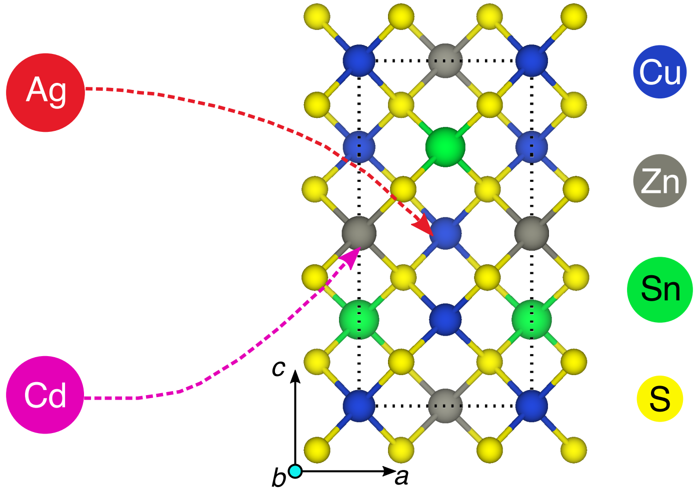

Effects of Cd and Ag doping in Cu_2ZnSnS_4 solar cells

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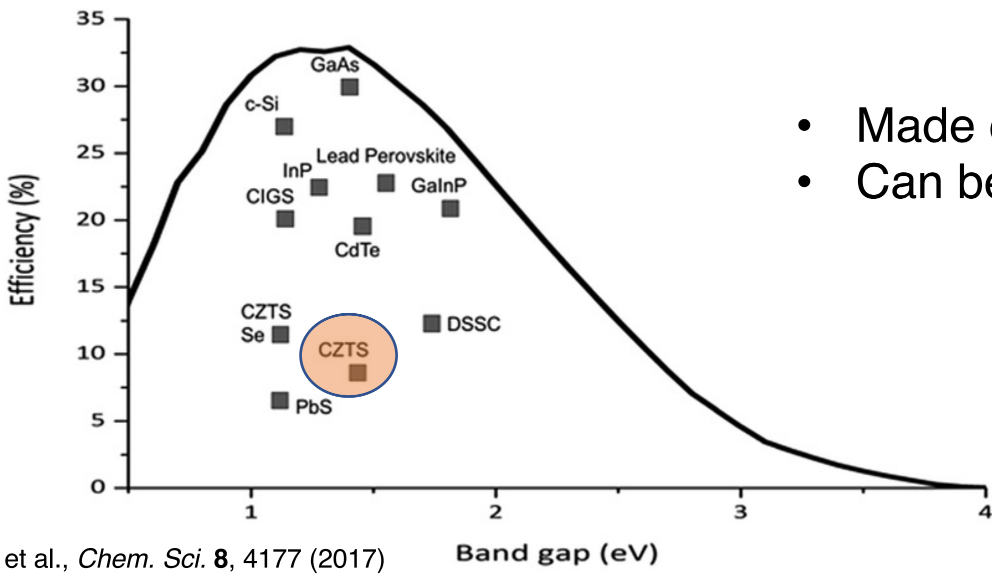
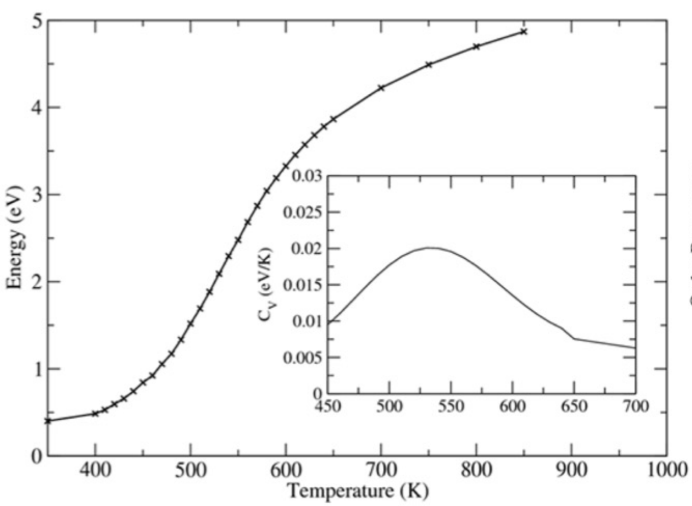
Symposium C4: Photovoltaics, solar energy materials and technologies
XXVII International Materials Research Congress
Aug 21, 2018

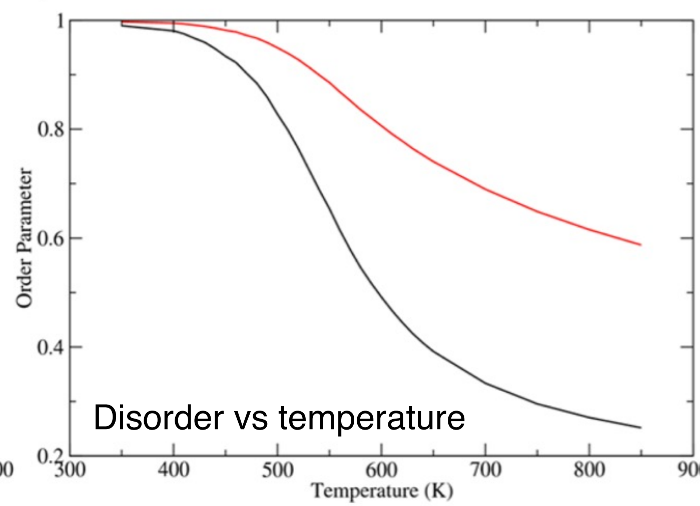
Cu_2ZnSnS_4 (CZTS) is a promising candidate for beyond-Si solar cells



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

- Made of abundant elements
- Can be synthesized through wet-chemistry



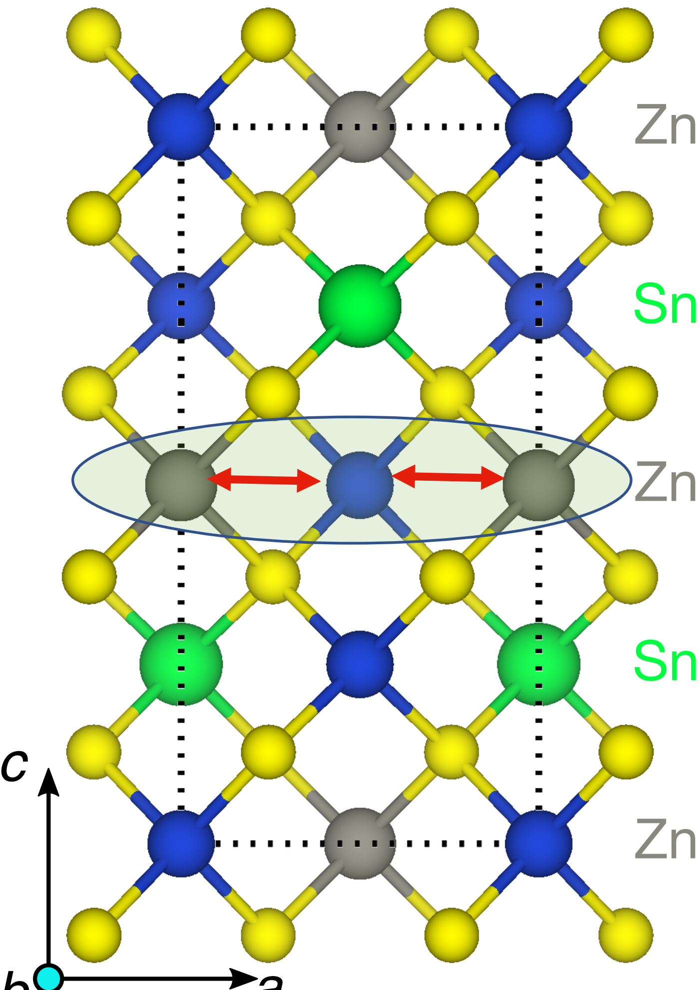


Often suffers from low efficiencies (~12%)

- Si is > 20%
- Due to disorder in Cu-Zn sub-lattice

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

Disorder ≡ Antisites ≡ Defects

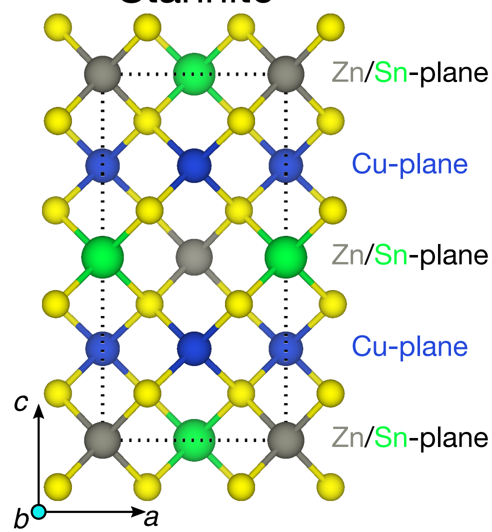


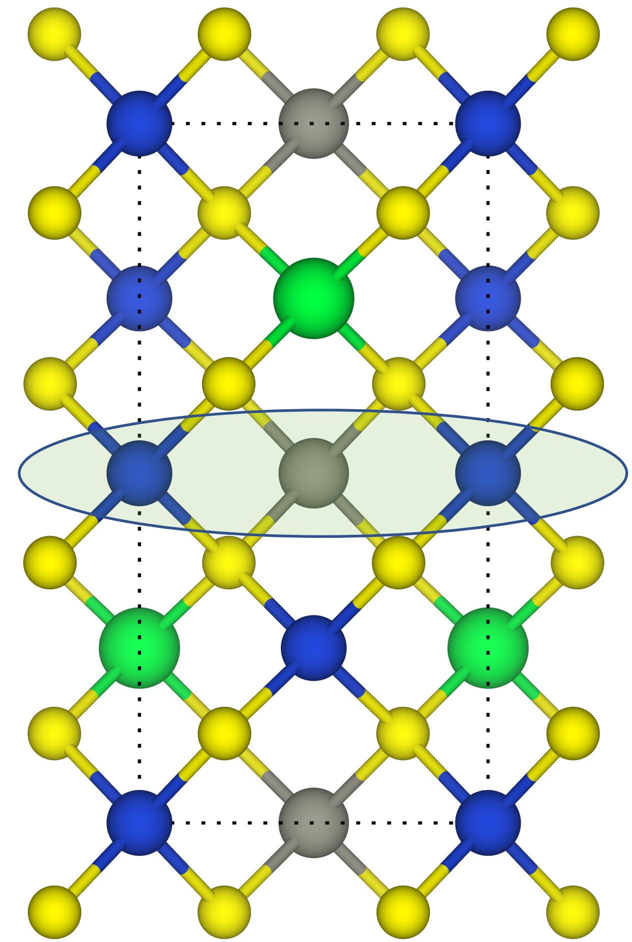
Kesterite

Anti-site formation

$Cu_{Zn} + Zn_{Cu}$

Stannite





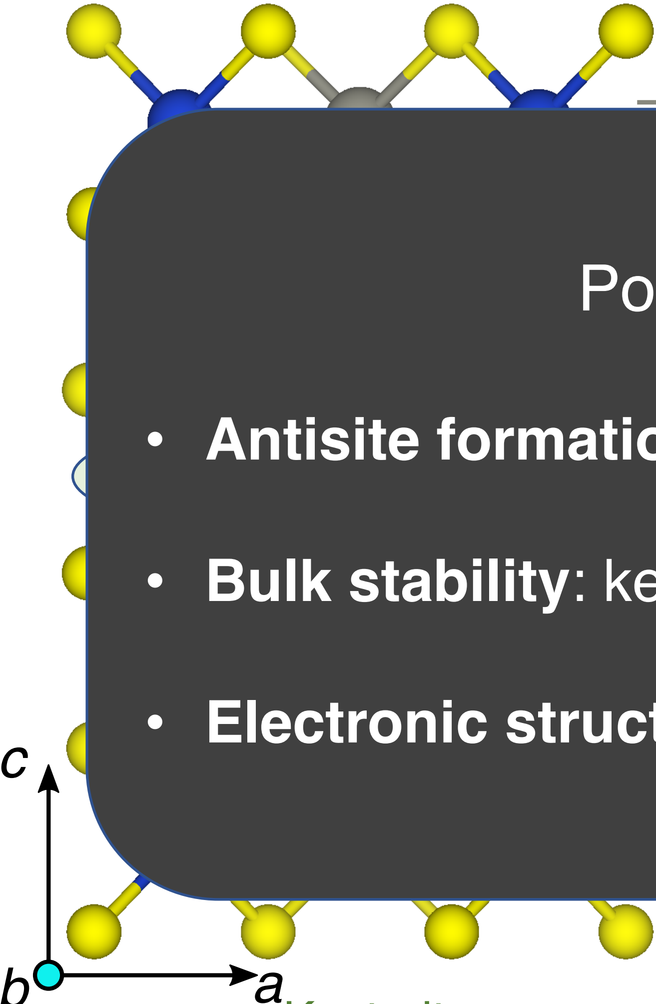
Disordered-Kesterite

Cu-Zn: similar atomic radii

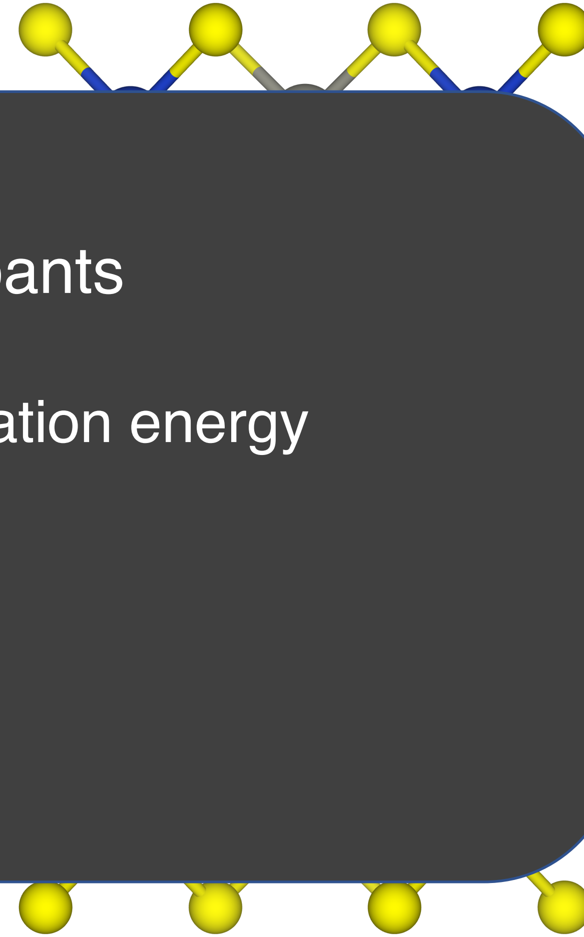
Kesterite-Stannite near degeneracy

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

Disorder ≡ Antisites ≡ Defects



Kesterite



Disordered-Kesterite

Potential impacts of dopants

- **Antisite formation**: change defect formation energy
- **Bulk stability**: kesterite vs. stannite
- **Electronic structure**: change band gap

Can doping reduce the occurrence of **disorder-inducing antisites**?

- **Large isovalent** dopants?
  - Cd for Zn; Ag for Cu

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

Methods

How do we evaluate the influence of dopants?

Density functional theory for defects

For "charged" defects

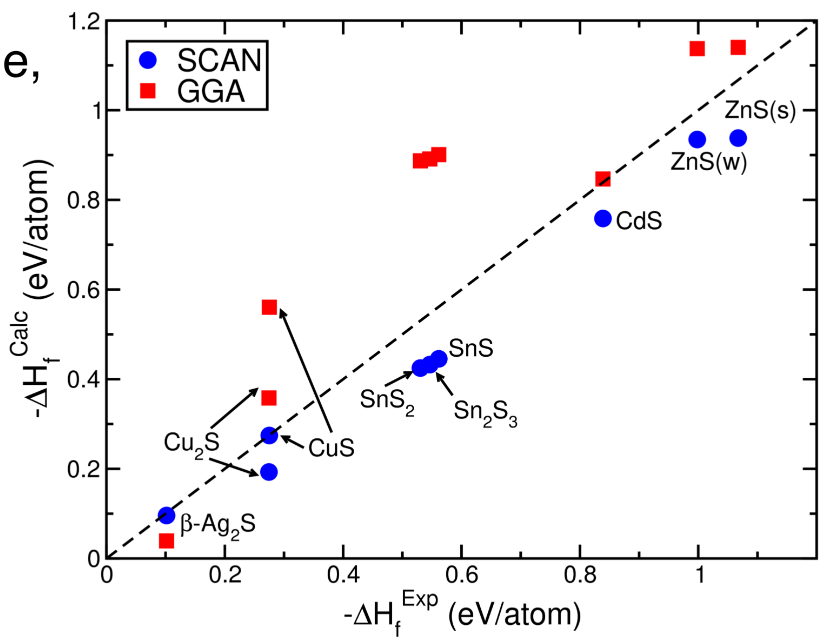
$$E_{disorder} \equiv E^{formation}_{anti-site} = E^{defected}_{bulk} - E^{pristine}_{bulk} + \Sigma_i n_i \mu_i + qE_F + E_{corr}$$

Kesterite with anti-sites 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?

For CZTS to be stable,



1. Sun et al., *Phys. Rev. Lett.* **115**, 036402 (2015)

Charged defects: ionized electrons or holes

Density functional theory for defects

For "charged" defects

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

Kesterite with anti-sites

Pure Kesterite

Synthesis/doping/operating conditions

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

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 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

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

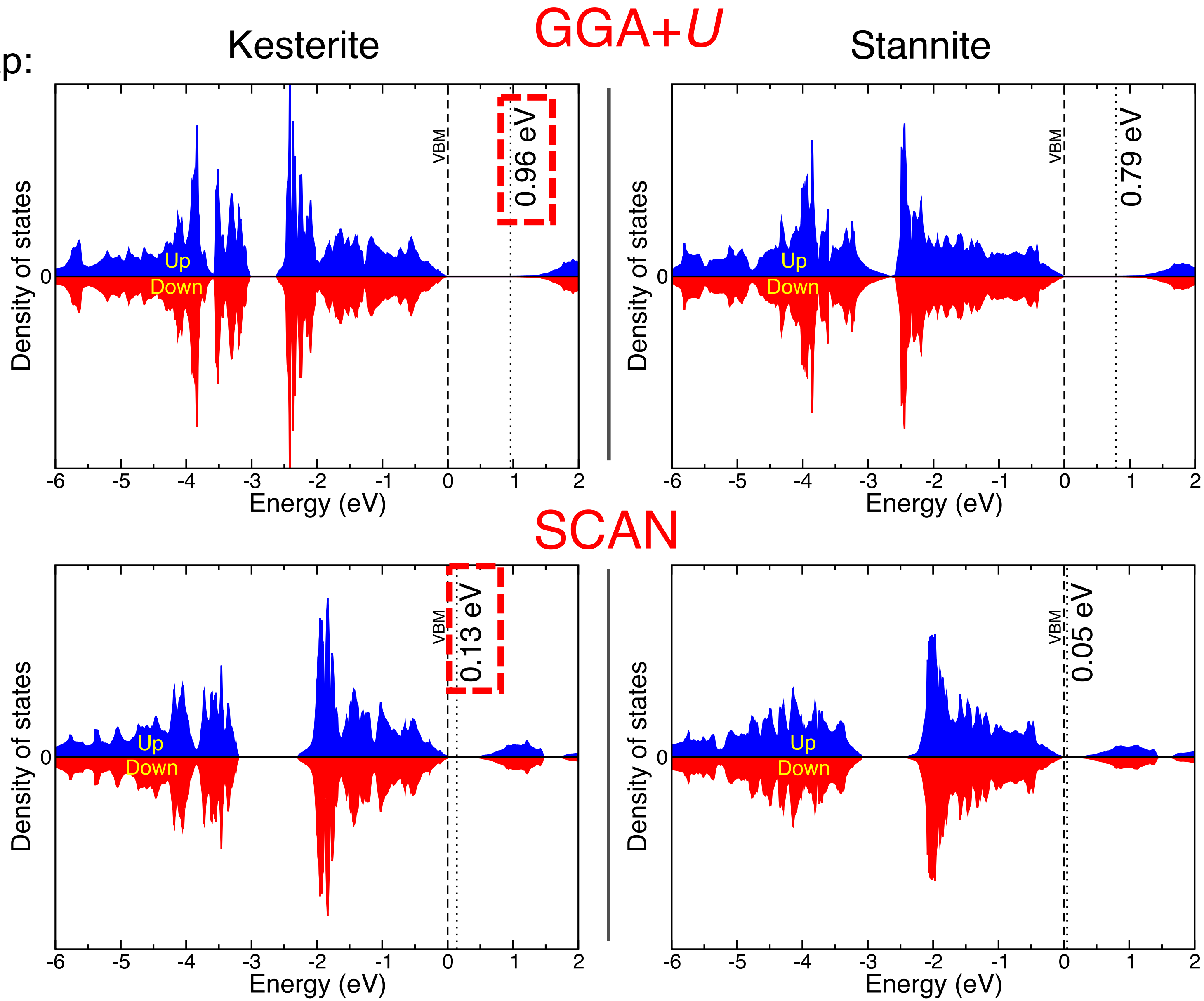
μ_{Ag} or μ_{Cd} chosen as the maximum possible value at all 3 conditions, provided CZTS is stable

Charged defects: ionized electrons or holes

1. Sun et al., *Phys. Rev. Lett.* **115**, 036402 (2015)

SCAN does have the “band-gap” problem

scGW gap: 1.64 eV
Exp: ~1.5 eV



scGW gap: 1.33 eV
Exp: ~1.3 eV

GW gap: Botti *et al.*, **Appl. Phys. Lett. 2011**, 98, 241915

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

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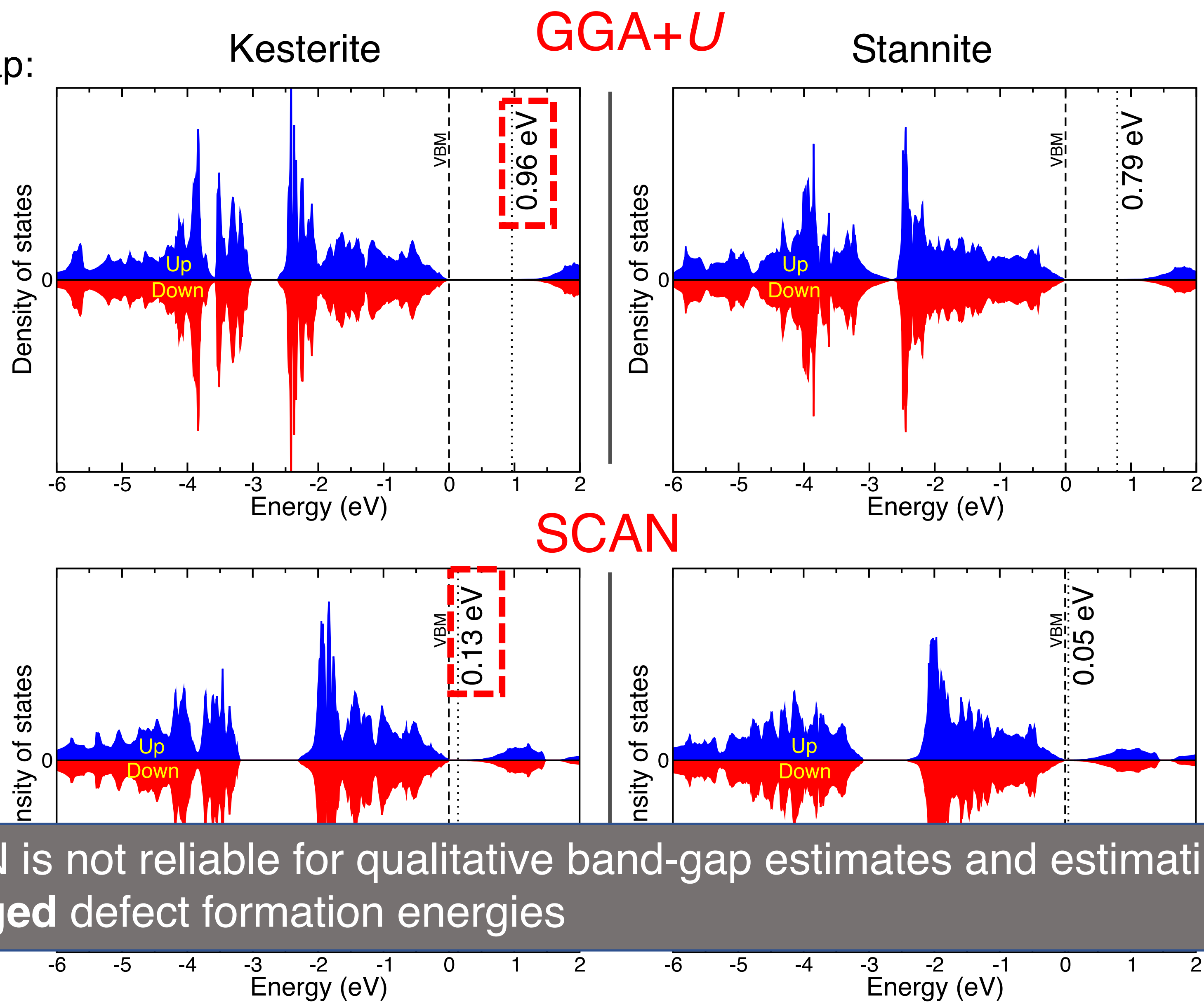


scGW gap: 1.33 eV
Exp: ~1.3 eV

SCAN is not reliable for qualitative band-gap estimates and estimating **charged** defect formation energies

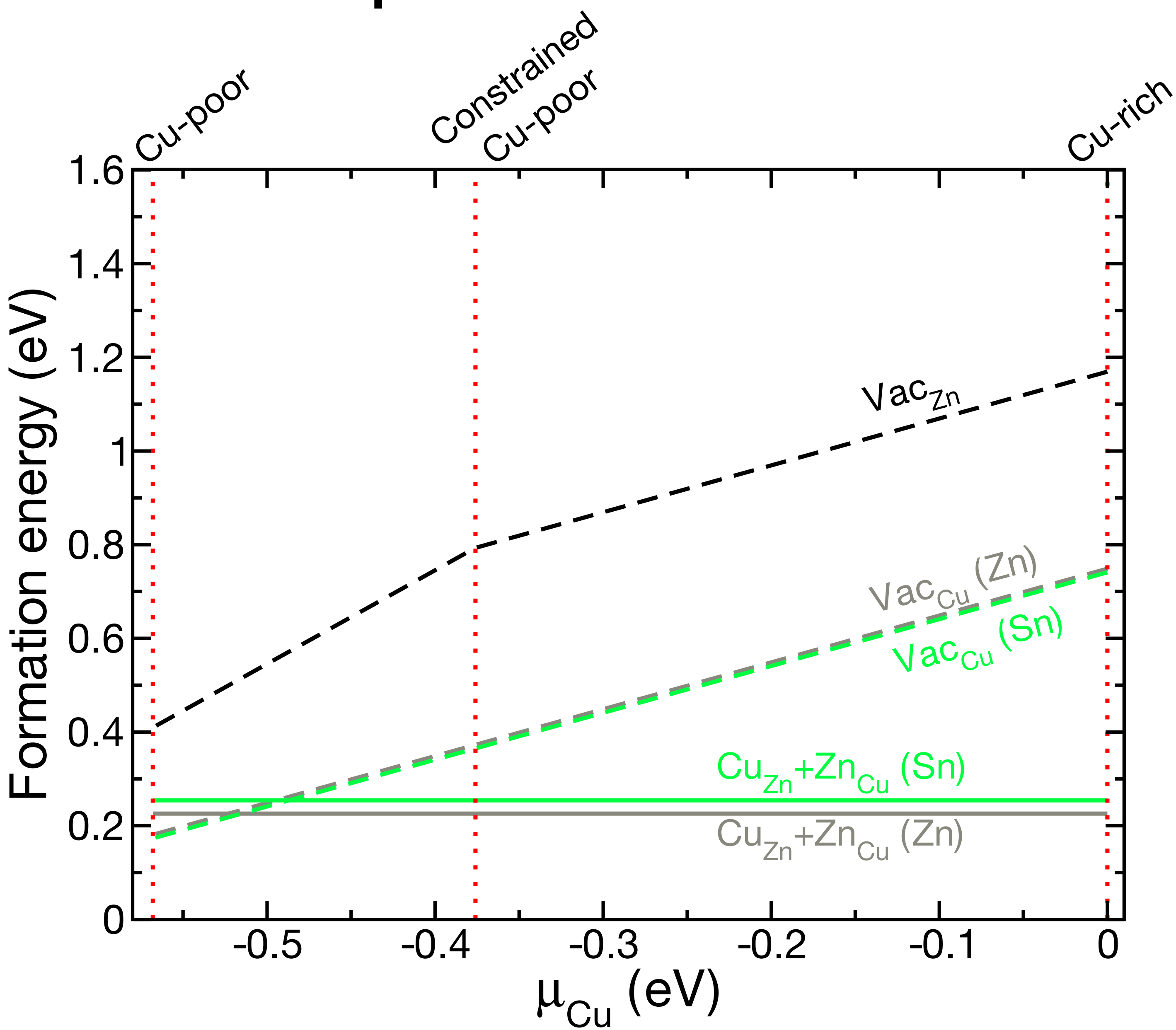
GW gap: Botti *et al.*, **Appl. Phys. Lett. 2011**, 98, 241915

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

How do Cd- or Ag- influence CZTS?

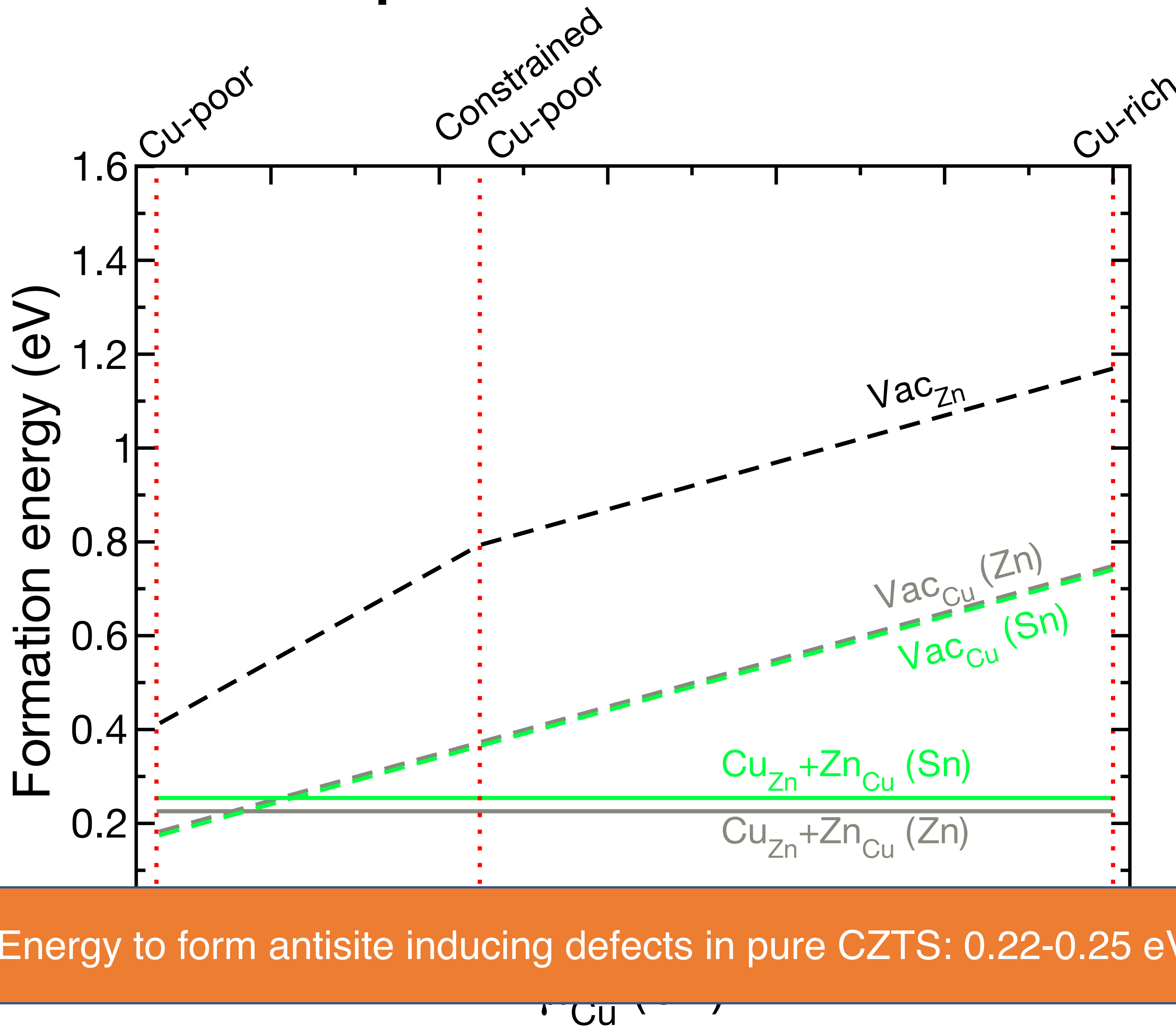
Results from defect formation and surface energetics

Pure CZTS expected to show disorder



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

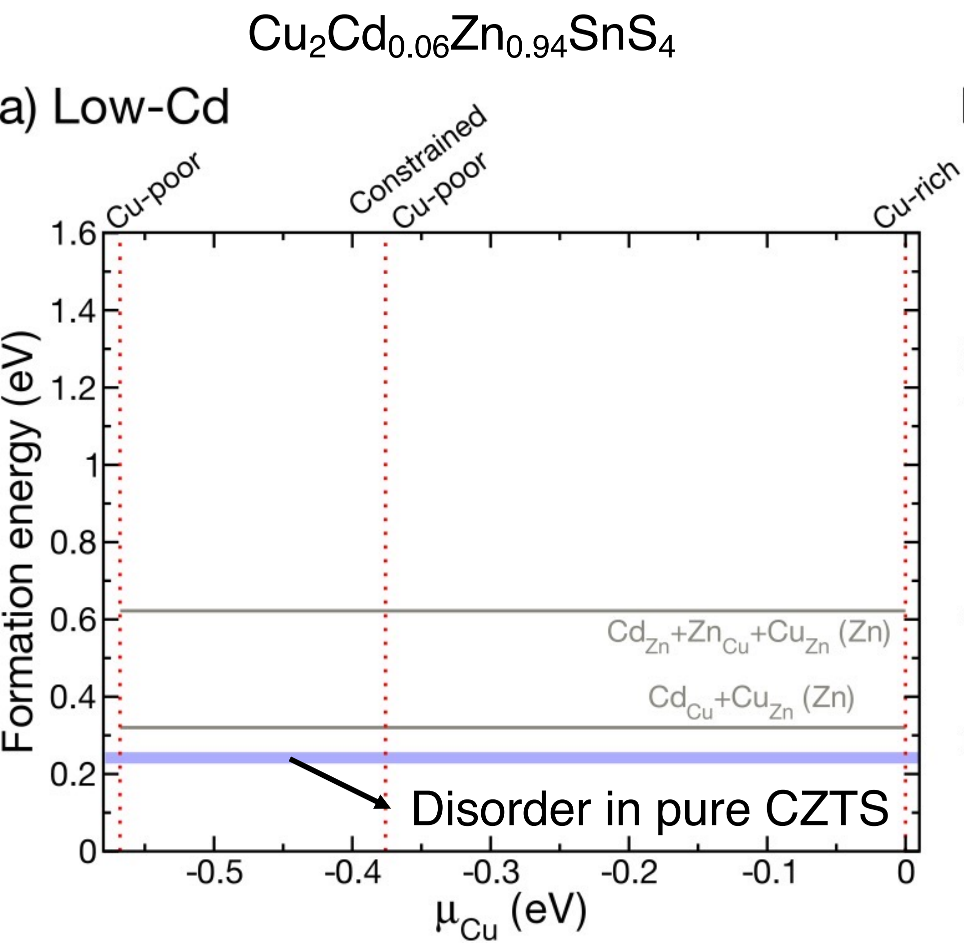
Pure CZTS expected to show disorder

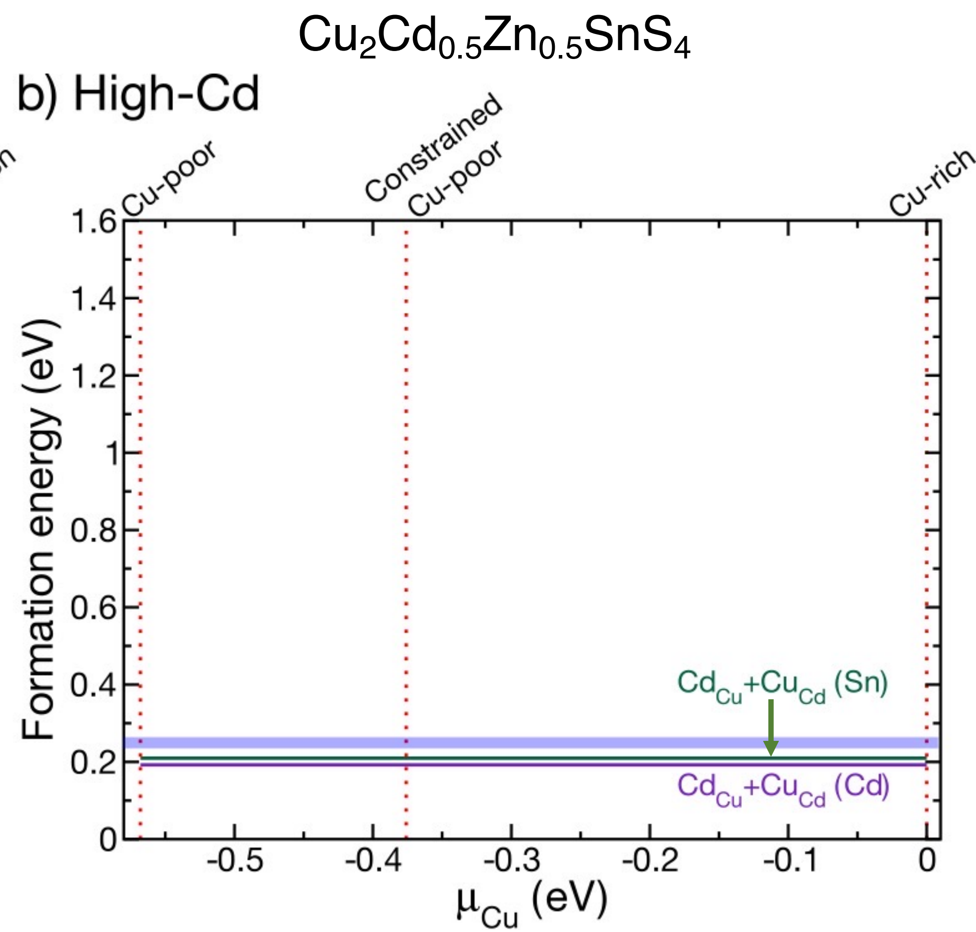


Energy to form antisite inducing defects in pure CZTS: 0.22-0.25 eV

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

Low Cd-doping = less disorder

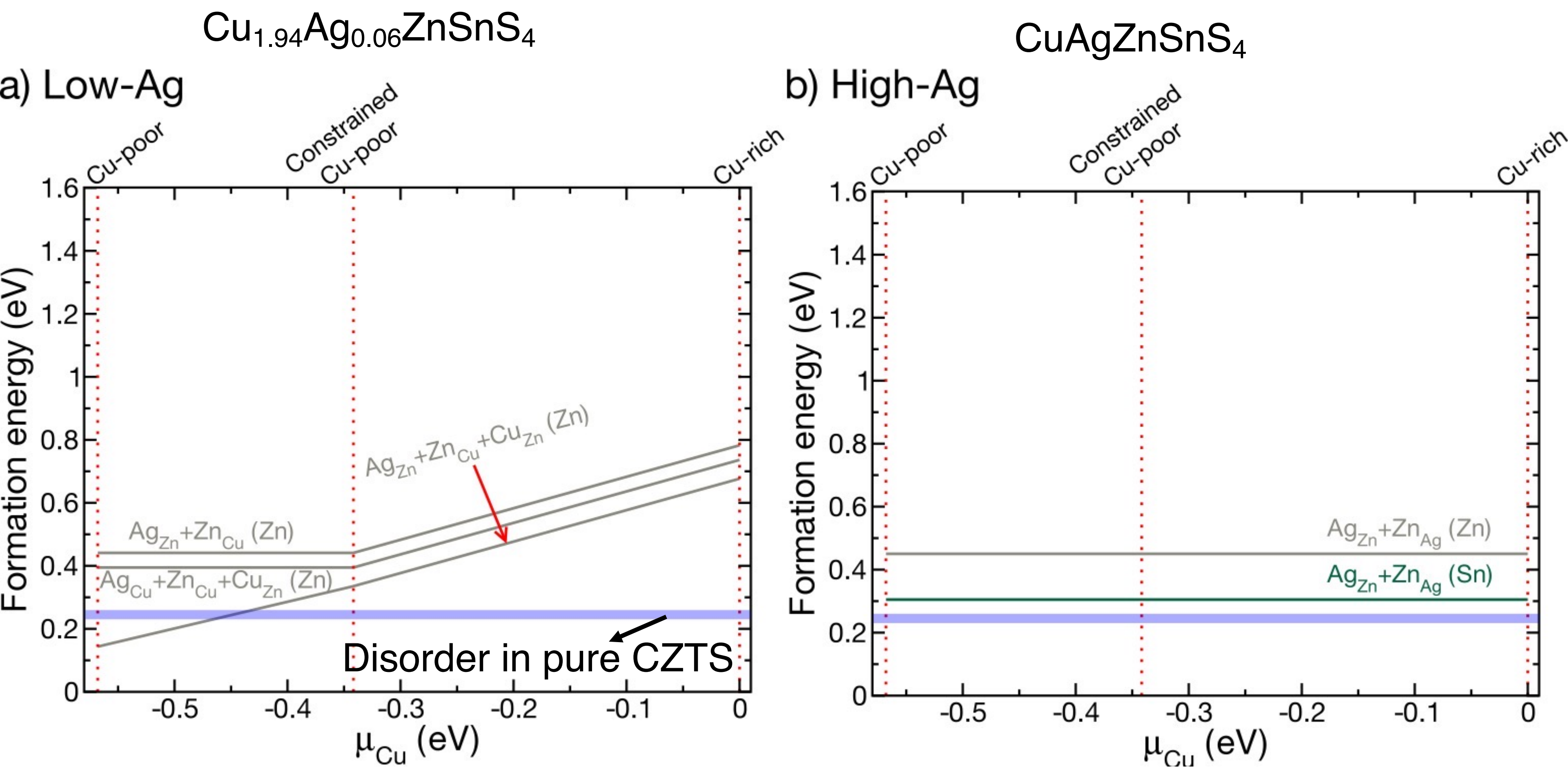




Energy to disorder higher at low Cd-doping

Note: SCAN-calculations

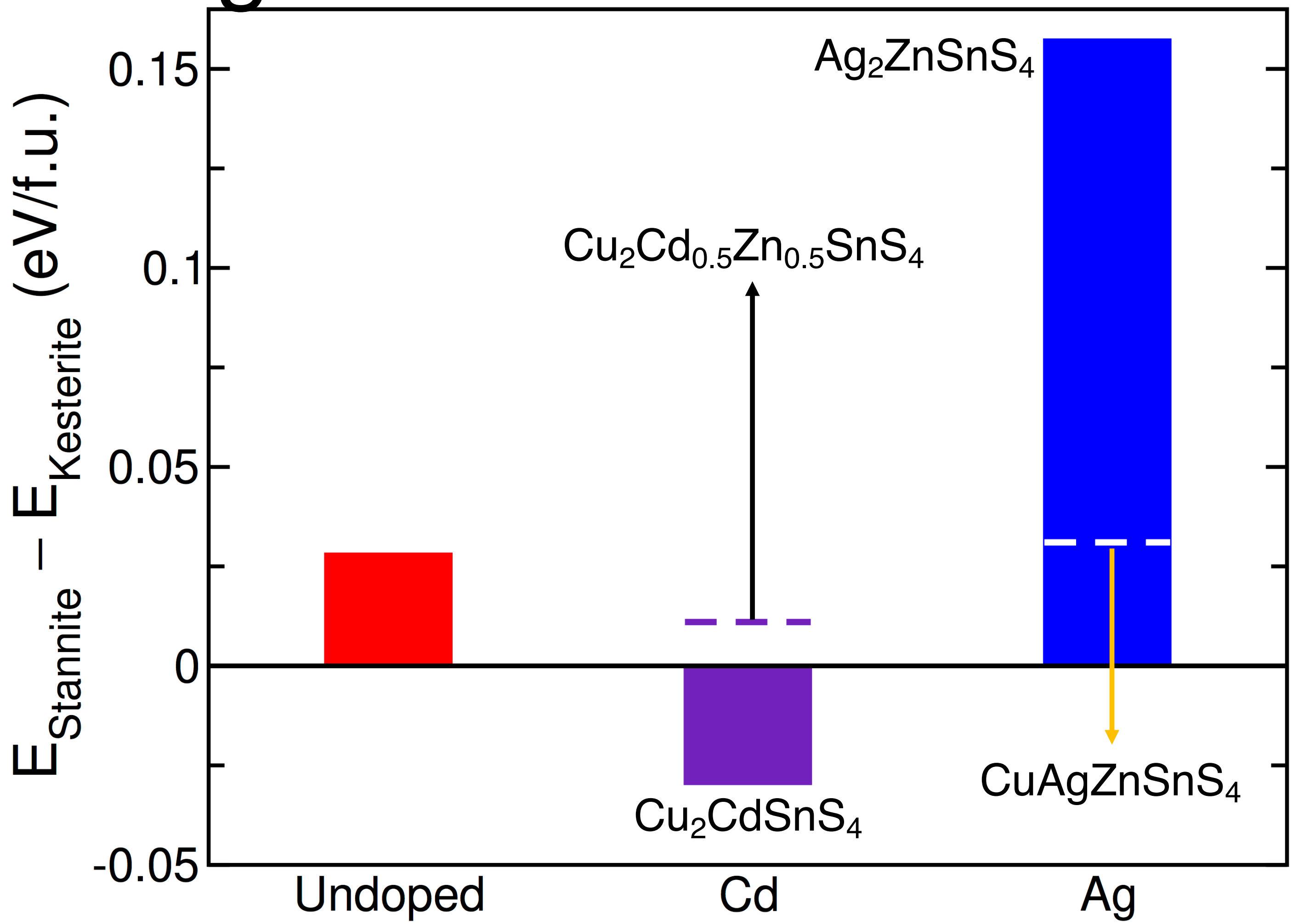
Low Ag-doping = less disorder*

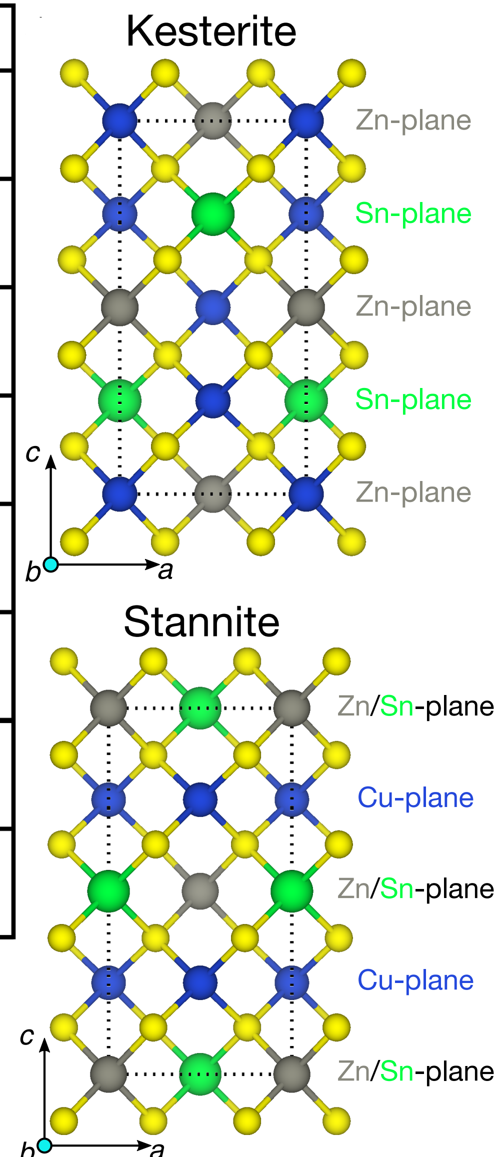


*Low Ag-doping only beneficial at constrained Cu-poor (Zn+Sn rich) to Cu-rich conditions
High Ag-doping should generally be beneficial in suppressing anti-sites

Note: SCAN-calculations

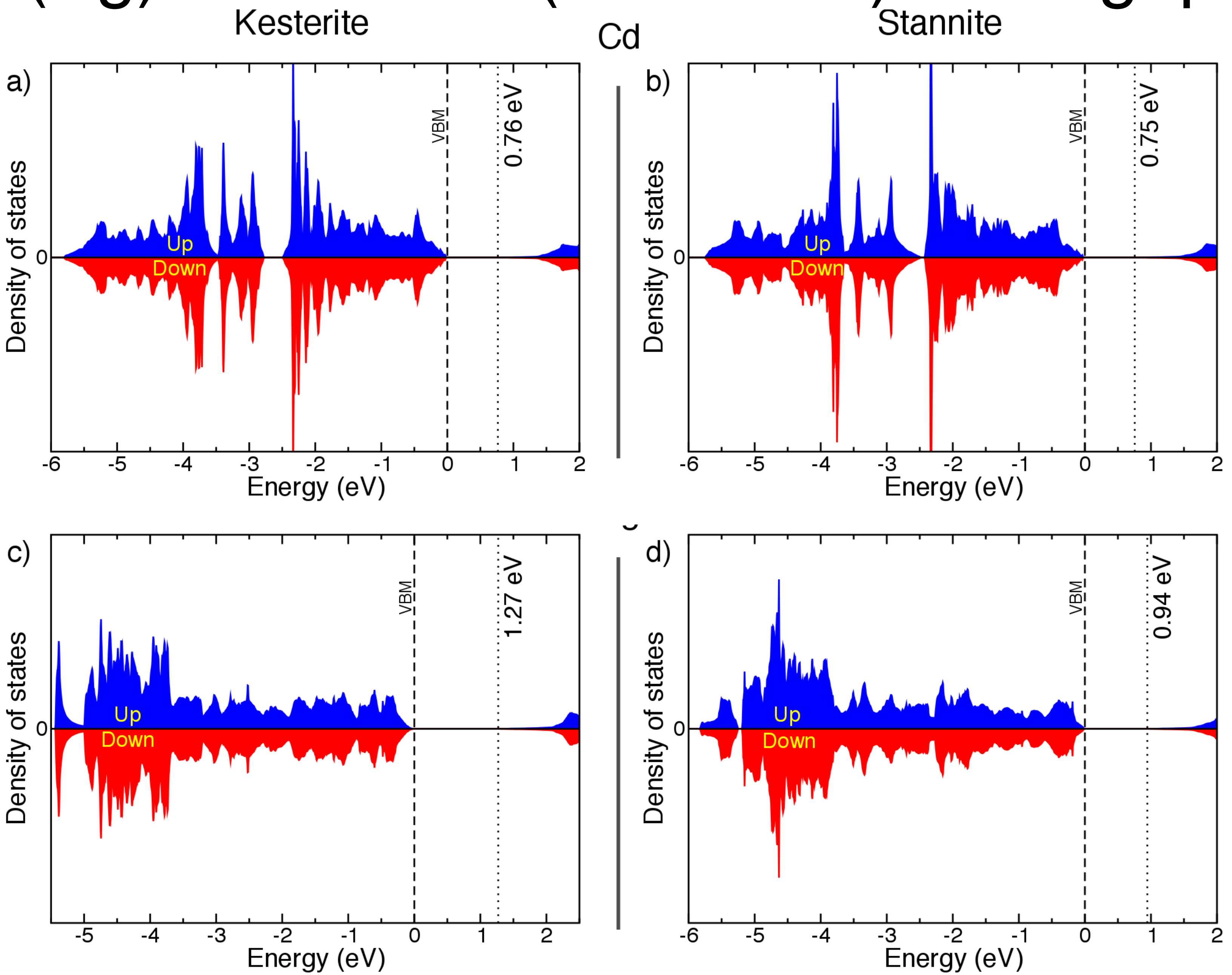
High Ag stabilizes kesterite
High Cd stabilizes stannite





Note: SCAN-calculations

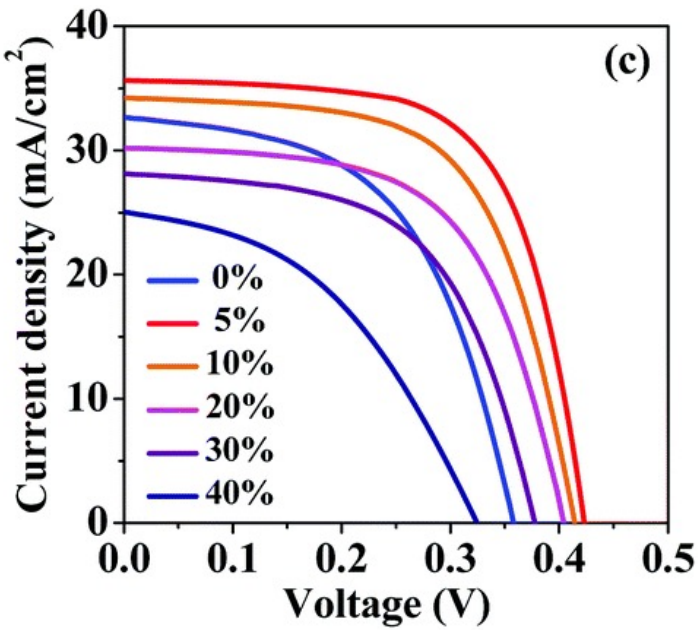
Cd (Ag) decreases (increases) band-gap

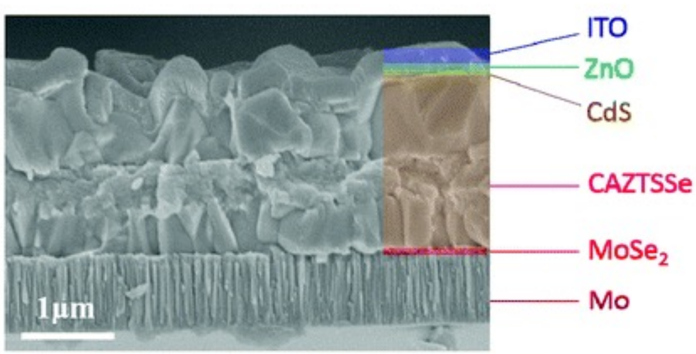


GGA+*U* gap, pure kesterite: **0.96 eV** GGA+*U* gap, pure stannite: **0.79** eV

Isovalent doping in kesterite: experiments report improved performance

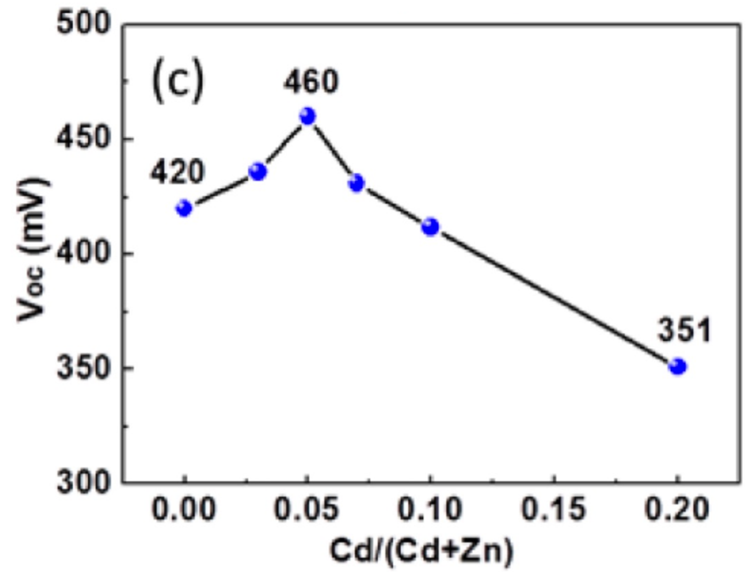
Ag_{Cu}

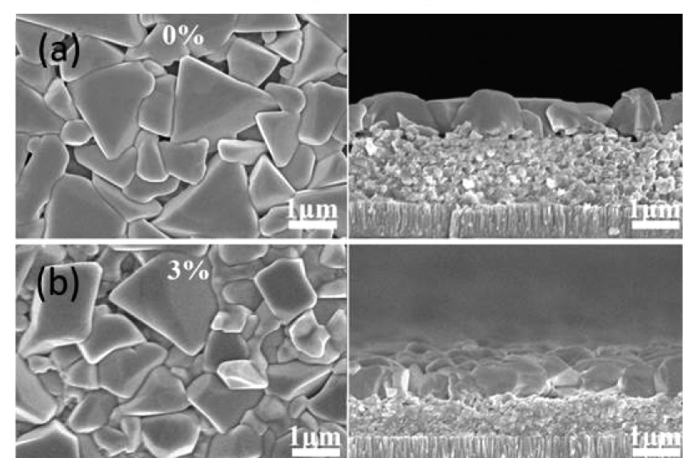




Qi et al., *Energy Environ. Sci.* **10**, 2401 (2017)

Cd_{Zn}





Fu et al., *Chem. Mater.* **28**, 5821 (2016)

Isovalent doping in kesterite:
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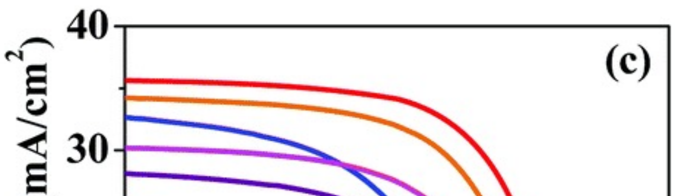
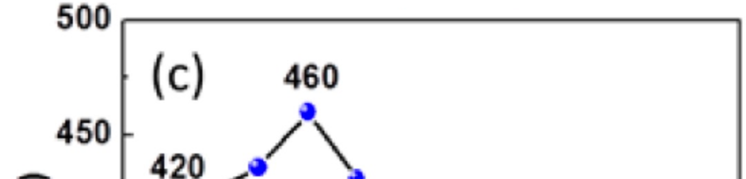
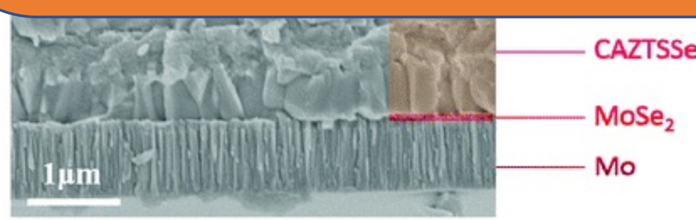


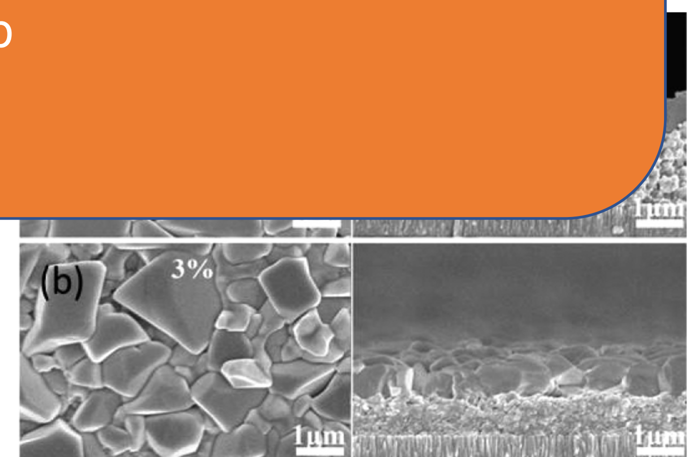
Cd_{Zn}



- 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



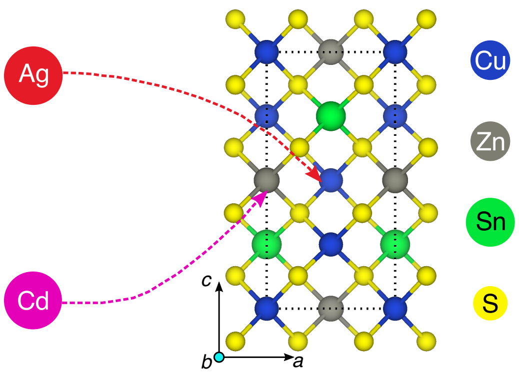


Qi et al., *Energy Environ. Sci.* **10**, 2401 (2017)

Fu et al., *Chem. Mater.* **28**, 5821 (2016)

Summary

- Despite being a promising semiconductor for PVs, CZTS solar cells suffer from poor efficiencies
  - Attributed to detrimental disorder-inducing antisites
  - Antisites may be suppressed with isovalent doping (Cd for Zn and Ag for Cu)
- Dopants influence multiple quantities
  - Defect formation, bulk stability and electronic structure
  - Use density functional theory to evaluate
- Low Cd = Less disorder; High Cd = More disorder
  - High Cd stabilizes stannite
  - Explains “peak” efficiencies observed in experiments

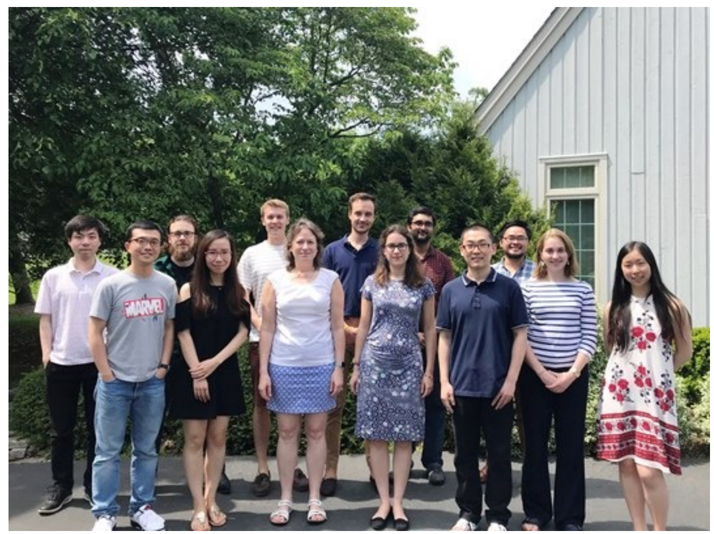


- Low Ag = More disorder with less Cu; High Ag = Less disorder
  - High Ag stabilizes kesterite; but also increases band-gap of kesterite
  - Ag-doping may also exhibit “peak” efficiencies
- Alternate dopants? Ag is rare and Cd is toxic

Acknowledgments

Prof. Thomas P. Senftle

Prof. Emily A. Carter



"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