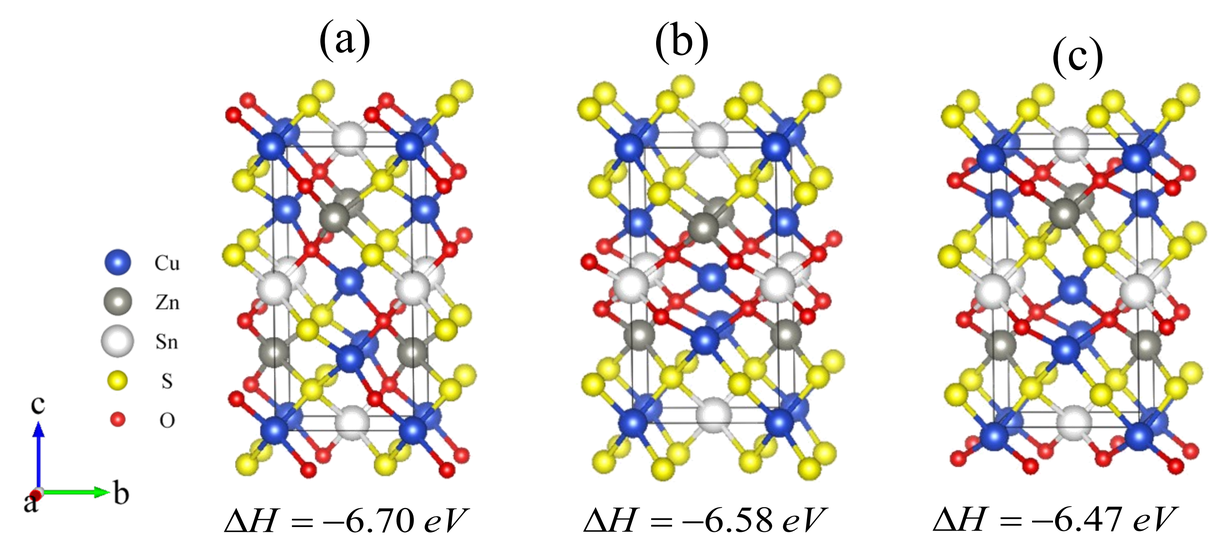

Fig. 2. Ball and stick diagram of the primitive simulation cell for CZTSO alloys with x=2 showing 3 of the 10 unique configurations. (a) structure with lowest energy (b) a high symmetry configuration. (c) structure with the highest energy configuration.

Conclusions

- Oxygen incorporation in the CZTS lattice is energetically favorable.
- $Cu_2ZnSnS_xO_{4-x}$ crystals are stable only for the small range of $3.3 < x < 4.0$.
- For CZTSO alloys, O have preferred configurations in which O sites are not concentrated in any a -b plane.
- The energy difference between the highest and lowest energy structures for x=2.0 system is 0.2 eV.

Reference

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