Optoelectronic & Mechanical Properties of $Cu_2CdGe(S_xSe_{1-x})_4$ via First Principles

Dr. Sanjay V. Khare

(http://astro1.panet.utoledo.edu/~khare/index.html)

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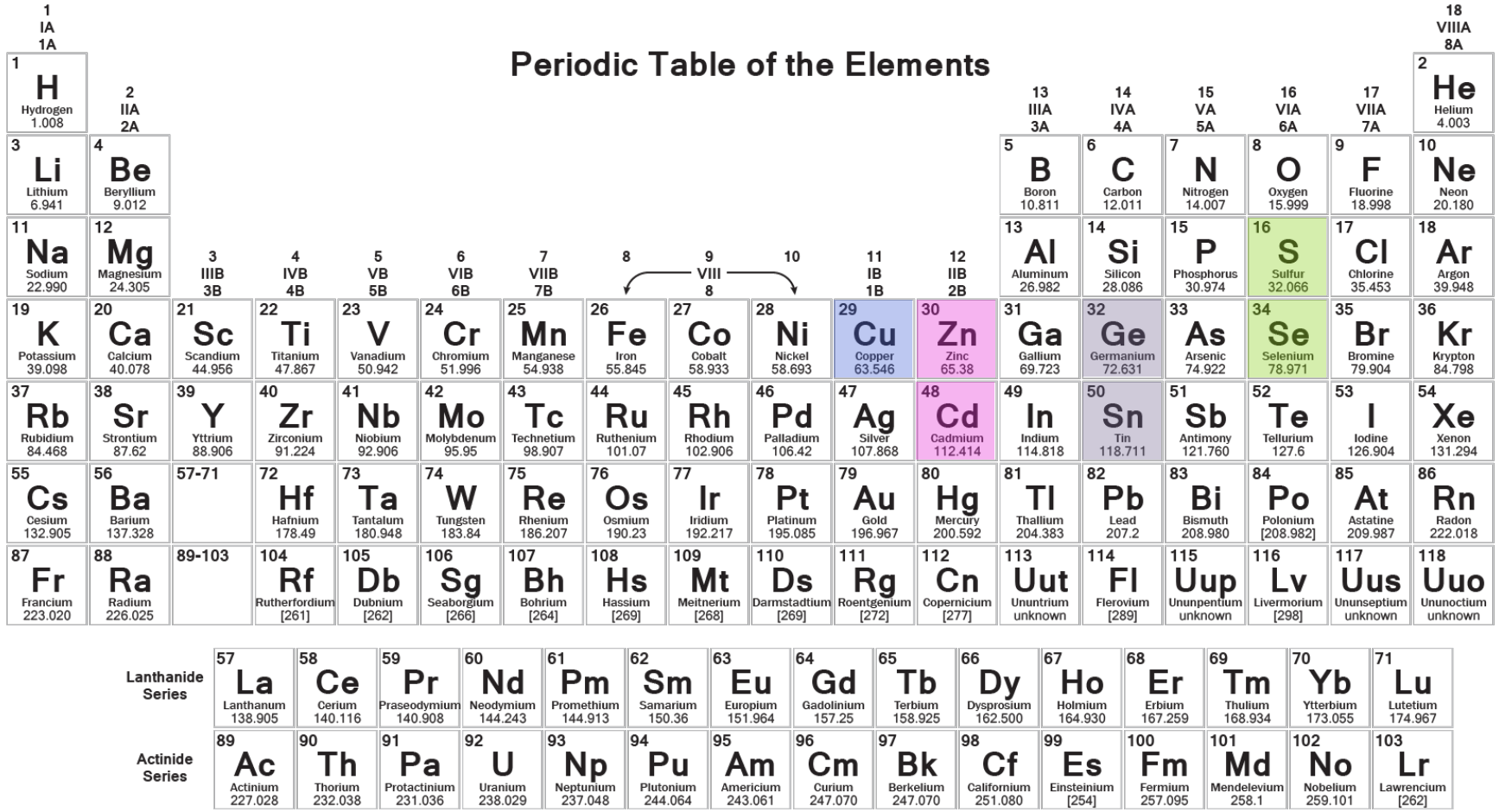
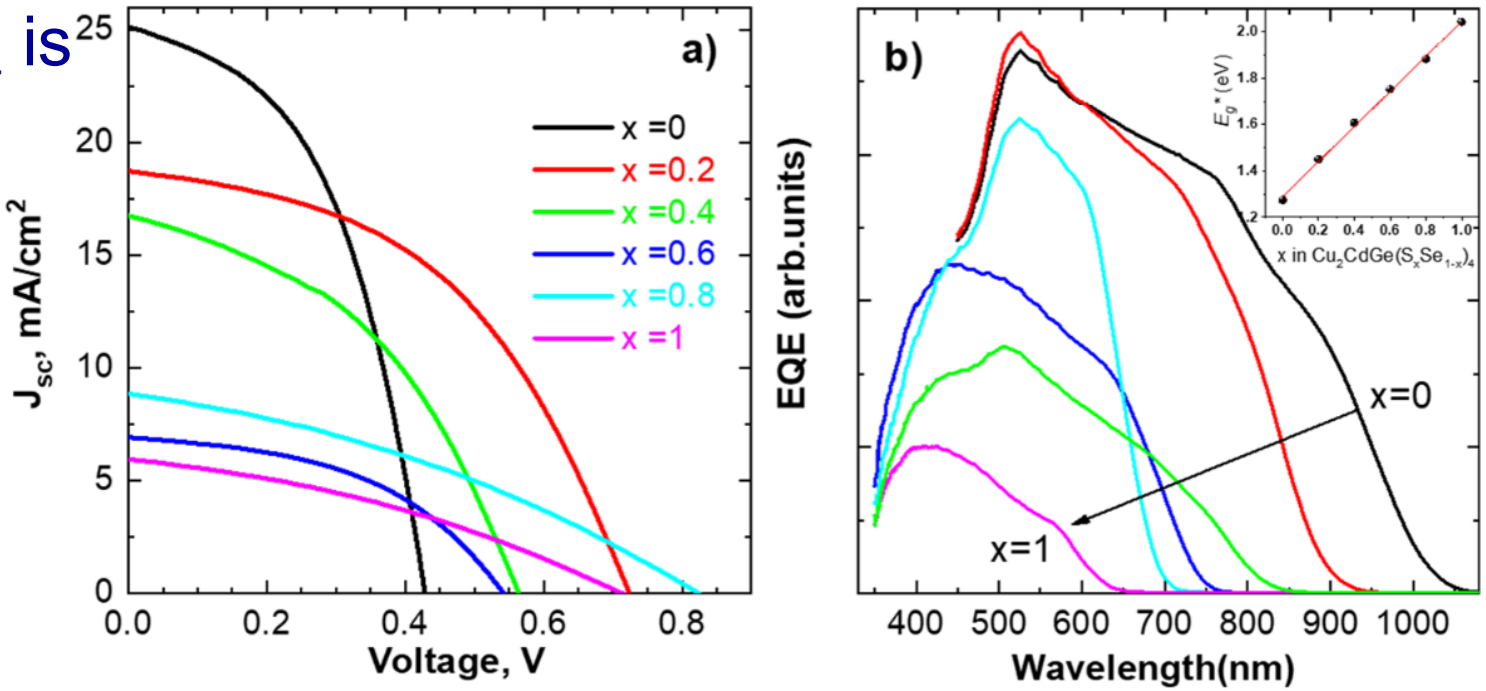
Background: Cu_2-Zn-Sn-S Semiconductors

- Currently Si, CdTe, GaAs, Cu(In, Ga)Se_2 dominate PV market
- Perovskites: Use Pb, which is toxic; unstable
- Replacements motivated by:
  - In, Ga rare elements – expensive
  - Cd toxic
- Most successful replacement class: $Cu_2ZnSn(S_{0.25}Se_{0.75})_4$; power conversion efficiency of 12.6%.
  - Long-standing problems: bulk defects → band tailing, short carrier lifetimes → limit open circuit voltage



Background: $Cu_2CdGeSe_4$ & Cu_2CdGeS_4

- Previous work[1,2,3]: $Cu_2CdGeSe_4$ is promising for PV applications.
- Can be made better through alloying
- Li et al, 2020: First study into $Cu_2CdGe(S_xSe_{1-x})_4$ alloy
  - Experimental study
  - Mostly orthorhombic system
  - Created solar cell devices
- No other studies on intermediate x exist



JV curves and EQE measurements of $Cu_2CdGe(S_xSe_{1-x})_4$ PV devices from Li *et al*[2]

1: M. Kauk-Kuusik, X. Li, M. Pilvet, K. Timmo, M. Grossberg, T. Raadik, M. Danilson, V. Mikli, M. Altosaar, J. Krustok, and J. Raudoja, Thin Solid Films 666, 15 (2018)

2: X. Li, M. Pilvet, K. Timmo, M. Grossberg, V. Mikli, and M. Kauk-Kuusik, Solar Energy 209, 646 (2020)

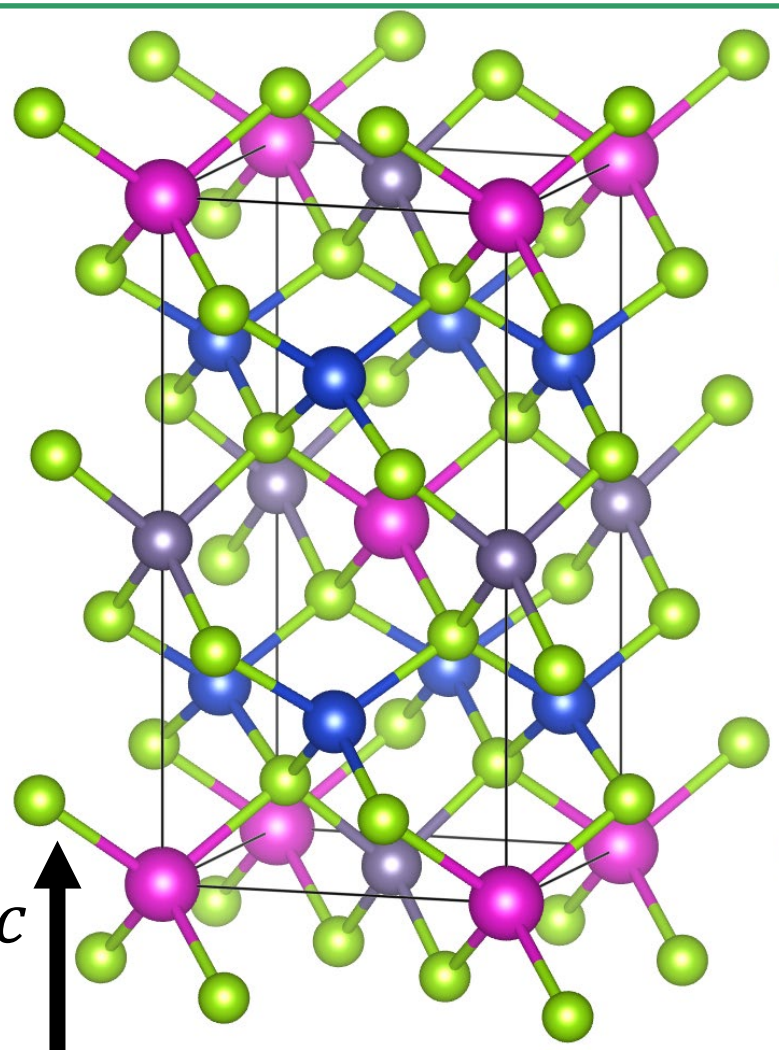
3: M. Grossberg, T. Raadik, J. Krustok, M. Kauk-Kuusik, K. Timmo, R. Kaupmees, V. Mikli, and A. Mere, Thin Solid Films 666, 44 (2018)

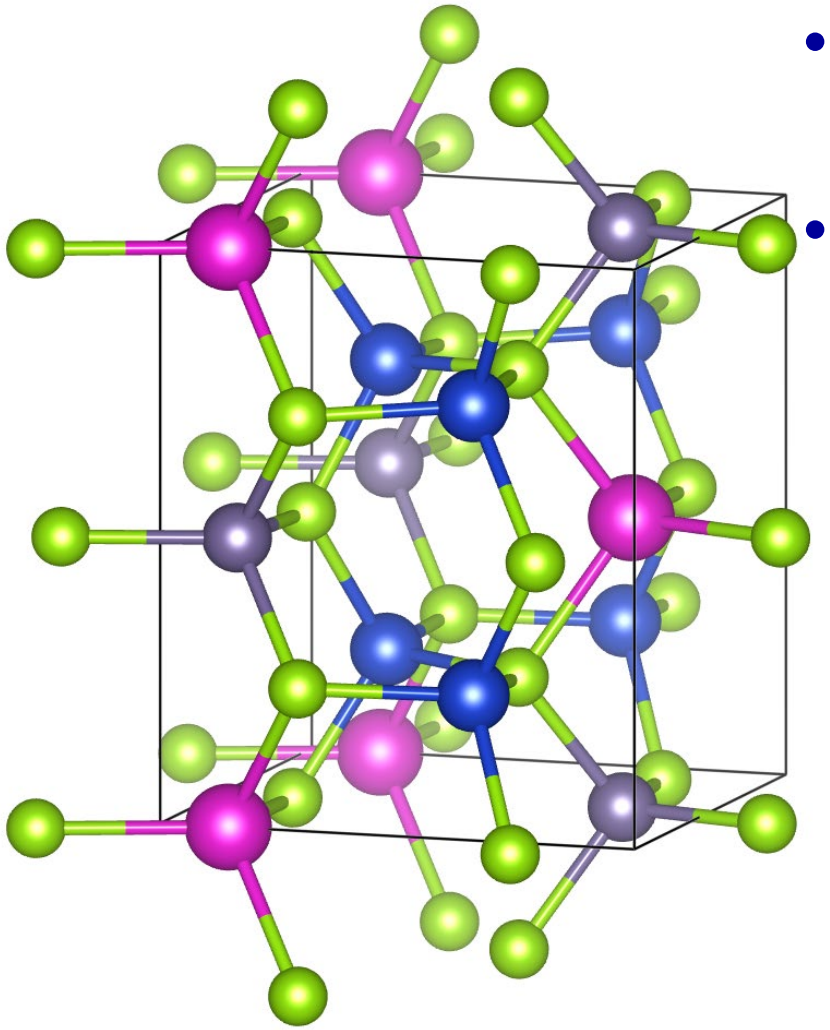
Methods: Density Functional Theory

- DFT+: Vienna Ab Initio Simulation Package (VASP[4])
- Charge analysis: Henkelman Group's[5] Bader Charge Analysis code
- COHP: Local Orbital Basis Suite Towards Electronic-structure Reconstruction (LOBSTER[6])
- Energy-strain method: Elastic properties[7]

4: G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
5: G. Henkelman, A. Arnaldsson, and H. Jónsson, Computational Materials Science 36, 354 (2006)
6: V. L. Deringer, A. L. Tchougréeff, and R. Dronskowski, J. Phys. Chem. A 115, 5461 (2011)
7: V. Adhikari, Z. T. Y. Liu, N. J. Szymanski, I. Khatri, D. Gall, P. Sarin, and S. V. Khare, Journal of Physics and Chemistry of Solids 120, 197 (2018)

Atomic Models: $Cu_2CdGe(S_xSe_{1-x})_4$





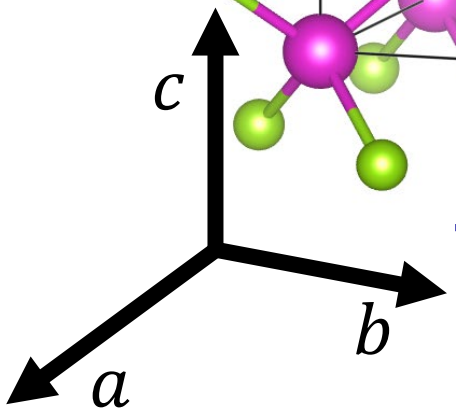
- Number of atoms = 16 = 2 × (formula unit)
- 1×1×1 conventional unit cell

Cu

Cd

Ge

S / Se



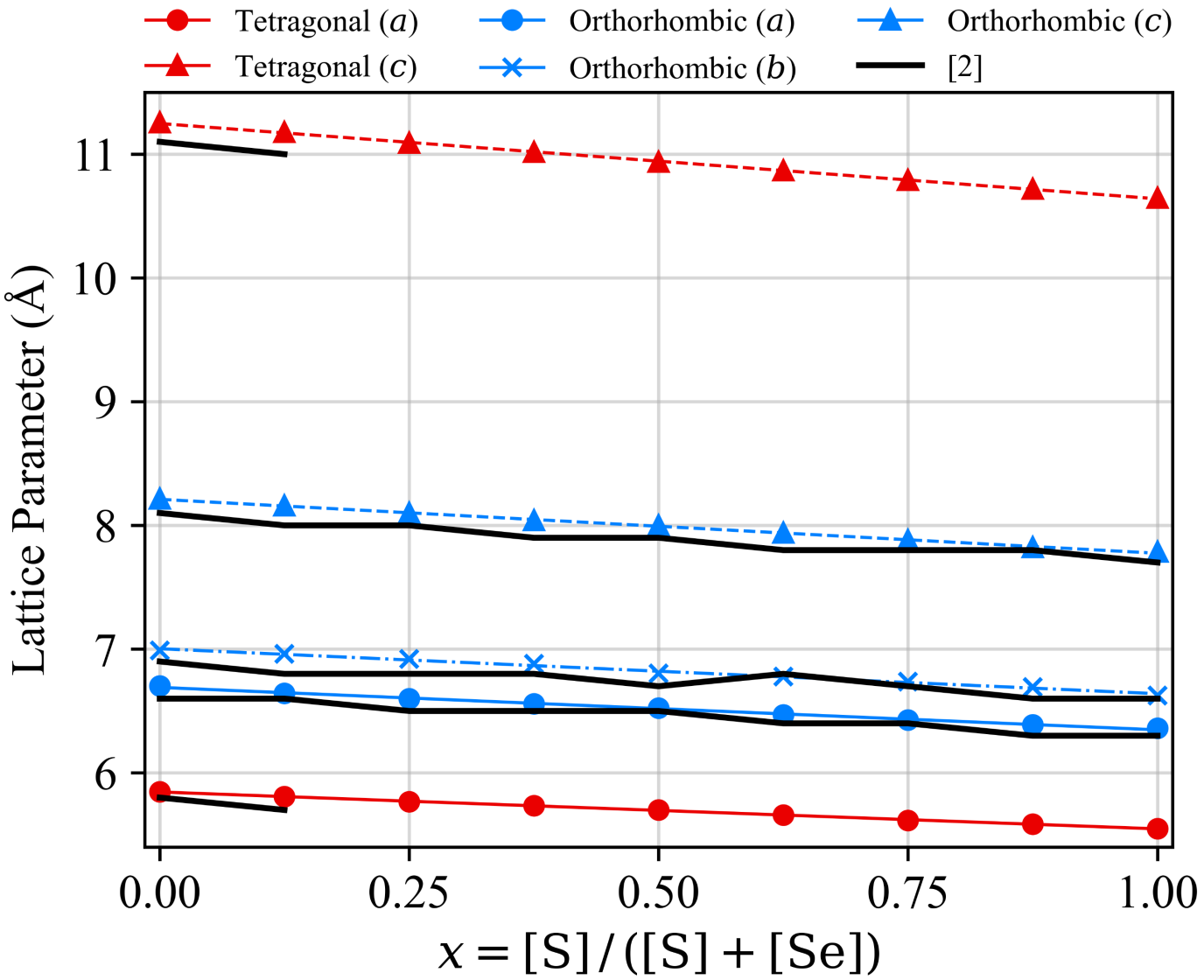
Tetragonal (Stannite, $I\bar{4}2m$)

Orthorhombic (Wurtzite, $Pmn2_1$)

$$x = \frac{[S]}{[S] + [Se]}$$

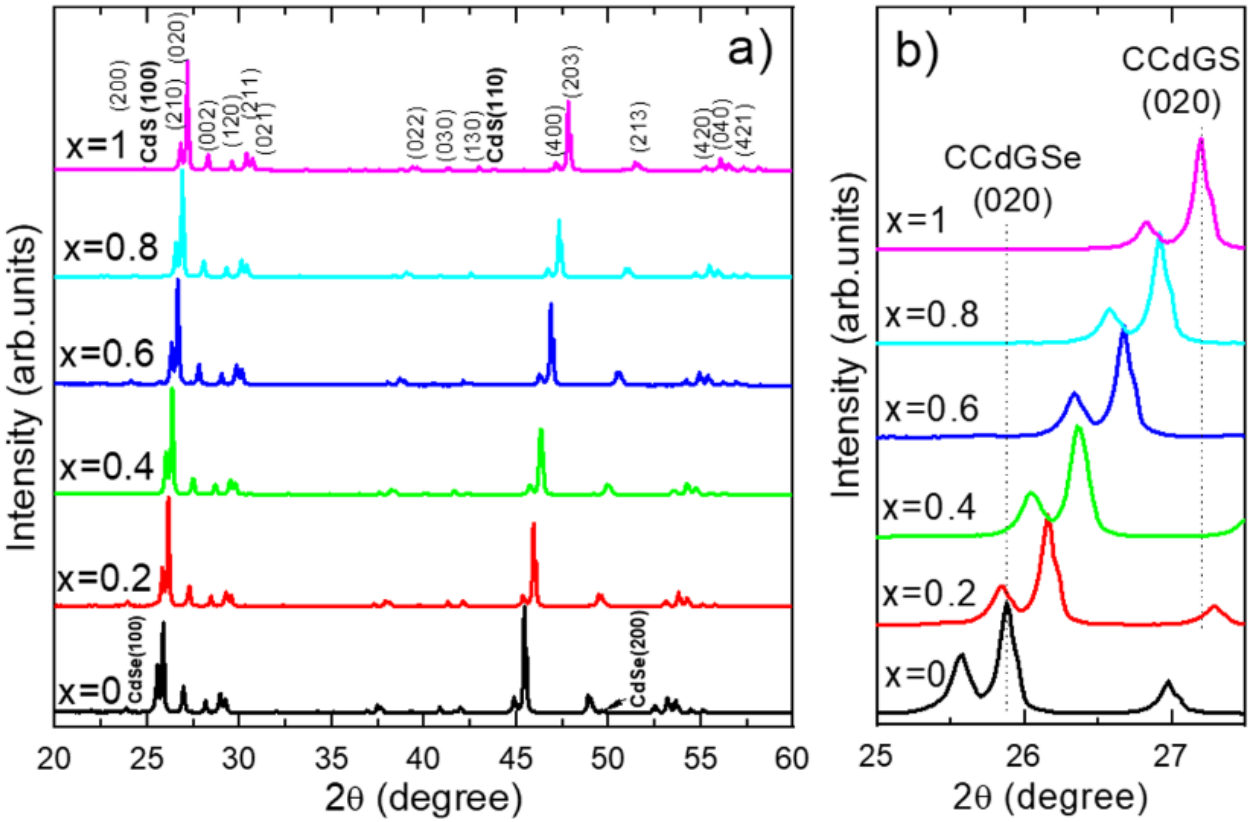
Lattice Parameters: $Cu_2CdGe(S_xSe_{1-x})_4$

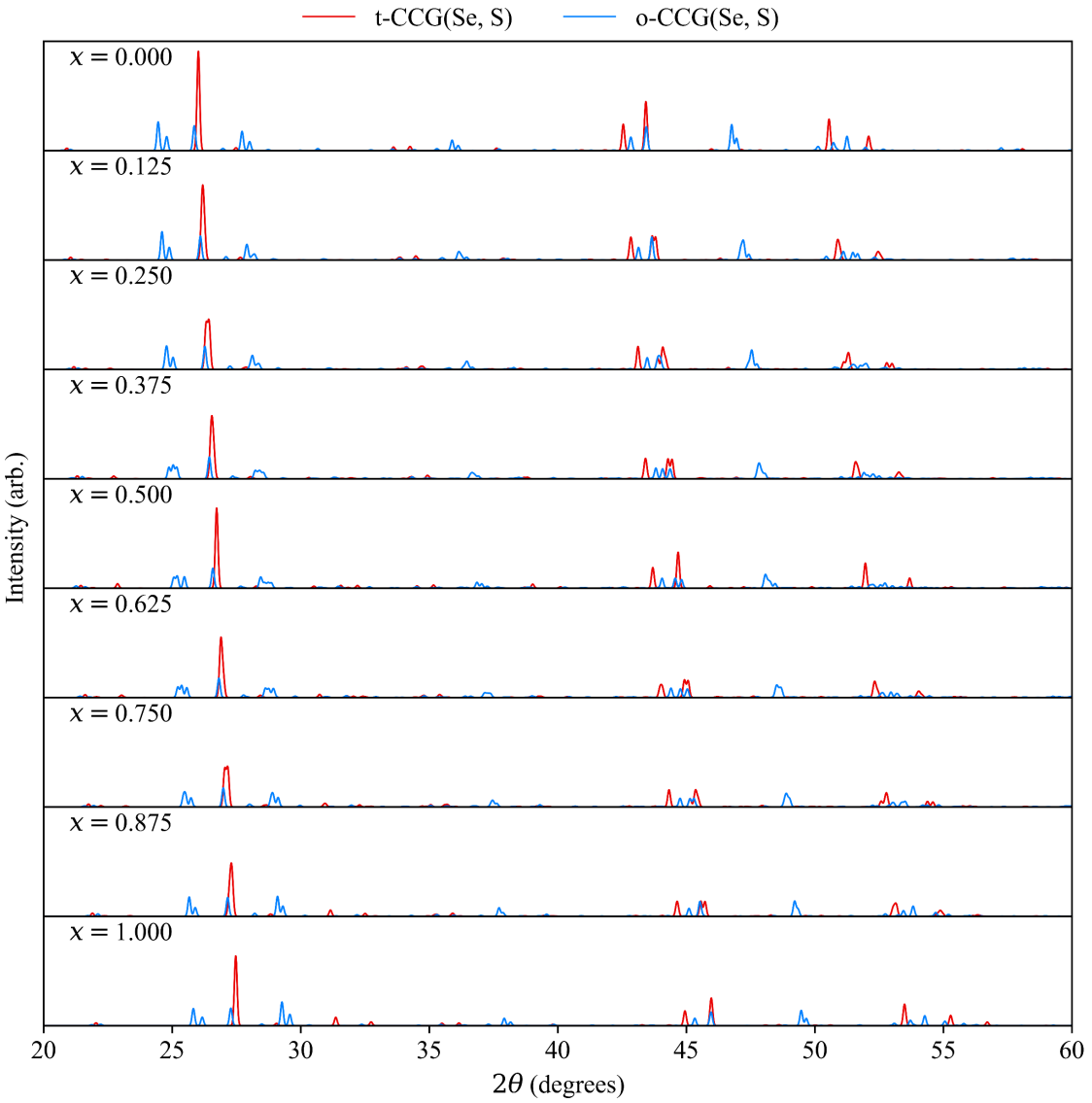
- Lattice Parameters: monotonic decrease with x
- Tetragonal:
  - c/a = constant = 1.9
- Orthorhombic:
  - b/a = constant = 1.0
  - $c/a = c/b$ = constant = 1.2



2: X. Li, M. Pilvet, K. Timmo, M. Grossberg, V. Mikli, and M. Kauk-Kuusik, Solar Energy 209, 646 (2020)

Simulated XRD: $Cu_2CdGe(S_xSe_{1-x})_4$





Experimental XRD[2] (orthorhombic) ↑↑↑

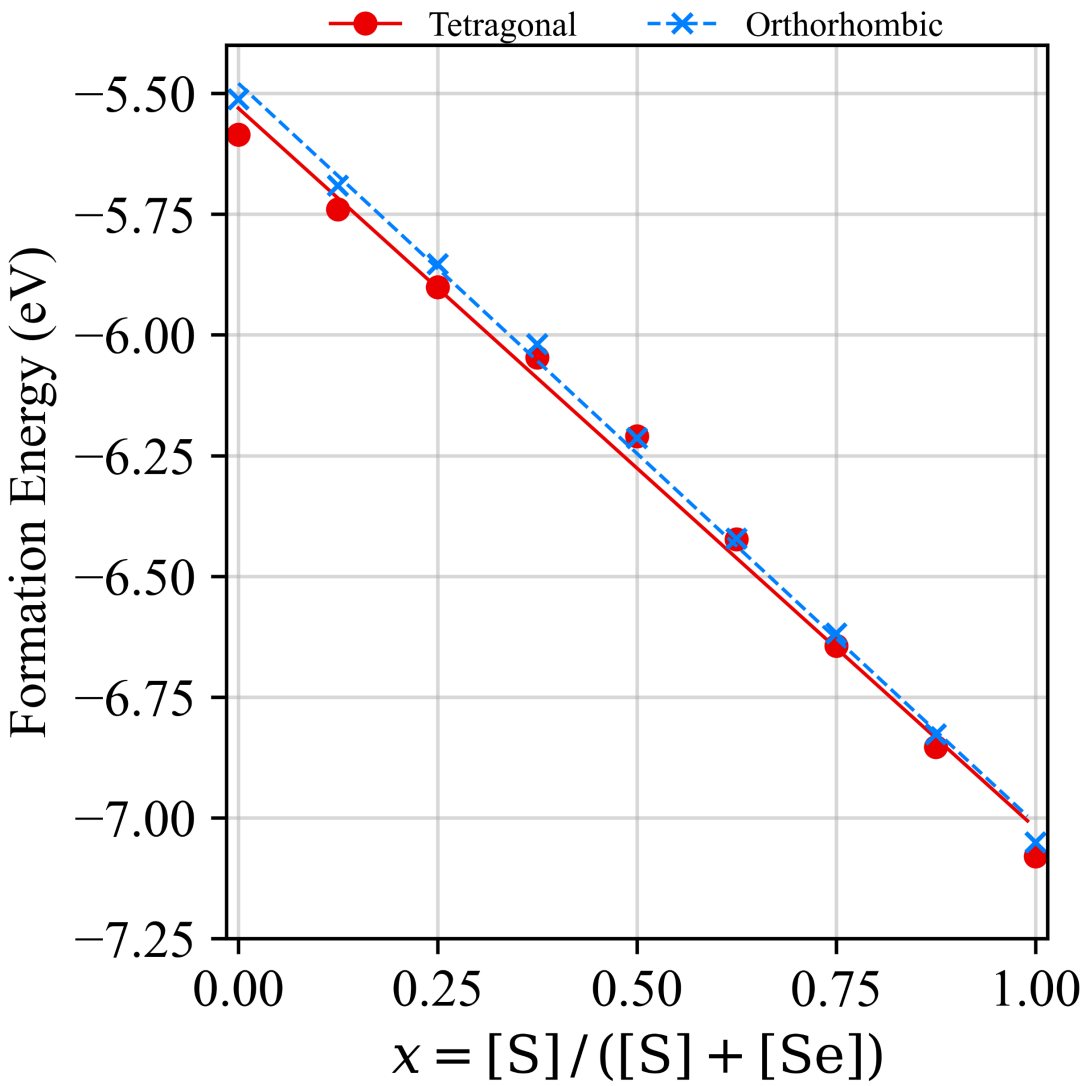
Simulated XRD (both systems) →→→
(λ = identical to [2])

2: X. Li, M. Pilvet, K. Timmo, M. Grossberg, V. Mikli, and M. Kauk-Kuusik, Solar Energy 209, 646 (2020)

Energetics: $Cu_2CdGe(S_xSe_{1-x})_4$

- Formation energies: monotonic decrease with x
- Tetragonal < Orthorhombic
- Compare with:
  - $Cu_2ZnSnSe_4$: -4.06 eV[8]
  - Cu_2ZnSnS_4: -4.84 eV[9]

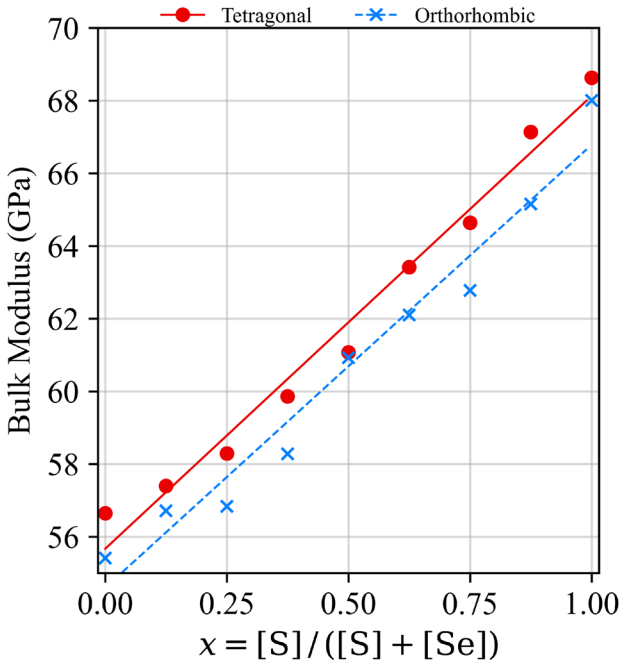
$$E_{\text{form}}(x) = E_{\text{CCG(Se,S)}}(x) - 2E_{\text{Cu}} + E_{\text{Cd}} + \ldots$$
$$\ldots E_{\text{Ge}} + 4[E_{\text{S}}x + E_{\text{Se}}(1-x)]$$

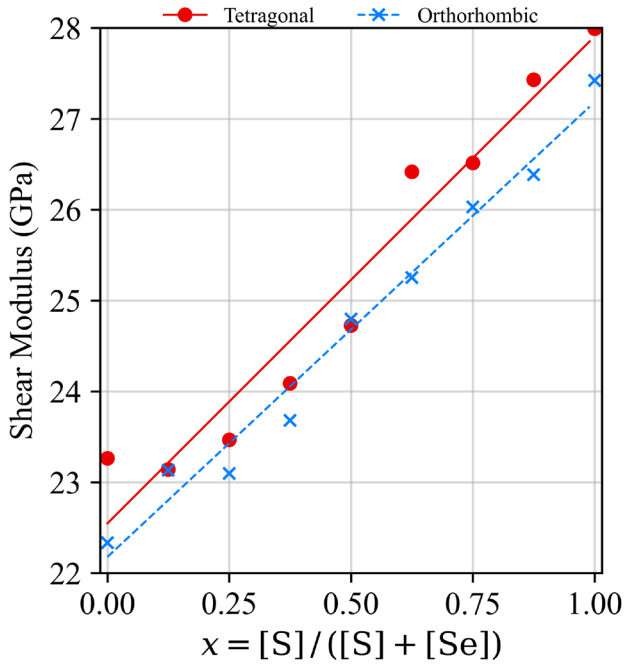


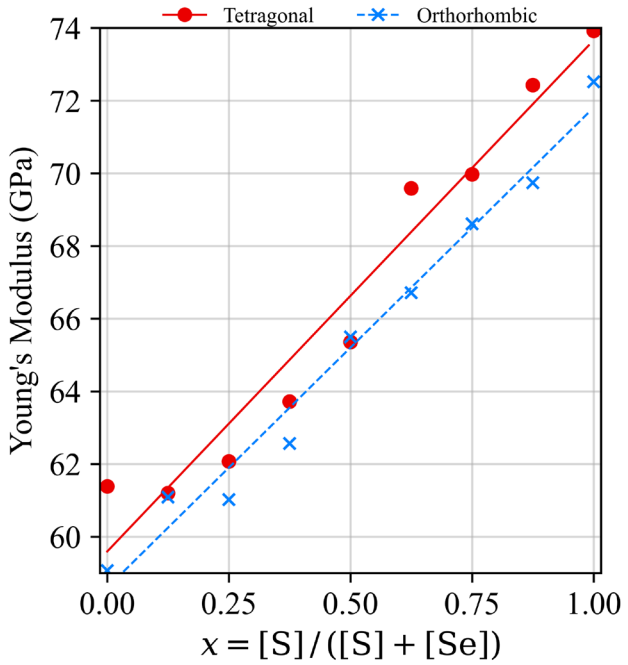
8: T. A. Stolyarov, E. A. Brichkina, A. V. Baranov, and E. G. Osadchii, Inorganic Materials 755-757 (2019)

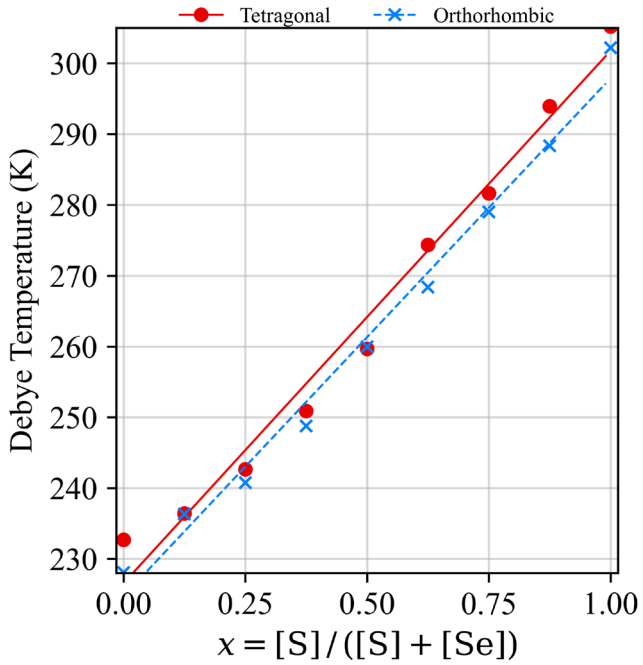
9: T. A. Stolyarov, E. G. Osadchii , A. V. Baranov, Geochemistry International, 109-111 (2019)

Elastic Moduli: $Cu_2CdGe(S_xSe_{1-x})_4$









- Constant Poisson's ratio ν = 0.32
- Constant Vicker's Hardness H_V = 3 GPa
- All stable according to Born stability criteria:

$$\begin{cases} C_{ii} > 0 \text{ for i} \in \{1, 4, 5, 6\} \\ C_{11}C_{22} - C_{12}^2 > 0 \\ C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 > 0 \end{cases}$$

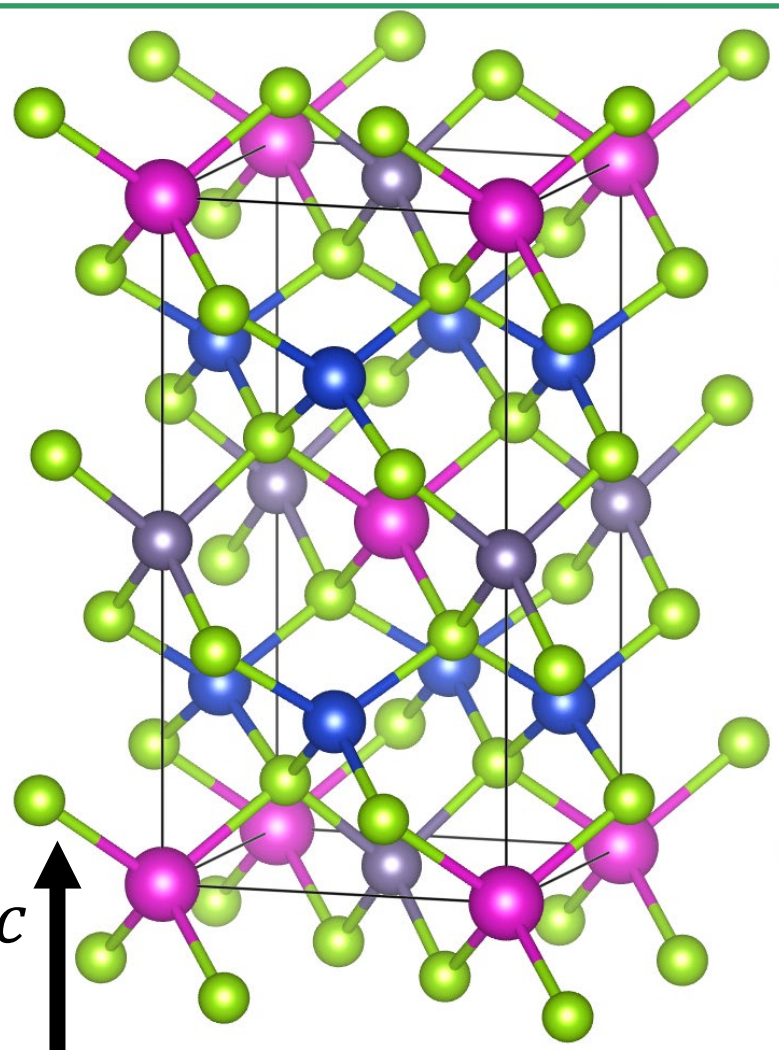
Other tetragonal results (theoretical):

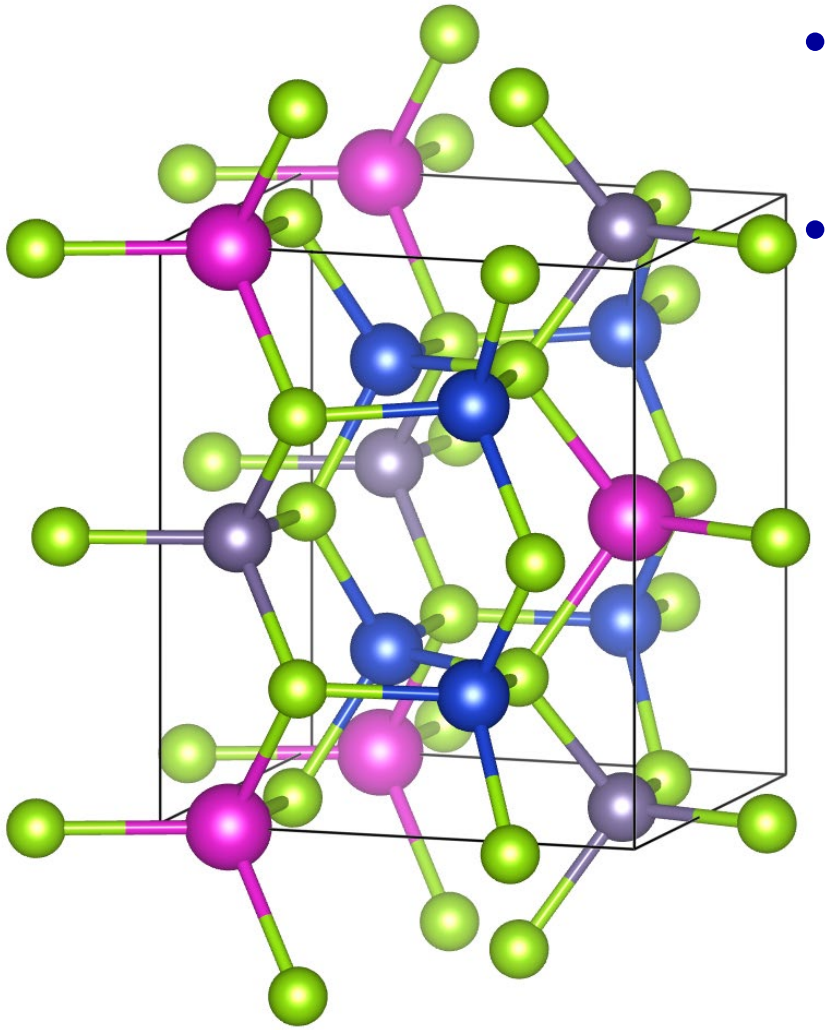
x = 0.000: Bulk Modulus: 58[10], 60[11] GPa
Shear Modulus: 22[10], 26[11] GPa
Young's Modulus: 69[11] GPa

x = 1.000: Bulk Modulus: 70[10] GPa
Shear Modulus: 28[10] GPa

10: S. Hasan, K. Baral, N. Li, and W.-Y. Ching, Sci Rep 11, 9921 (2021)
11: T. V. Vu et. al., Journal of Electronic Materials 48, 705 (2019)

Atomic Models: $Cu_2CdGe(S_xSe_{1-x})_4$





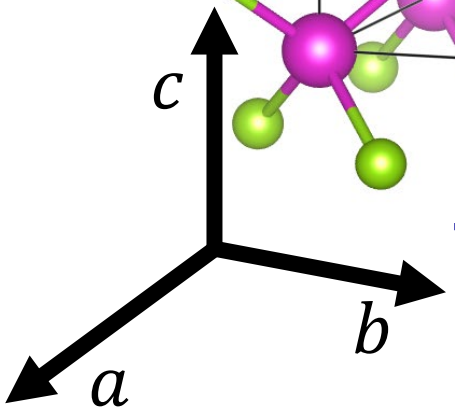
- Number of atoms = 16 = 2 × (formula unit)
- 1×1×1 unit = conventional unit cell

Cu

Cd

Ge

S / Se

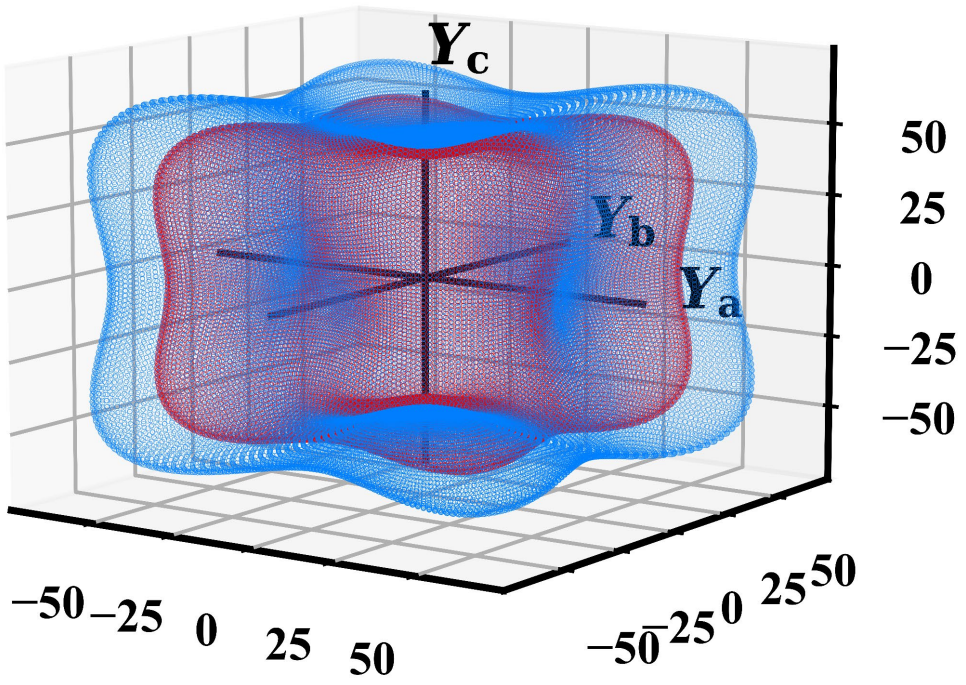


Tetragonal (Stannite, $I\bar{4}2m$)

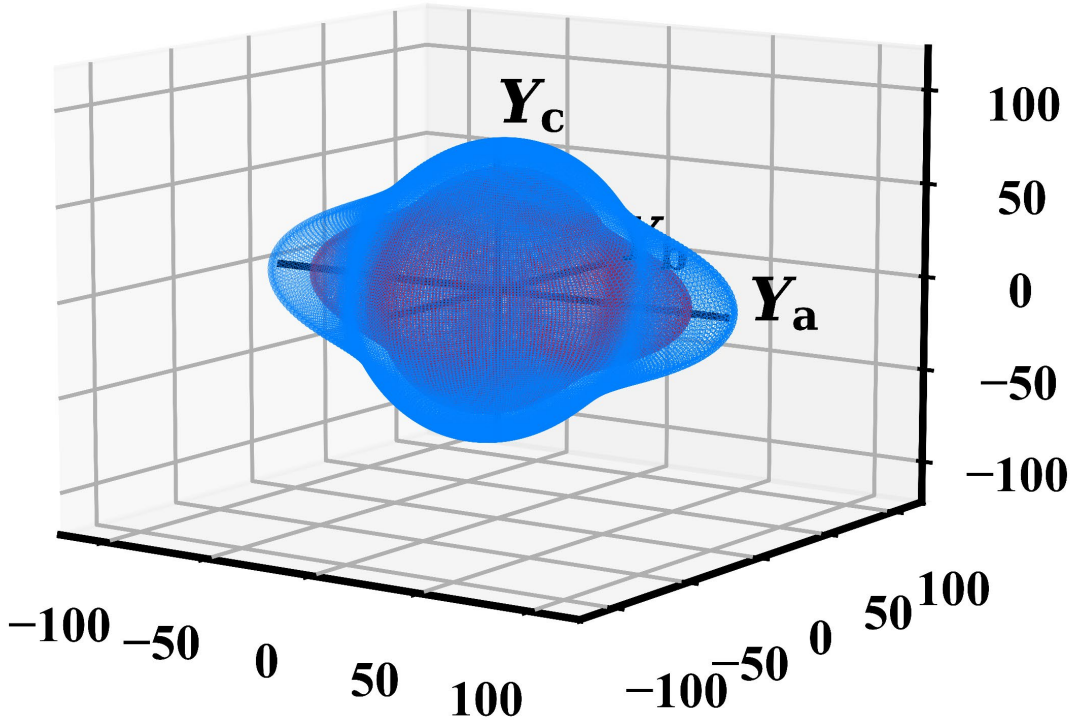
Orthorhombic (Wurtzite, $Pmn2_1$)

$$x = \frac{[S]}{[S] + [Se]}$$

Directional Young's Moduli: $Cu_2CdGe(S_xSe_{1-x})_4$

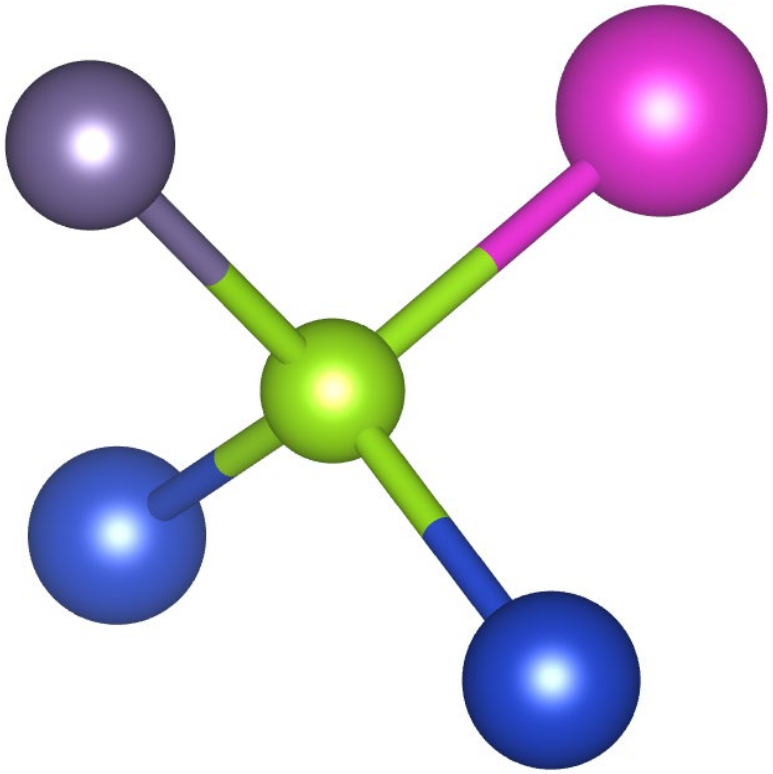


Tetragonal:
Strongest in diagonal directions (GPa units)



Orthorhombic:
strongest in a, b, c directions (GPa units)

Bader Charge Analysis



$Cu_2CdGeSe_4$

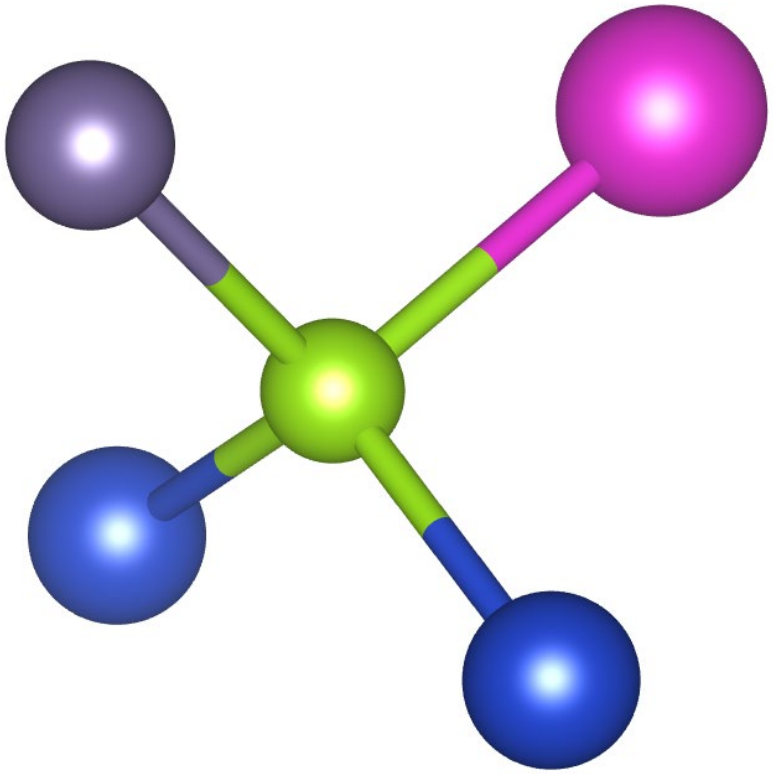
- Cu = + 0.4 *e*
- Cd = + 0.7 *e*
- Ge = + 0.9 *e*
- Se = - 0.6 *e*

Cu_2CdGeS_4

- Cu = + 0.5 *e*
- Cd = + 0.9 *e*
- Ge = + 1.2 *e*
- S = - 0.8 *e*

Tetragonal and Orthorhombic nearly identical charge transfers

Bader Charge Analysis



$Cu_2CdGeSe_4$

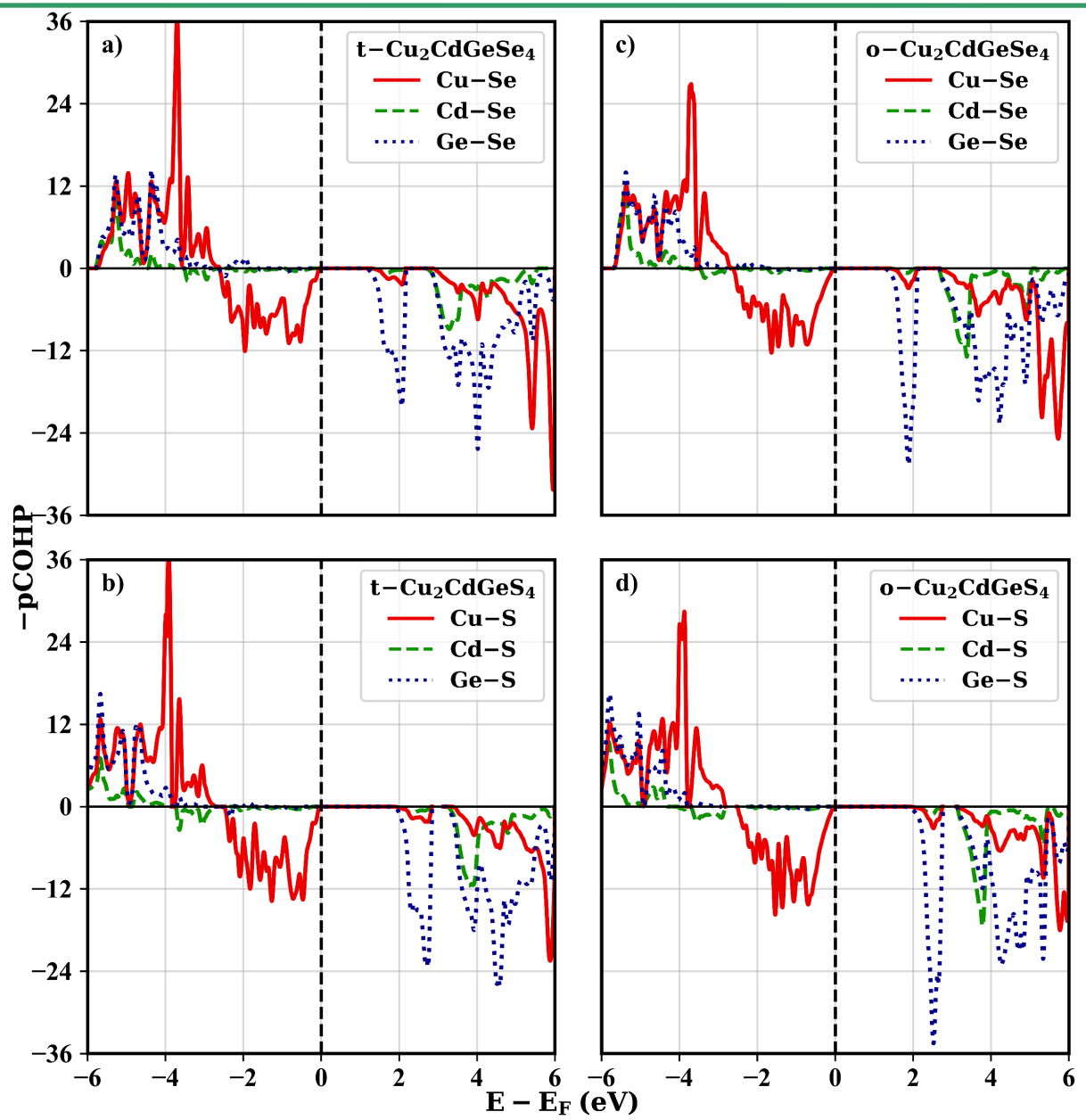
- Cu = + 0.36 *e*
- Cd = + 0.71 *e*
- Ge = + 0.85 *e*
- Se = - 0.57 *e*

Cu_2CdGeS_4

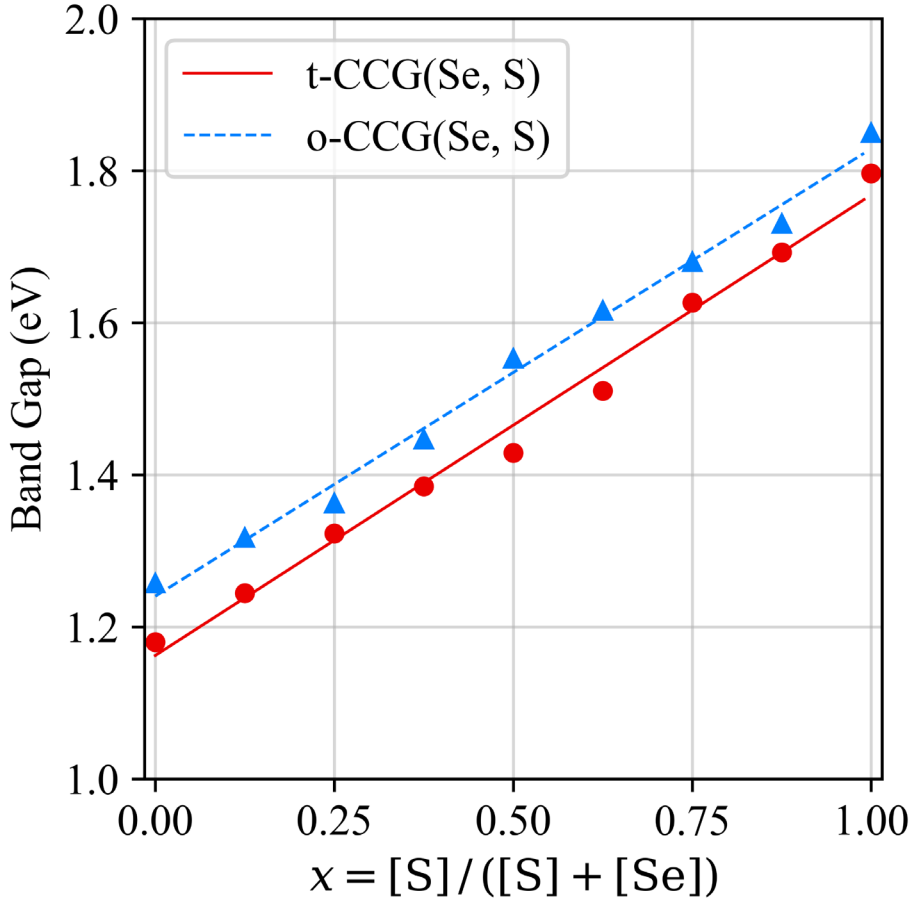
- Cu = + 0.49 *e*
- Cd = + 0.86 *e*
- Ge = + 1.20 *e*
- S = - 0.76 *e*

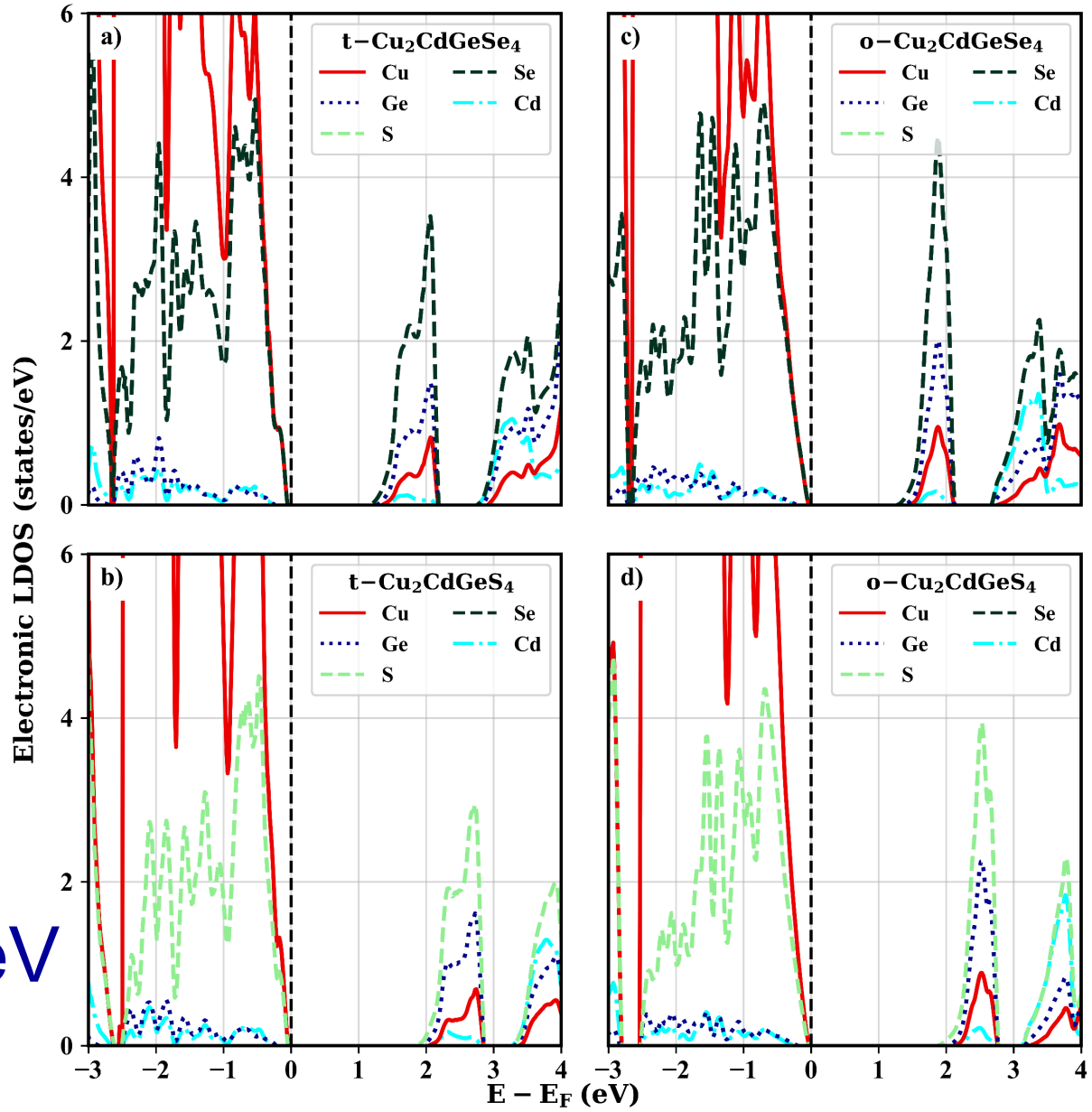
COHP: $Cu_2CdGe(S_xSe_{1-x})_4$

- Cu: majority of population
- Mostly antibonding states 2 eV below fermi level: small elastic strength
- Negative integrated COHP until 6 eV: structures are stable



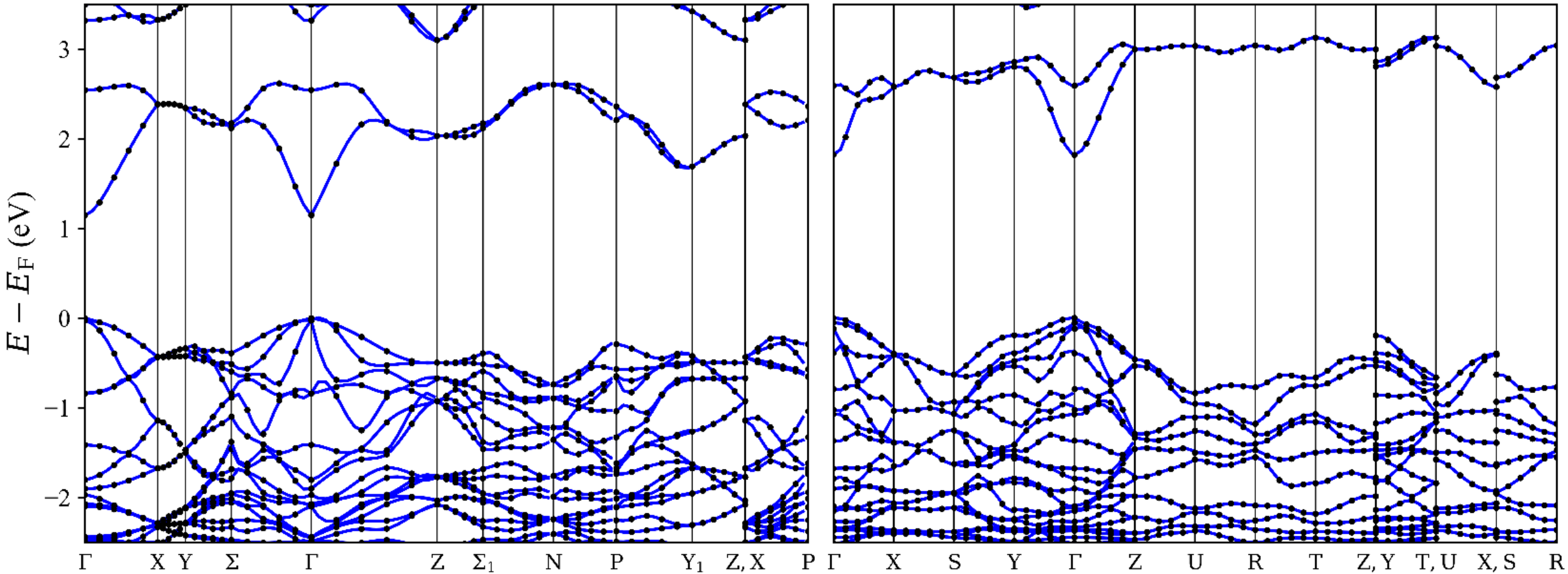
Density of States: $Cu_2CdGe(S_xSe_{1-x})_4$





- Tetragonal gap: ~ 1.2 → 1.8 eV
- Orthorhombic gap: ~ 1.3 → 1.9 eV
- Linear increase with x: 0 → 1

Band Structure



Tetragonal
$Cu_2CdGeSe_4$

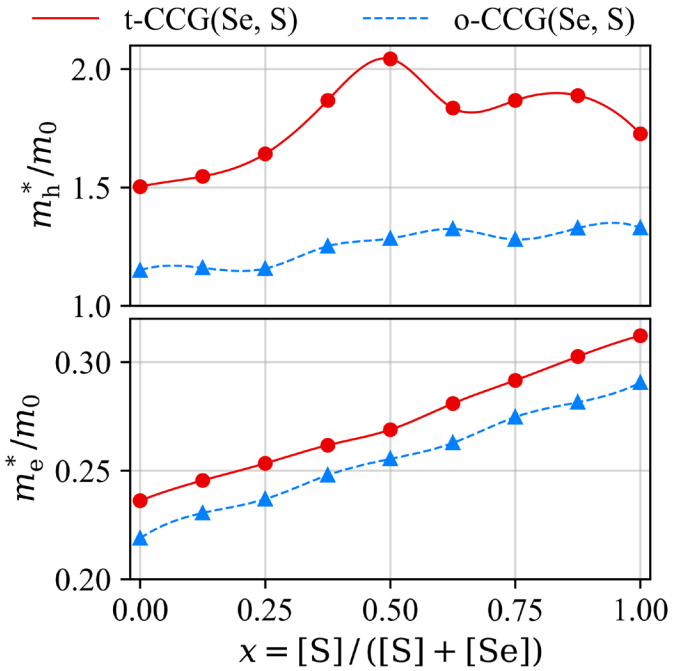
Orthorhombic
Cu_2CdGeS_4

Effective Masses: $Cu_2CdGe(S_xSe_{1-x})_4$

High symmetry directions: $(\alpha - \gamma: x = 0.000 \rightarrow x = 1.000)$

	m_h^*/m_0			m_e^*/m_0		
System	**a**	**b**	**c**	**a**	**b**	**c**
Tetragonal	0.77 – 0.79	0.77 – 0.79	0.46 – 0.55	0.17 – 0.24	0.17 – 0.24	0.11 – 0.18
Orthorhombic	1.35 – 1.58	1.41 – 1.73	0.77 – 0.81	0.17 – 0.24	0.16 – 0.24	0.17 – 0.24

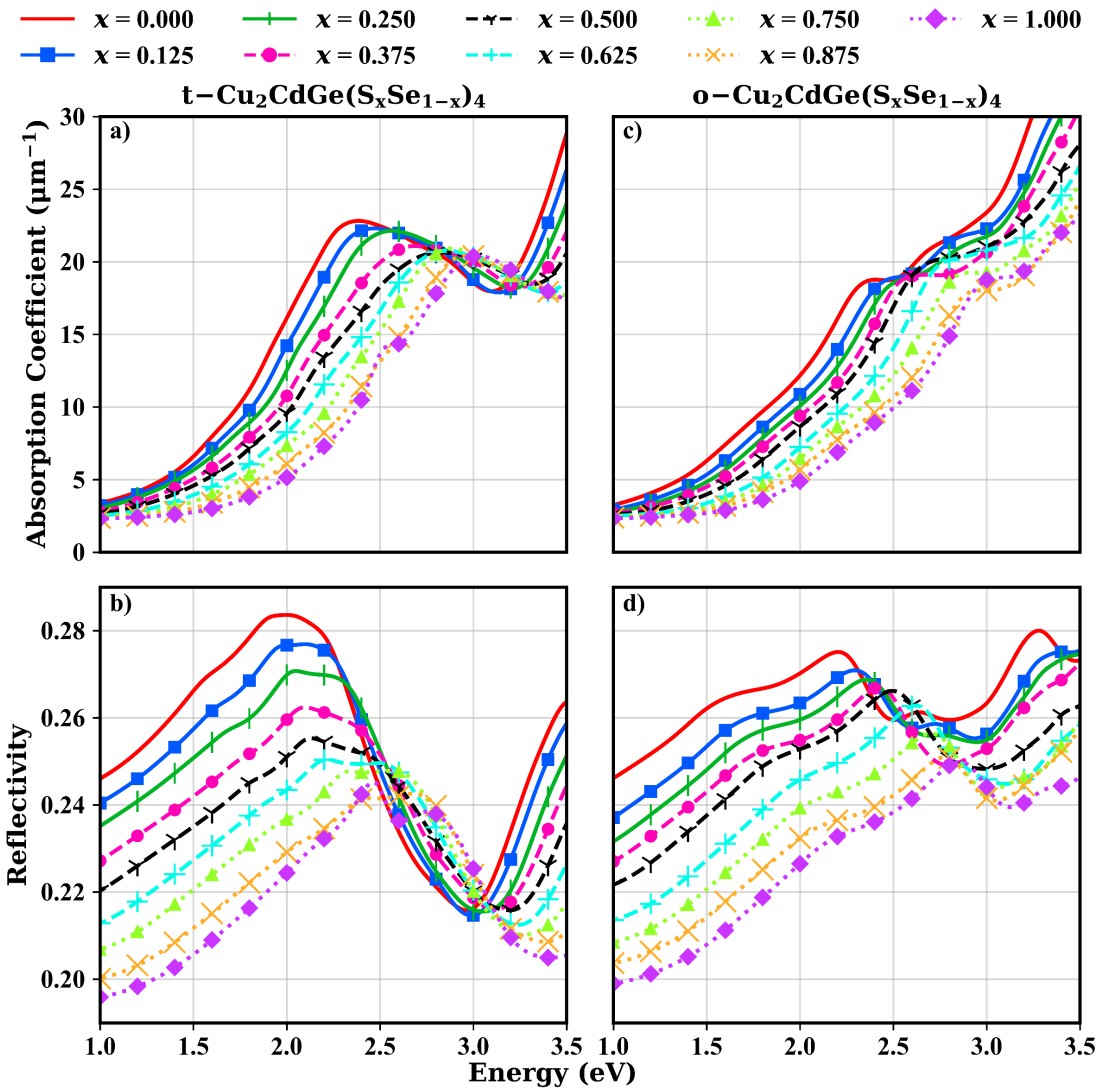
Average over all directions:



- Average hole masses ≫ high symmetry masses (exception: Orthorhombic system **a** and **b** directions)
- Hole mass lightest in **c** direction

Optical Response: $Cu_2CdGe(S_xSe_{1-x})_4$

- Features blue-shifted with increasing x
- Absorption comparable to common PV materials:
  - CdTe[12]: 13 μm^{-1} max
  - Si[13]: 15 μm^{-1} max
- Mild reflectivity compared to:
  - CdTe[12]: 0.18 min
  - Si[13]: 0.33 min



12: B. B. Dumre, N. J. Szymanski, V. Adhikari, I. Khatri, D. Gall, and S. V. Khare, Solar Energy 194, 742 (2019)

13: M. A. Green and Keevers, M. J, Progress in Photovoltaics: Research and Applications, vol. 3, pp. 189 - 192, 1995.

Summary: Results, Future Work

- Computed elastic and optoelectronic properties of $Cu_2CdGe(S_xSe_{1-x})_4$
- Properties vs. x: linear
- Optoelectronic properties: both structures suitable for photovoltaic applications
- Elastic properties: tetragonal system slightly stronger than orthorhombic
  - Caveat: Creating tetragonal structure with high x may be difficult
- Methods for growing tetragonal structure could be further explored

Thank you!

Extra: DFT Parameters

- Structural Calculations:
  - GGA XC Functional
  - 550 eV PW cutoff
  - 0.001 eV/A force tolerance
  - 8×8×7 Γ-centered k-point mesh
  - σ = 0.04 eV gaussian-type smearing for partial occupancies
- Optoelectronic Calculations:
  - HSE06 XC Functional
  - 550 eV PW cutoff
  - 6×6×5 Γ-centered k-point mesh
  - Tetrahedron smearing for partial occupancies
  - Number of bands = 3 × (the default)

Extra: Simulated XRD

- Relative integrated intensity[14]:

$$I = \frac{p}{V^2}\left[\frac{1+\cos^2(2\theta_{\mathrm{B}})}{\sin^2(\theta_{\mathrm{B}})\cos(\theta_{\mathrm{B}})}\right]|F_{\mathrm{hkl}}|^2\exp\left(-\frac{2B\sin^2(\theta_{\mathrm{B}})}{\lambda^2}\right)$$

- Structure factor:

$$F_{\mathrm{hkl}} = \sum_{j=\mathrm{atoms}} f_{\mathrm{j}}\exp\left(i2\pi(hx_{\mathrm{j}} + ky_{\mathrm{j}} + zl_{\mathrm{j}})\right)$$

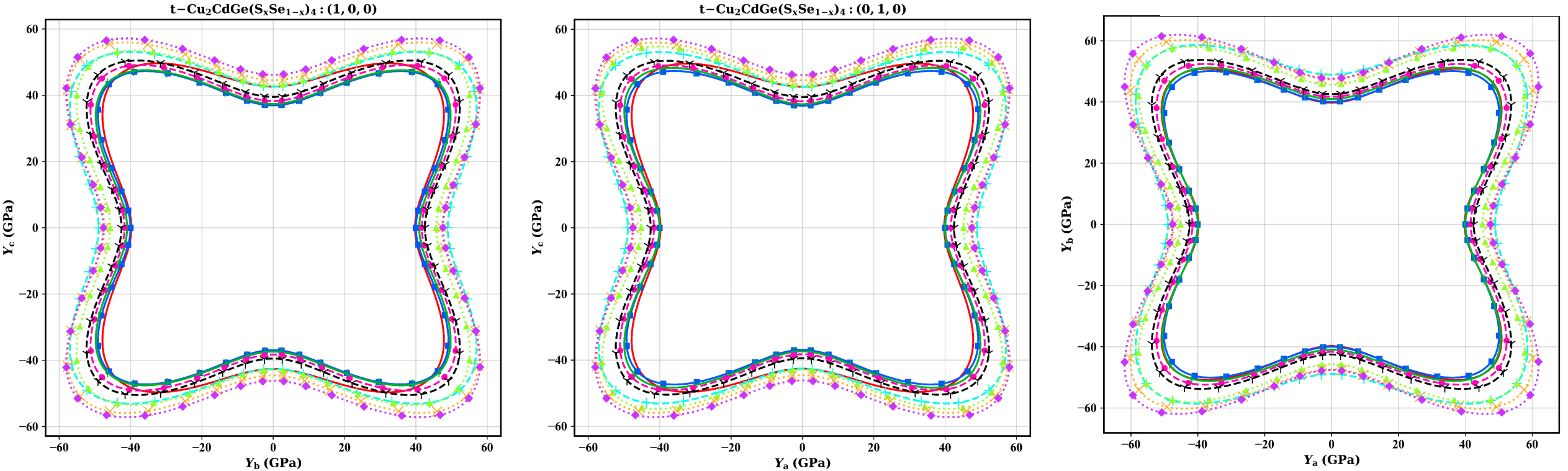
- Atomic scattering factor:

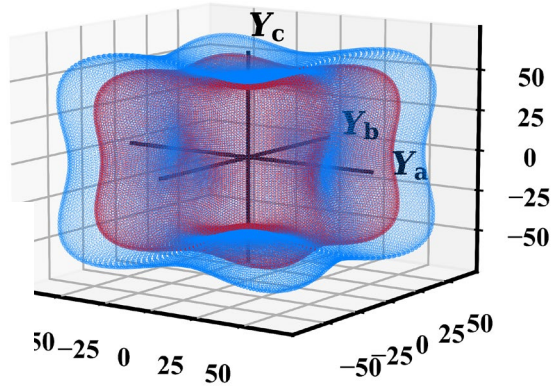
$$f_{\mathrm{j}} \approx \sum_{k=1}^{4} a_{\mathrm{jk}}\exp\left(-b_{\mathrm{jk}}\left(\frac{2\left(\frac{2\pi}{\lambda}\right)}{4\pi}\sin(\theta_{\mathrm{B}})\right)^2\right) + c_{\mathrm{j}}$$

14: H.W.G. Spraget, Computers Education, vol. 13, pp. 101 – 108, 1989

Extra: Directional Young's Modulus (planes)

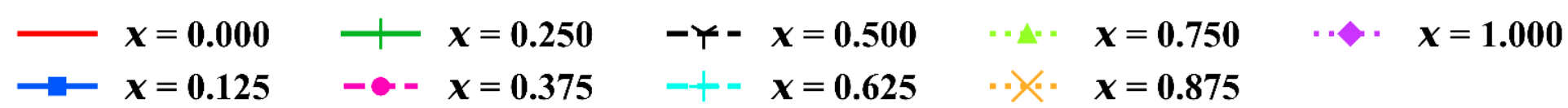
- Tetragonal Phase
- Views along planes normal to the a, b, c axes

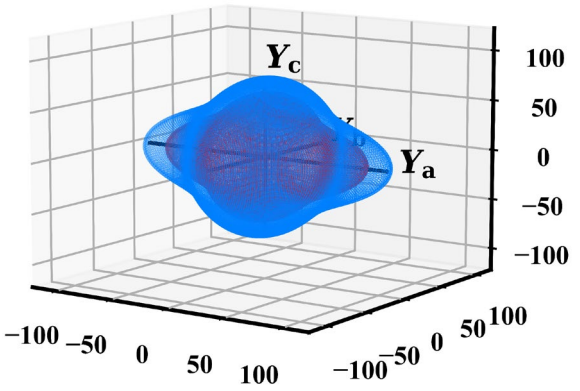


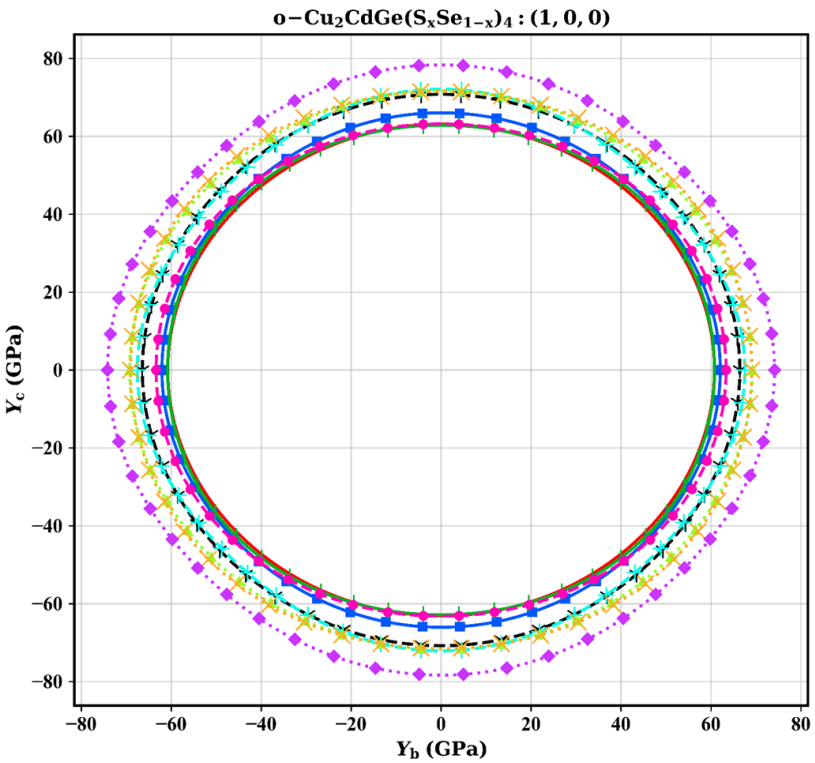


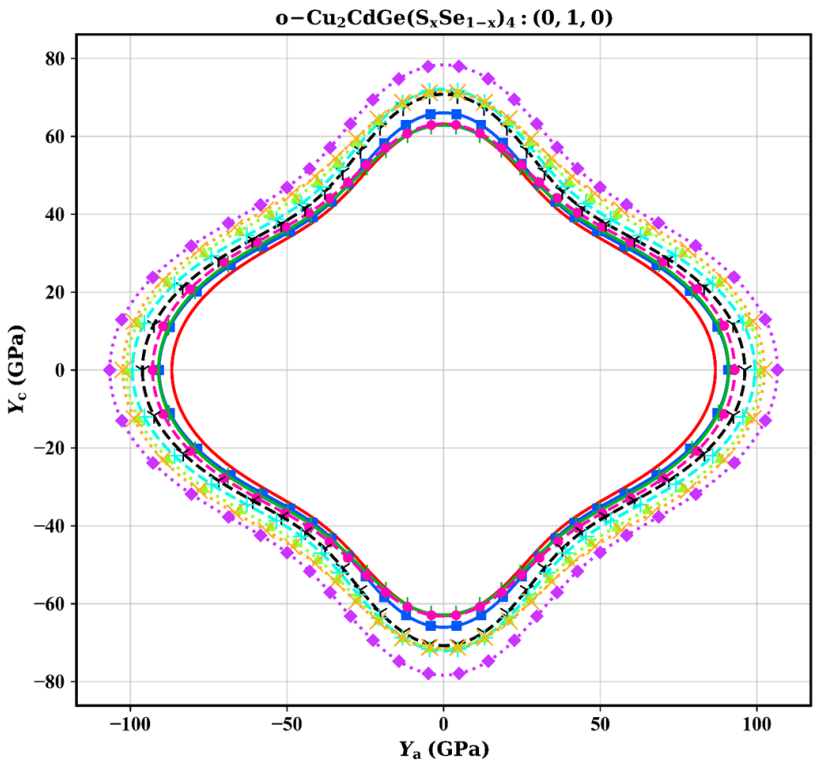
Extra: Directional Young's Modulus (planes)

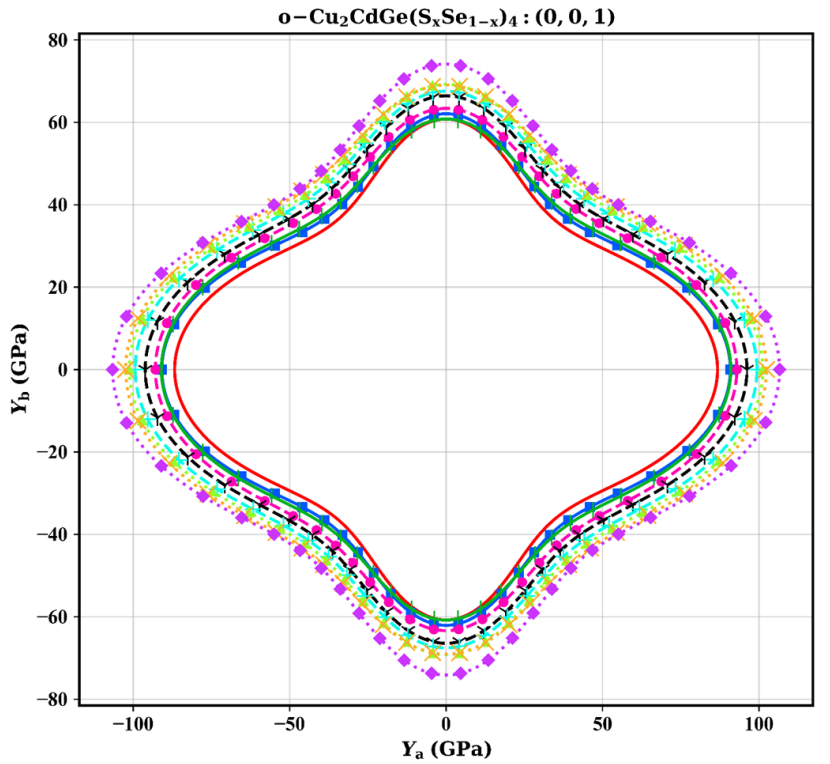
- Orthorhombic Phase
- Views along planes normal to the a, b, c axes











Extra: Standard AM 1.5 Solar Spectrum

- Maximum between 1.8 – 2.8 eV (red lines)