$Cu_2ZnSnS_xO_{4-x}$ and $Cu_2ZnSnS_xSe_{4-x}$: First principles simulations of optimal alloy configurations and their energies

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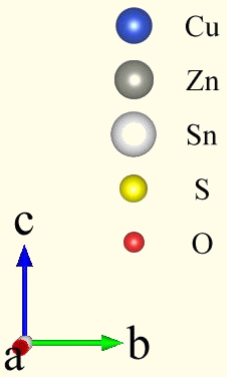
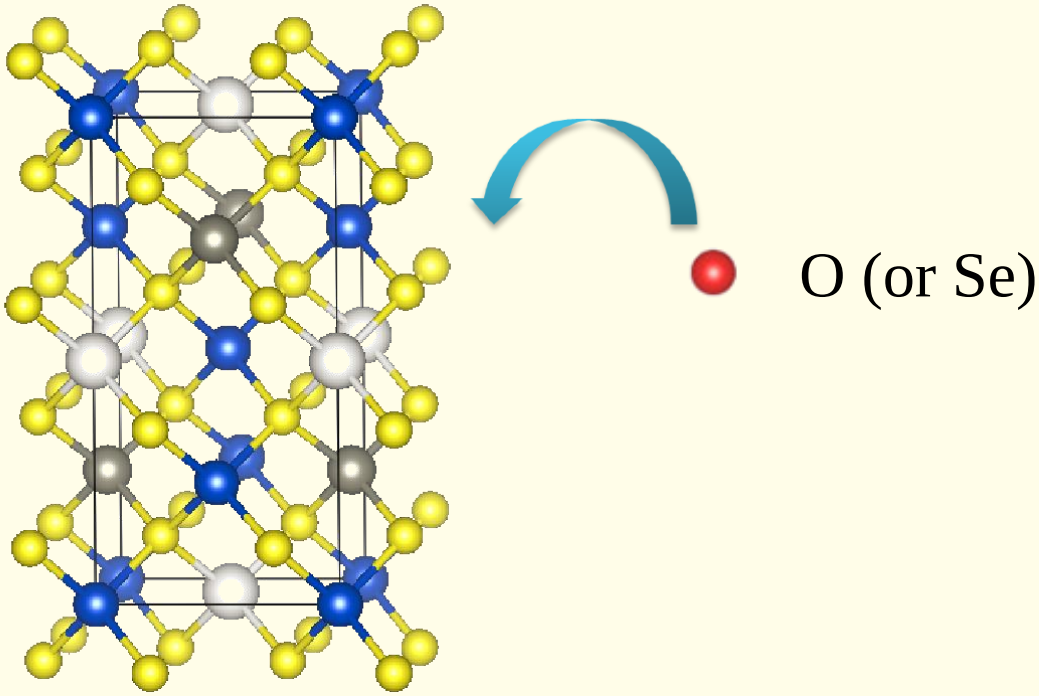
Questions: Does Oxidation occur?





Kesterite structure of pure Cu_4ZnSnS_4 (CZTS)

Outline

- Fabrication of pure materials
- Phase diagrams & Stable region
- Alloys: Lattice Parameters Variations
- Prediction of Oxidation and Selenization
- Possible Fabrication Methods
- Energetically Structure of CZTSO/CZTSSe

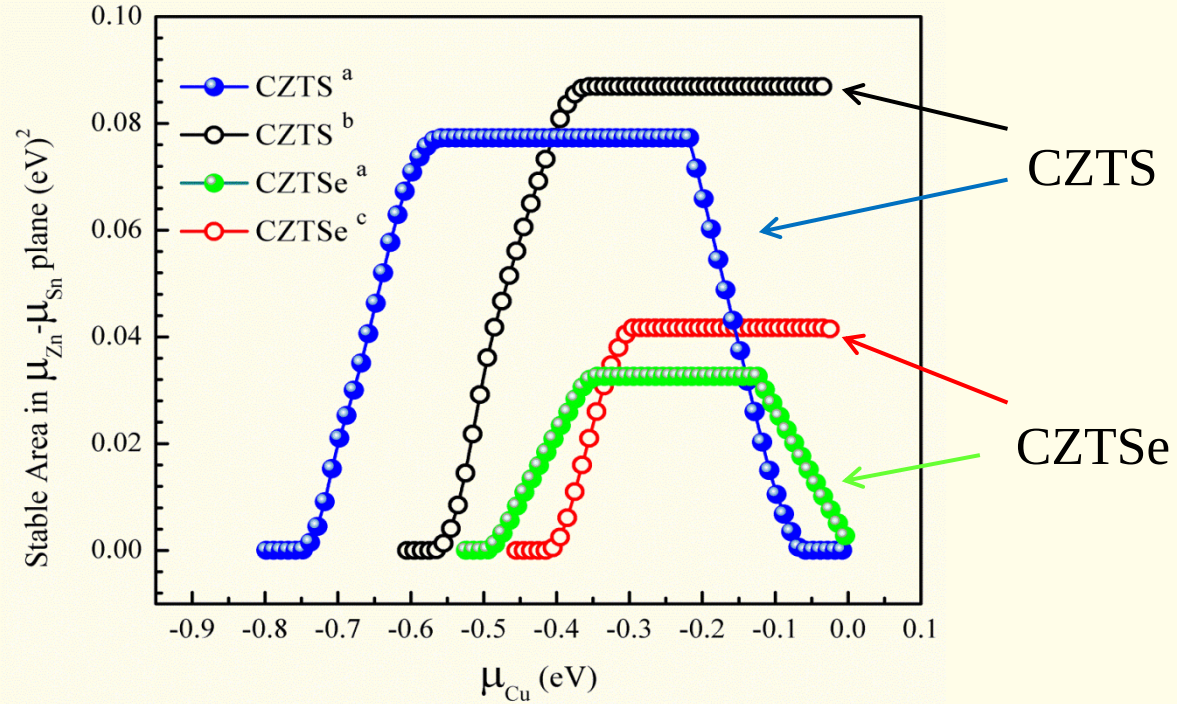
Fabrication of pure materials

Possible synthesis reactions for CZTS family of compounds.

Starting materials	Product	ΔH^R_{cal}	
$Cu_2S+ZnS+SnS_2$	Cu_2ZnSnS_4	-0.573	Exothermic
$2CuS+ZnS+SnS$	Cu_2ZnSnS_4	-0.326	
Cu_2SnS_3+ZnS	Cu_2ZnSnS_4	-0.142	
$Cu_2Se+ZnSe+SnSe_2$	$Cu_2ZnSnSe_4$	-0.536	
$2CuSe+ZnSe+SnSe$	$Cu_2ZnSnSe_4$	-0.288	
Cu_2SnSe_3+ZnSe	$Cu_2ZnSnSe_4$	-0.063	
$Cu_2O+ZnO+SnO_2$	Cu_2ZnSnO_4	1.679	Endothermic
$2CuO+ZnO+SnO$	Cu_2ZnSnO_4	0.374	
Cu_2SnO_3+ZnO	Cu_2ZnSnO_4	0.073	

Phase diagrams & Stable region

Materials	Calculated	Experimental (CRC)
Cu_2S	-0.931 [a], -0.52 [b]	-0.824
Cu_2Se	-0.610 [a], -0.24 [c]	-0.677



Plot of Cu versus area in the Zn-Sn plane defining the regions of stability of CZTS and CZTSe, comparing the results of the present work (a) to those of Ref. (b) and Ref. (c).

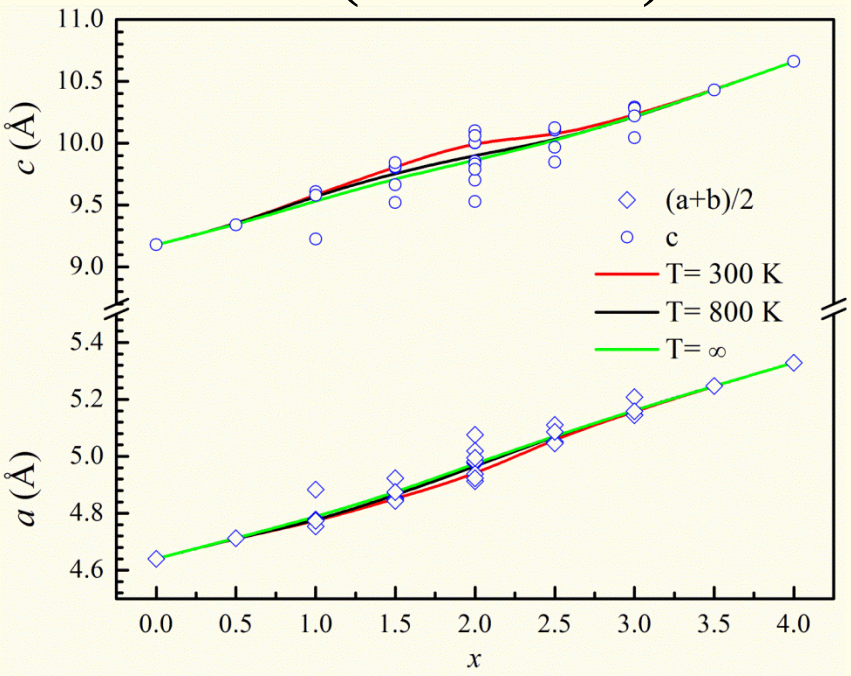
a Present work.

b A. Walsh, et al, Advanced Energy Materials **2**, 400 (2012).

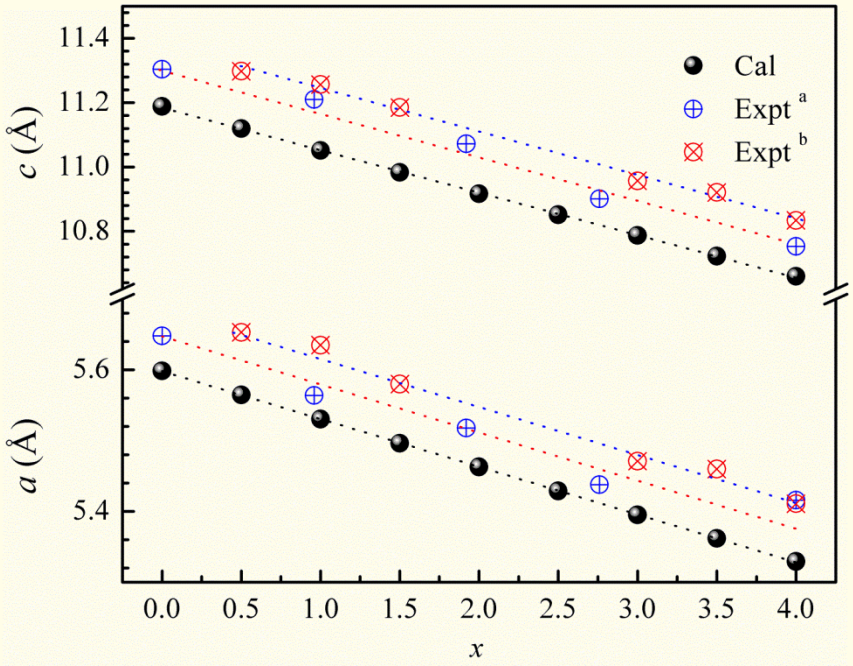
c S. Chen, et al, Advanced materials **25**, 1522 (2013).

Alloys: Lattice Parameters Variations

(A: CZTSO)



(B: CZTSSe)



The calculated lattice parameters $(a+b)/2$ and c as a function of x, which indicates the concentration of sulfur for $Cu_2ZnSnS_xO_{4-x}$ (A) and $Cu_2ZnSnS_xSe_{4-x}$ (B). All the data are based on calculation of conventional cell.

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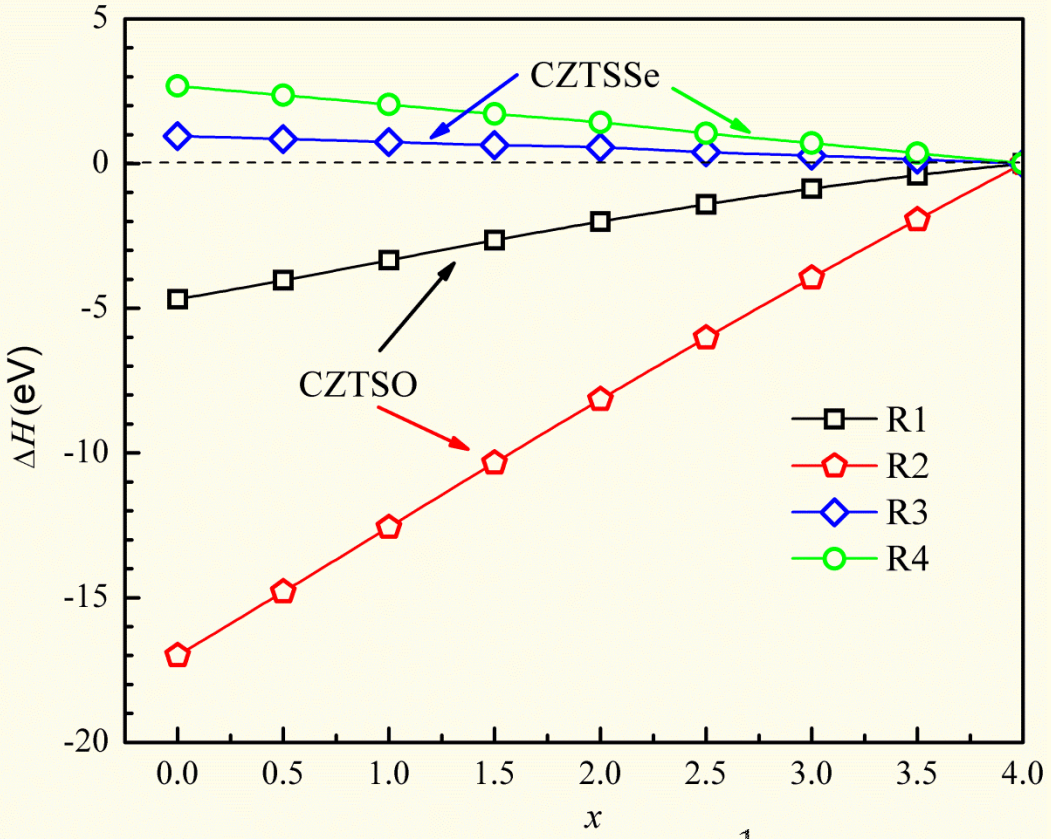
a J. He, et al, Journal of Alloys and Compounds **529**, 34 (2012).

b S. Levcenco, et al, Optical Materials **34**, 1362 (2012).

Prediction of Oxidation and Selenization



Calculated reaction energies or *R*1, *R*2, *R*3, and *R*4 averaged over all alloy configurations and plotted as a functions of *x*. *x* is the concentration of sulfur. *R*3 and *R*4 discuss the solid and gas state of the S/Se respectively.

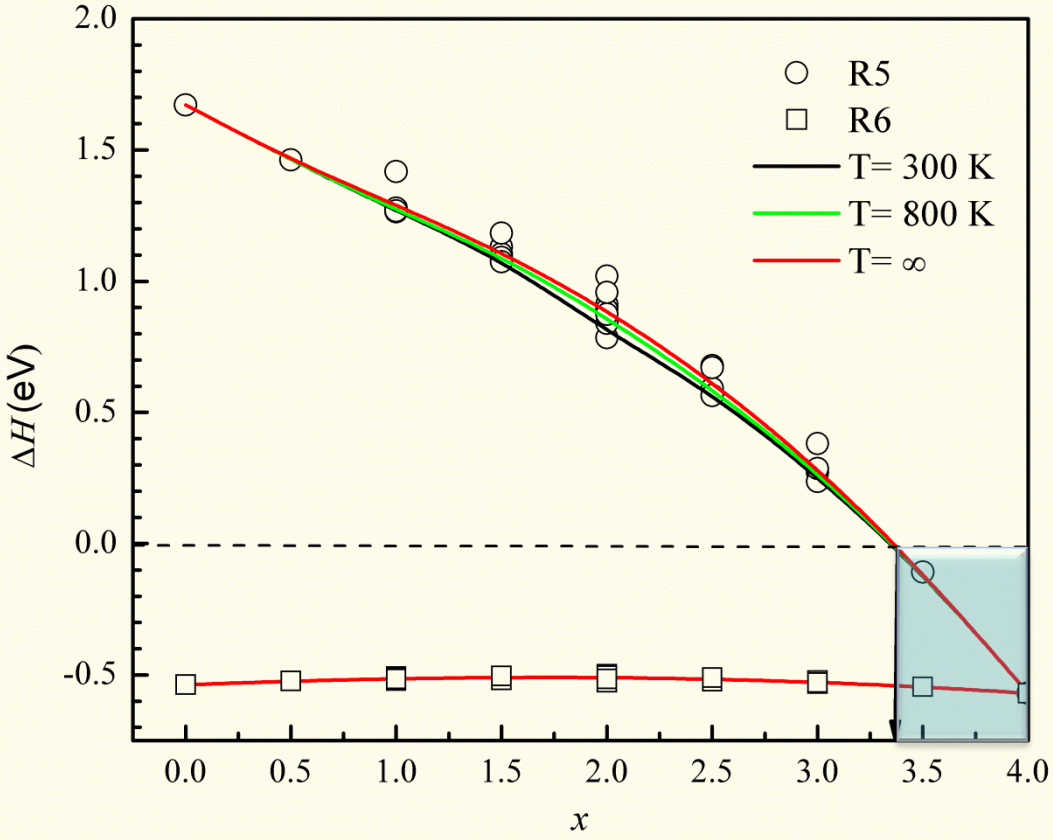
$$R1: \quad Cu_2ZnSnS_4 + (4-x)\frac{1}{2}O_2 \rightarrow Cu_2ZnSnS_xO_{4-x} + (4-x)S$$

$$R2: \quad Cu_2ZnSnS_4 + (4-x)\frac{3}{2}O_2 \rightarrow Cu_2ZnSnS_xO_{4-x} + (4-x)SO_2$$

$$R3: \quad Cu_2ZnSnS_4 + (4-x)Se_s \rightarrow Cu_2ZnSnS_xSe_{4-x} + (4-x)S_s$$

$$R4: \quad Cu_2ZnSnS_4 + (4-x)Se_g \rightarrow Cu_2ZnSnS_xSe_{4-x} + (4-x)S_g$$

Possible Fabrication Methods

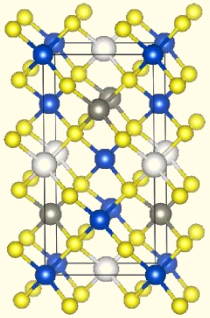


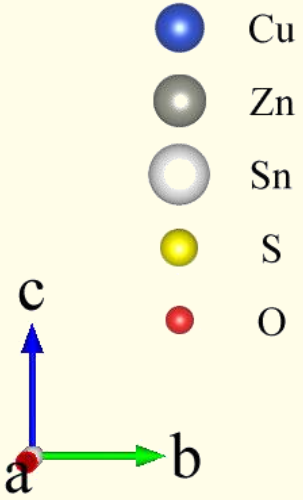
Reaction energies for formation of CZTSO (reaction R5) and formation of CZTSSe (reaction R6).

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

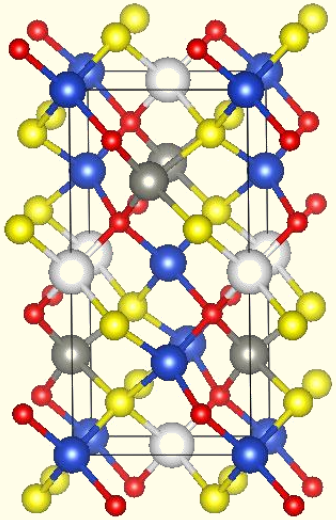
$$R6: \quad \frac{x}{4}(Cu_2S + ZnS + SnS_2) + (1-\frac{x}{4})(Cu_2Se + ZnSe + SnSe_2) \rightarrow Cu_2ZnSnS_xSe_{4-x}$$

Energetically structure of CZTSO/CZTSSe



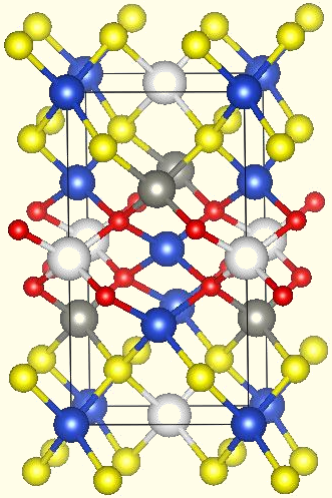


(A)



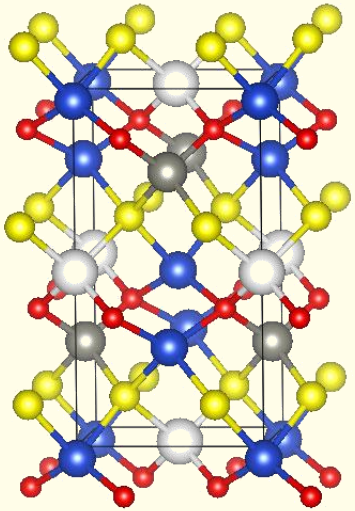
$\Delta H = -6.70\ eV$

(B)



$\Delta H = -6.58\ eV$

(C)



$\Delta H = -6.47\ eV$

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

CZTO is meta-stable in the kesterite structure. Oxygen incorporation in the CZTS lattice is very likely to occur.

$Cu_2ZnSnS_xO_{4-x}$ alloys are only stable for small range ($3.3 < x < 4.0$) with respect to binary oxides and sulfides.

For CZTSO alloys, O have preferred configuration, which avoids concentration in any a -b plane.

For CZTSSe, the alloys have random distributions of Se.

It is easier to synthesize CZTS than CZTSe, while it is energetically more favorable to sulfurize CZTSe than to selenize CZTS.

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