

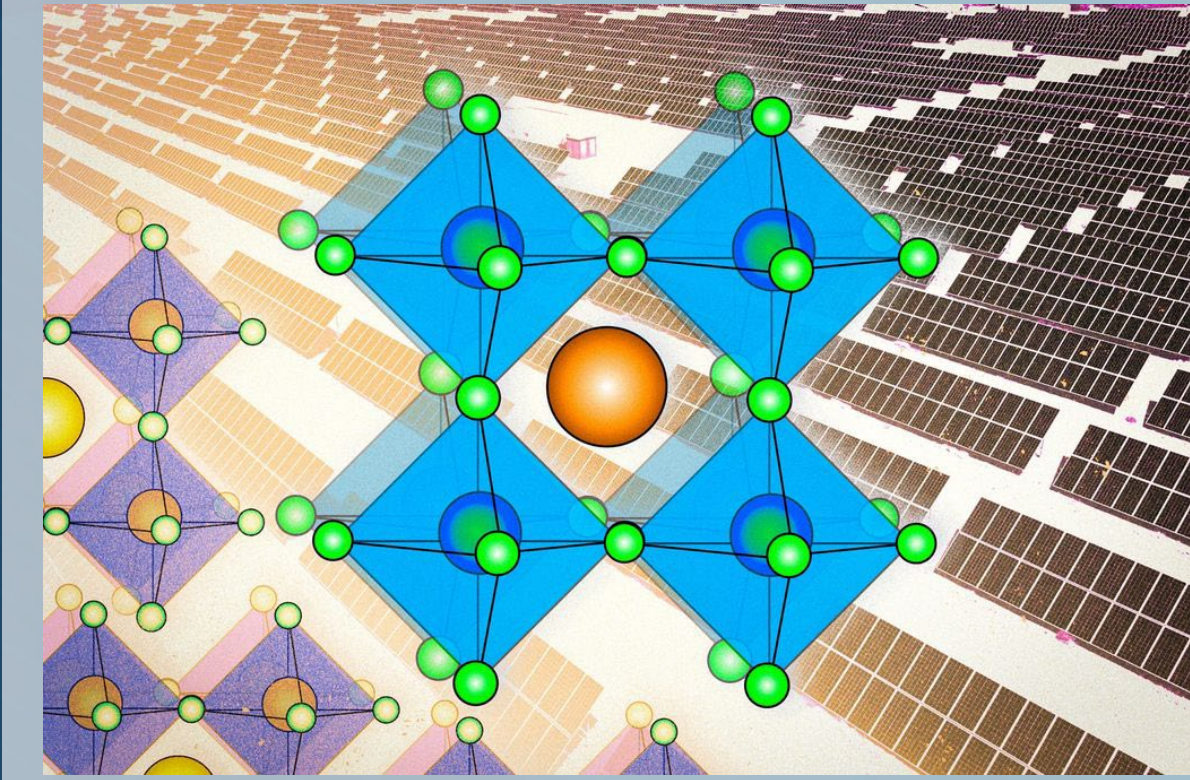
Computational Investigations of the Bulk and Surface Properties of CaSnS₃

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INTRODUCTION

In recent years, the demand for sustainable energy sources increased rapidly in efforts to decarbonize various sectors.^[1] Photovoltaic conversion has long been on the horizon as the most compelling technological option for producing 'green' energy from widely available sunlight. Harnessing this energy and designing our infrastructure around it will mitigate the adverse environmental and societal consequences of climate change.



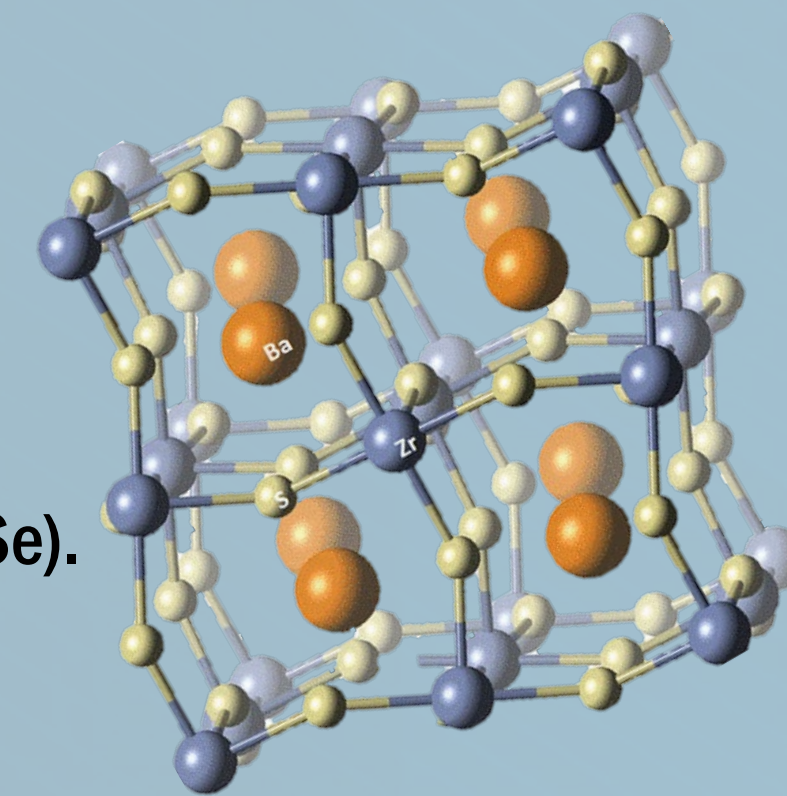
Hybrid organic-inorganic lead halide perovskites (HOIPs) have attracted significant attention recently as one of the most promising photovoltaic technologies owing to their high efficiency, low-cost, solution-processibility, and exceptional optoelectronic properties.^{[4][5]}

The record PCE of halide perovskites (over 25% in single-junction cells and over 29% in tandem cells with silicon) shows a great promise.^[6]

However, the toxicity of the lead content and the intrinsic instability of lead-halide perovskites materials have remained significant challenges to their large-scale applications and commercialization.

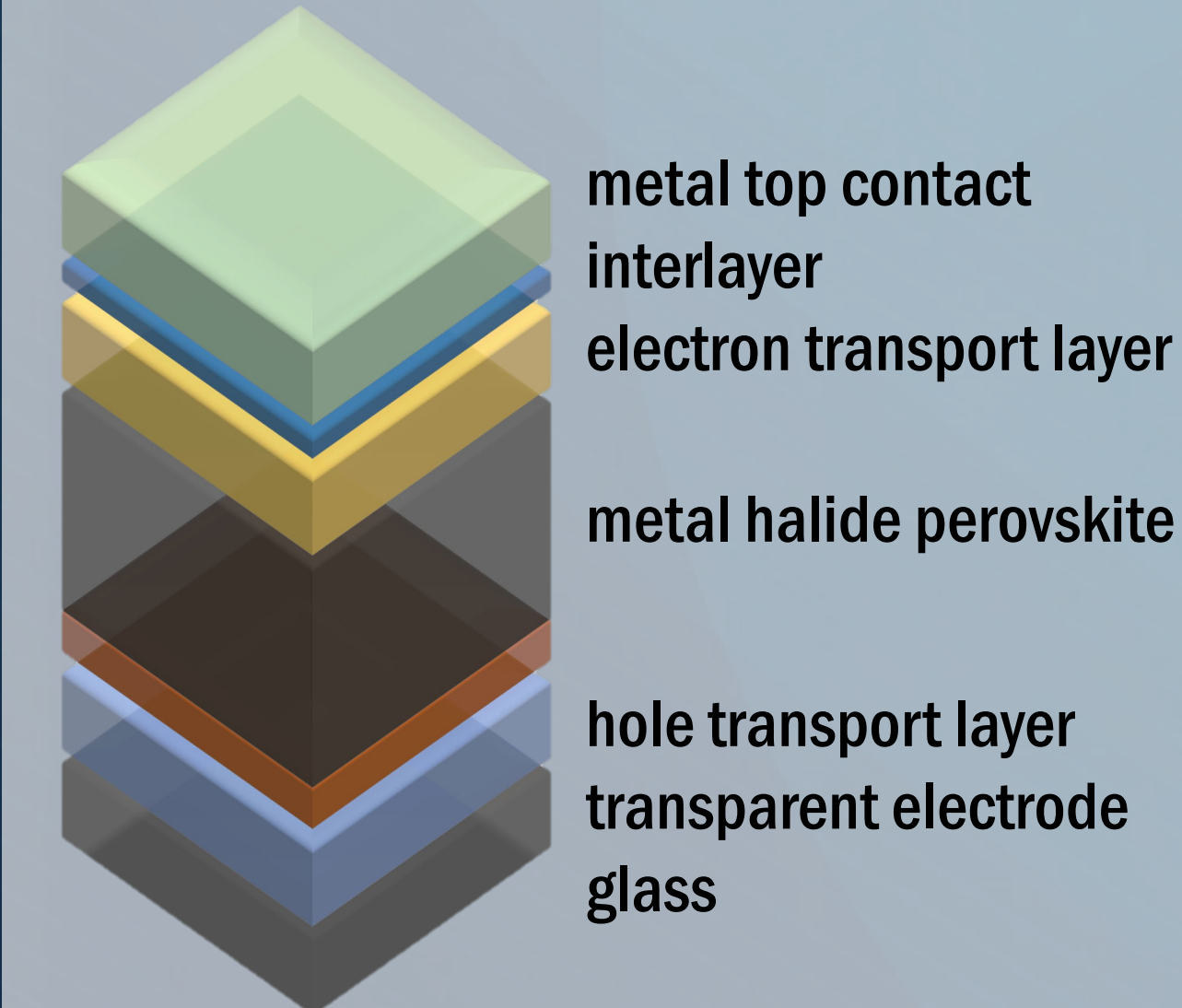
CHALCOGENIDE PEROVSKITES

- Chalcogenide perovskites have recently emerged promising alternatives to HOIPs owing to their remarkable chemical and thermal stability up to 600 degrees Celsius and under-water immersion.^[7]
- They are characterized by record-high dielectric polarizability, while also featuring tunable bandgap (E_g) in the visible and near infrared region of the solar spectrum (1.4–2.1 eV).^[8]
- Possess high absorption coefficients near the band edge ($\sim 10^5 \text{ cm}^{-1}$ in contrast to 10^4 cm^{-1} for CdTe and Si).^[9]
- PV device simulation shows that 38% efficiency can be reached in a chalcogenide perovskite/crystalline Si tandem architecture.^[10]
- They have huge compositional degrees of freedom (ABX_3), where A and B are metals with a combined valence of 6 and X stand for S or Se). Examples: BaZrS₃, BaZrSe₃, SrZrS₃, CaZrSe₃, CaSnS₃, etc.



RESEARCH OBJECTIVES

The nature of the surface of the absorber material (i.e., the composition and stability) dictates its interfacial structures with charge transport layers.



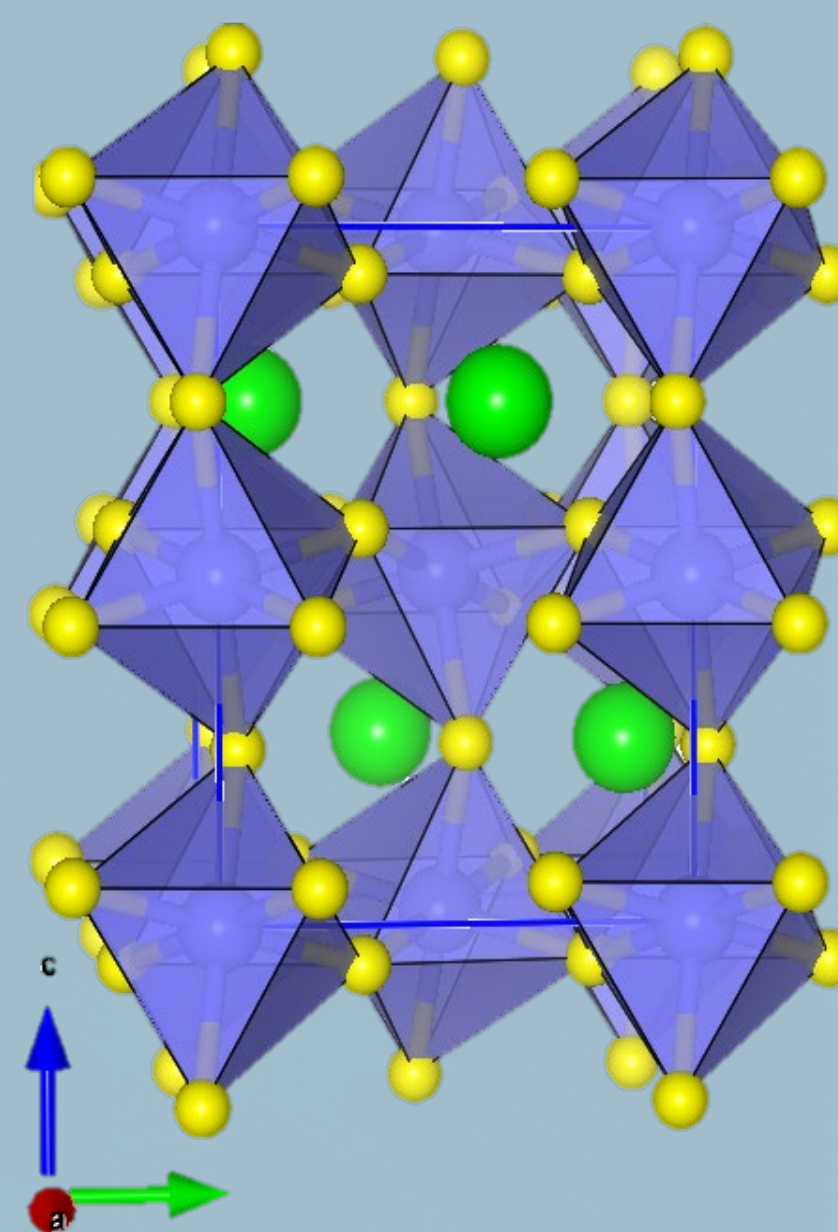
- Determine the structural parameters of CaSnS₃
- Accurately predict the bandgap and electronic structures (band structure and density of states) of CaSnS₃.
- Predict the optical properties (absorption coefficient, dielectric constant, reflectivity, refractive index, etc.) of CaSnS₃.

- Characterize the surface structures, composition and relative stabilities of the different Miller-index surfaces of CaSnS₃.
- Determine the electronic properties (i.e., the work function, ionization potential, and electron affinity) of the different surfaces of CaSnS₃.

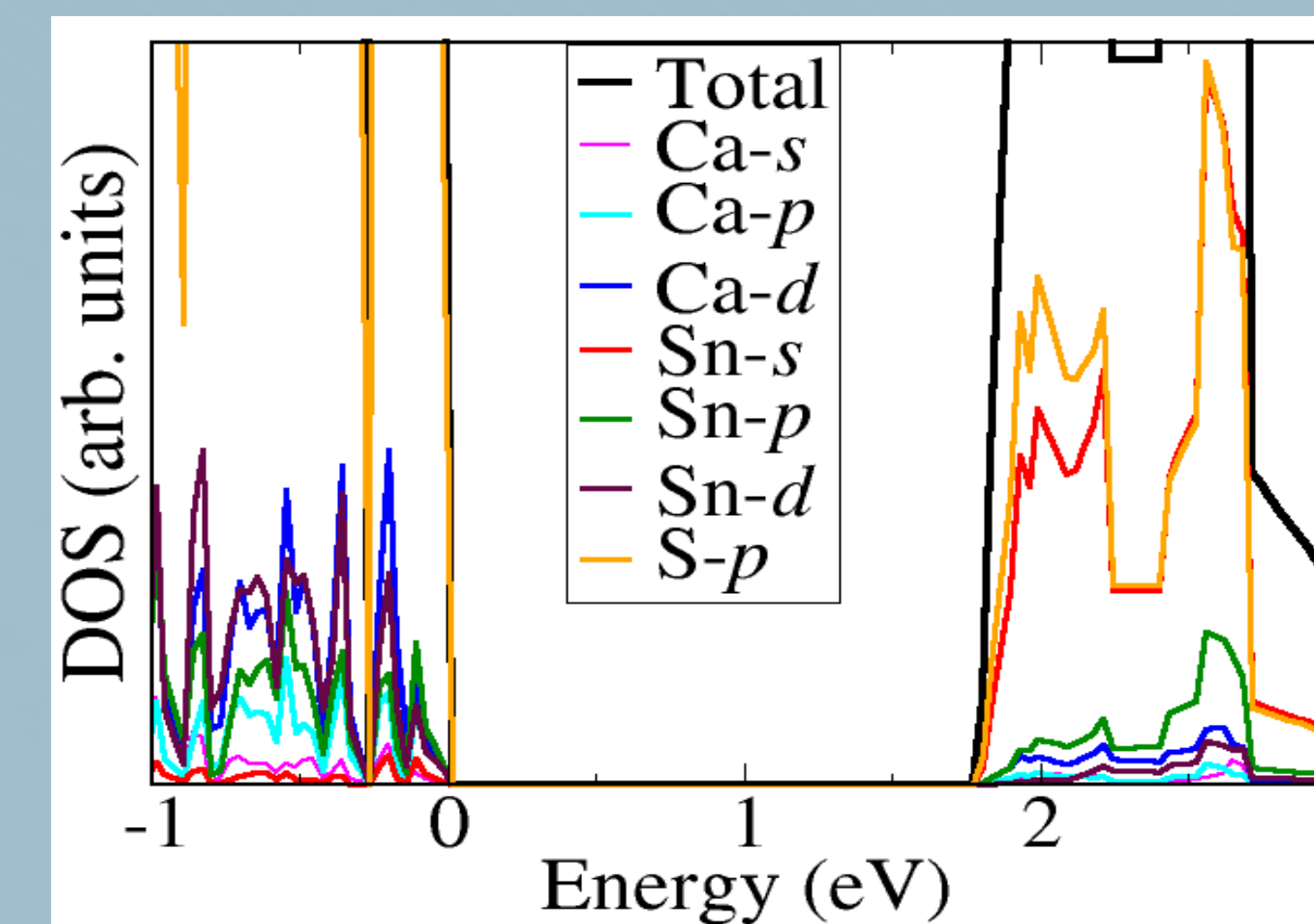
STRUCTURAL AND ELECTRONIC PROPERTIES OF BULK CASNS3

CaSnS₃ Crystallizes in the orthorhombic phase

Space group: Pnma



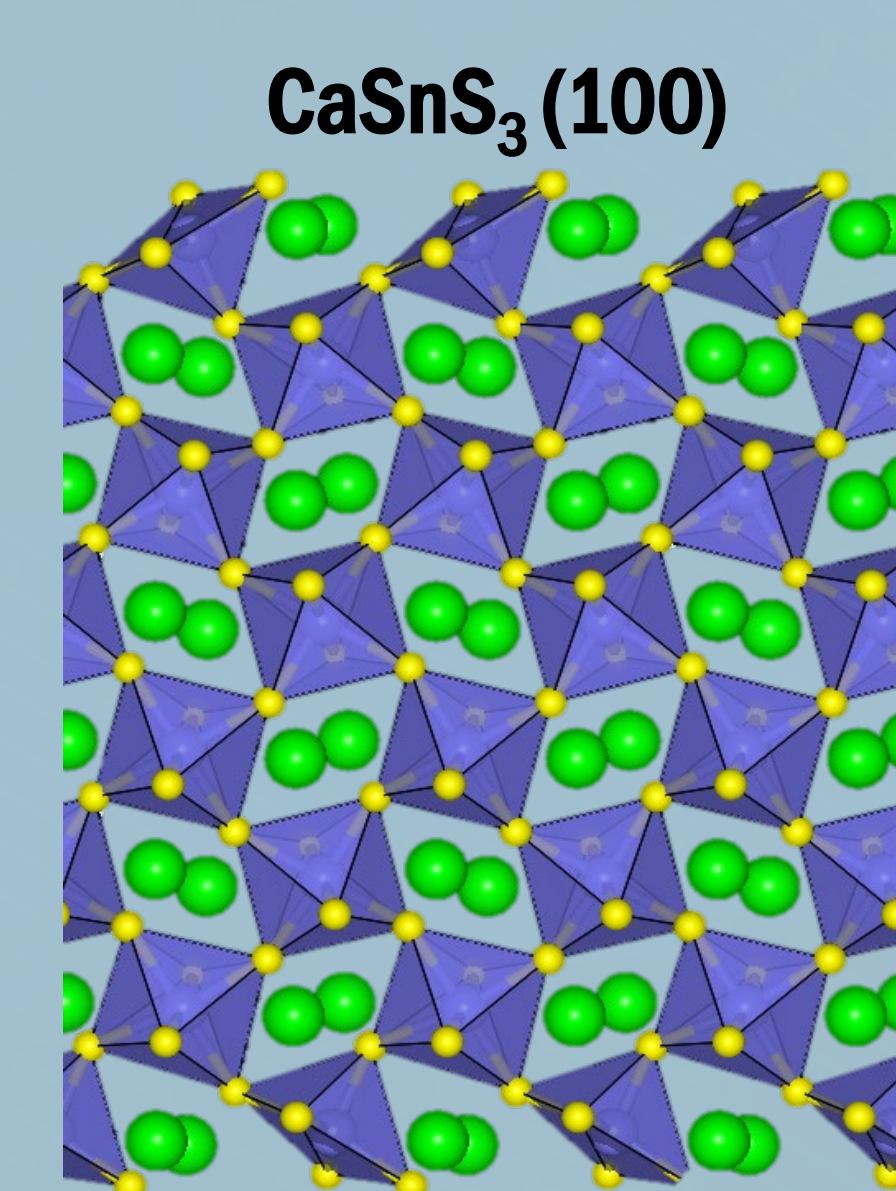
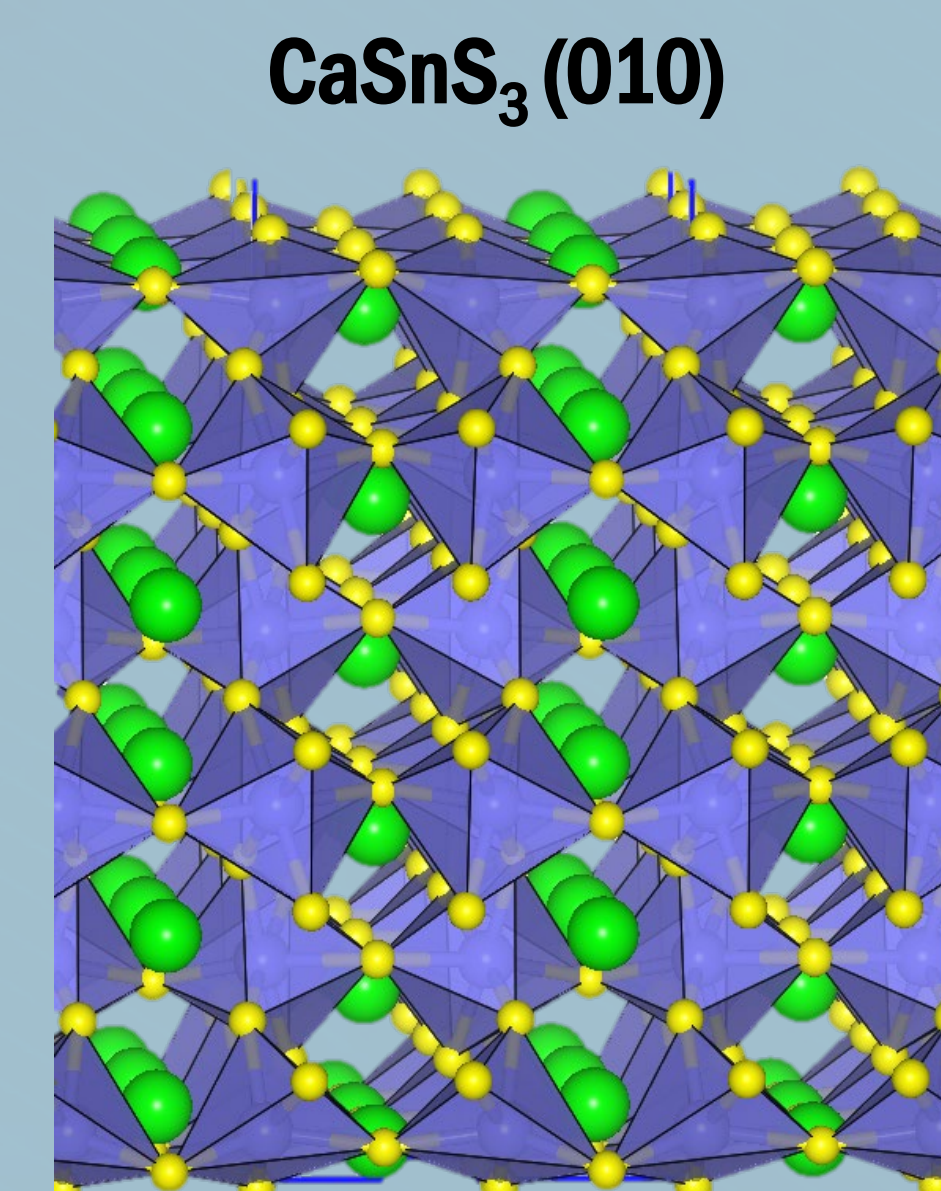
Lattice parameter	DFT-D3	Experiment ^[2]	Band Gap	E_g (eV)
a (Å)	6.647	6.687	DFT-D3	1.76
b (Å)	7.033	7.084	Experiment ^[2]	1.72
c (Å)	9.580	11.286		



SURFACE COMPOSITION AND STABILITY ANALYSIS

The surface stability trend is predicted to be: (010) < (100) < (011) < (111) < (001) < (110)

Surfaces Energies [γ (Jm ⁻²)]	CaSnS ₃ (010)	CaSnS ₃ (100)
(001)	0.5983	
(010)	0.4527	
(100)	0.5257	
(011)	0.5456	
(101)	0.6613	
(110)	0.6415	
(111)	0.5642	

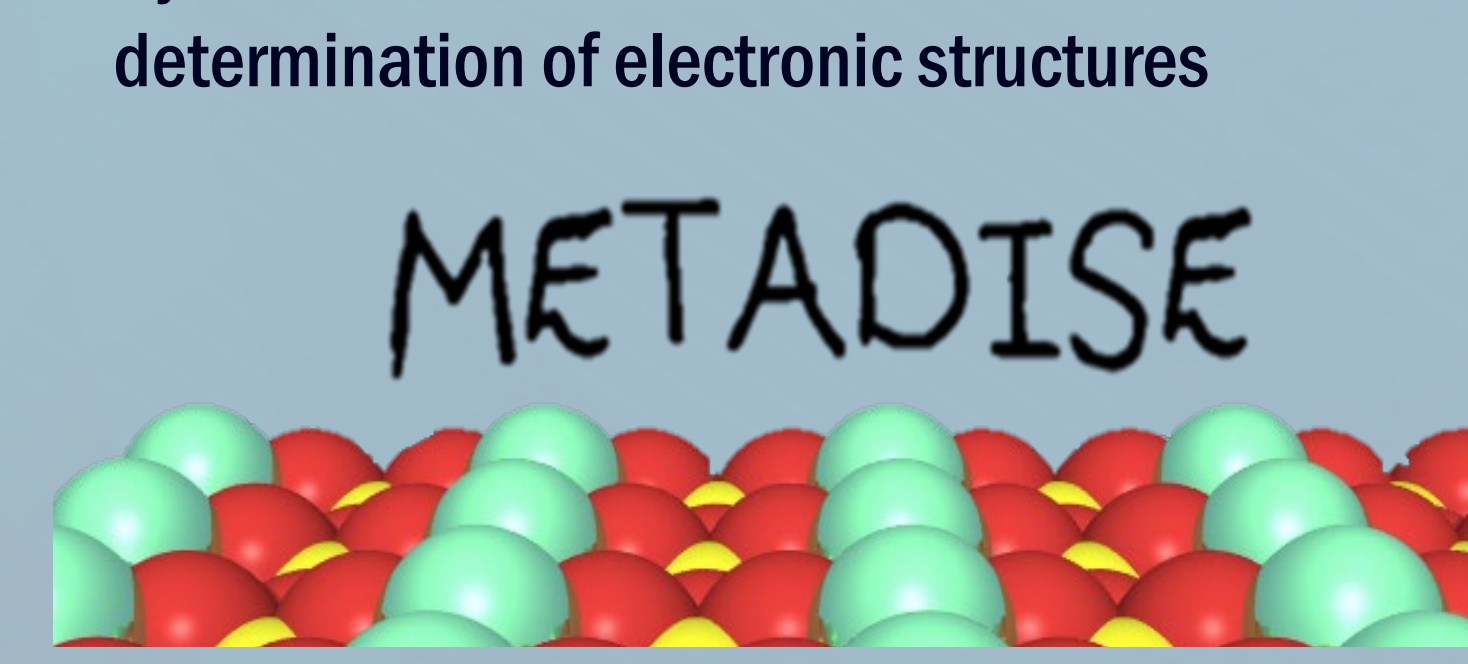


METHODOLOGY & COMPUTATIONAL DETAILS

Surface stability analysis:

$$\gamma_r = \frac{E_{slab}^{relaxed} - nE_{bulk}}{2A}$$

- State-of-the-art methodology of Density Functional Theory (DFT) implemented using the VASP package
- Dispersion correction accounted for via the Grimme's scheme
- Hybrid HSE06 was used for accurate determination of electronic structures



CONCLUSIONS

In summary, we have characterized the bulks and surface properties of CaSnS₃ using first-principles DFT methodology with Grimme's dispersion correction and Hybrid HSE06 functional.

- The orthorhombic structural parameters are predicted in good agreement with experiment
- The Electronic bandgap is predicted at 1.76 eV, which is consistent UV-vis measurement
- Both the valence band edge of CaSnS₃ is dominated by S-p states whereas the conduction band edge has major contribution from both the S-p and Sn-s states
- The most stable surface of CaSnS₃ is predicted to be the (010) surface with a surface energy of 0.45 Jm⁻².

Ongoing and future calculations will systematically characterize optical properties of the bulk CaSnS₃

We will also characterize the electronic properties (work function, ionization potential, and electron affinity) of the different surfaces of CaSnS₃

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ACKNOWLEDGEMENTS

I would like to express my sincere gratitude towards my supervisor, Dr. Nelson Dzade, and his PhD student, Henry Igwebuikwe, for their guidance and support throughout the research process.

I would also like to thank the Department of Energy and Mineral Engineering in the Penn State College of Earth and Mineral Sciences for funding this project and providing me with invaluable research experience.