

# Optoelectronic & Mechanical Properties of $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$ via First Principles

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*Dr. Sanjay V. Khare*

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

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Ohio Supercomputer Center



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# Background: Cu<sub>2</sub>-Zn-Sn-S Semiconductors

- Currently Si, CdTe, GaAs, Cu(In, Ga)Se<sub>2</sub> 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<sub>2</sub>ZnSn(S<sub>0.25</sub>Se<sub>0.75</sub>)<sub>4</sub>; power conversion efficiency of 12.6%.

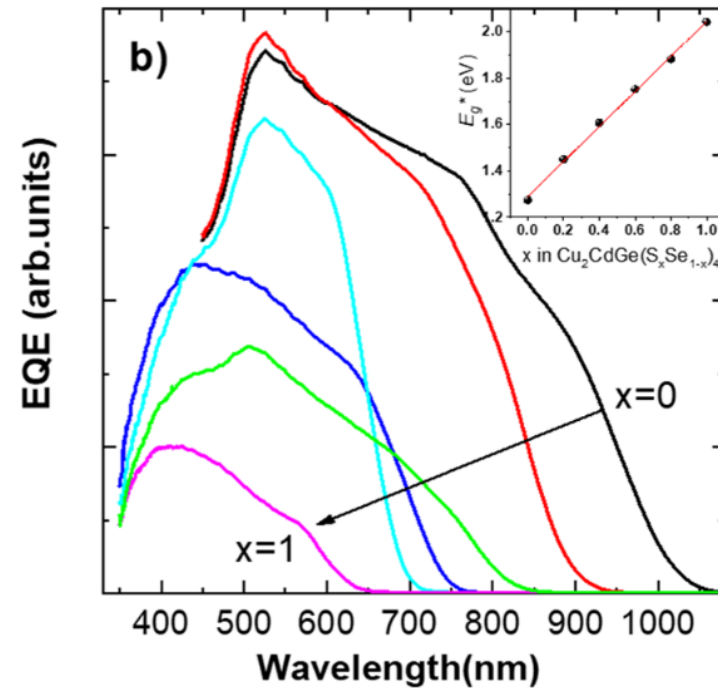
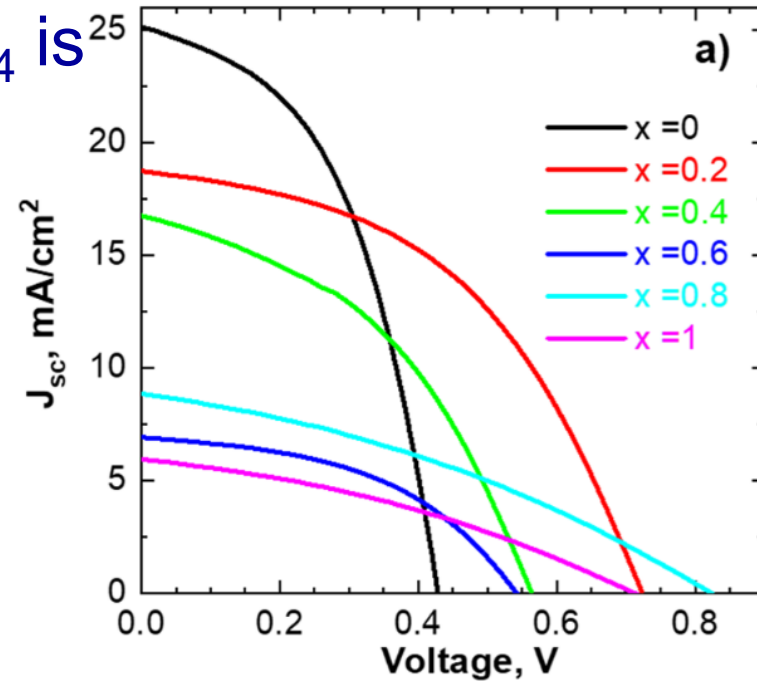
Periodic Table of the Elements

1 IA 1A																	18 VIIIA 8A
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.798
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown
		Lanthanide Series	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
		Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

- Long-standing problems: bulk defects → band tailing, short carrier lifetimes → limit open circuit voltage

# Background: $\text{Cu}_2\text{CdGeSe}_4$ & $\text{Cu}_2\text{CdGeS}_4$

- Previous work<sup>[1,2,3]</sup>:  $\text{Cu}_2\text{CdGeSe}_4$  is promising for PV applications.
- Can be made better through alloying
- Li et al, 2020: First study into  $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$  alloy
  - Experimental study
  - Mostly orthorhombic system
  - Created solar cell devices
- No other studies on intermediate  $x$  exist



JV curves and EQE measurements of  $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$  PV devices from Li *et al*<sup>2</sup>

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

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

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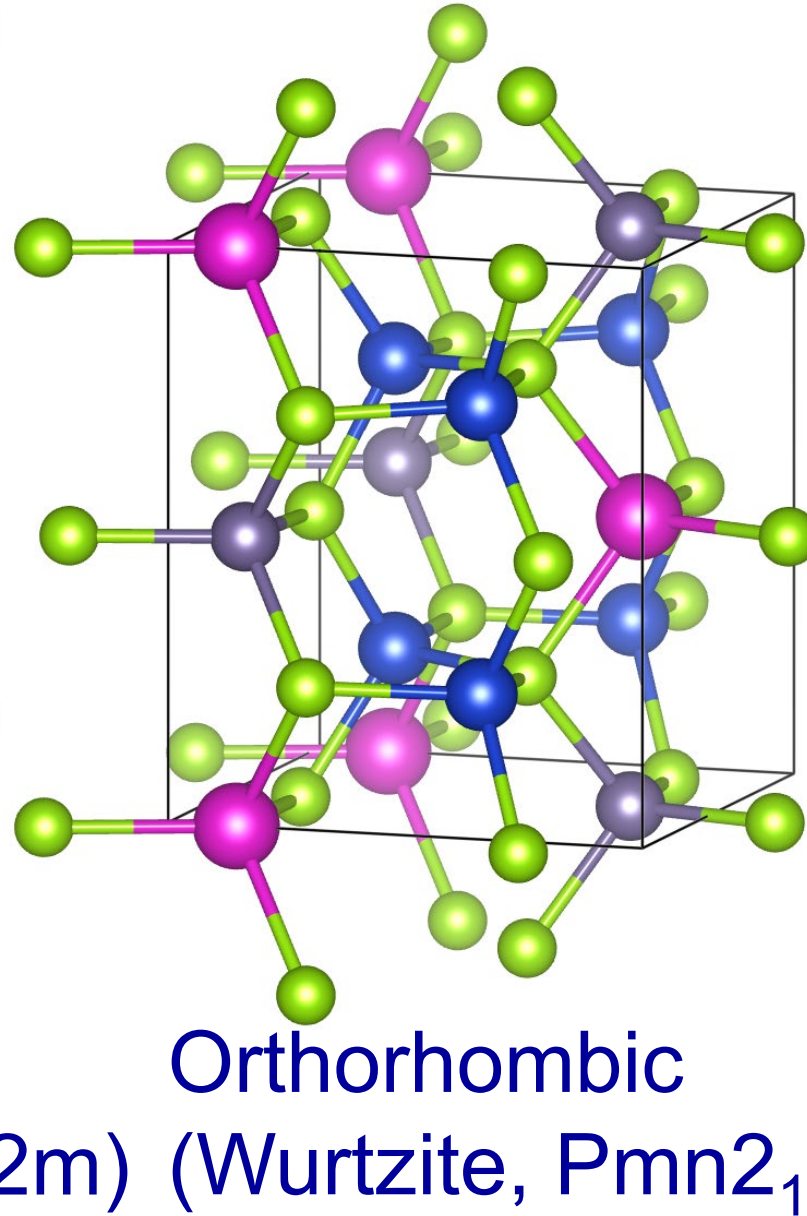
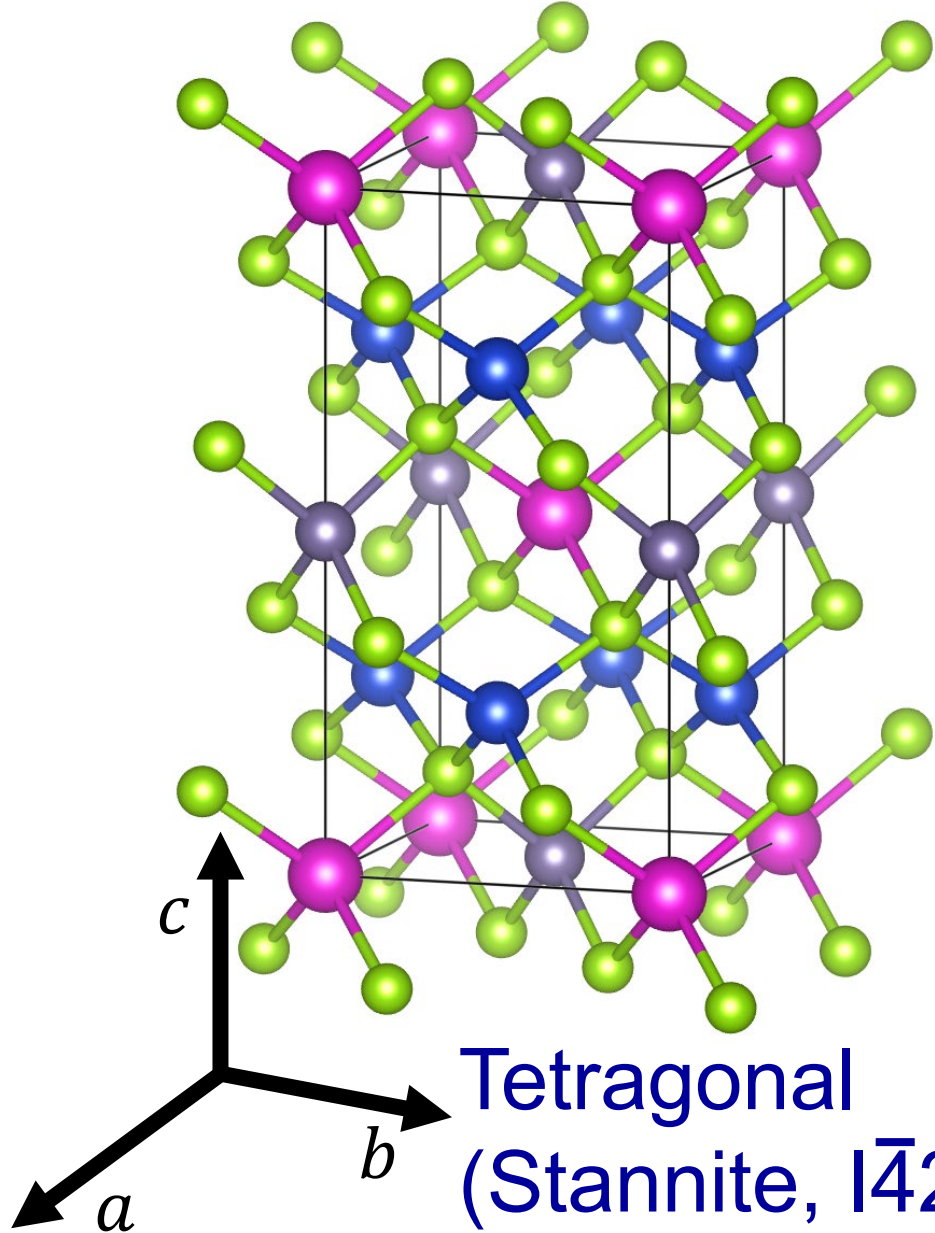
4: G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).

5: G. Henkelman, A. Arnaldsson, and H. Jónsson, Computational Materials Science 36, 354 (2006)

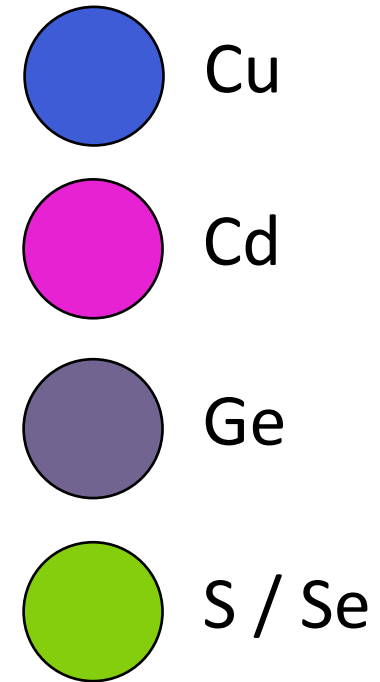
6: V. L. Deringer, A. L. Tchougréeff, and R. Dronskowski, J. Phys. Chem. A 115, 5461 (2011)

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: $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$



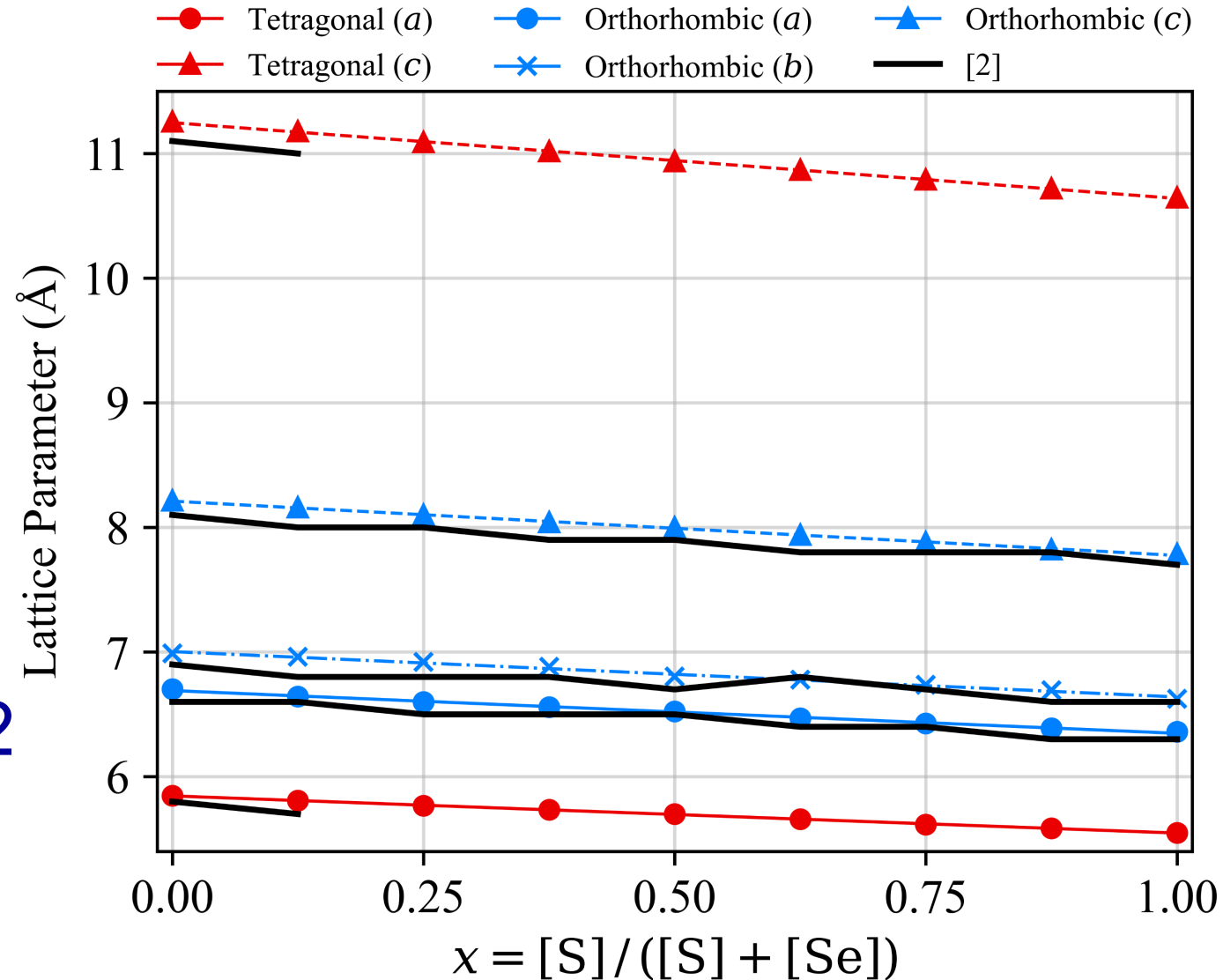
- Number of atoms = 16  
= 2 × (formula unit)
- 1×1×1 conventional unit cell



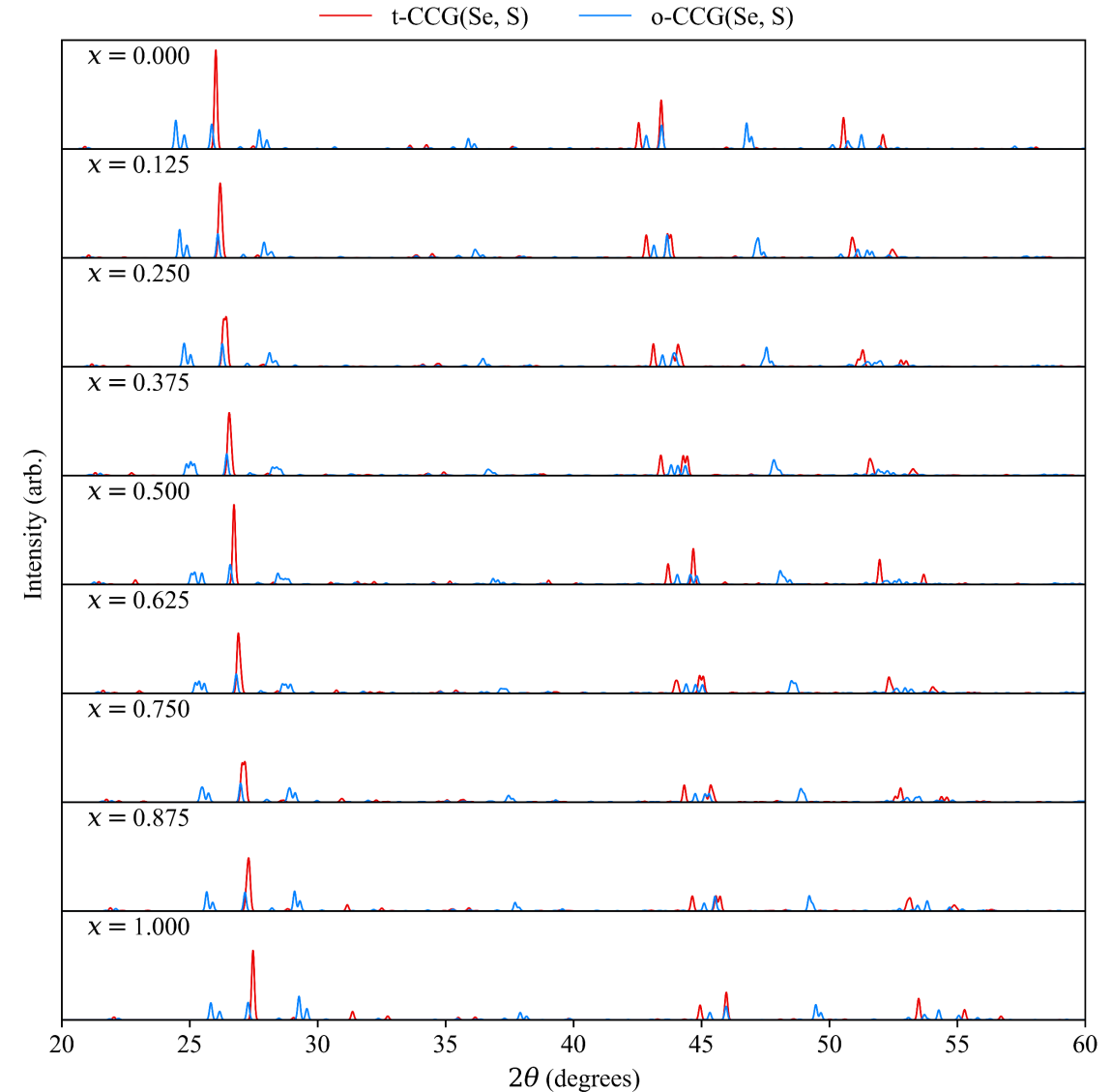
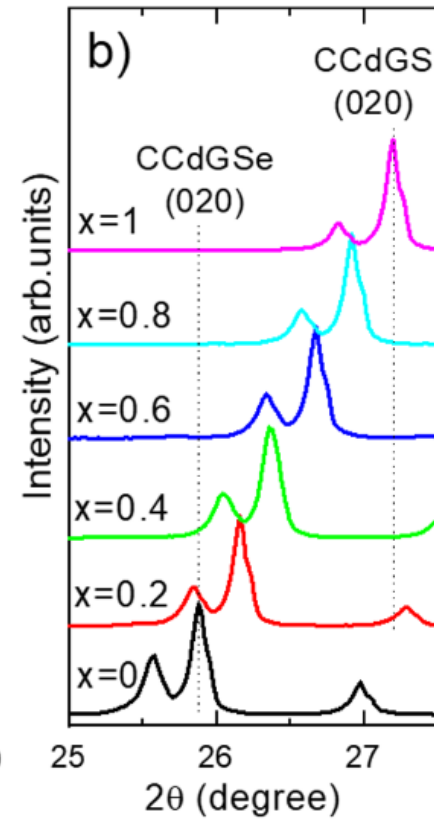
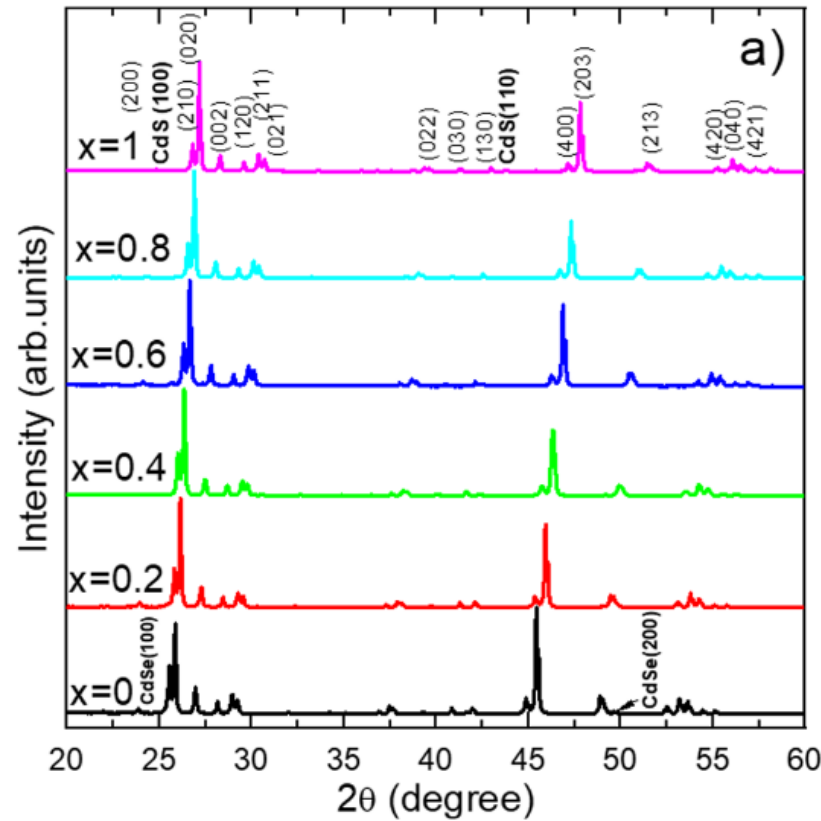
$$x = \frac{[\text{S}]}{[\text{S}] + [\text{Se}]}$$

# Lattice Parameters: $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$

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



# Simulated XRD: $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$



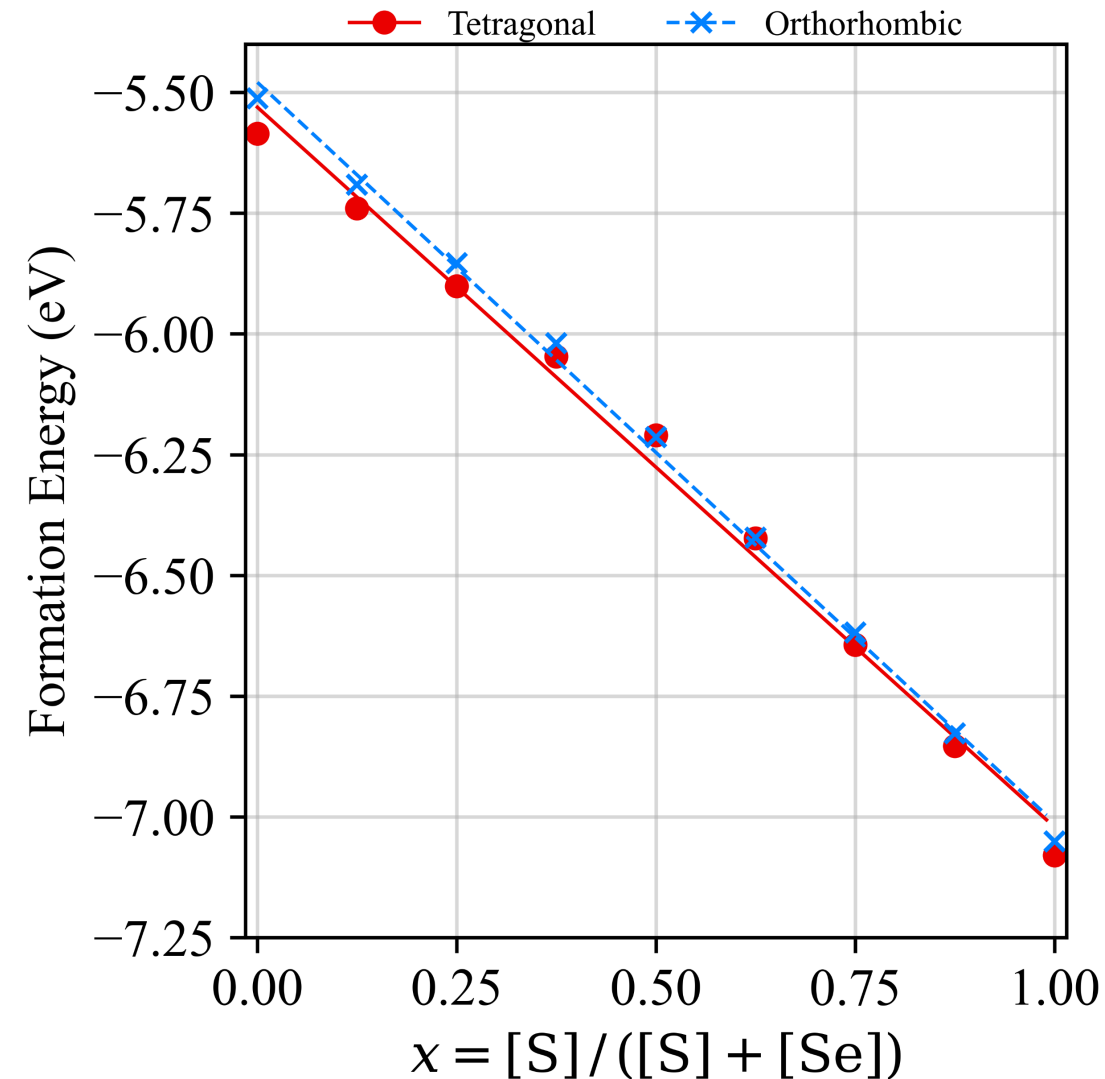
Experimental XRD<sup>2</sup> (orthorhombic) ↑↑↑

Simulated XRD (both systems) →→→  
( $\lambda$  = identical to [2])

# Energetics: $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$

- Formation energies: monotonic decrease with  $x$
- Tetragonal < Orthorhombic
- Compare with:
  - $\text{Cu}_2\text{ZnSnSe}_4$ : -4.06 eV<sup>[8]</sup>
  - $\text{Cu}_2\text{ZnSnS}_4$ : -4.84 eV<sup>[9]</sup>

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

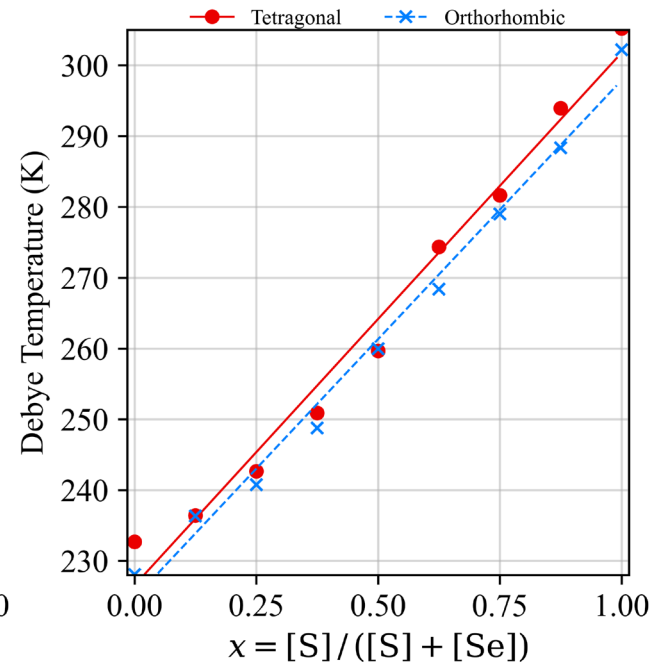
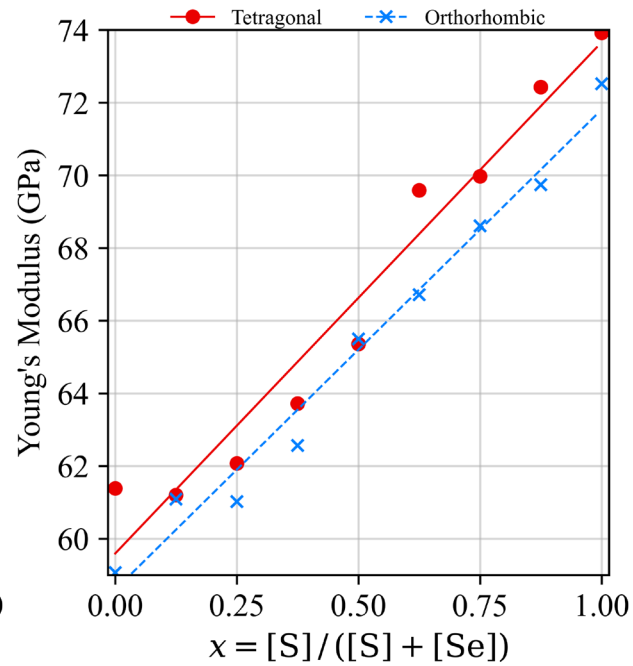
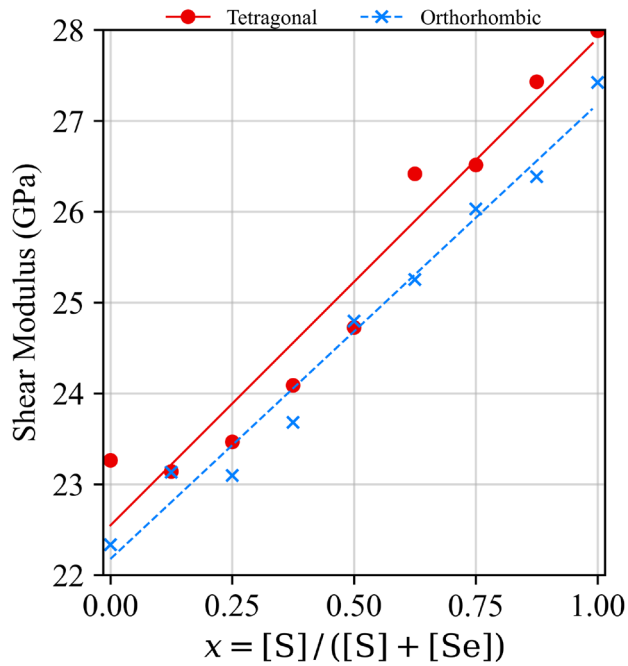
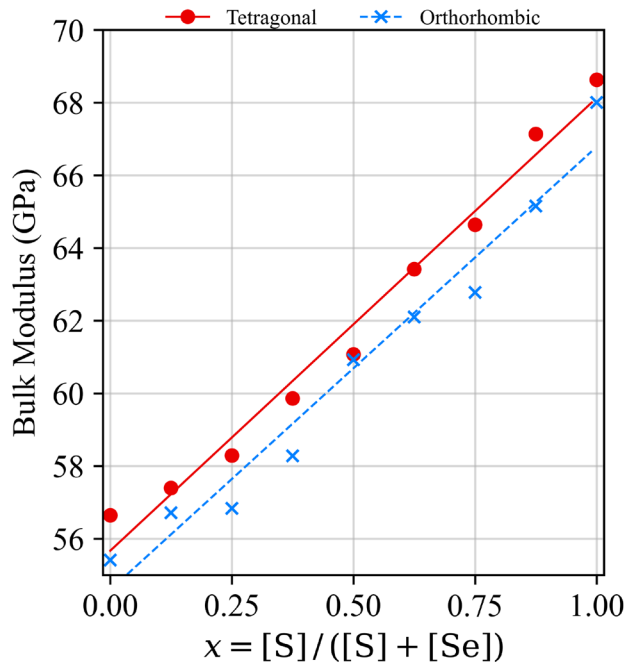


8: T. A. Stolyarov, E. A. Brichkina, A. V. Baranov, and E. G. Osadchii, Inorganic Materials 755-757 (2019)

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



# Elastic Moduli: $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$



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

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

Other tetragonal results (theoretical):

$x = 0.000$ : Bulk Modulus: 58<sup>[10]</sup>, 60<sup>[11]</sup> GPa

Shear Modulus: 22<sup>[10]</sup>, 26<sup>[11]</sup> GPa

Young's Modulus: 69<sup>[11]</sup> GPa

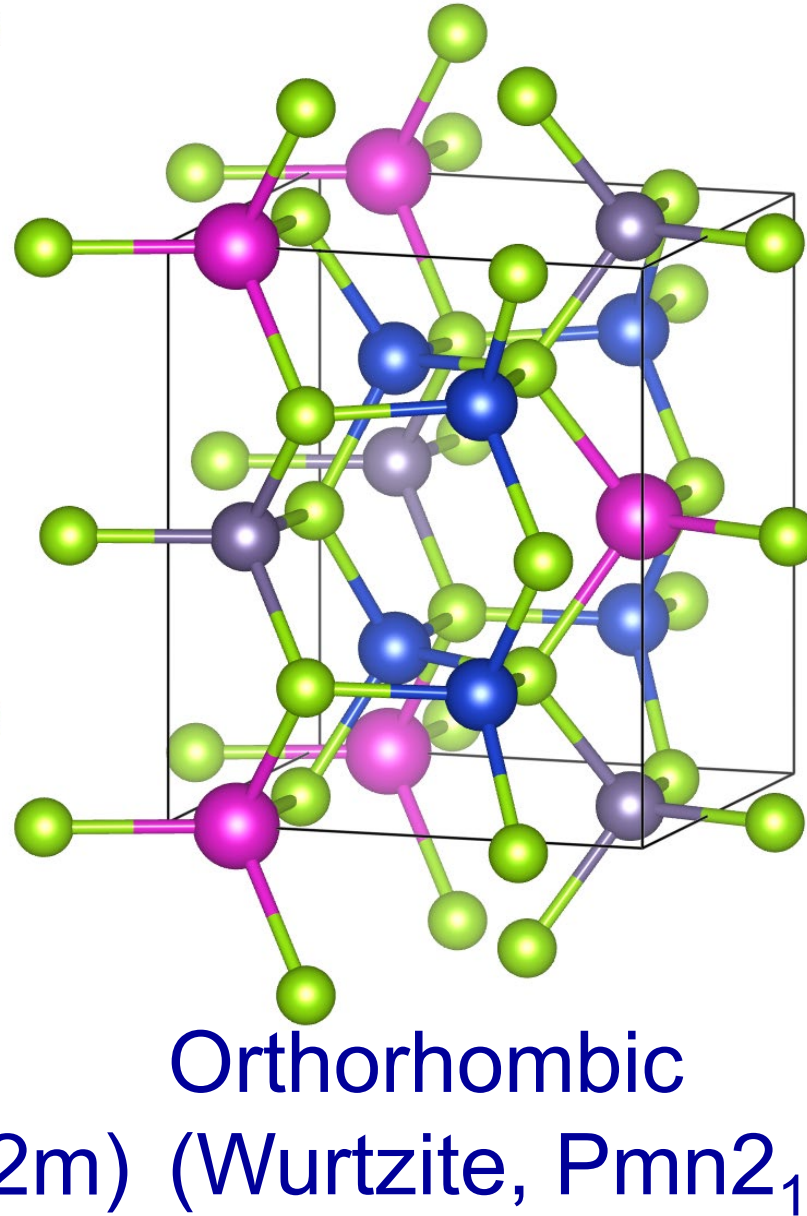
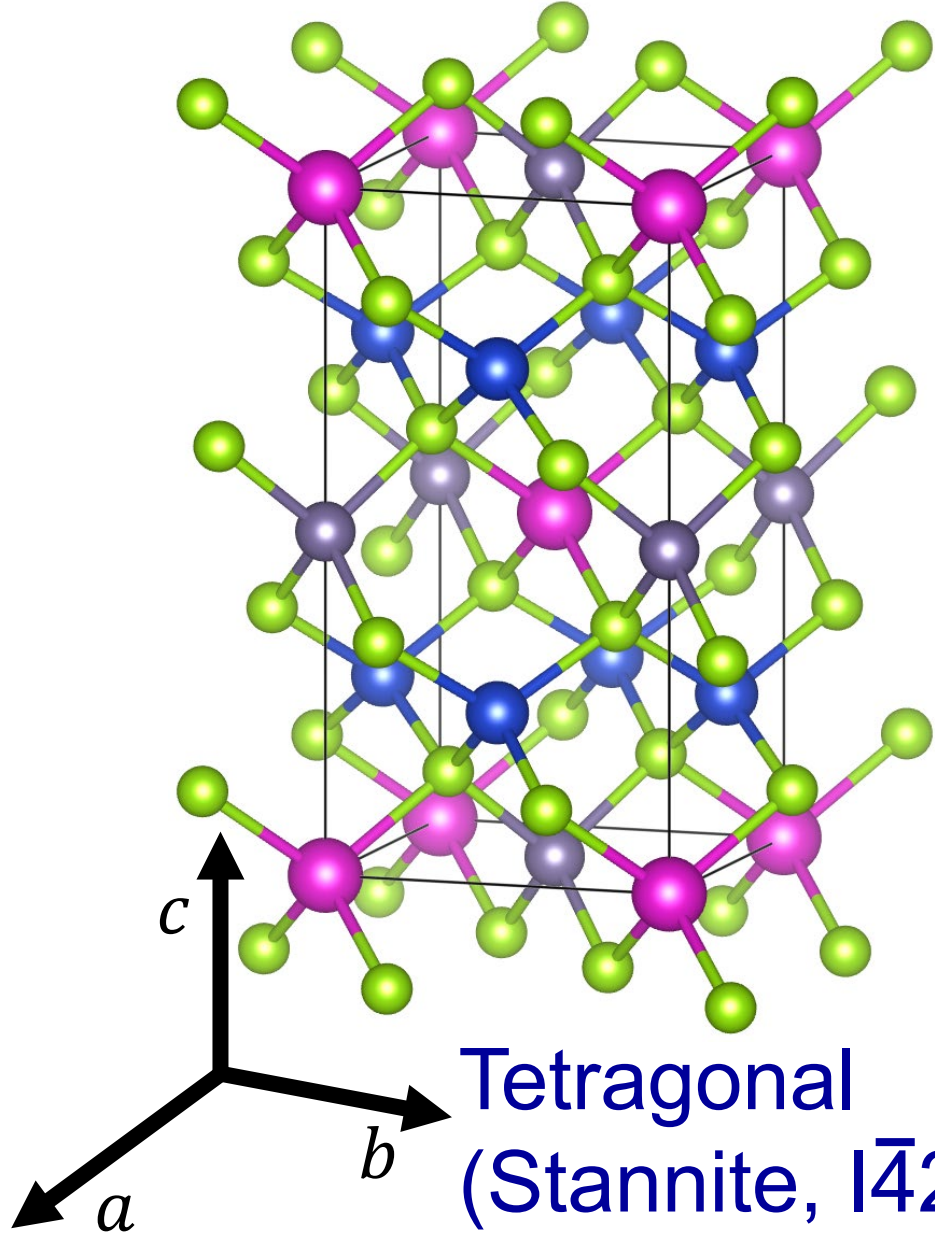
$x = 1.000$ : Bulk Modulus: 70<sup>[10]</sup> GPa

Shear Modulus: 28<sup>[10]</sup> GPa

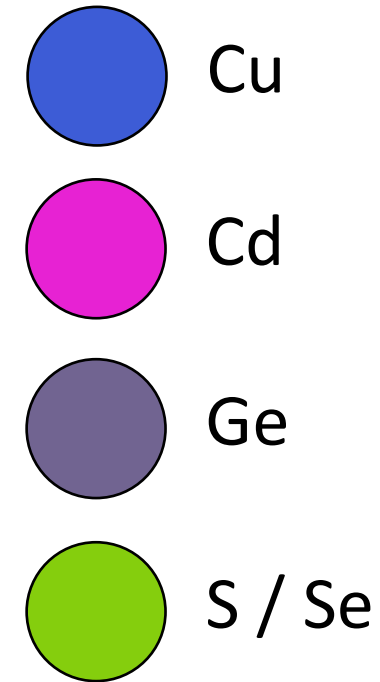
**10:** S. Hasan, K. Baral, N. Li, and W.-Y. Ching, Sci Rep 11, 9921 (2021)

**11:** T. V. Vu et. al., Journal of Electronic Materials 48, 705 (2019)

# Atomic Models: $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$

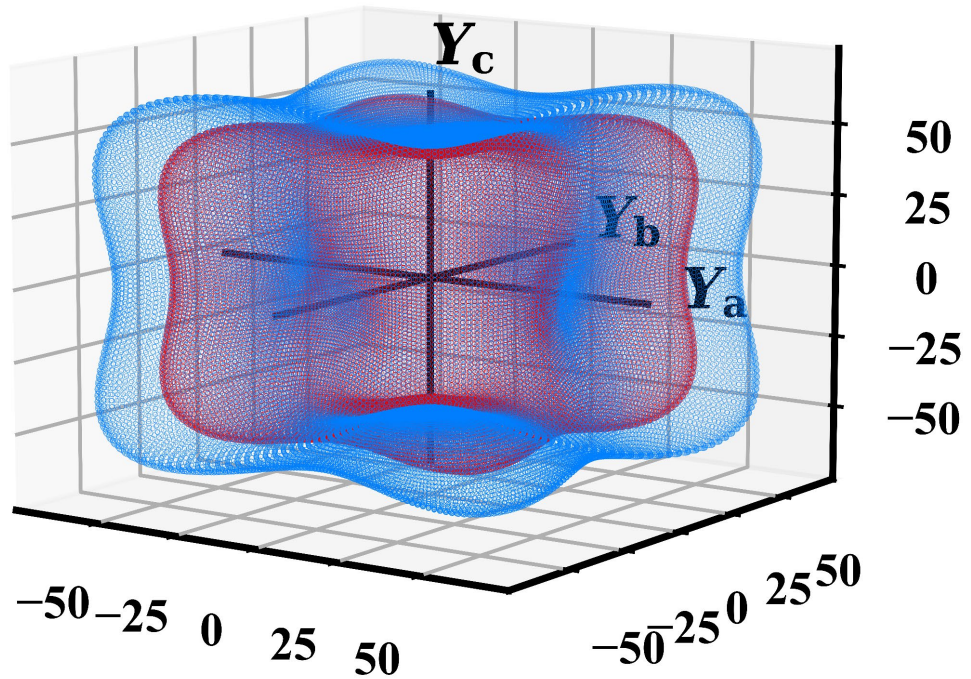


- Number of atoms = 16  
=  $2 \times$  (formula unit)
- $1 \times 1 \times 1$  unit =  
conventional unit cell

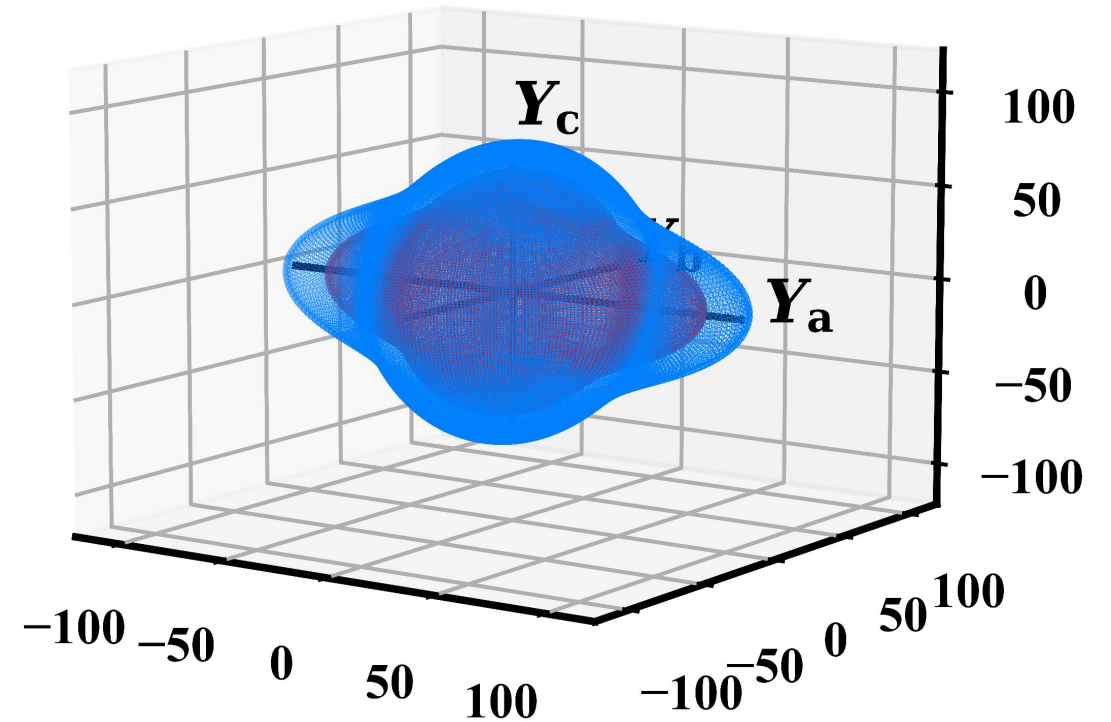


$$x = \frac{[\text{S}]}{[\text{S}] + [\text{Se}]}$$

# Directional Young's Moduli: $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$

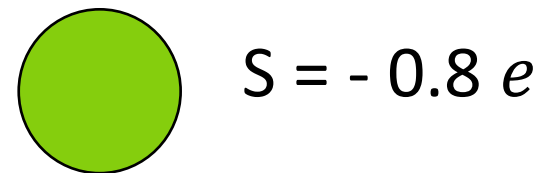
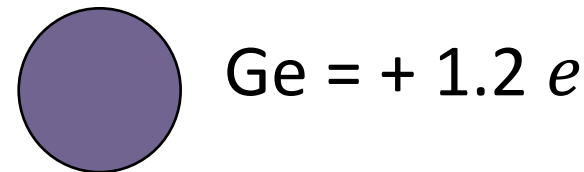
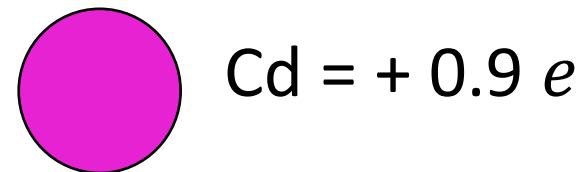
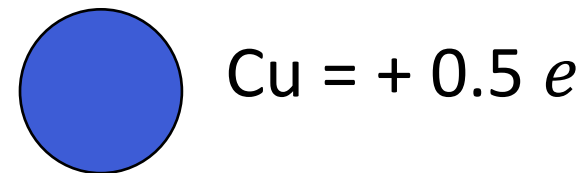
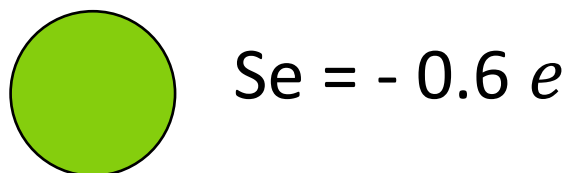
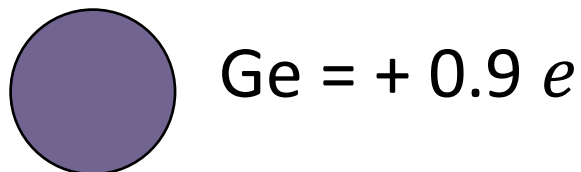
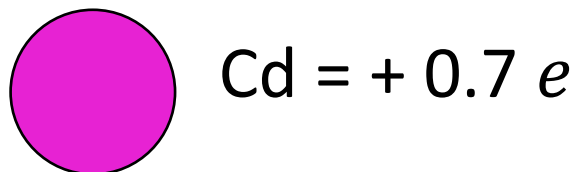
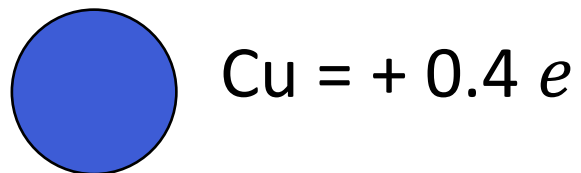
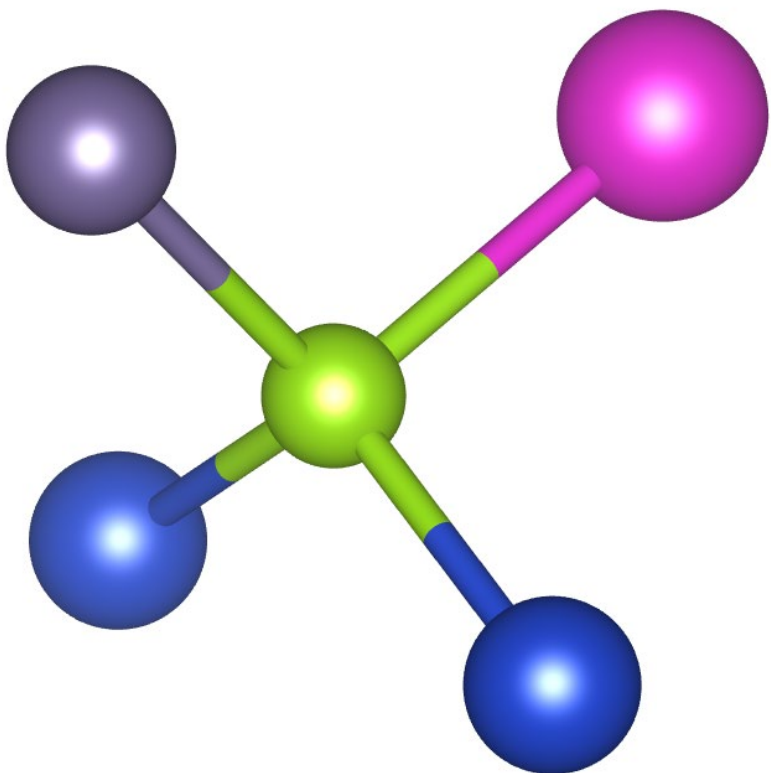


Tetragonal:  
Strongest in diagonal  
directions (GPa units)



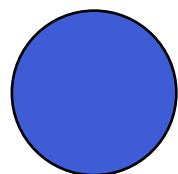
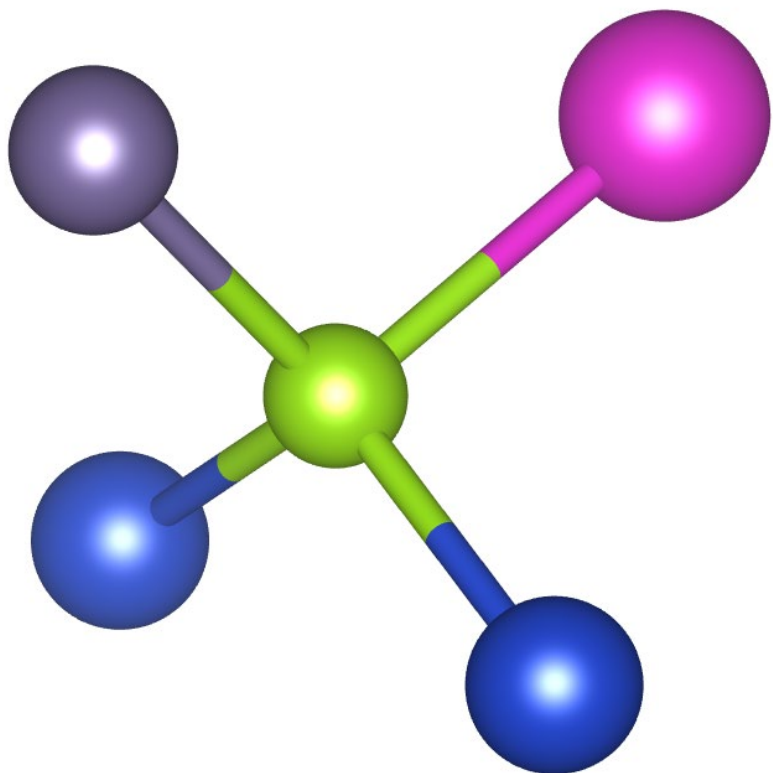
Orthorhombic:  
strongest in  $a, b, c$   
directions (GPa units)

# Bader Charge Analysis

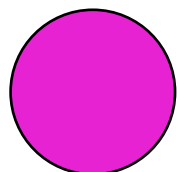


**Tetragonal and Orthorhombic nearly identical charge transfers**

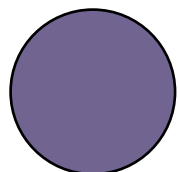
# Bader Charge Analysis



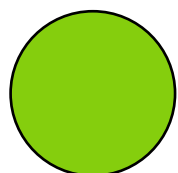
$$\text{Cu} = + 0.36 e$$



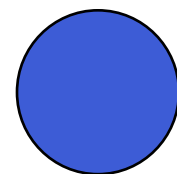
$$\text{Cd} = + 0.71 e$$



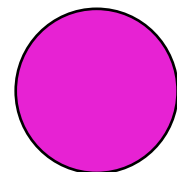
$$\text{Ge} = + 0.85 e$$



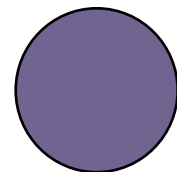
$$\text{Se} = - 0.57 e$$



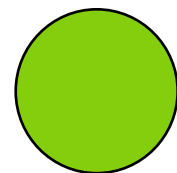
$$\text{Cu} = + 0.49 e$$



$$\text{Cd} = + 0.86 e$$



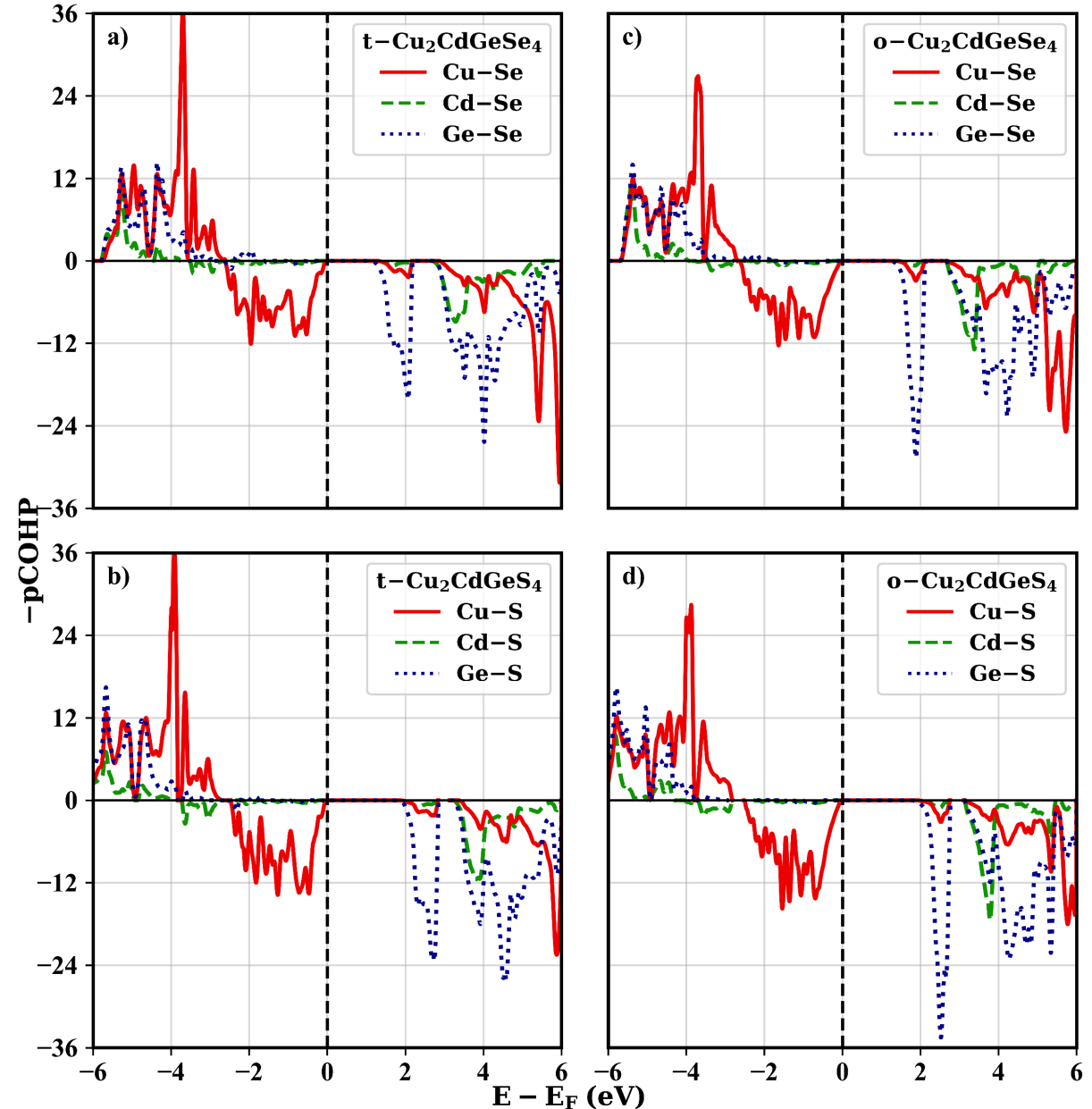
$$\text{Ge} = + 1.20 e$$



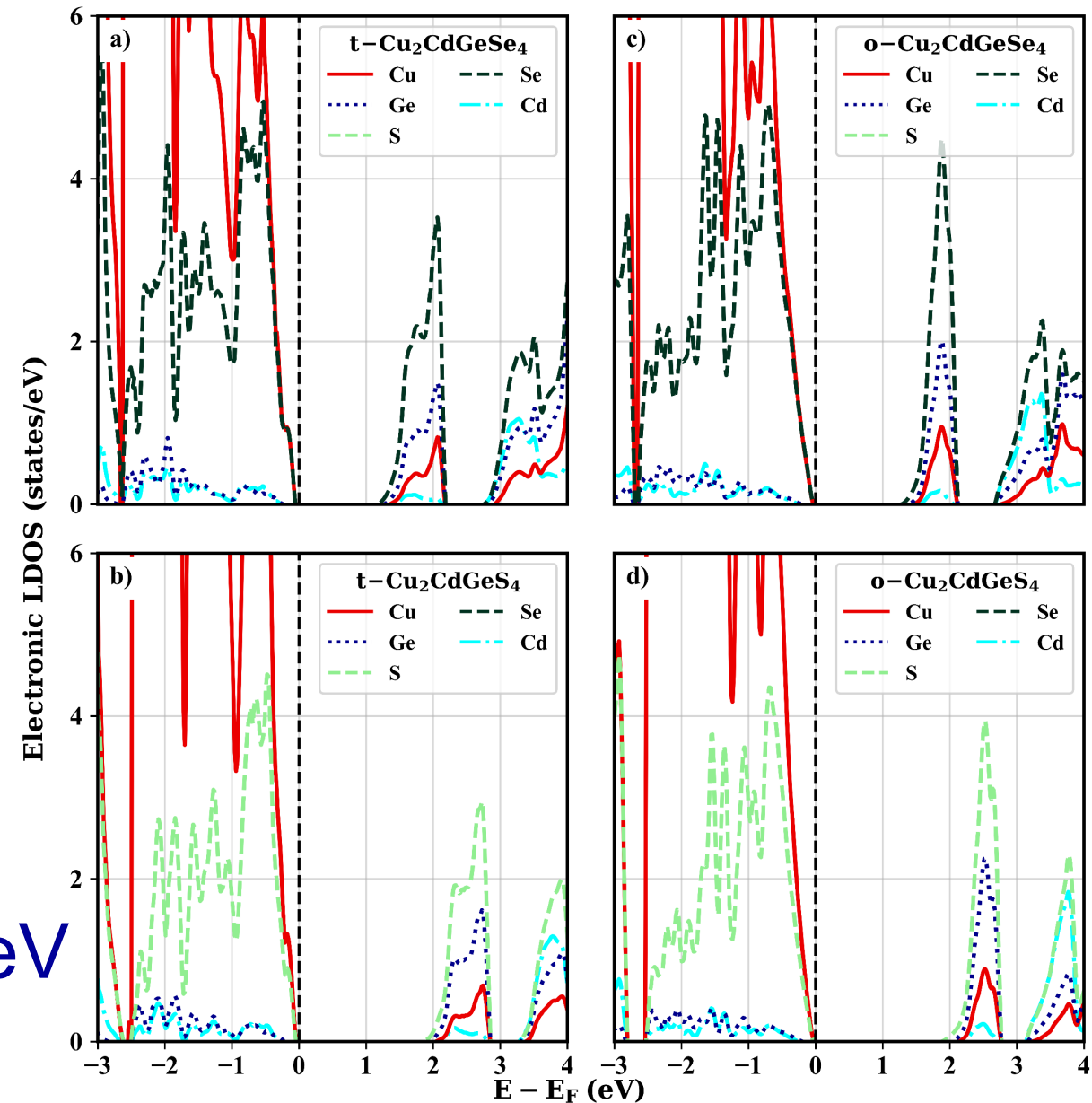
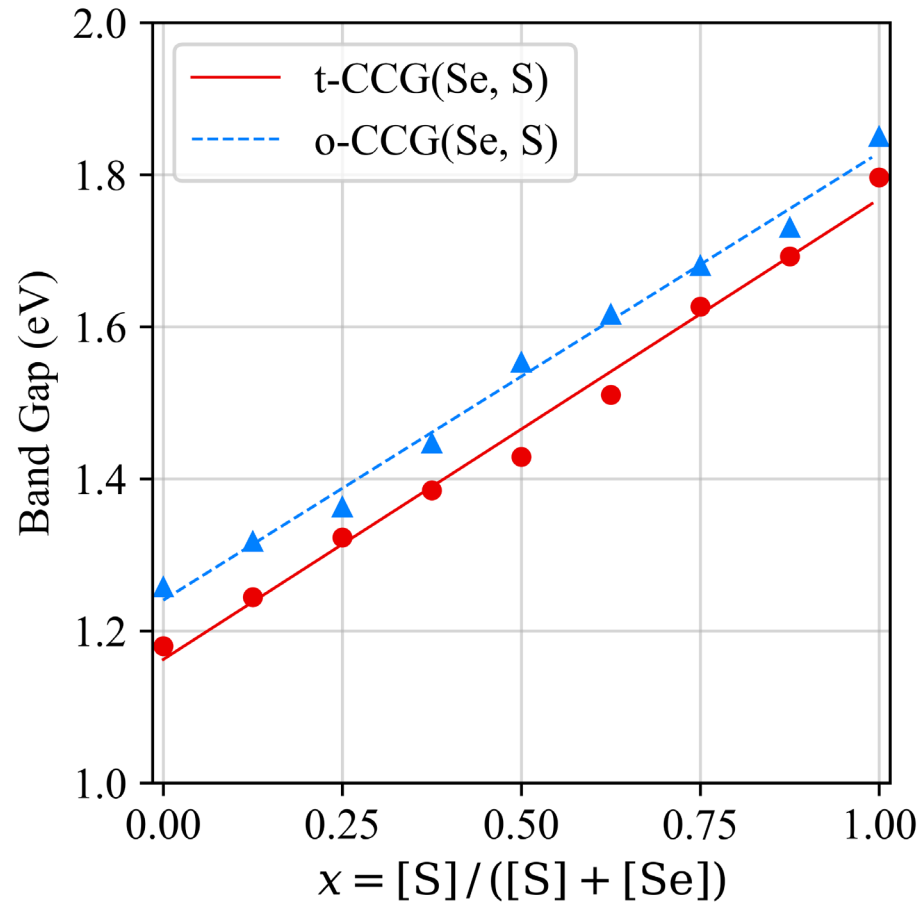
$$\text{S} = - 0.76 e$$

# COHP: $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$

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

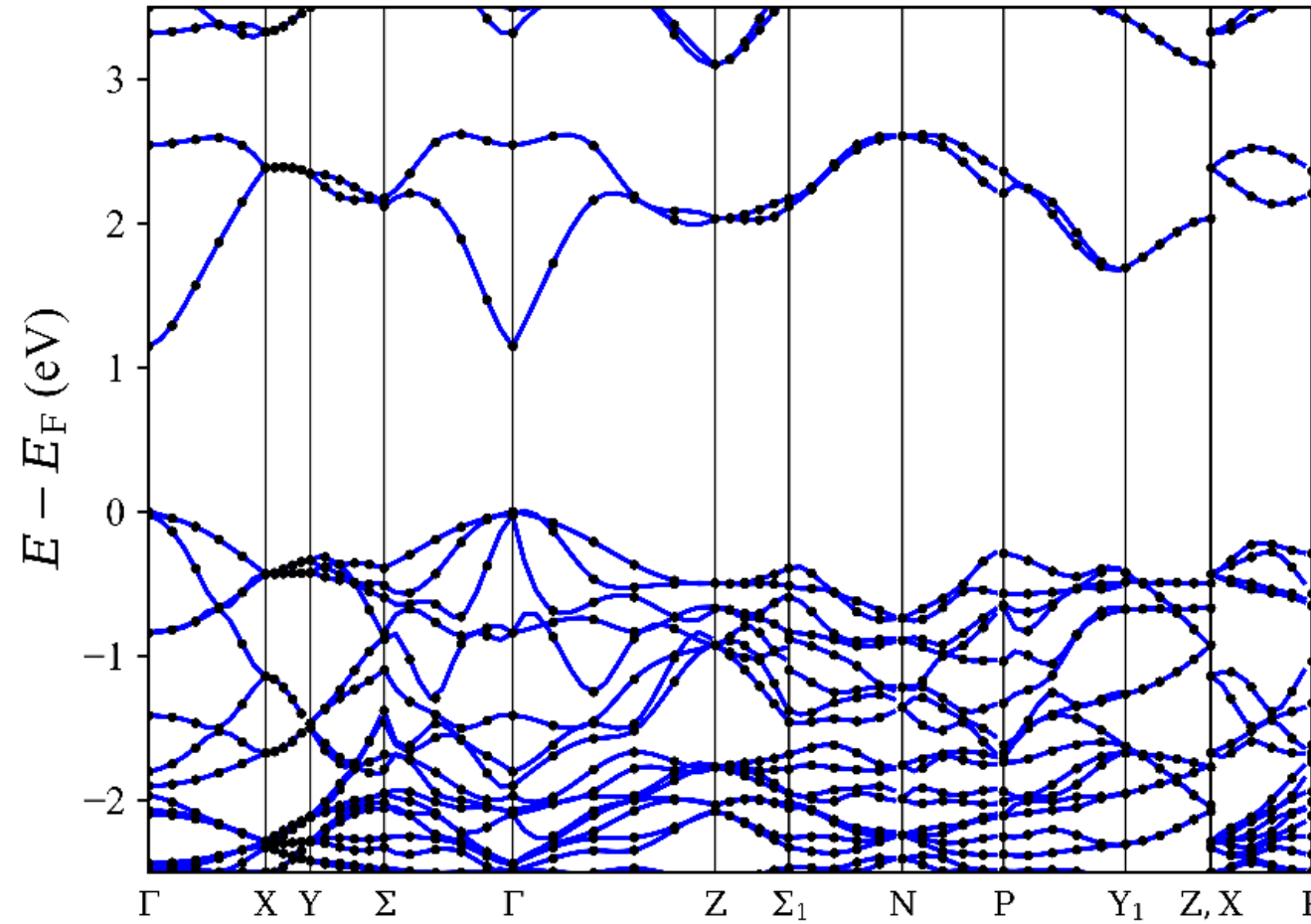


# Density of States: $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$

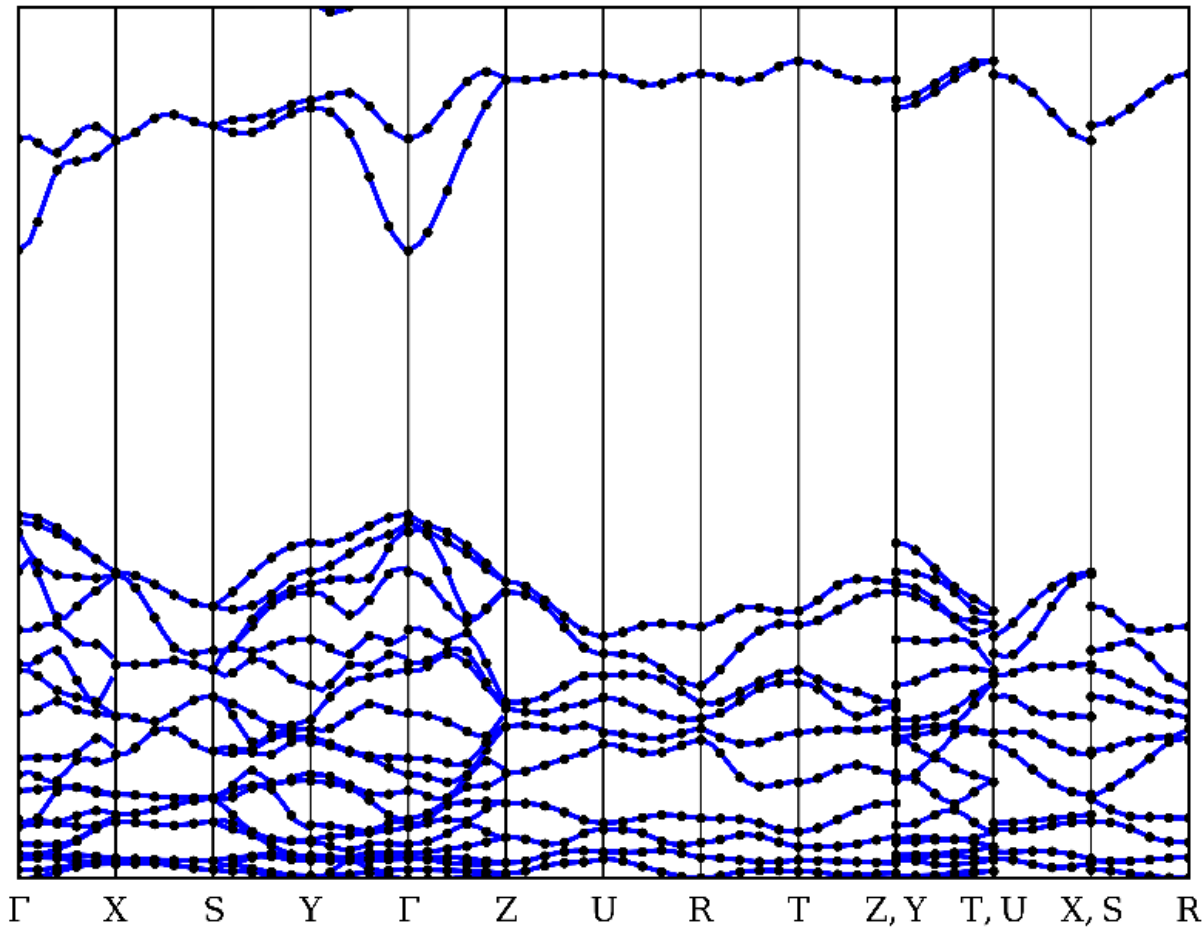


- Tetragonal gap:  $\sim 1.2 \rightarrow 1.8$  eV
- Orthorhombic gap:  $\sim 1.3 \rightarrow 1.9$  eV
- Linear increase with  $x$ :  $0 \rightarrow 1$

# Band Structure



Tetragonal  
 $\text{Cu}_2\text{CdGeSe}_4$



Orthorhombic  
 $\text{Cu}_2\text{CdGeS}_4$

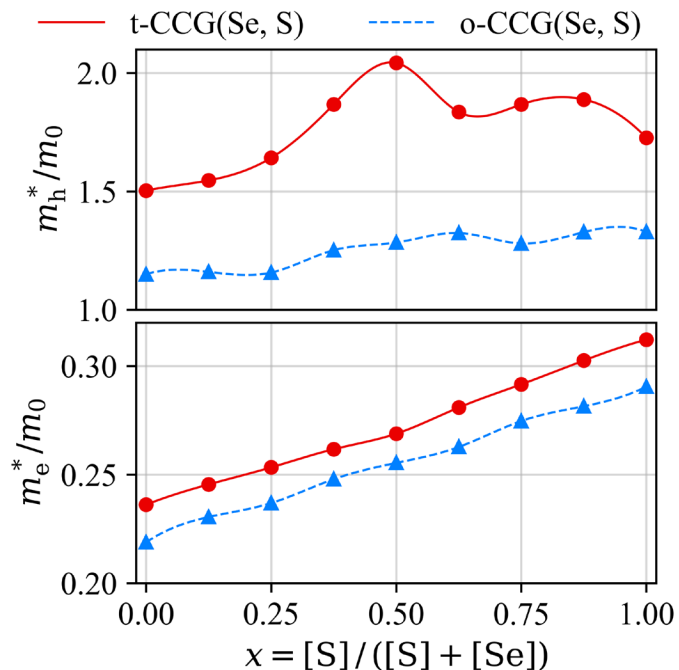


# Effective Masses: $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$

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

System	$m_h^*/m_0$			$m_e^*/m_0$		
	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

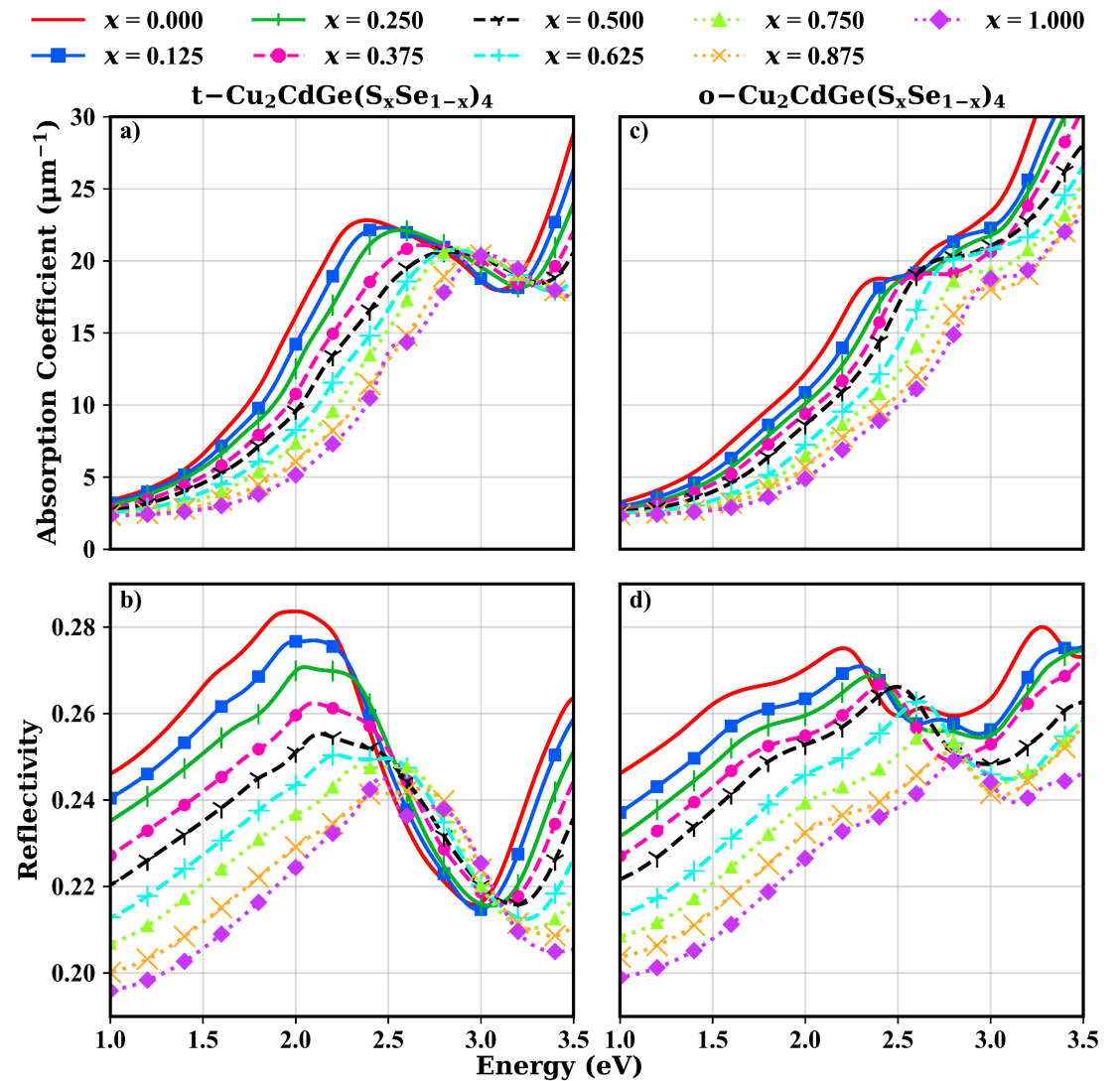
Average over all directions:



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

# Optical Response: $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$

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

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- Computed elastic and optoelectronic properties of  $\text{Cu}_2\text{CdGe}(\text{S}_x\text{Se}_{1-x})_4$
- 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

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

# Extra: Simulated XRD

- Relative integrated intensity<sup>[14]</sup>:

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

- Structure factor:

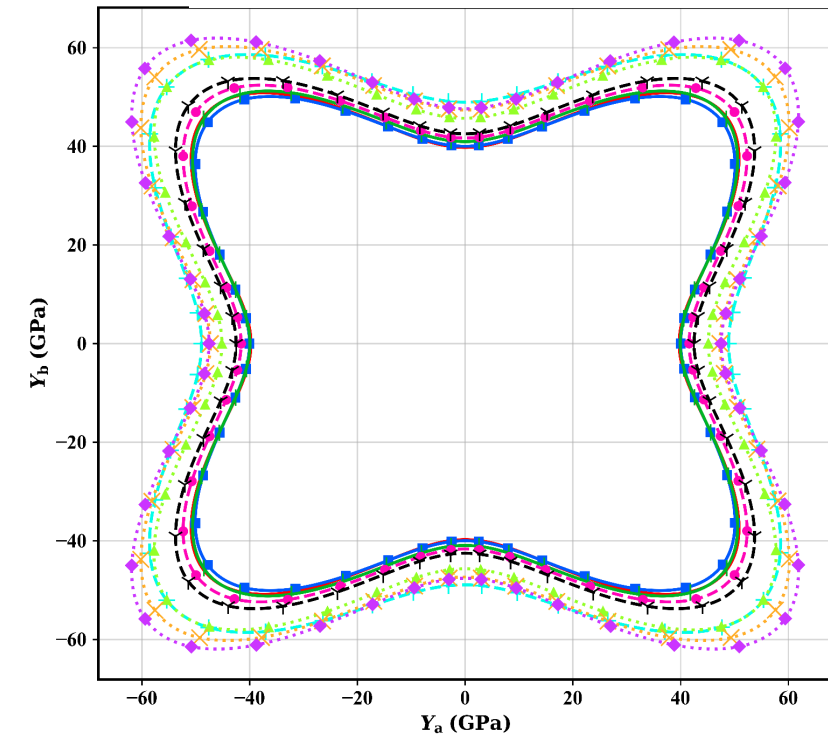
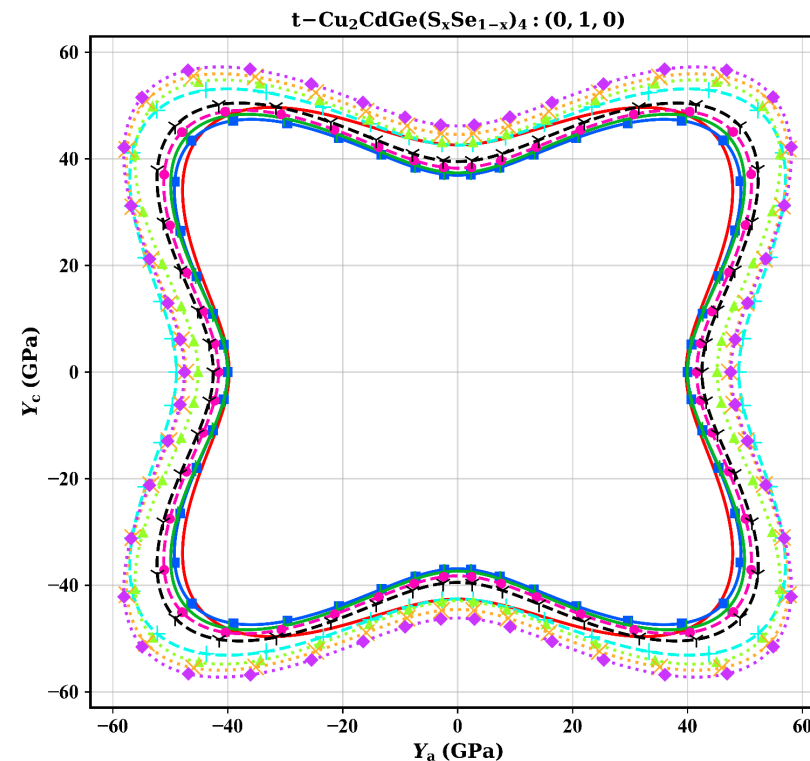
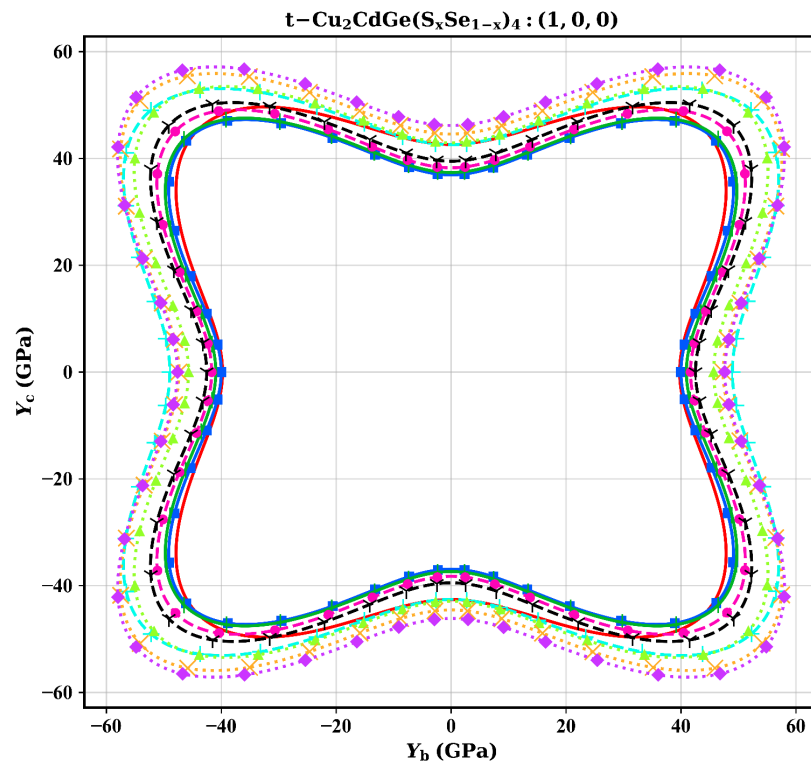
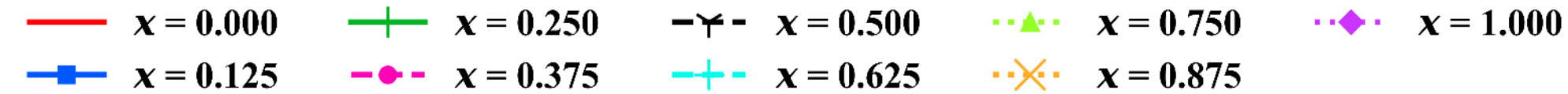
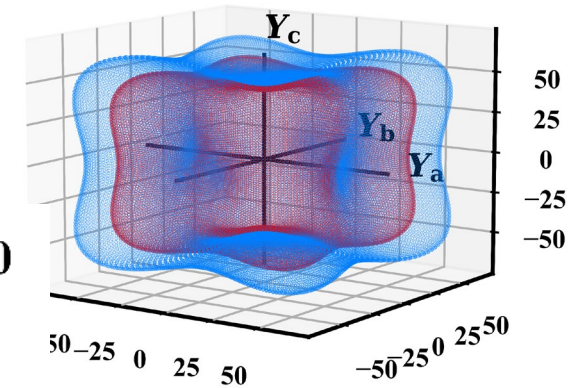
$$F_{hkl} = \sum_{j=\text{atoms}} f_j \exp(i2\pi(hx_j + ky_j + zl_j))$$

- Atomic scattering factor:

$$f_j \approx \sum_{k=1}^4 a_{jk} \exp\left(-b_{jk} \left(\frac{2\left(\frac{2\pi}{\lambda}\right)\sin(\theta_B)}{4\pi}\right)^2\right) + c_j$$

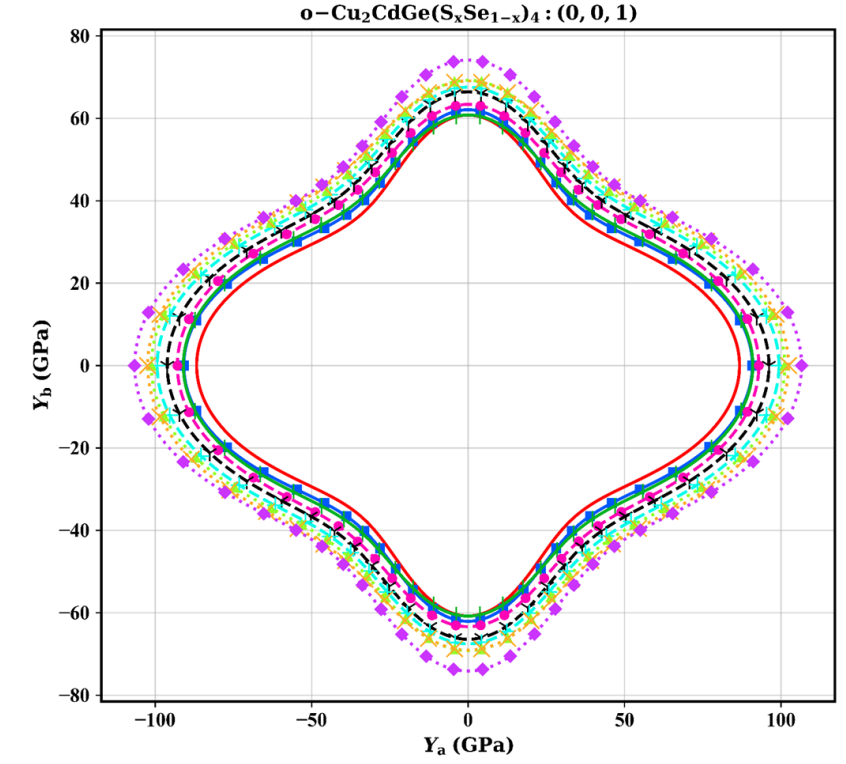
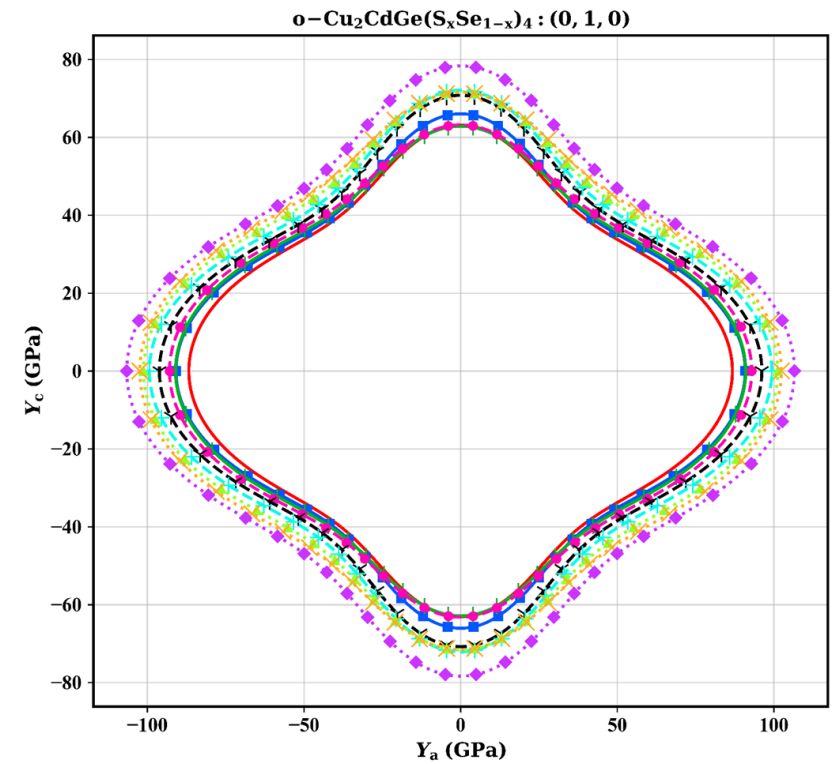
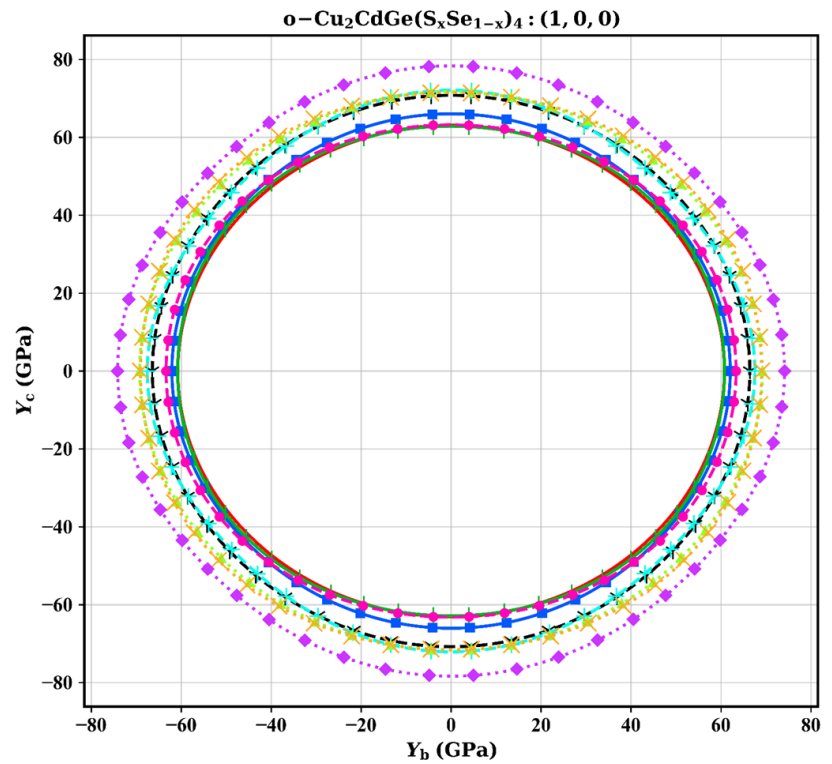
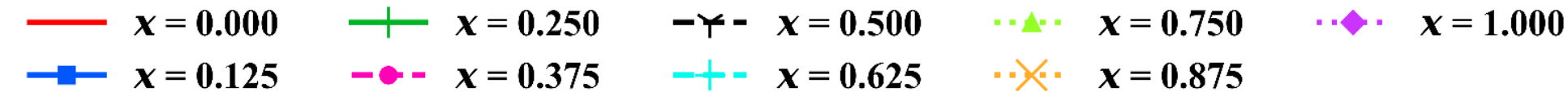
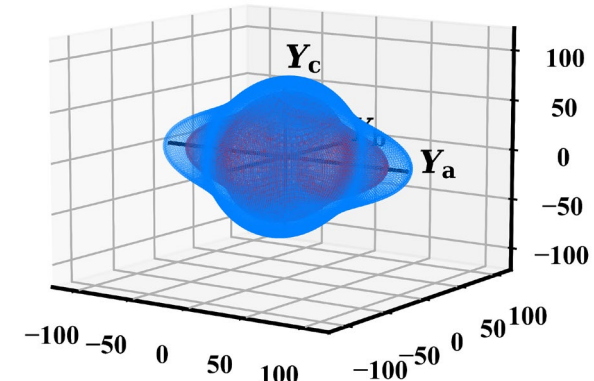
# Extra: Directional Young's Modulus (planes)

- 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)

