Role of functional defects in Cu_2ZnSnS_4 solar cells

Sai Gautam Gopalakrishnan, Kuang Yu, Samuel Berman and Emily A. Carter

Princeton University
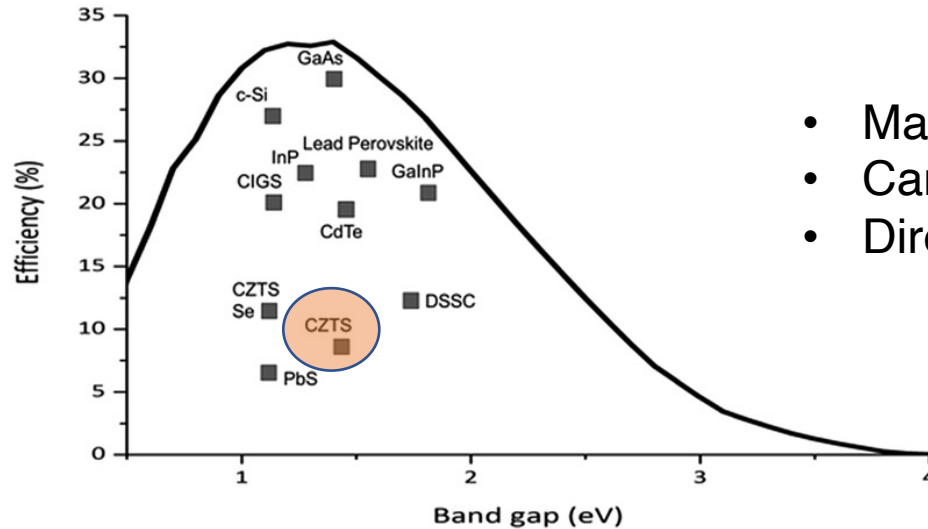
gautam91@princeton.edu

Cu$_2$ZnSnS$_4$ (CZTS) is a promising candidate for beyond-Si solar cells

Mathews et al., *Chem. Sci.* **8**, 4177 (2017)

- Made of abundant elements
- Can be synthesized through wet chemistry
- Direct band gap, 1.4-1.6 eV

Eff = 12.6%
FF = 69.8%
V_{oc} = 513.4mV
J_{sc} = 35.2mA/cm^2
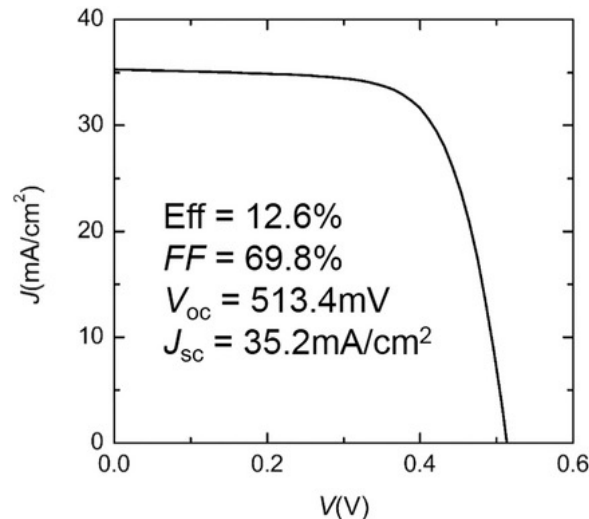
Wang et al., *Adv. Energy Mater.* **4**, 1301465 (2014)

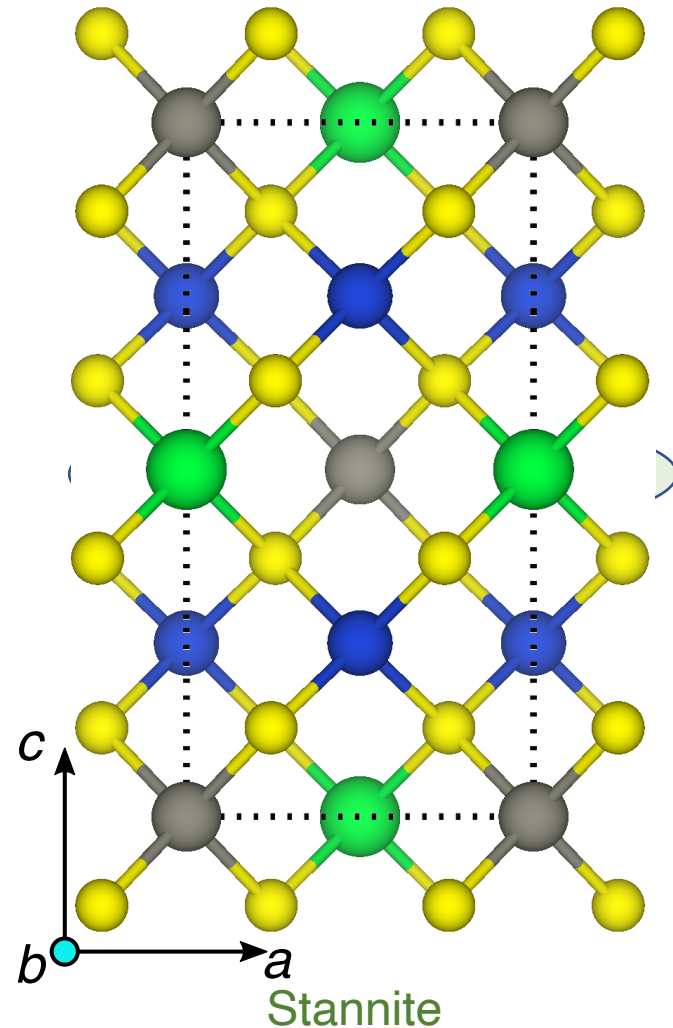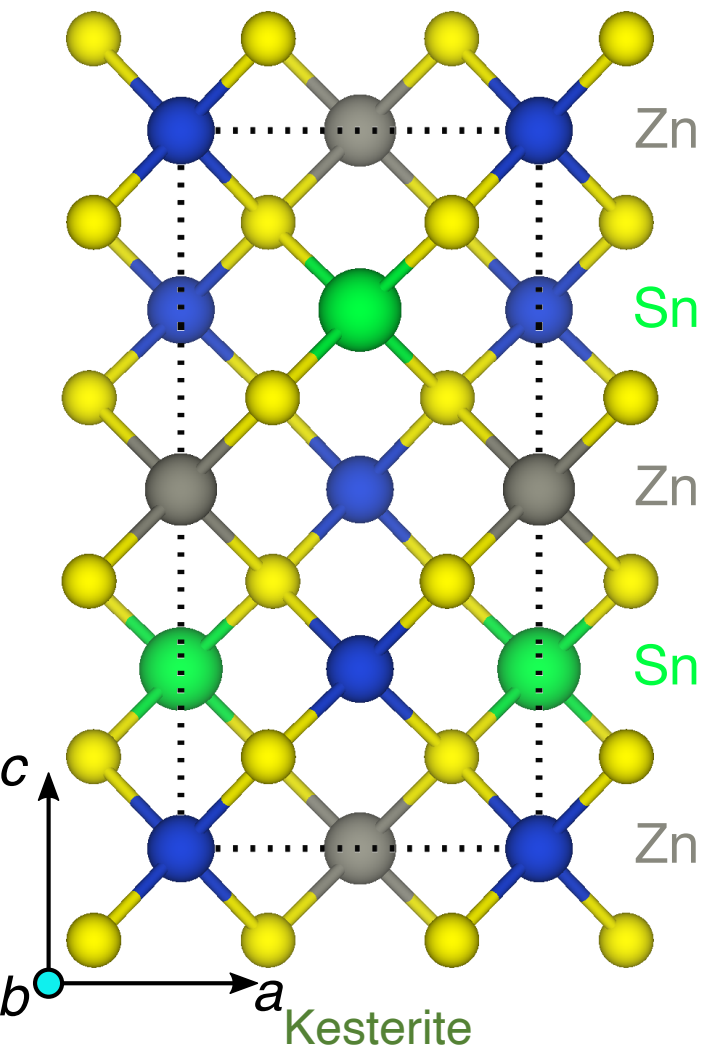Often suffers from low efficiencies (~12%)
- Si is > 20%
- Due to disorder in Cu-Zn sub-lattice

Se frequently added to tune band gap

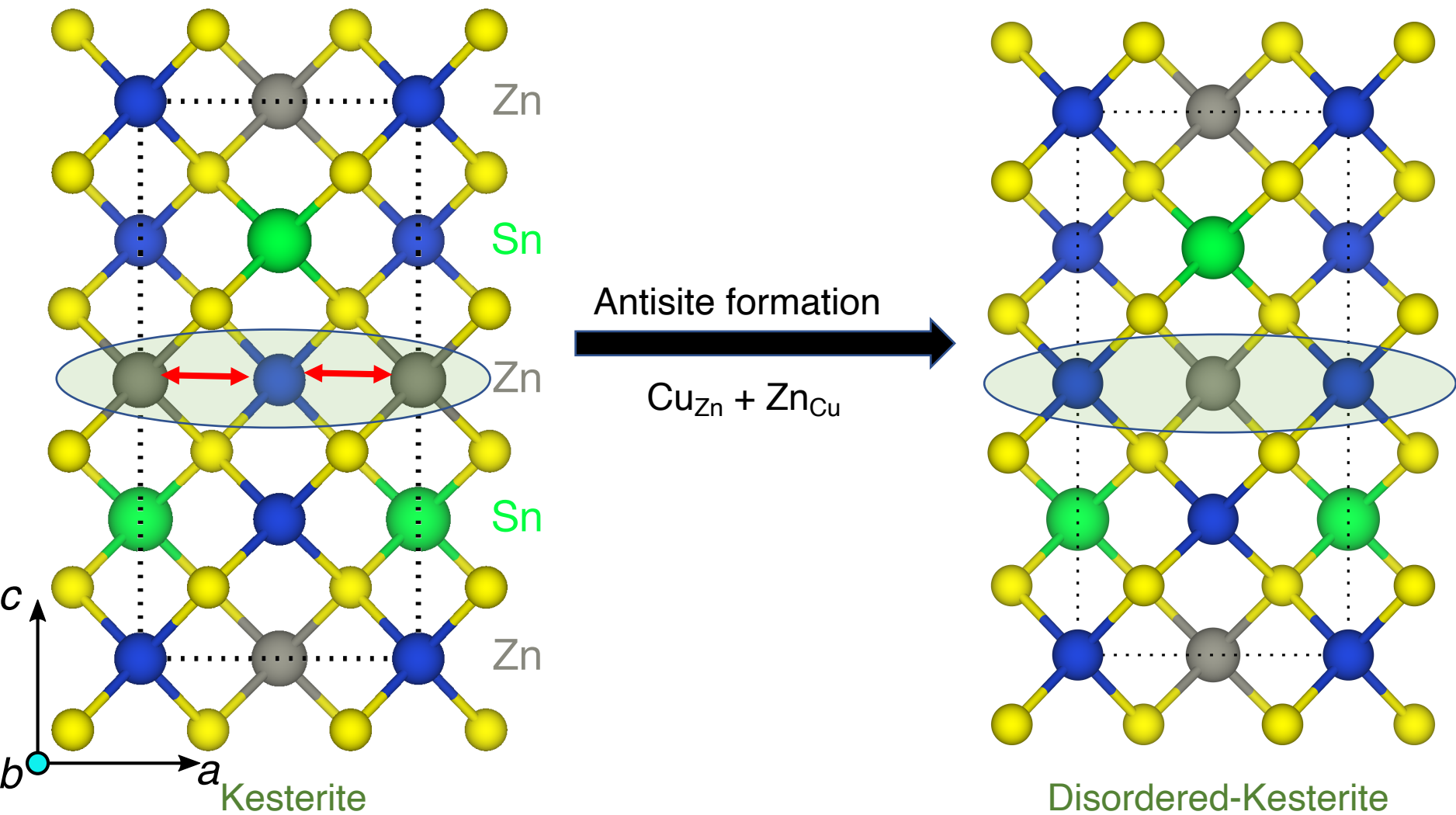High temperature annealing to improve crystal size
- Often leads to elemental loss and defect production
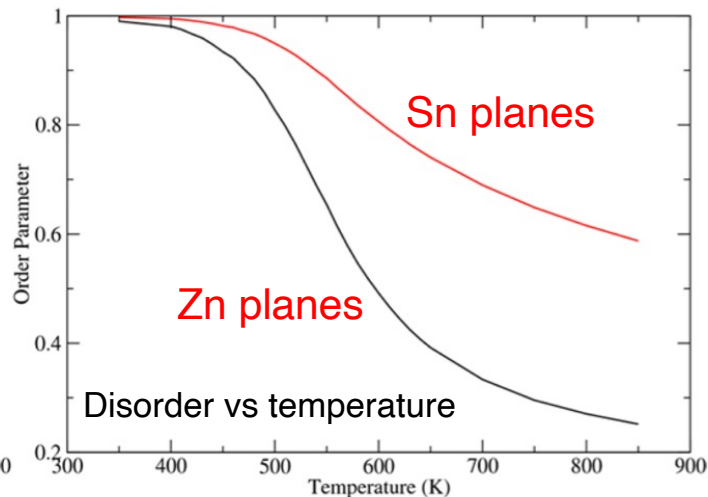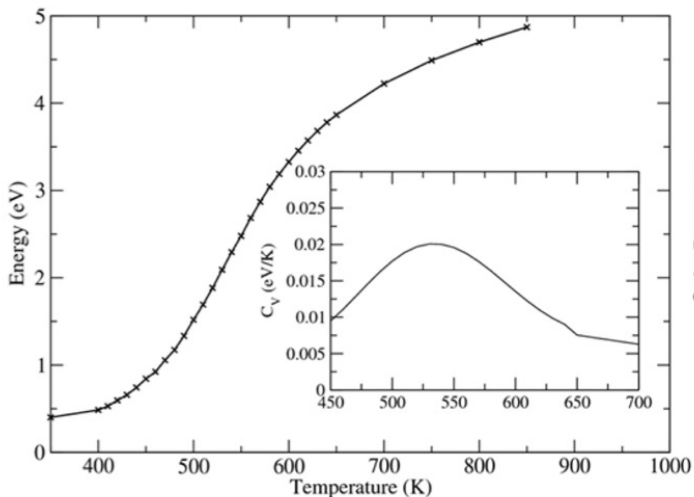
Disorder ≡ Antisites ≡ Defects

Kesterite

Stannite

Cu-Zn: similar atomic radii
Kesterite-Stannite near degeneracy (~3 kJ/mol)

G.S. Gautam et al., *Chem. Mater.* **2018**, *30*, 4543; Yu and Carter, *Chem. Mater.* **27**, 2920 (2015)

Disorder ≡ Antisites ≡ Defects

Antisite formation

$Cu_{Zn} + Zn_{Cu}$

Kesterite

Disordered-Kesterite

Cu-Zn: similar atomic radii
Kesterite-Stannite near degeneracy (~3 kJ/mol)

G.S. Gautam et al., *Chem. Mater.* **2018**, *30*, 4543; Yu and Carter, *Chem. Mater.* **27**, 2920 (2015)

Disorder in CZTS is thermodynamically favored under annealing conditions

Cluster-expansion + Monte-Carlo used to model disorder within Zn and Sn planes in CZTS

Disorder vs temperature

Average energy and average "disorder" increase with temperature
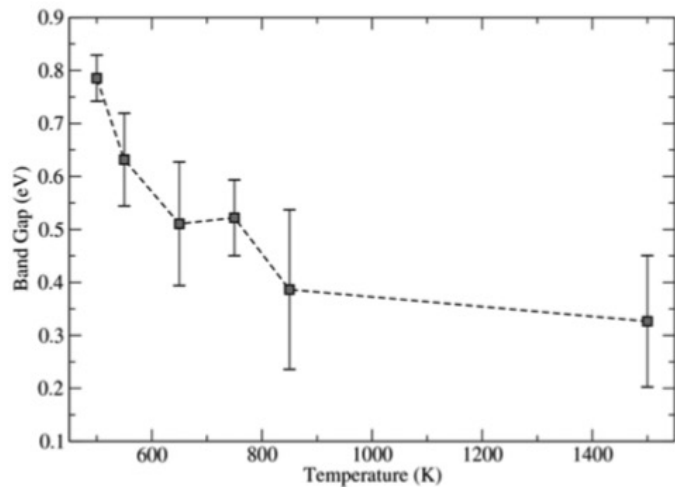
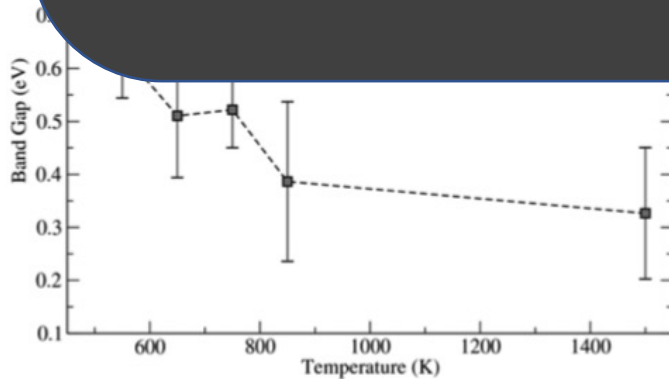
Band gap decreases with increasing disorder in CZTS

Can doping reduce the occurrence of **disorder-inducing antisites**?
- **Large isovalent** dopants?
  - Cd for Zn; Ag for Cu
  - Ca for Zn; Na for Cu
- What **properties** will a dopant affect?

Yu and Carter, *Chem. Mater.* **27**, 2920 (2015); *Chem. Mater.* **28**, 864 (2016); *Chem. Mater.* **28**, 4415 (2016)

Disorder in CZTS is thermodynamically favored under annealing conditions

Potential impacts of dopants

- **Antisite formation**: change defect formation energy

- **Bulk stability**: kesterite vs. stannite

- **Electronic structure**: change band gap

decreases with increasing disorder in CZTS

- **Large isovalent** dopants?
  - Cd for Zn; Ag for Cu
  - Ca for Zn; Na for Cu
- What **properties** will a dopant affect?

Yu and Carter, *Chem. Mater.* **27**, 2920 (2015); *Chem. Mater.* **28**, 864 (2016); *Chem. Mater.* **28**, 4415 (2016)

Methods

How do we evaluate the influence of dopants?

Density functional theory for defects

$$E_{disorder} \equiv E_{anti-site}^{formation} = \boxed{E_{bulk}^{defect}} - \boxed{E_{bulk}^{pristine}} + \boxed{\Sigma_i n_i \mu_i} + \boxed{qE_F + E_{corr}}$$

Kesterite with antisites   Pure Kesterite   Synthesis/doping/operating conditions

For "neutral" defects ($q = 0$), the strongly constrained and appropriately normed (SCAN)[1] functional is used to describe electronic exchange-correlation within Density Functional Theory (DFT)

- SCAN satisfies 17 known constraints on the behavior of an exchange-correlation functional
- SCAN for defect energetics? Band gaps? Chemical potential limits?
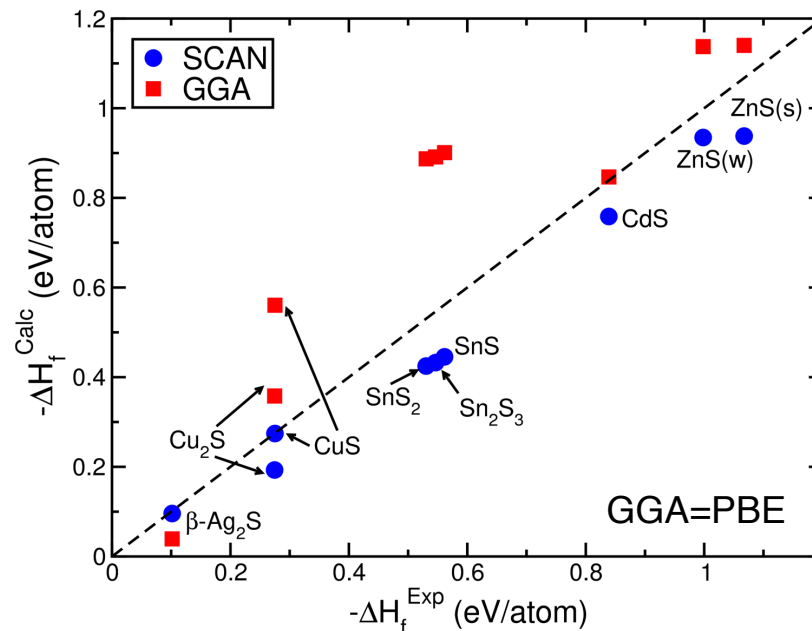
1. Sun et al., *Phys. Rev. Lett.* **115**, 036402 (2015)

Charged defects: ionized electrons or holes

Chemical potentials

For "charged" defects

$$E_{disorder} \equiv E_{anti-site}^{formation} = E_{bulk}^{defect} - E_{bulk}^{pristine} + \Sigma_i n_i \mu_i + qE_F + E_{corr}$$

Kesterite with antisites   Pure Kesterite   Synthesis/doping/operating conditions

$$E_{defect}^{formation} = f(\mu_{Cu}, \mu_{Zn}, \mu_{Sn}, \mu_{Ag}, \mu_{Cd}, \mu_{Na}, \mu_{Ca})$$

Independent variable   Possible constraints   Doping conditions

For CZTS to be stable, $\Delta G_f^{CZTS} = 2\mu_{Cu} + \mu_{Zn} + \mu_{Sn} + 4\mu_S$

Three Cu-chemical-potential conditions considered

Cu-rich

$\mu_{Cu} = Cu\ metal$
$\mu_{Zn} = \Delta G_f^{ZnS} - \mu_S$ (Zn-rich)
$\mu_{Sn} = \Delta G_f^{SnS} - \mu_S$ (Sn-rich)

Constrained Cu-poor

$\mu_{Cu} = \min(\mu_{Cu})\ at\ \Delta G_f^{CZTS}$
$\mu_{Zn} = \Delta G_f^{ZnS} - \mu_S$ (Zn-rich)
$\mu_{Sn} = \Delta G_f^{SnS} - \mu_S$ (Sn-rich)

Cu-poor

$\mu_{Cu} = \min(\mu_{Cu})\ at\ \Delta G_f^{CZTS}$

μ_{dopant} chosen as the maximum possible value at all 3 conditions, provided CZTS is stable

G.S. Gautam et al., *Chem. Mater.* **2018**, *30*, 4543

SCAN does have the "band gap" problem
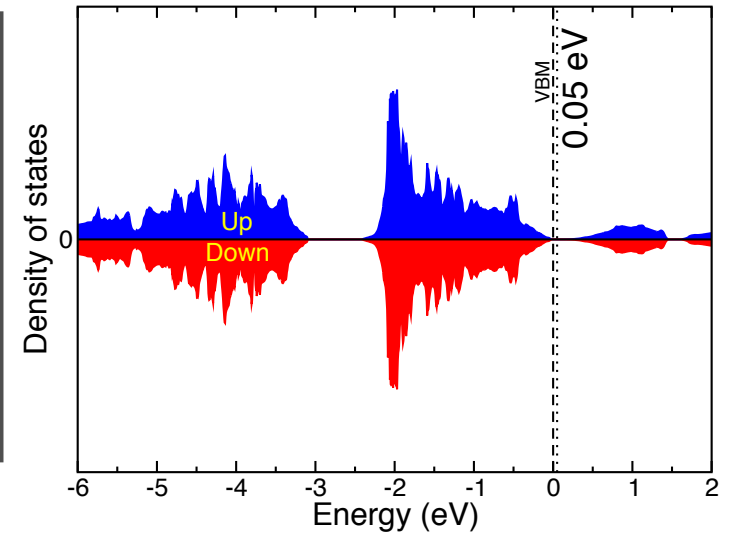

scGW gap: 1.64 eV
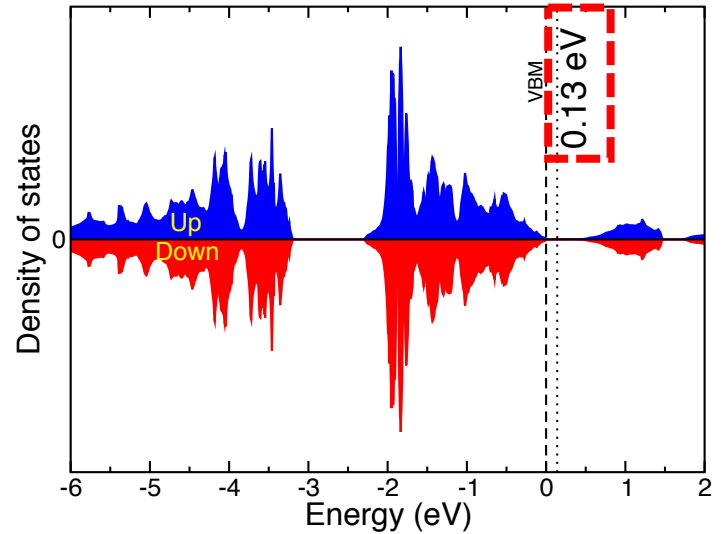Exp: ~1.5 eV

GGA+*U*

Kesterite

Stannite

scGW gap: 1.33 eV
Exp: ~1.3 eV
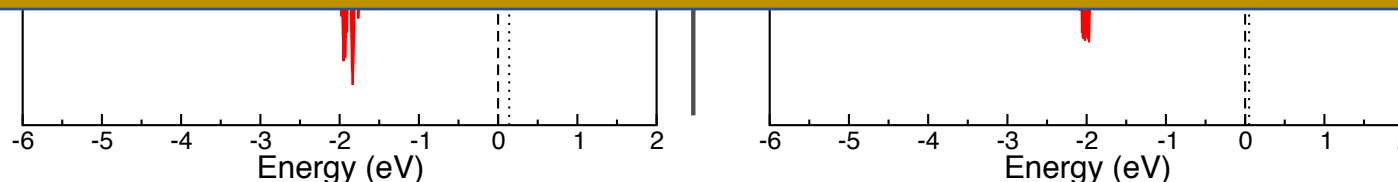
SCAN

SCAN does have the "band gap" problem

Kesterite

GGA+*U*
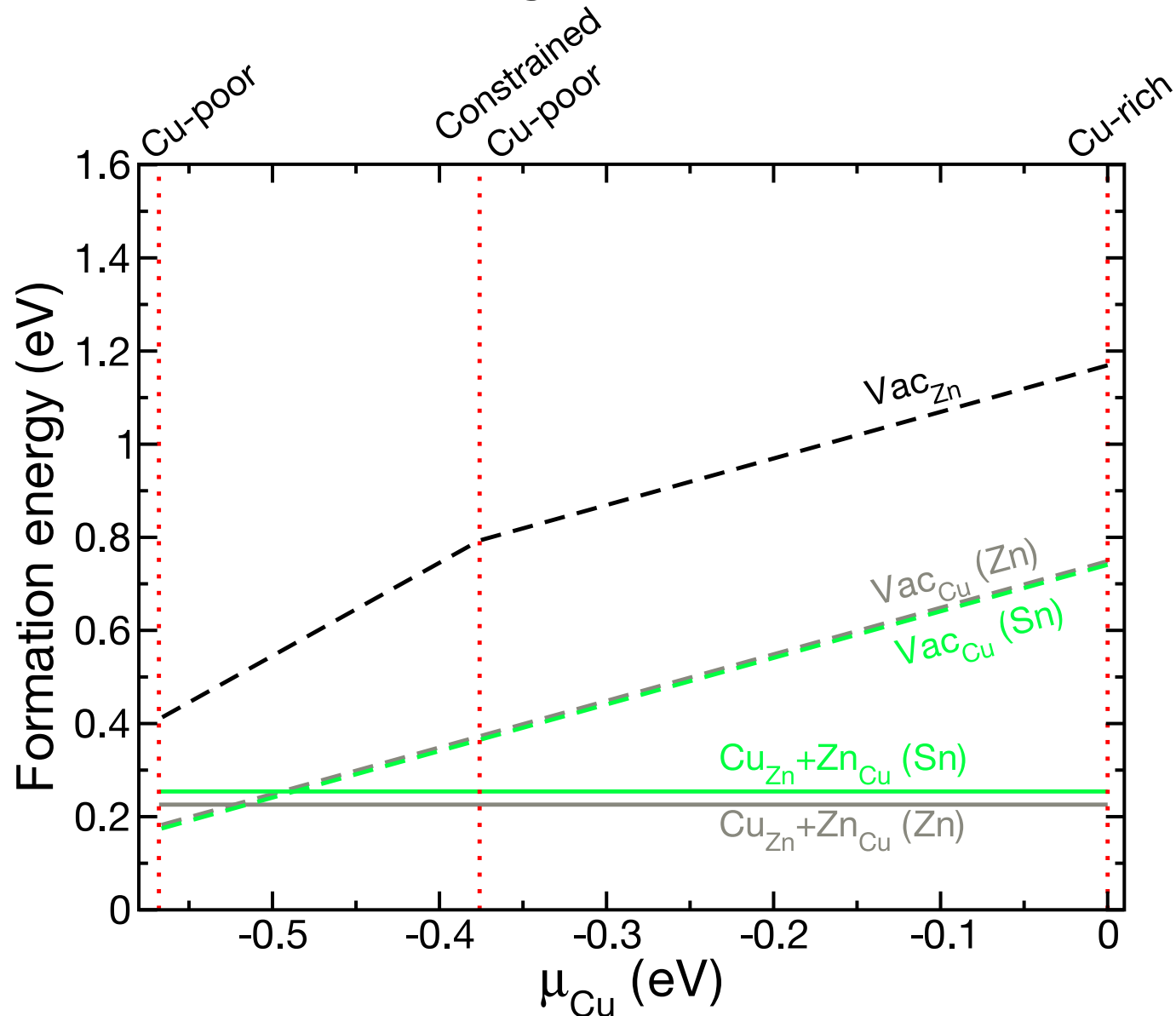
Stannite

scGW gap:
1.64 eV
Exp:
~1

scGW gap:
1.33 eV
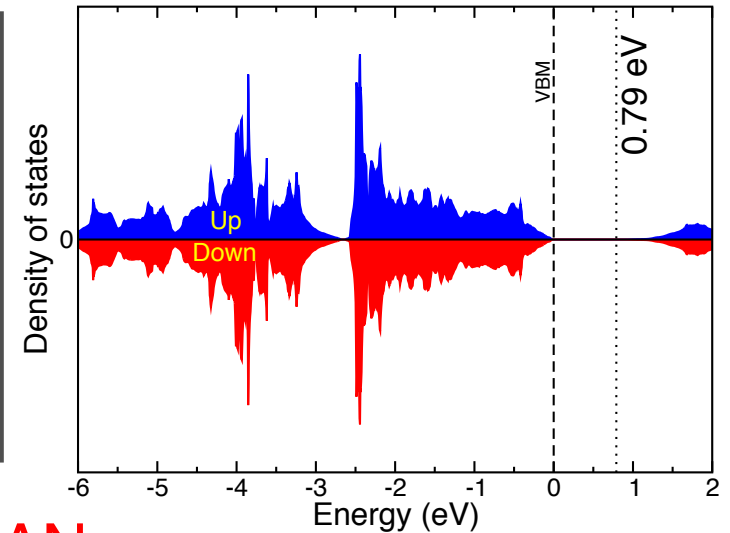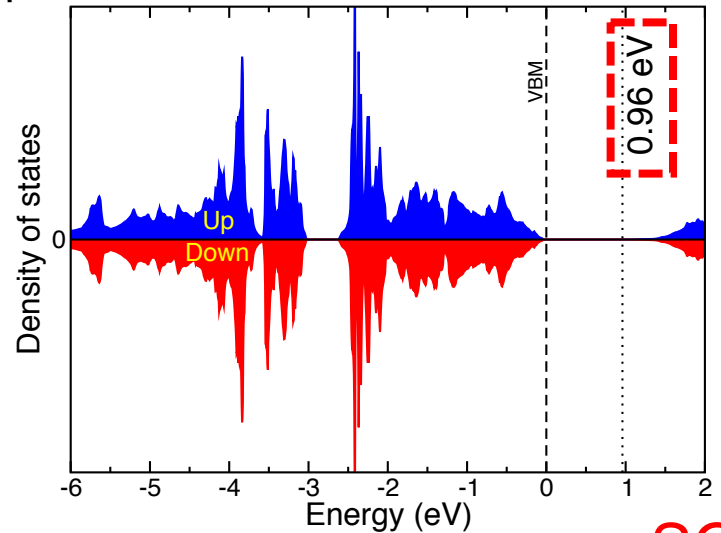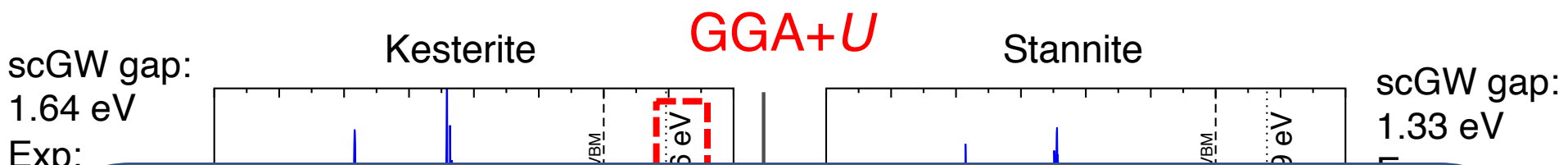
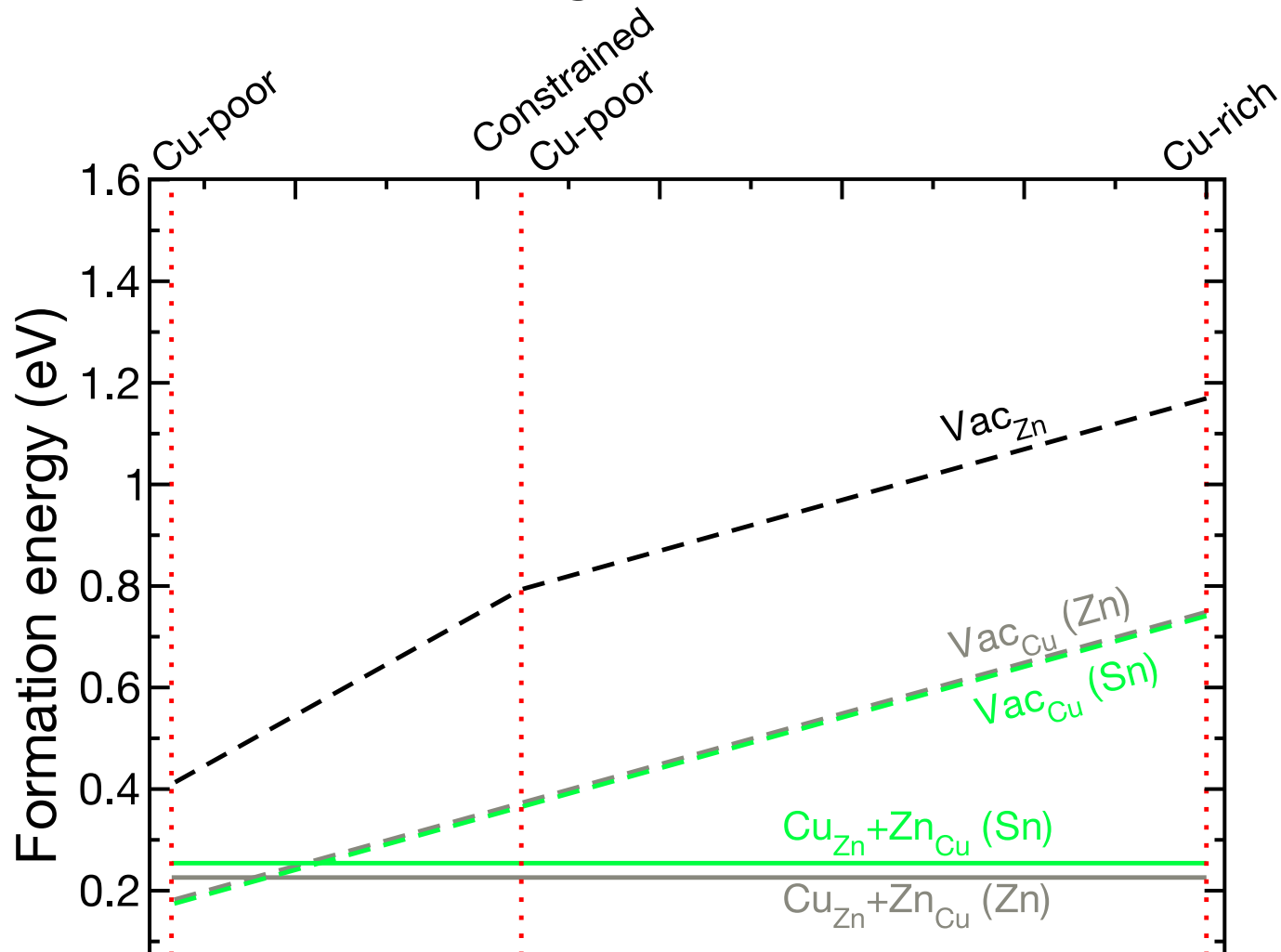**SCAN is not reliable for qualitative band gap estimates and estimating charged defect formation energies**

For a more detailed benchmarking of SCAN, refer to
"Evaluating transition metal oxides within DFT-SCAN and SCAN+*U*
frameworks for solar thermochemical applications",
G.S. Gautam and E.A. Carter, *Phys. Rev. Mater.* **2**, 095401 (2018)
Poster: CM01.03 (Nov 26, 8pm)

Energy (eV)

Energy (eV)

Pure CZTS expected to show disorder: SCAN is reliable for defect energetics

SCAN-calculations in agreement with previous GGA+U estimates [Yu and Carter, *Chem. Mater.* **27**, 2920 (2015)]

Pure CZTS expected to show disorder: SCAN is reliable for defect energetics

Cu-poor

Constrained Cu-poor

Cu-rich

Formation energy (eV)

Vac_{Zn}

Vac_{Cu} (Zn)

Vac_{Cu} (Sn)

$Cu_{Zn}+Zn_{Cu}$ (Sn)

$Cu_{Zn}+Zn_{Cu}$ (Zn)

Energy to form antisite inducing defects in pure CZTS: 0.22-0.25 eV

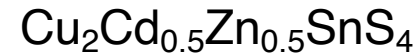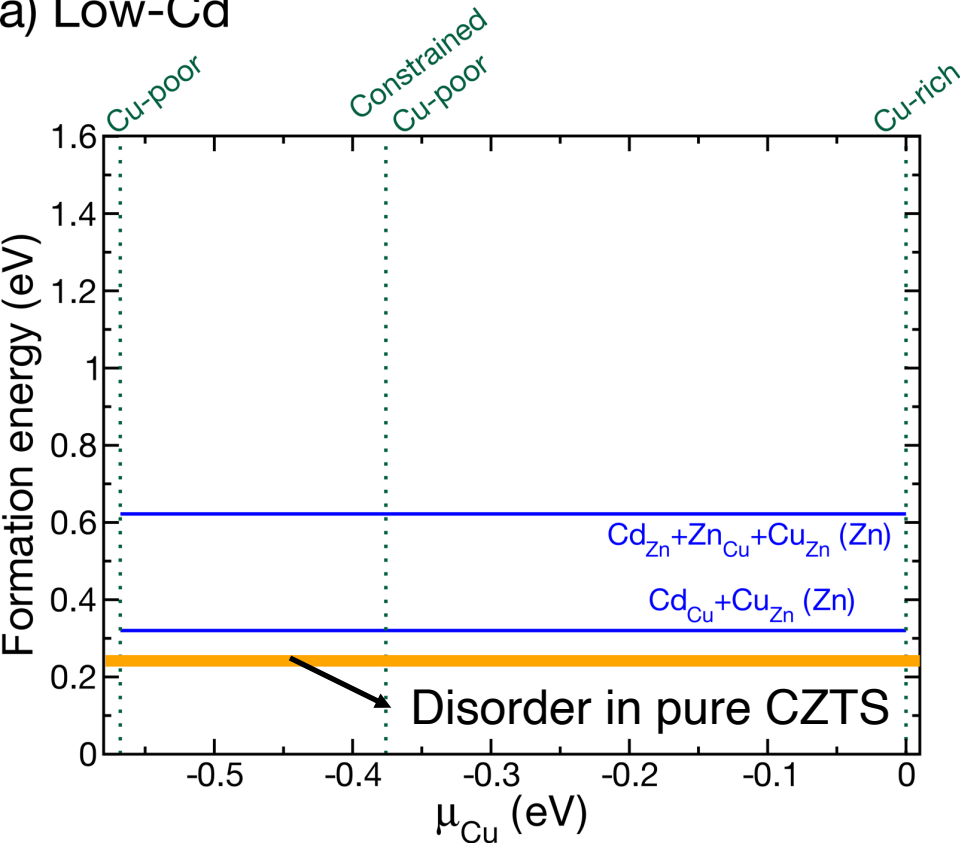SCAN-calculations in agreement with previous GGA+U estimates [Yu and Carter, *Chem. Mater.* **27**, 2920 (2015)]

How do Cd or Ag influence CZTS?

Results from defect formation and electronic structure

Low Cd-doping = less disorder

$Cu_2Cd_{0.06}Zn_{0.94}SnS_4$
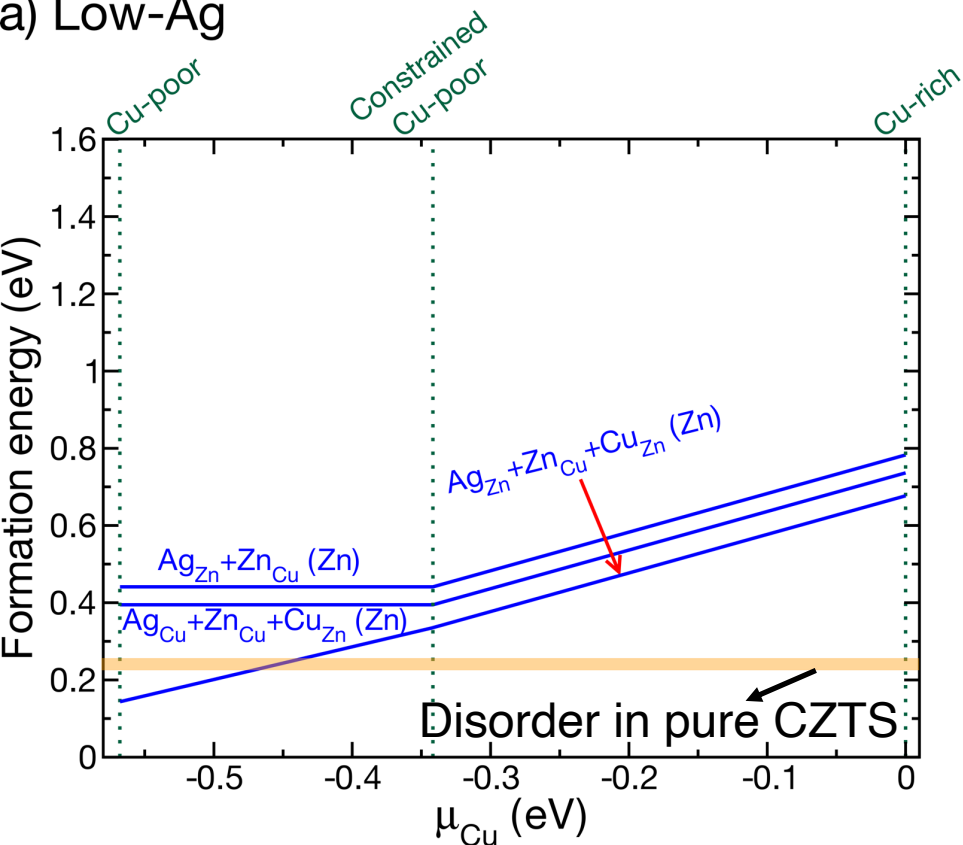
$Cu_2Cd_{0.5}Zn_{0.5}SnS_4$

a) Low-Cd

Cu-poor   Constrained Cu-poor   Cu-rich

Formation energy (eV)

$Cd_{Zn}+Zn_{Cu}+Cu_{Zn}$ (Zn)

$Cd_{Cu}+Cu_{Zn}$ (Zn)

Disorder in pure CZTS

μ_{Cu} (eV)

b) High-Cd

Cu-poor   Constrained Cu-poor   Cu-rich

Formation energy (eV)

$Cd_{Cu}+Cu_{Cd}$ (Sn)

$Cd_{Cu}+Cu_{Cd}$ (Cd)

μ_{Cu} (eV)
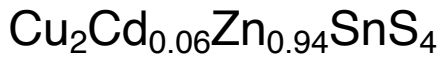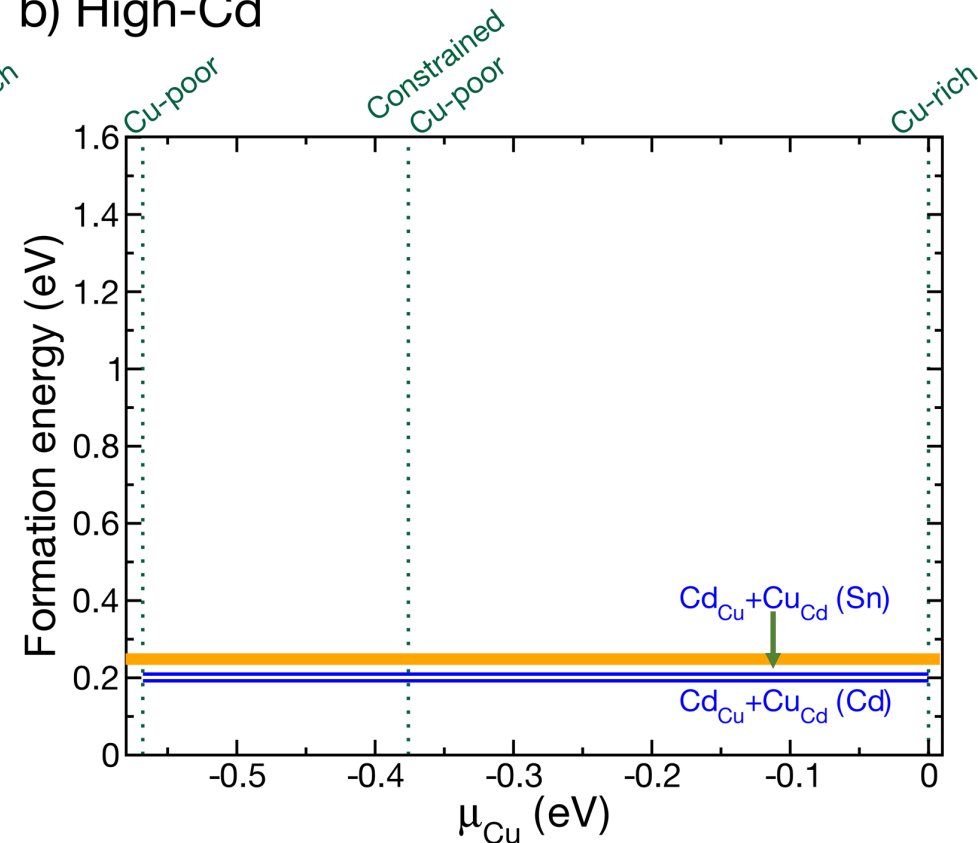
Energy to disorder higher at low Cd-doping

Note: SCAN-calculations
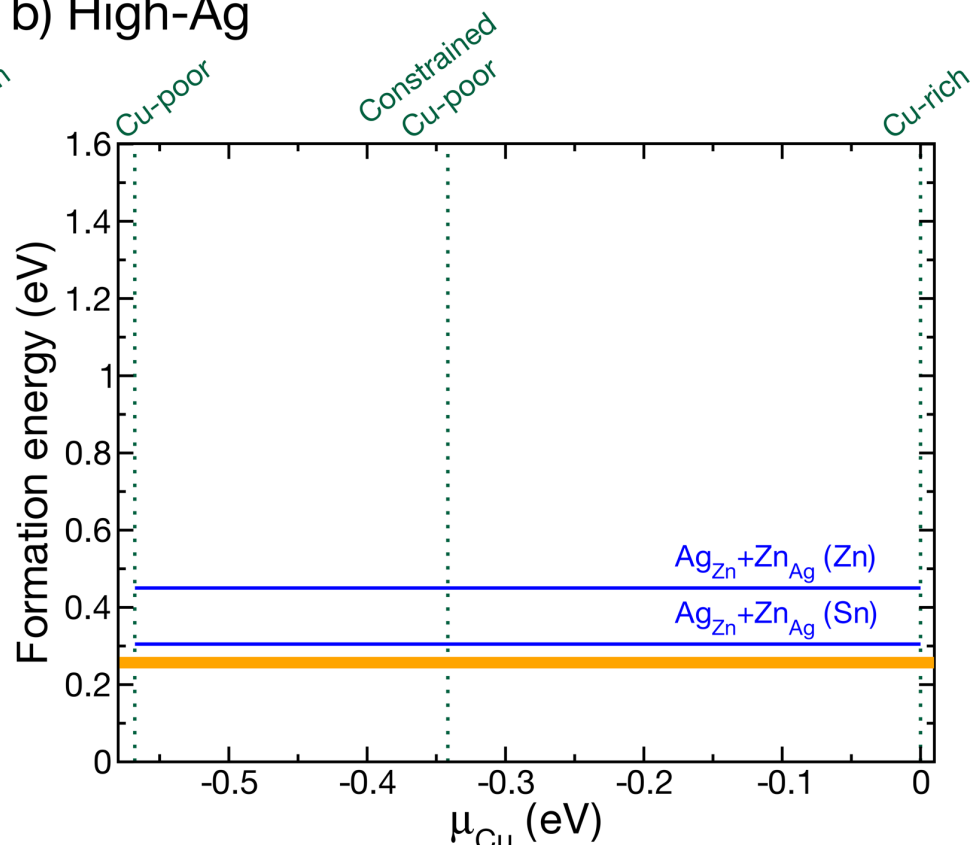
Low Ag-doping = less disorder*

$Cu_{1.94}Ag_{0.06}ZnSnS_4$
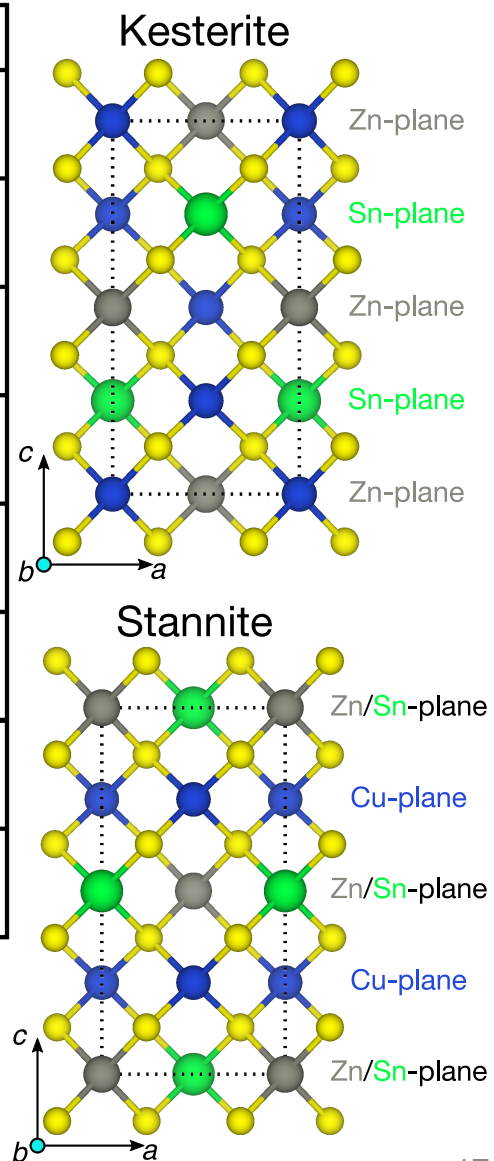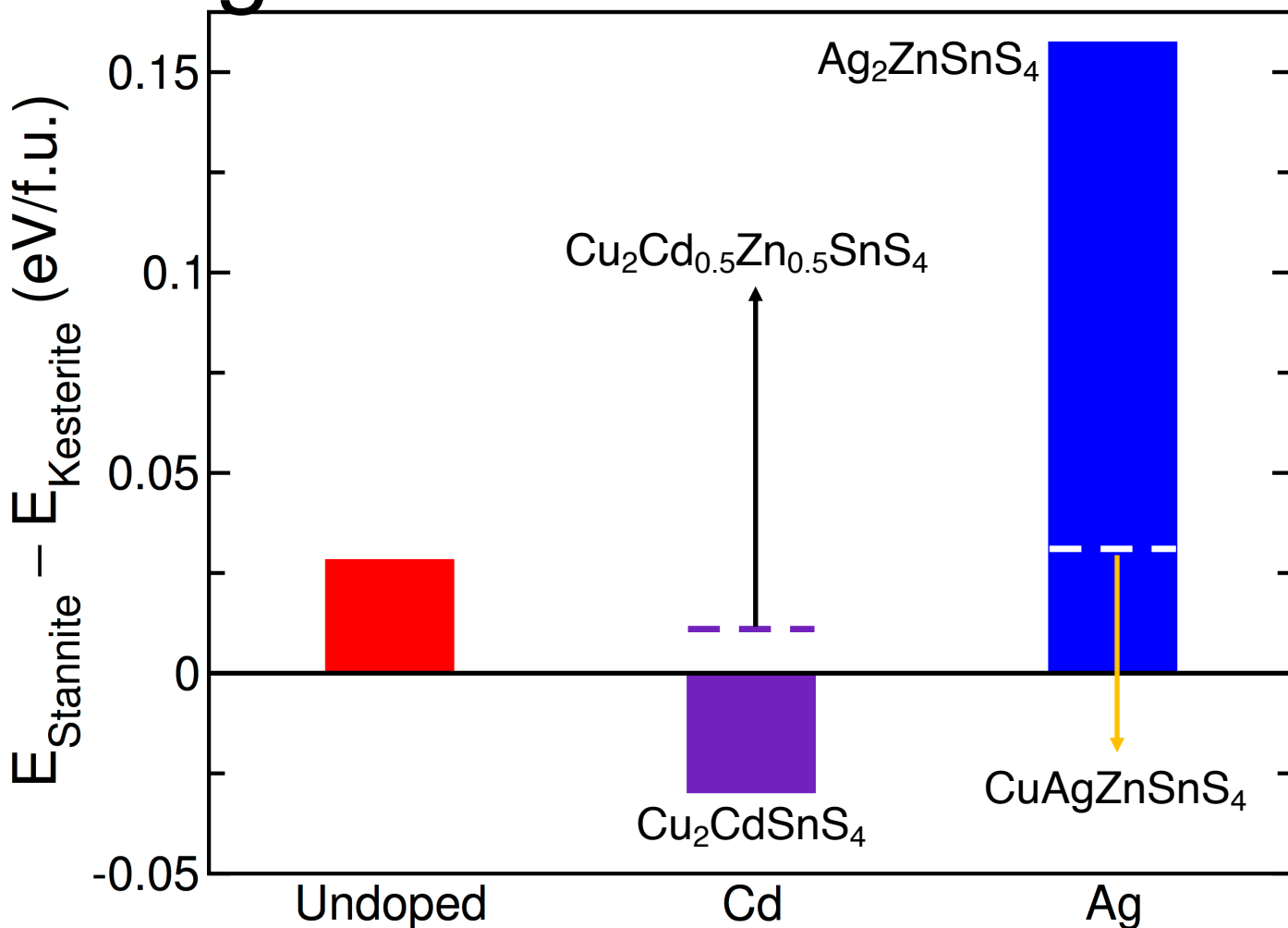
$CuAgZnSnS_4$

a) Low-Ag

b) High-Ag

*Low Ag-doping only beneficial at constrained Cu-poor (Zn+Sn rich) to Cu-rich conditions
High Ag-doping should generally be beneficial in suppressing antisites

Note: SCAN-calculations

High Ag stabilizes kesterite
High Cd stabilizes stannite

$E_{Stannite} - E_{Kesterite}$ (eV/f.u.)

Ag_2ZnSnS_4

$Cu_2Cd_{0.5}Zn_{0.5}SnS_4$

Undoped

Kesterite

Stannite

Zn/Sn-plane
Cu-plane
Zn/Sn-plane
Cu-plane
Zn/Sn-plane

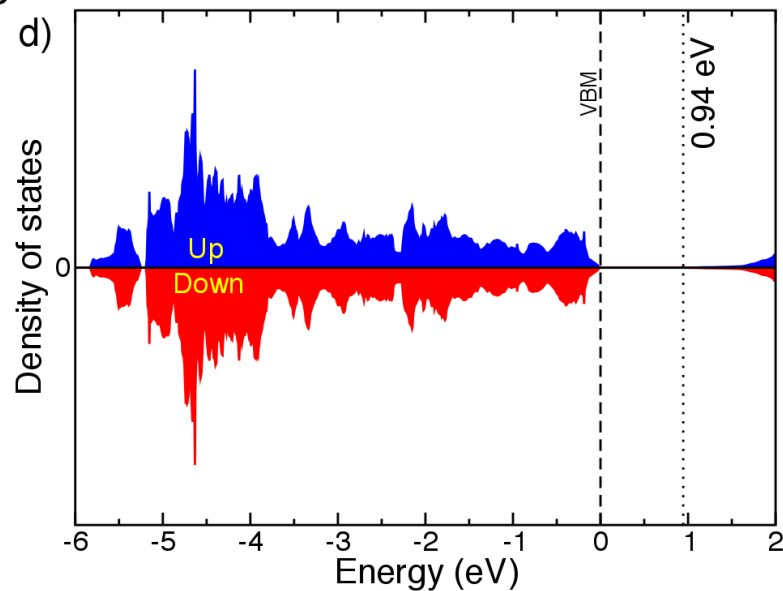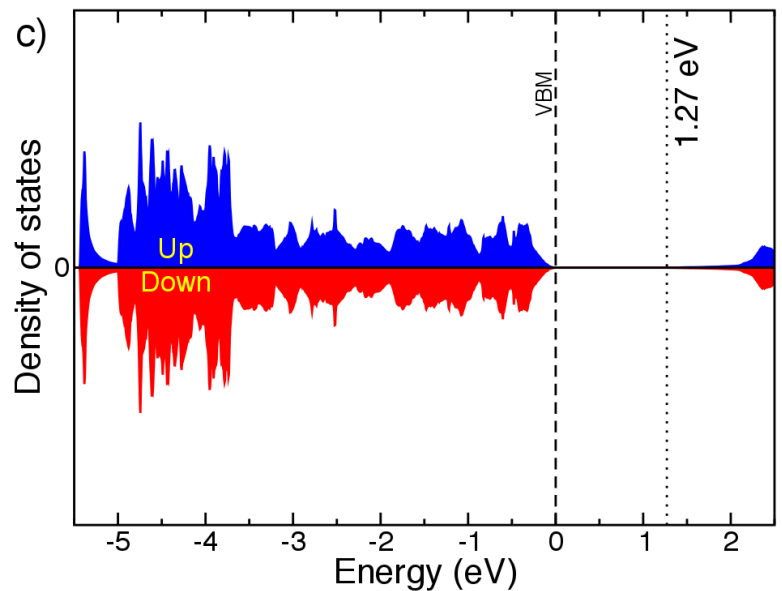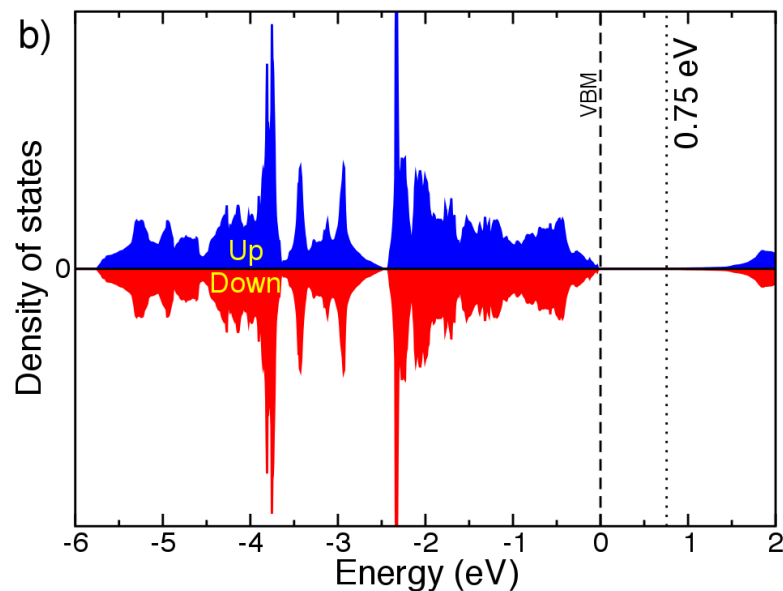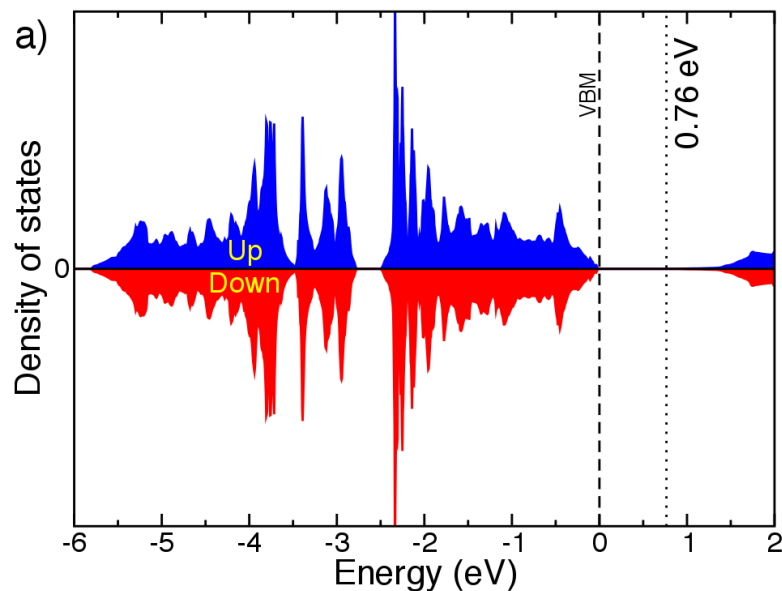Ag_2ZnSnS_4 and Cu_2CdSnS_4 are thermodynamically stable

Note: SCAN-calculations

17

Cd (Ag) decreases (increases) band gap

Kesterite   Cd   Stannite

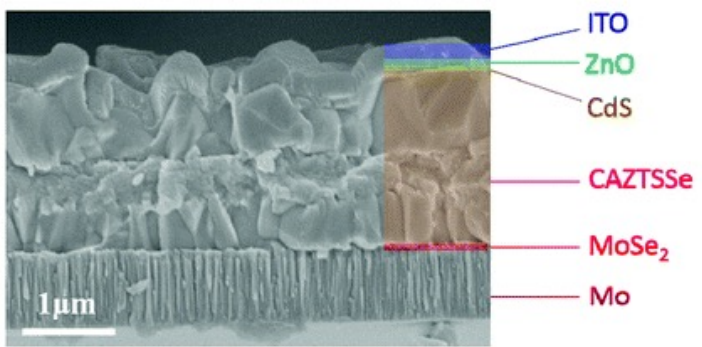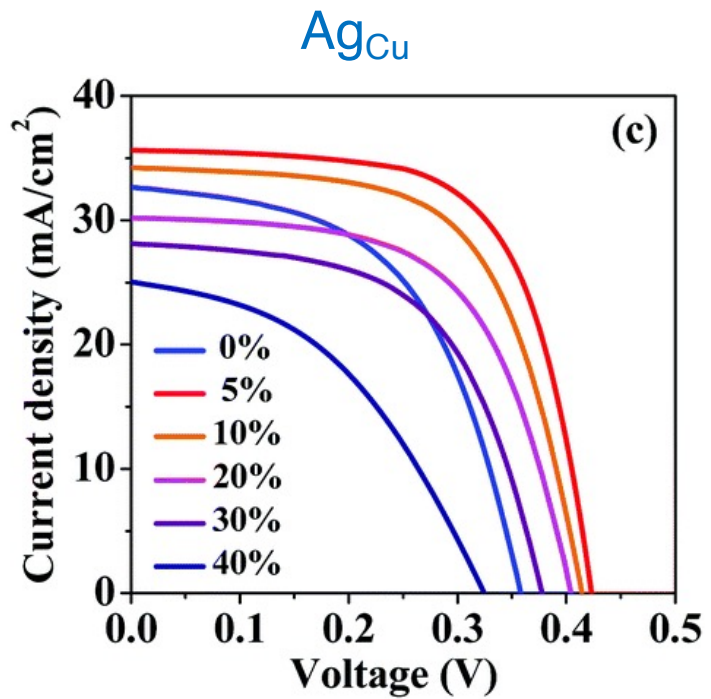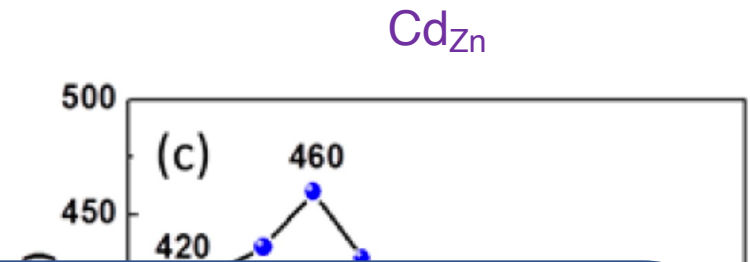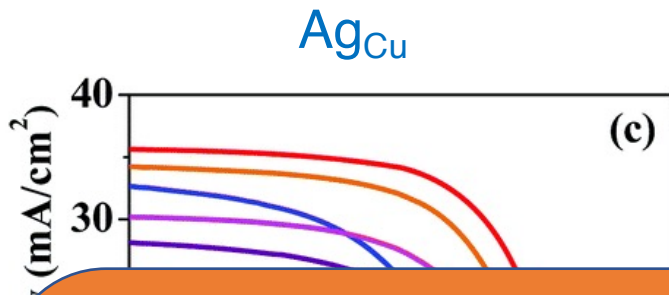GGA+*U* gap, pure kesterite: **0.96 eV**   GGA+*U* gap, pure stannite: **0.79** eV

Isovalent doping in kesterite:
experiments report improved performance
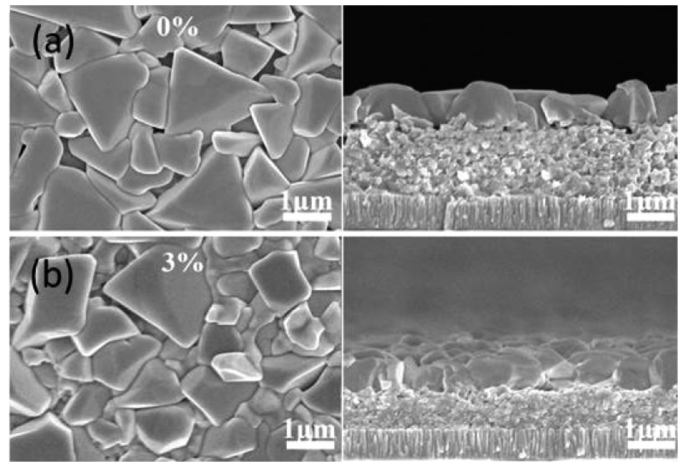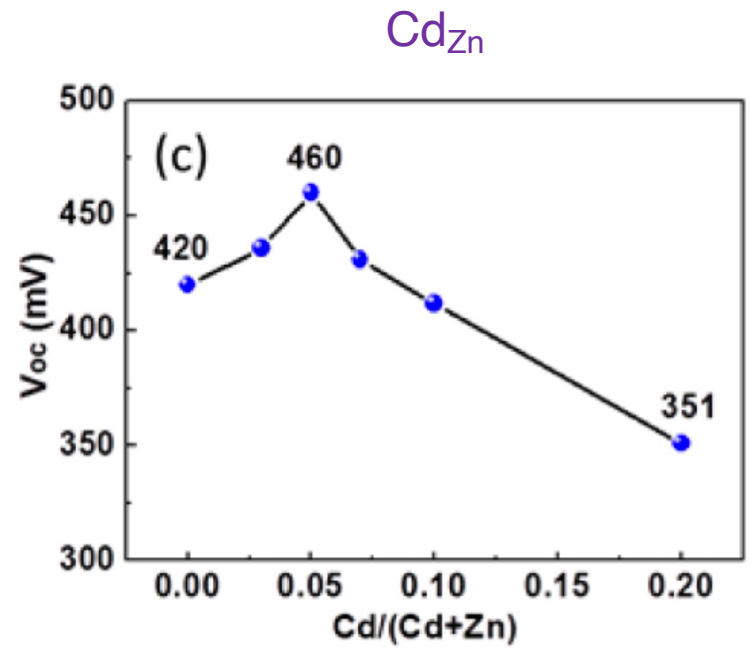
Ag_{Cu}

Cd_{Zn}

Isovalent doping in kesterite:
experiments report improved performance

Ag_{Cu}

Cd_{Zn}

- Both Ag and Cd doping increase efficiencies: but only up to a certain doping content (~ 5%)

- Cd = high Cd, higher disorder, efficiency drop
- Ag = high Ag, higher band gap, efficiency drop

Alternate dopants? Ag is rare and Cd is toxic

CAZTSSe

MoSe₂

Mo

1 μm

3%

1μm

1μm

Qi et al., *Energy Environ. Sci.* **10**, 2401 (2017)

Fu et al., *Chem. Mater.* **28**, 5821 (2016)
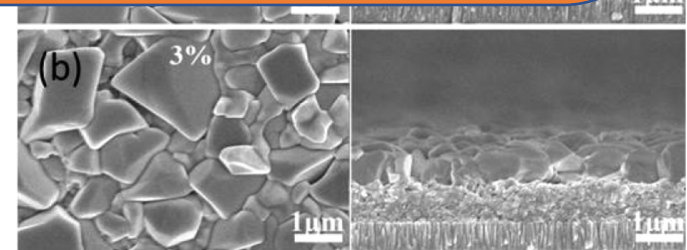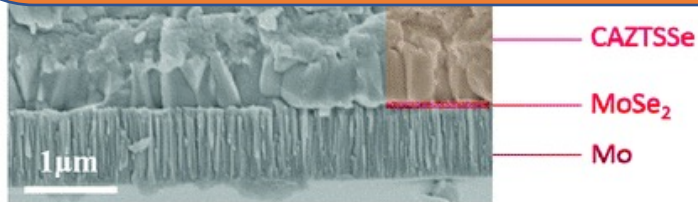
Na/Ca doping in CZTS

Influence on defect, bulk and electronic properties

Na-doping = less disorder

$Cu_{1.94}Na_{0.06}ZnSnS_4$　　　　　　　$CuNaZnSnS_4$

a) Low Na

Cu-poor　Constrained Cu-poor　Cu-rich

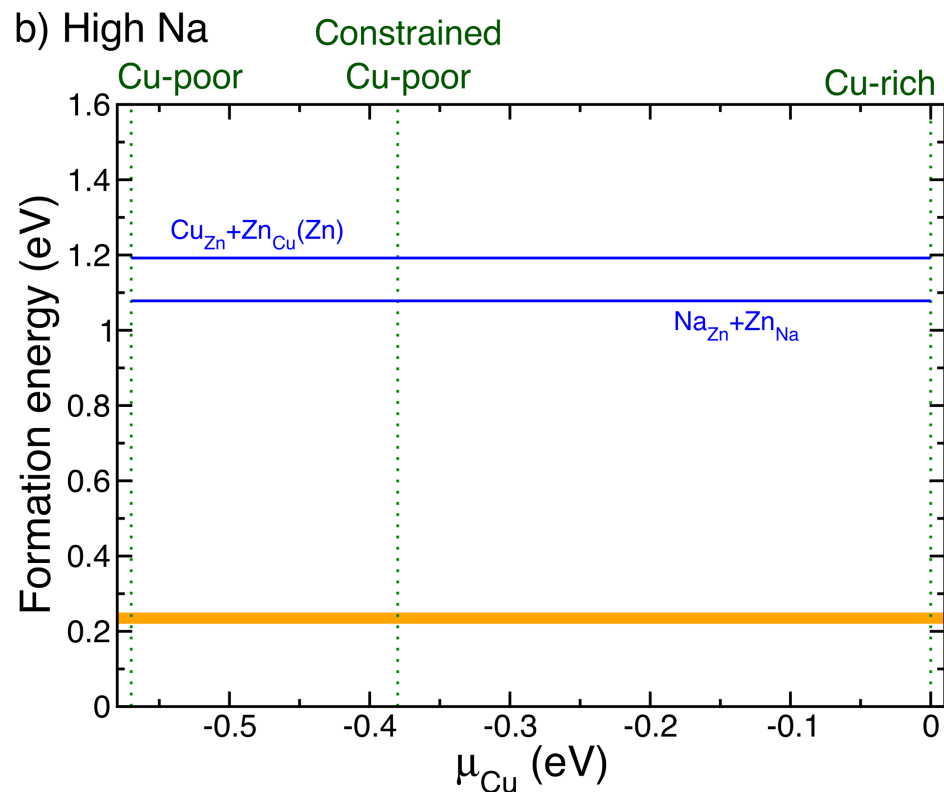Formation energy (eV)

$Na_{Cu}+Cu_{Zn}+Zn_{Cu}(Zn)$

$Na_{Zn}+Zn_{Cu}(Zn)$

$Na_{Zn}+Cu_{Zn}+Zn_{Cu}(Sn)$

Disorder in pure CZTS

μ_{Cu} (eV)

b) High Na

Cu-poor　Constrained Cu-poor　Cu-rich

Formation energy (eV)

$Cu_{Zn}+Zn_{Cu}(Zn)$

$Na_{Zn}+Zn_{Na}$

μ_{Cu} (eV)
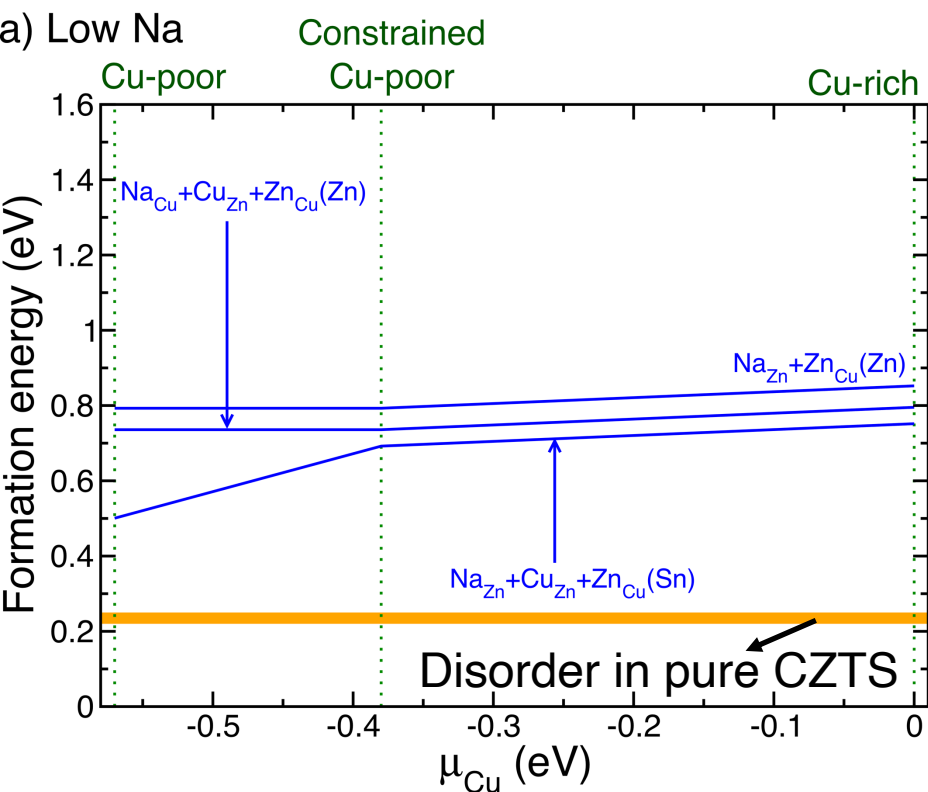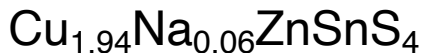
Na-doping can suppress disorder in CZTS, under low/high doping and across Cu-chemical potentials

Note: SCAN-calculations

Ca-doping = less disorder

$Cu_2Ca_{0.06}Zn_{0.94}SnS_4$ $Cu_2Ca_{0.5}Zn_{0.5}SnS_4$

a) Low Ca

Constrained
Cu-poor Cu-poor Cu-rich

Formation energy (eV)

$Ca_{Cu}+Cu_{Zn}+Zn_{Cu}(Zn)$

$Ca_{Zn}+Cu_{Zn}+Zn_{Cu}(Zn)$ $Ca_{Cu}+Cu_{Zn}(Zn)$

Disorder in pure CZTS

μ_{Cu} (eV)

b) High Ca

Constrained
Cu-poor Cu-poor Cu-rich

Formation energy (eV)

$Cu_{Ca}+Ca_{Cu}(Ca)$

$Cu_{Ca}+Ca_{Cu}(Sn)$

μ_{Cu} (eV)
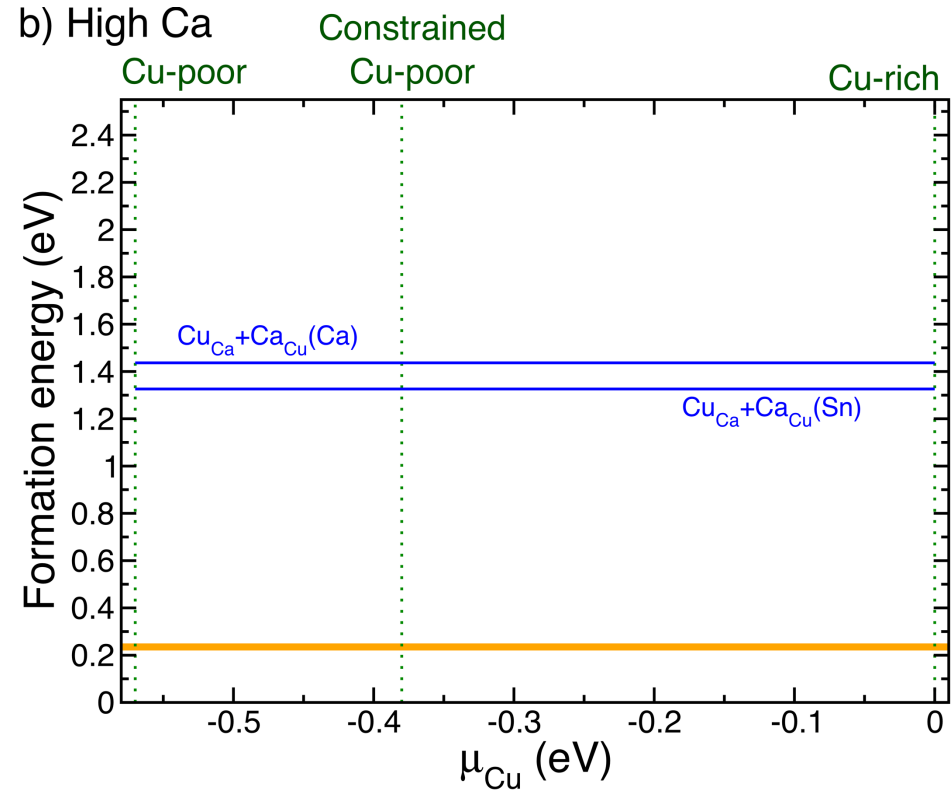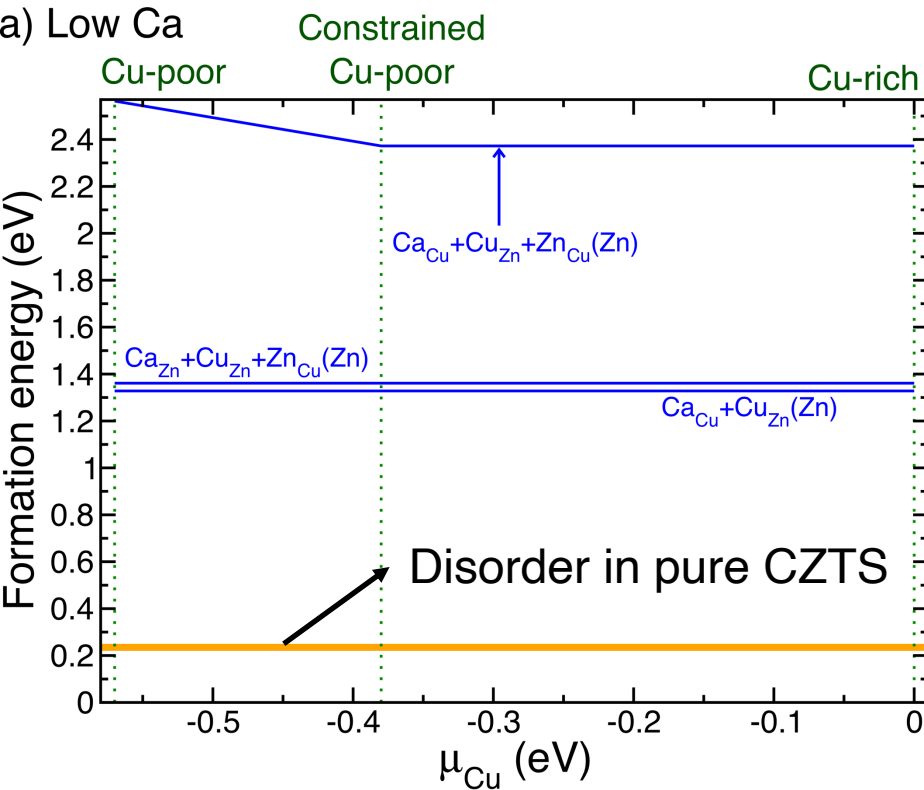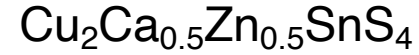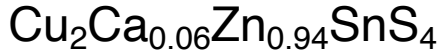
Ca suppresses disorder in CZTS, better than Na, across doping and Cu-conditions

Note: SCAN-calculations

Na stabilizes kesterite and phase separates
High Ca leads to decomposition of CZTS
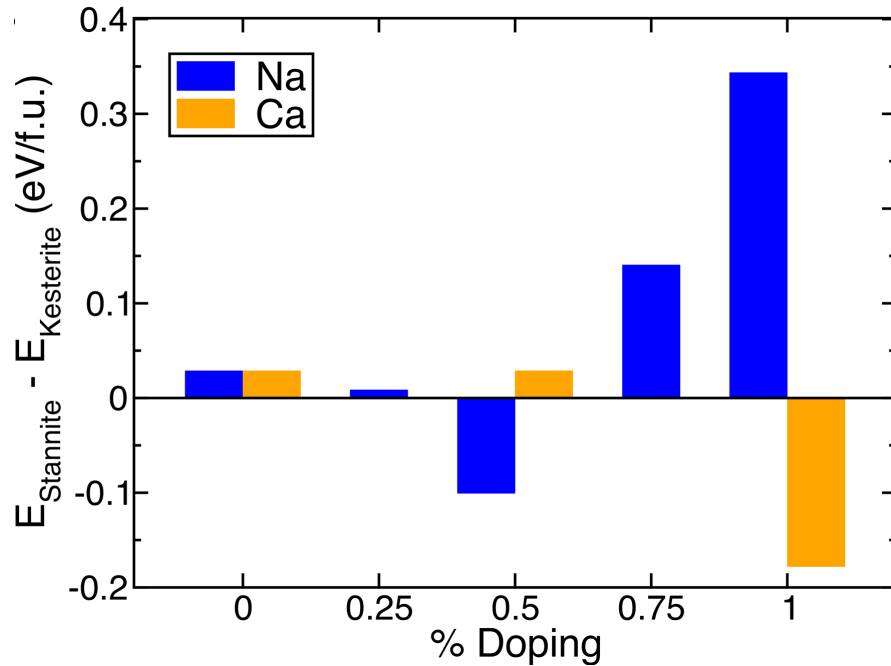
Na-doping follows non-monotonic trend in kesterite vs. stannite stability (different from Ag)

Ca-doping stabilizes stannite with increasing doping content (similar to Cd)
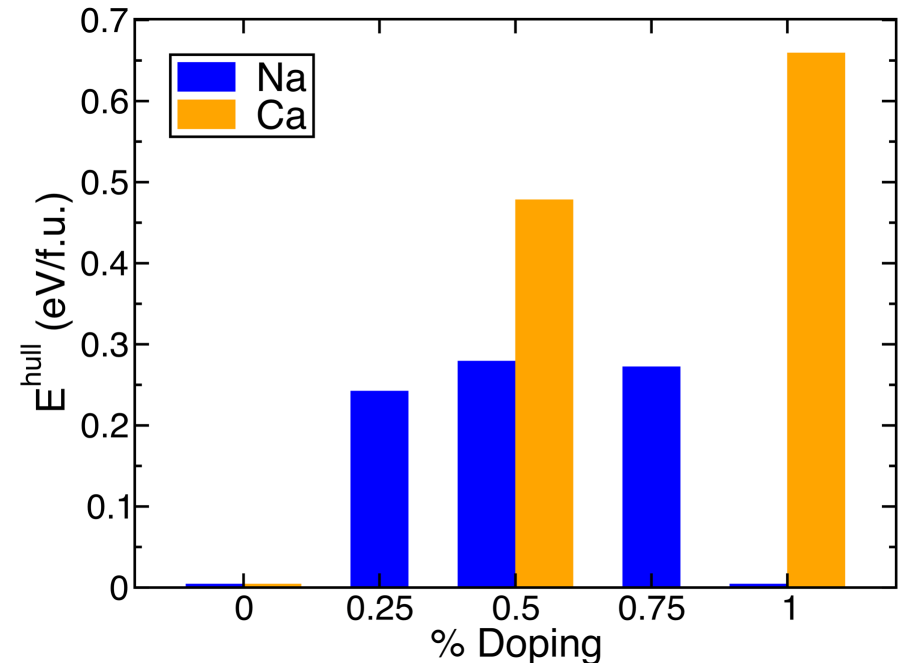
Energy above hull (at 0 K): measures metastability vs. ground-states

Cu_2ZnSnS_4 and Na_2ZnSnS_4 are thermodynamically stable
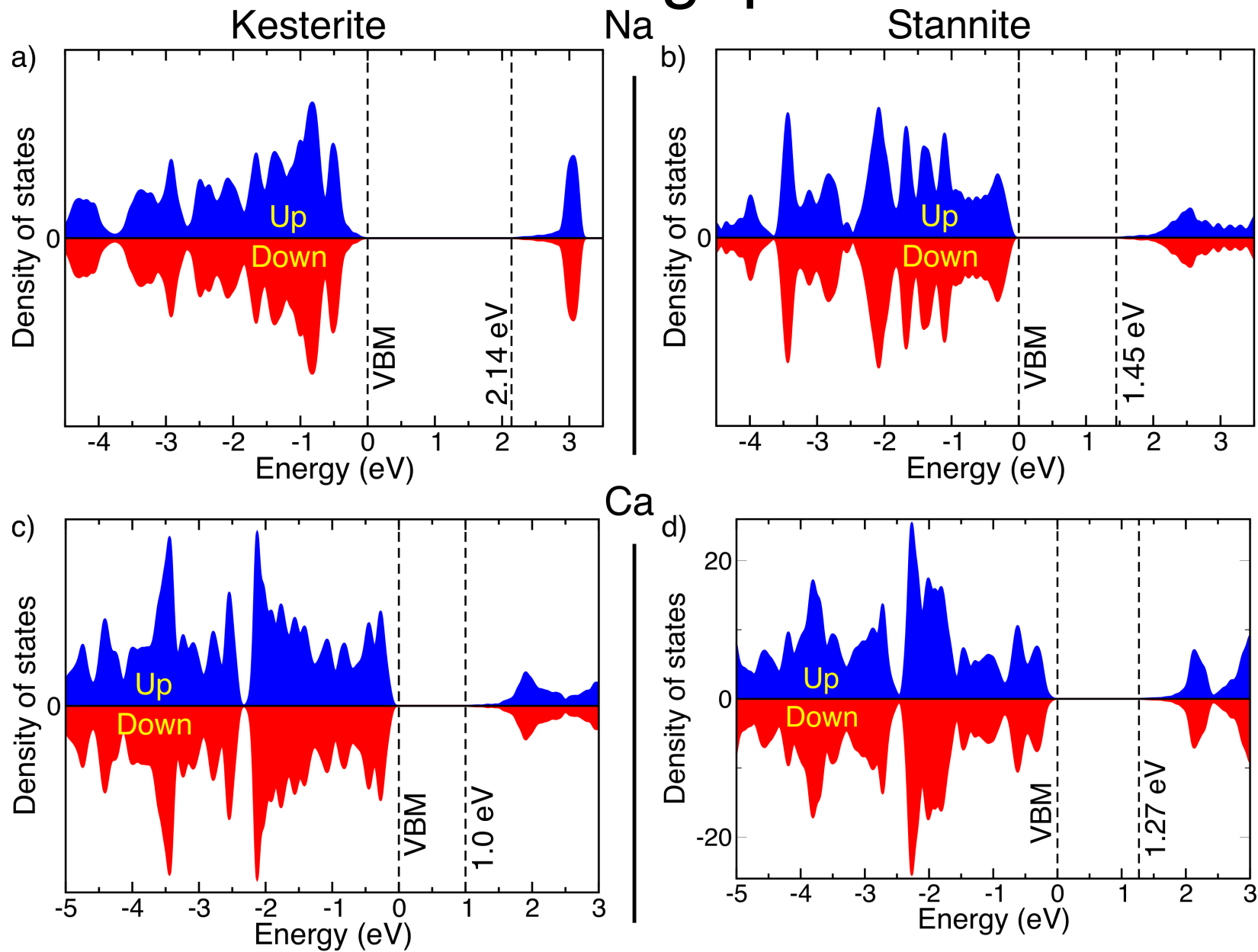- Na-doping should lead to Na-rich and Na-poor domains

Cu_2CaSnS_4 is thermodynamically unstable
- High levels of Ca-doping should result in decomposition of kesterite structure (Cu_2SnS_3+CaS)

Note: SCAN-calculations

Na/Ca increases band gap

Kesterite   Na   Stannite

a) Density of states — Up / Down — VBM, 2.14 eV — Energy (eV)

b) Density of states — Up / Down — VBM, 1.45 eV — Energy (eV)

Ca

c) Density of states — Up / Down — VBM, 1.0 eV — Energy (eV)
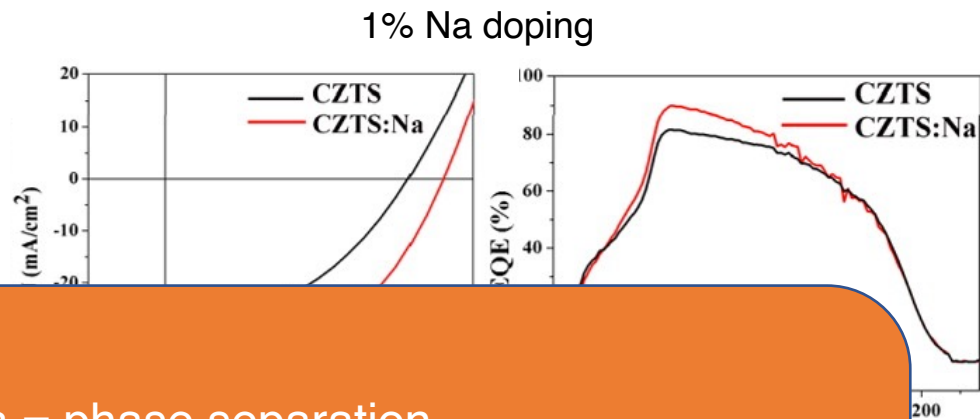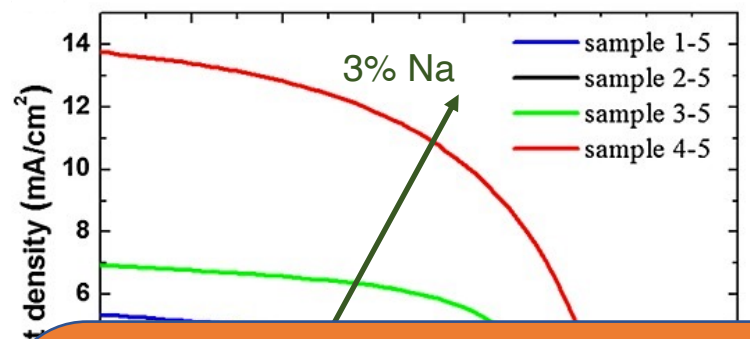
d) Density of states — Up / Down — VBM, 1.27 eV — Energy (eV)
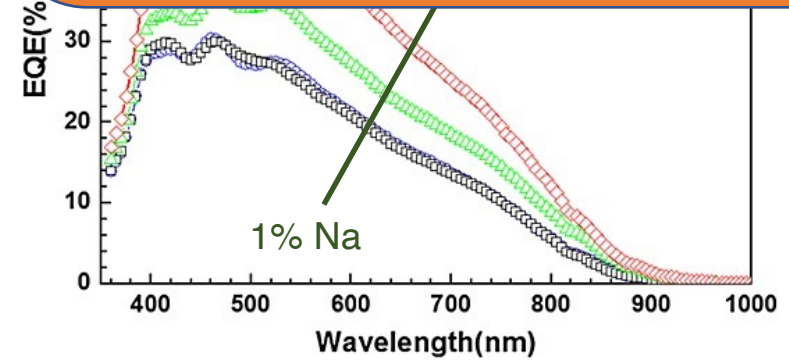
GGA+*U* gap, pure kesterite: **0.96 eV**   GGA+*U* gap, pure stannite: **0.79** eV

Na-doping indeed improves efficiency

3% Na

1% Na doping

- Na: low Na = low disorder, high Na = phase separation
  - Low Na-doping should be beneficial

- Ca: low Ca = low disorder; high Ca = instability
  - Low Ca, if feasible, will be beneficial

1% Na

No evidence of Ca-doping improving performance in CZTS cells, experimentally

K-J Yang et al., *Prog. Photovolt: Res. Appl.* **23**, 862 (2015)

Na-doping indeed improves efficiency
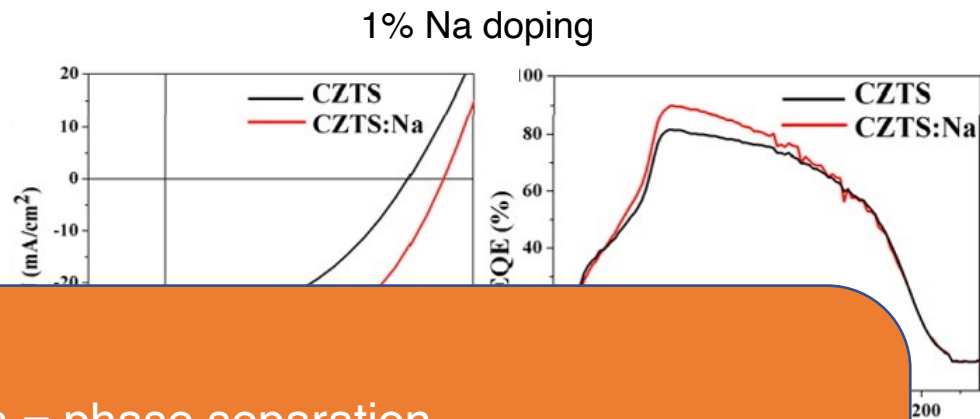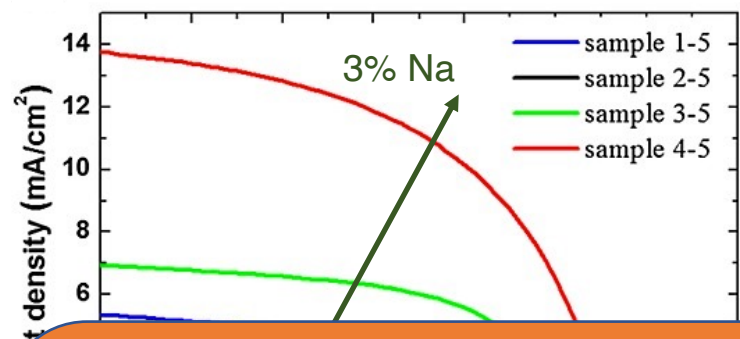

1% Na doping

- Na: low Na = low disorder, high Na = phase separation
  - Low Na-doping should be beneficial

- Ca: low Ca = low disorder; high Ca = instability
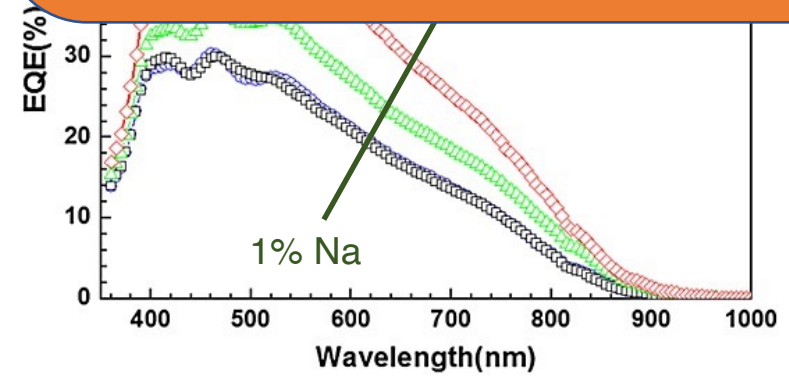 - Low Ca, if feasible, will be beneficial

No evidence of Ca-doping improving performance in CZTS cells, experimentally

K-J Yang et al., *Prog. Photovolt: Res. Appl.* **23**, 862 (2015)

Summary

- Despite being a promising semiconductor for PVs, CZTS solar cells suffer from poor efficiencies
  - Attributed to detrimental disorder-inducing antisites; may be suppressed by isovalent doping

- Dopants influence multiple quantities
  - Defect formation, bulk stability and electronic structure

- Low Cd = Less disorder; High Cd = More disorder
  - Explains "peak" efficiencies observed in experiments

- Low Ag = More disorder with less Cu; High Ag = Less disorder
  - High Ag stabilizes kesterite; but also increases band gap of kesterite
  - Ag-doping may also exhibit "peak" efficiencies

- Low Na = Less disorder; High Na = phase separation
  - Low Na will be beneficial in improving efficiencies

- Low Ca = Less disorder; High Ca = Instability
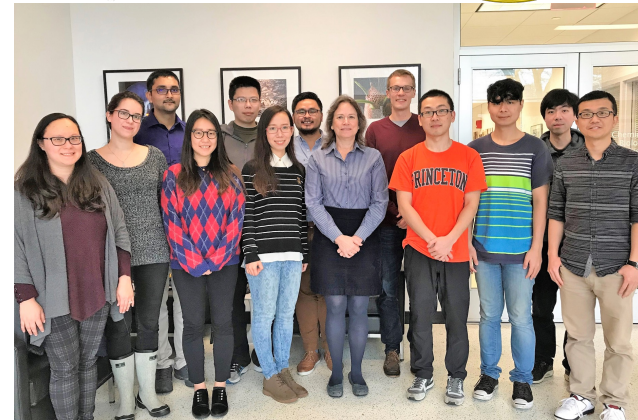 - Low Ca, if possible, will improve performance

Search for other *feasible* and *better* dopants will be useful
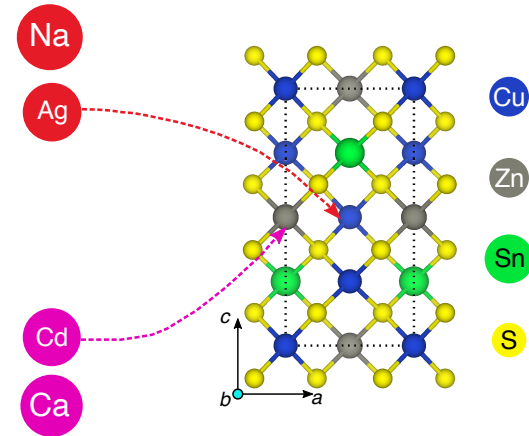
Acknowledgments

Prof. Emily A. Carter

Prof. Thomas P. Senftle

Dr. Kuang Yu
Samuel Berman

TIGER   TIGER

"Novel solar cell materials: insights from first-principles", G.S. Gautam, T.P. Senftle, N. Alidoust and E.A. Carter, *J. Phys. Chem. C* **2018** (Article ASAP)

"Understanding the effects of Cd and Ag doping in Cu_2ZnSnS_4 solar cells", G.S. Gautam, T.P. Senftle and E.A. Carter, *Chem. Mater.* **2018**, *30*, 4543-4555

"Role of Na and Ca as isovalent dopants in Cu_2ZnSnS_4 solar cells", S. Berman, G.S. Gautam, and E.A. Carter, *under review*

"Elucidating structural disorder and the effects of Cu vacancies on the electronic properties of Cu_2ZnSnS_4", K. Yu and E.A. Carter, *Chem. Mater.* **2016**, 28, 864-869

gautam91@princeton.edu