Carl von Ossietzky Universität Oldenburg

# Exploring Binary Cesium-based Photocathode Materials via High-Throughput Density Functional Theory Calculations

Holger-Dietrich Saßnick[1] and Caterina Cocchi[1,2]

[1]Carl von Ossietzky Universität Oldenburg, Physics Department, 26129 Oldenburg
[2]Humboldt-Universität zu Berlin, Physics Department and IRIS Adlershof, 12489 Berlin

22nd September, 2022

# Motivation and Goals

- Nowadays syntheses methods are still strongly relying on expensive trial-and-error approaches.
- Introduce a theoretical framework that gives insight into relationships between structural features and the material's properties.
- As a starting point we focus on "simple" binary systems that are well known and studied.

## Experimental Collaborators

HZB Helmholtz Zentrum Berlin

Prof. Dr. Thorsten Kamps,
Dr. Sonal Mistry
and team.

DESY.

Dr. Sven Lederer
and team.

## Sponsors

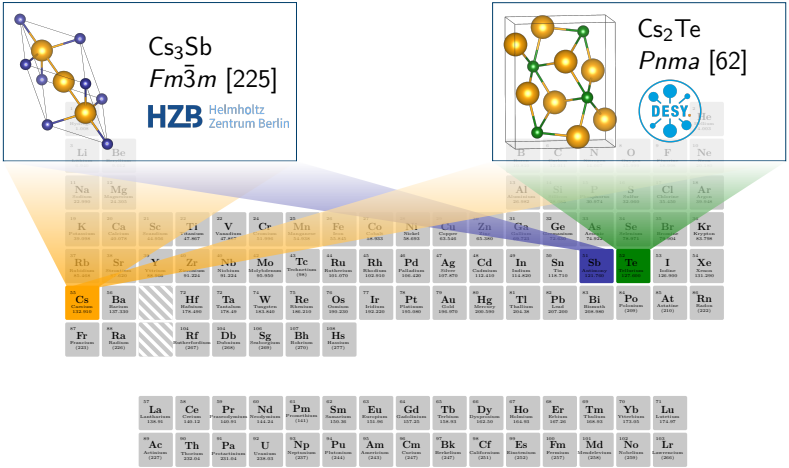
Bundesministerium für Bildung und Forschung

Niedersächsisches Ministerium für Wissenschaft und Kultur

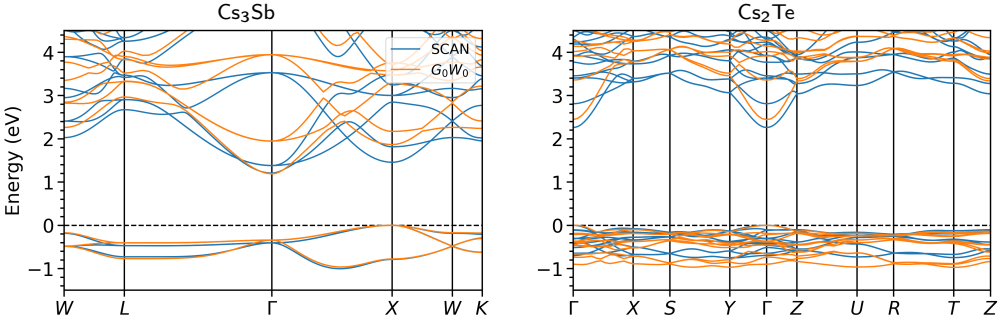
DFG
Project-id: 490940284

HLRN
Project-id: nic00069

*Ab-initio* methods like density functional theory (DFT) allow the calculation of material's properties without empirical parameters.



# Calculation results include electronic band structures

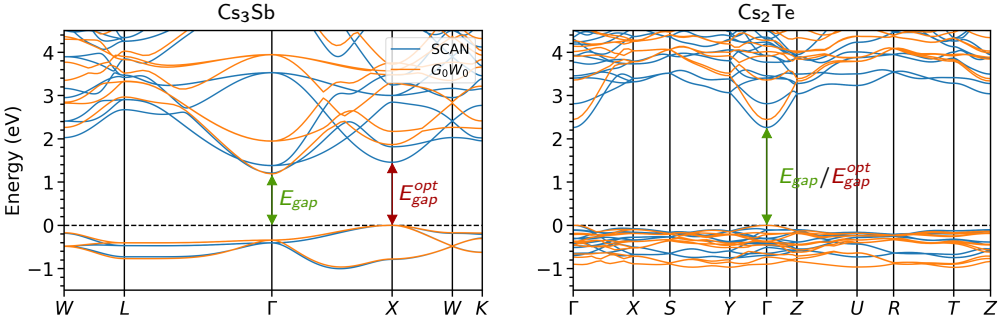



| | PBE | SCAN | SCAN+SOC | $G_0W_0$@PBE | BSE | Exp. |
|---|---|---|---|---|---|---|
| | | | **$Cs_3Sb$** | | | |
| $E_{gap}$ | 0.65 | 1.21 | 1.06 | 1.19 | | |
| $E_{gap}^{opt}$ (**k**-point) | 1.02 (Γ) | 1.46 (X) | 1.31 (X) | 1.53 (Γ) | 1.44 (Γ) | 1.6[1] |
| | | | **$Cs_2Te$** | | | |
| $E_{gap}$ | 1.76 | 2.26 | 2.06 | 2.45 | | |
| $E_{gap}^{opt}$ (**k**-point) | 1.76 (Γ) | 2.26 (Γ) | 2.06 (Γ) | 2.45 (Γ) | 1.60 (Γ) | 3.3[2] |

[1] Spicer, *Phys. Rev.* **1958**, 112, 114–122; doi: 10.1103/PhysRev.112.114
[2] Powell, Spicer, *et al.*, *Phys. Rev. B* **1973**, 8, 3987–3995; doi: 10.1103/PhysRevB.8.3987

Saßnick and Cocchi, *Electron. Struct.* **2021**, 3, 027001: doi: 10.1088/2516-1075/abfb08
Cocchi and Saßnick, *Micromachines* **2021**, 12(9), 1002; doi: 10.3390/mi12091002

# Calculation results include electronic band structures

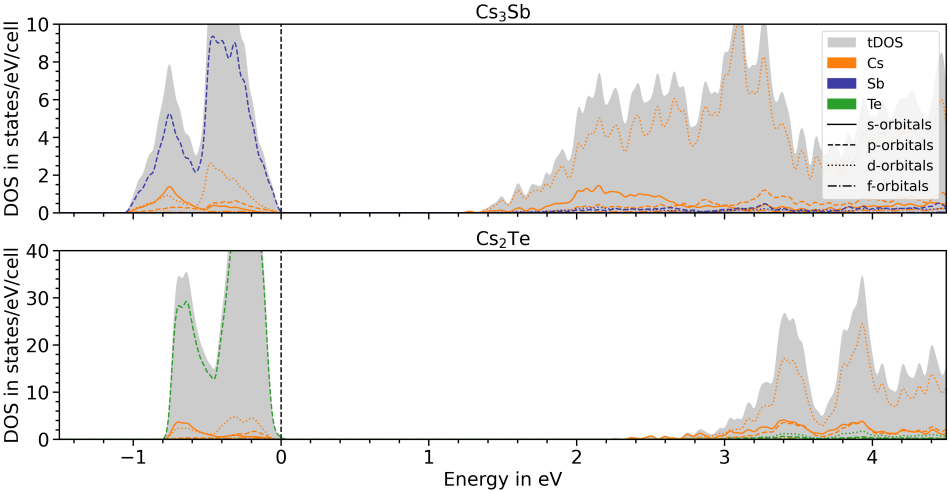



| | PBE | SCAN | SCAN+SOC | $G_0W_0$@PBE | BSE | Exp. |
|---|---|---|---|---|---|---|
| | | | **$Cs_3Sb$** | | | |
| $E_{gap}$ | 0.65 | 1.21 | 1.06 | 1.19 | | |
| $E_{gap}^{opt}$ (**k**-point) | 1.02 (Γ) | 1.46 (X) | 1.31 (X) | 1.53 (Γ) | 1.44 (Γ) | 1.6[1] |
| | | | **$Cs_2Te$** | | | |
| $E_{gap}$ | 1.76 | 2.26 | 2.06 | 2.45 | | |
| $E_{gap}^{opt}$ (**k**-point) | 1.76 (Γ) | 2.26 (Γ) | 2.06 (Γ) | 2.45 (Γ) | 1.60 (Γ) | 3.3[2] |

[1] Spicer, *Phys. Rev.* **1958**, 112, 114–122; doi: 10.1103/PhysRev.112.114
[2] Powell, Spicer, *et al.*, *Phys. Rev. B* **1973**, 8, 3987–3995; doi: 10.1103/PhysRevB.8.3987

Saßnick and Cocchi, *Electron. Struct.* **2021**, 3, 027001: doi: 10.1088/2516-1075/abfb08
Cocchi and Saßnick, *Micromachines* **2021**, 12(9), 1002; doi: 10.3390/mi12091002

# And the projected density of states of the electrons

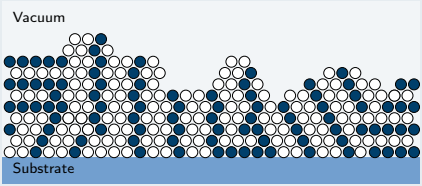



Saßnick and Cocchi, *Electron. Struct.* **2021**, 3, 027001: doi: 10.1088/2516-1075/abfb08

# High-throughput methods and their benefits

## Better insight into microstructure

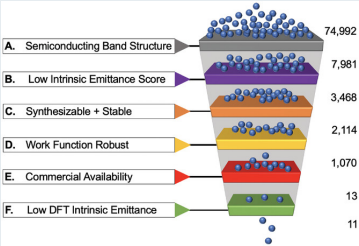
Synthesis route via PVD results in polycrystalline materials:




By restricting the screening space to a binary system, crystal structures that are likely to form during the syntheses process can be theoretically calculated.

## Identifying novel materials

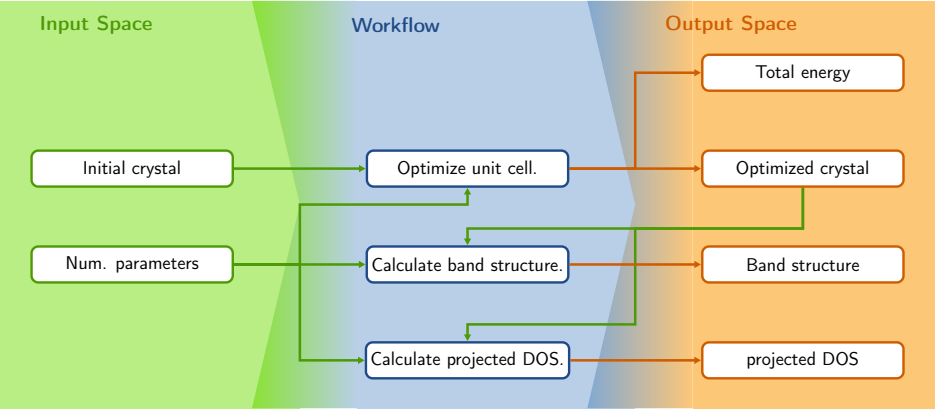
synthesis and experimental analysis of a large manifold of materials is very expensive.




Screening of a manifold of different material classes to check suitability for the application.

Antoniuk, Schindler, *et al.*, *Adv. Mater.* **2021**, 2104081; doi: 10.1002/adma.202104081

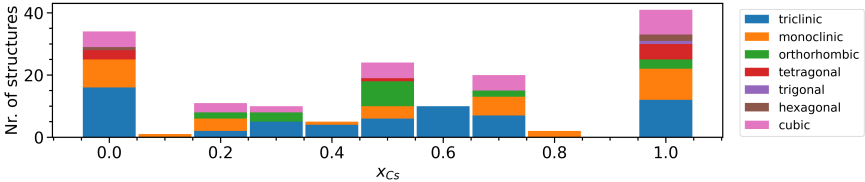
# The technical implementation of a high-throughput workflow



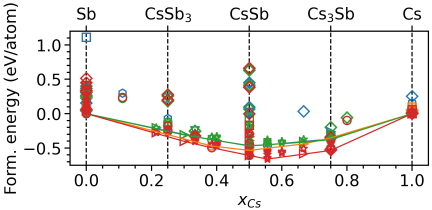

- The high-throughput workflow has been designed using AiiDA.
  Huber, Zoupanos *et al.*, *Scientific Data* **2020**, 7, 300; doi: 10.1016/j.commatsci.2020.110086
  Uhrin, Huber *et al.*, *Comp. Mat. Sci.* **2021**, 187; doi: 10.1016/j.commatsci.2020.110086

# The Cs-Sb system

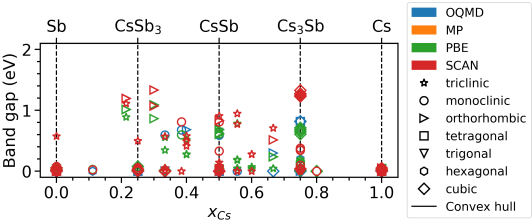
Distribution of the crystal structures:




Stability:




Band gap:

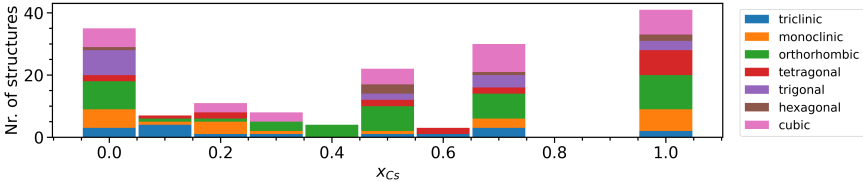



- $E_{form}(\mathrm{Cs}_x\mathrm{Sb}_{1-x}) = E(\mathrm{Cs}_x\mathrm{Sb}_{1-x}) - [xE(\mathrm{Cs}) + (1-x)E(\mathrm{Sb})]$

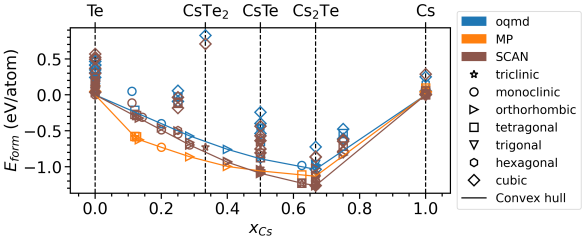
Cocchi and Saßnick, *Micromachines* **2021**, 12(9), 1002; doi: 10.3390/mi12091002

# The Cs-Te system

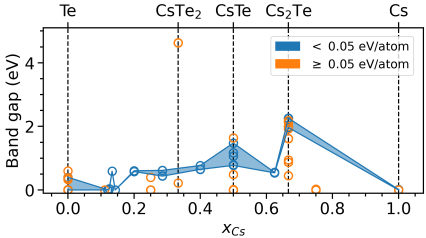
Distribution of the crystal structures:




Stability:



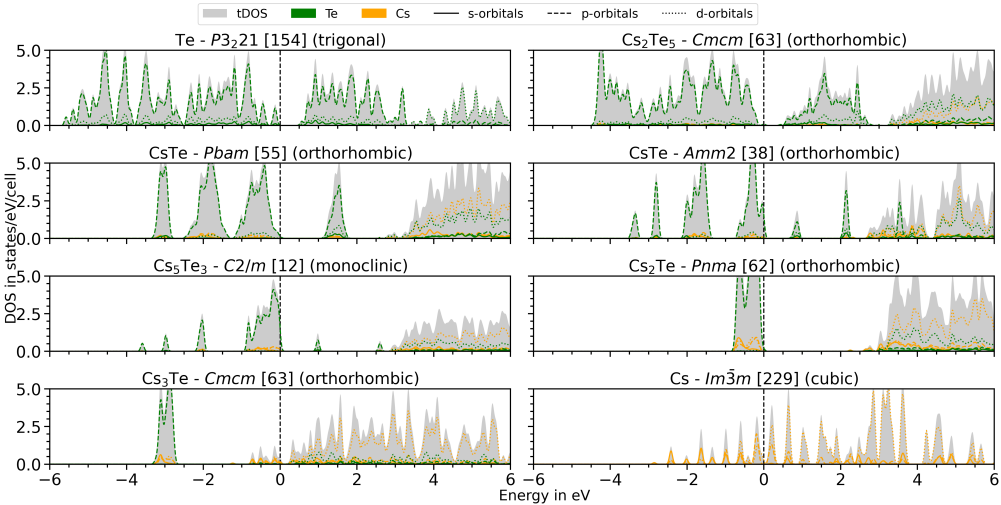

Band gap:




- $E_{form}(\mathrm{Cs}_x\mathrm{Te}_{1-x}) = E(\mathrm{Cs}_x\mathrm{Te}_{1-x}) - [xE(\mathrm{Cs}) + (1-x)E(\mathrm{Te})]$

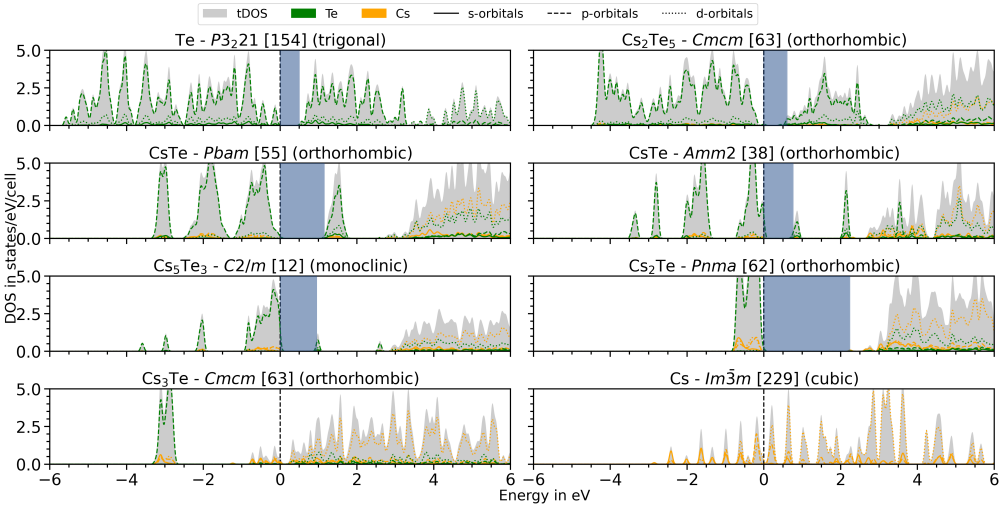
Saßnick and Cocchi, *J. Chem. Phys.* **2022**, **156**, 104108; doi: 10.1063/5.0082710

# Changing electronic character with composition




**0 eV is set to the valence band maximum (VBM).**
**Saßnick and Cocchi, *J. Chem. Phys.* 2022, 156, 104108; doi: 10.1063/5.0082710**

# Changing electronic character with composition

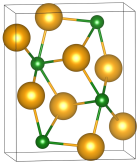



0 eV is set to the valence band maximum (VBM).
Saßnick and Cocchi, *J. Chem. Phys.* **2022**, 156, 104108; doi: 10.1063/5.0082710

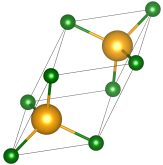
# Most stable phases with the experimental composition of 2:1 (1)

- 10 different crystals have a distance to convex hull smaller than 0.05 eV/atom.
- Based on their structural similarity 4 groups can be distinguished.
- For the latter calculations only the structure with the highest symmetry is considered:

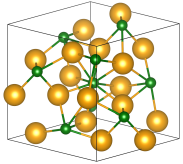
*Pnma* [62] (orthorhombic)



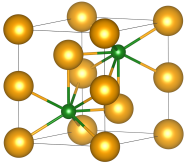
$Fm\bar{3}m$ [225] (cubic)



*R*3 [146] (trigonal)



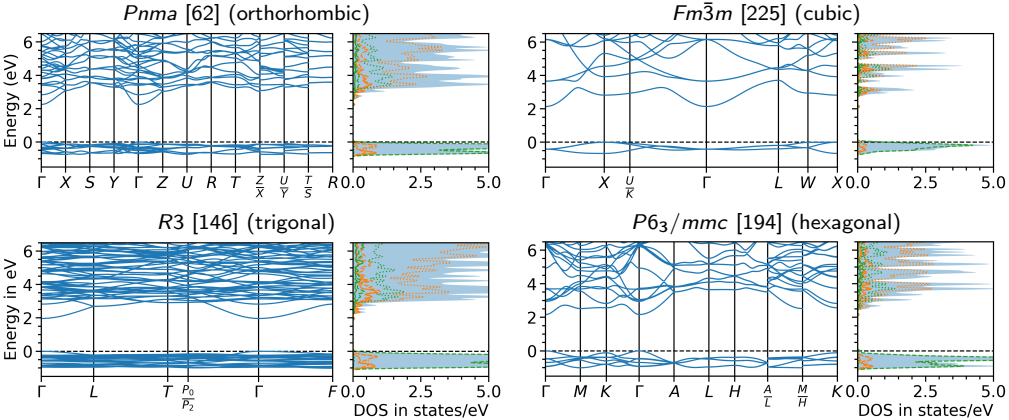
$P6_3/mmc$ [194] (hexagonal)



Cs Te

Saßnick and Cocchi, *J. Chem. Phys.* **2022**, 156, 104108; doi: 10.1063/5.0082710

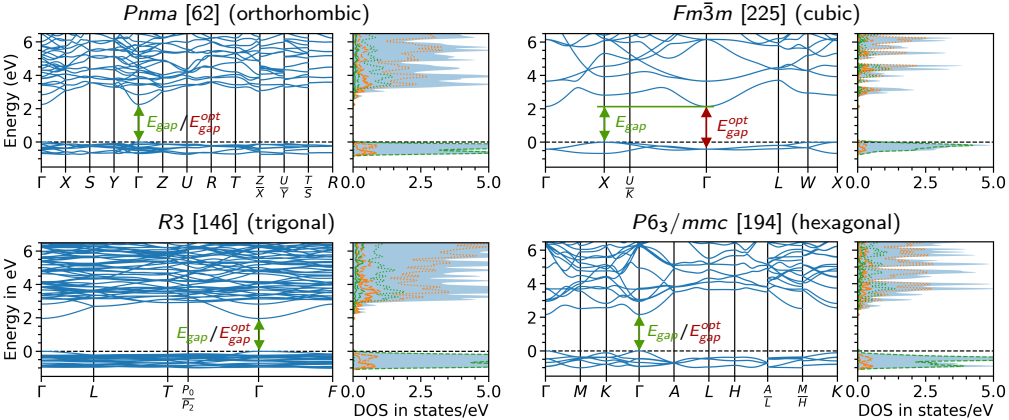
# Most stable phases with the experimental composition of 2:1 (2)




| | *Pnma* [62] | $Fm\bar{3}m$ [225] | *R*3 [146] | $P6_3/mmc$ [194] |
|---|---|---|---|---|
| $E_{gap}$ in eV (*k*-points) | 2.25 | 2.14 ($X \rightarrow \Gamma$) | 1.96 | 2.16 |
| $E_{gap}^{opt}$ in eV (*k*-point) | 2.25 ($\Gamma$) | 2.55 ($\Gamma$) | 1.96 ($\Gamma$) | 2.16 ($\Gamma$) |

0 eV is set to the valence band maximum (VBM).
Saßnick and Cocchi, *J. Chem. Phys.* **2022**, 156, 104108; doi: 10.1063/5.0082710

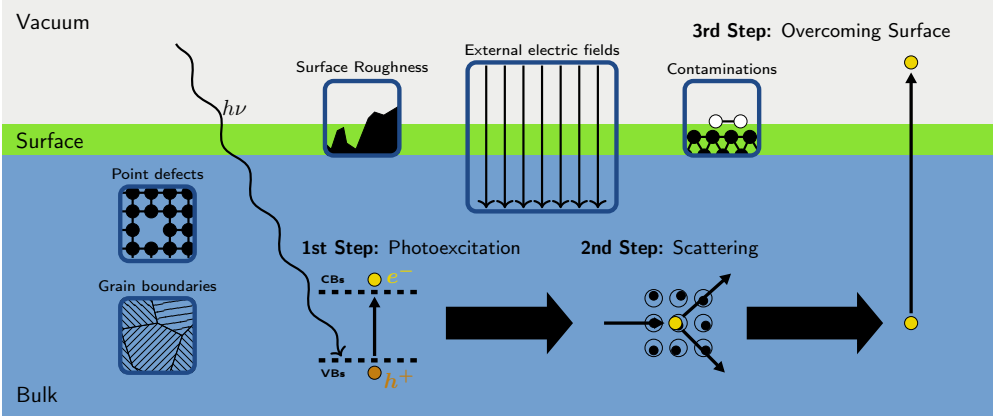
# Most stable phases with the experimental composition of 2:1 (2)




| | *Pnma* [62] | $Fm\bar{3}m$ [225] | *R*3 [146] | $P6_3/mmc$ [194] |
|---|---|---|---|---|
| $E_{gap}$ in eV (*k*-points) | 2.25 | 2.14 ($X \rightarrow \Gamma$) | 1.96 | 2.16 |
| $E_{gap}^{opt}$ in eV (*k*-point) | 2.25 (Γ) | 2.55 (Γ) | 1.96 (Γ) | 2.16 (Γ) |

0 eV is set to the valence band maximum (VBM).
Saßnick and Cocchi, *J. Chem. Phys.* **2022**, 156, 104108; doi: 10.1063/5.0082710

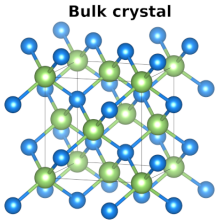
# The role of surfaces in the photoemission process

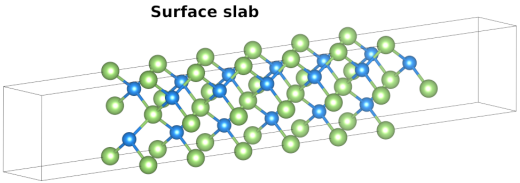



Cocchi and Saßnick, *Micromachines* **2021**, 12(9), 1002; doi: 10.3390/mi12091002

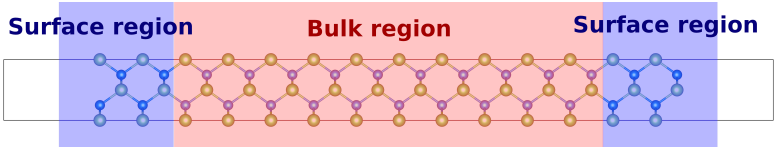
# How to model a surface?

The surface breaks the periodicity in one dimension, thus making it necessary to treat this direction with non-periodic boundary conditions:



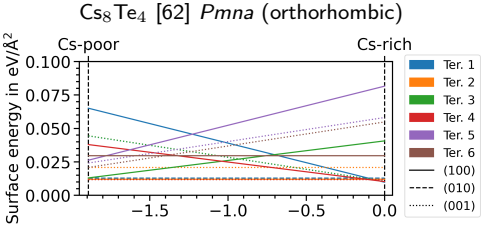



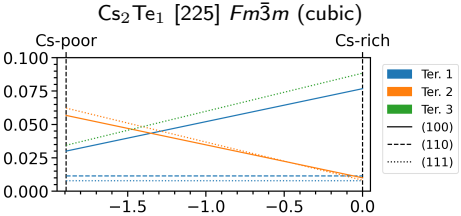

resulting in slabs which contain two surface facets:

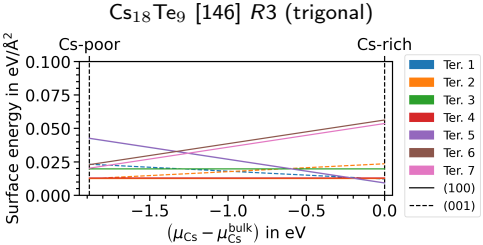


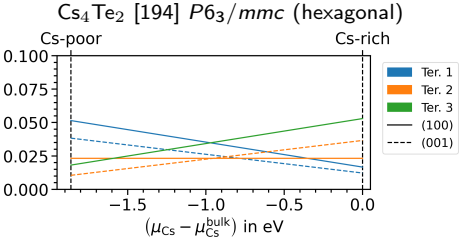

*Richard Schier is presenting a poster on the simulation of $CsK_2Sb$-surface facets (arxiv: 2208.05843).*

# Surface Stability



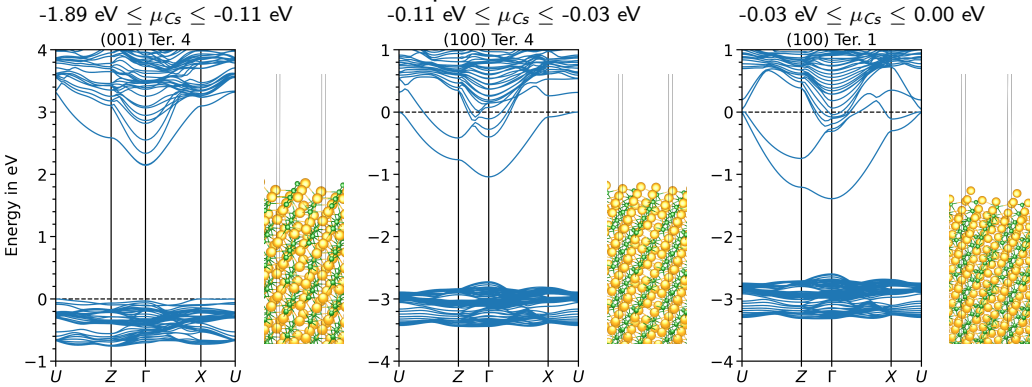




Saßnick and Cocchi, *in preparation*.

# Surface properties of the $Cs_8Te_4$ [62] *Pmna* phase

Cs-poor ⟶ Cs-rich

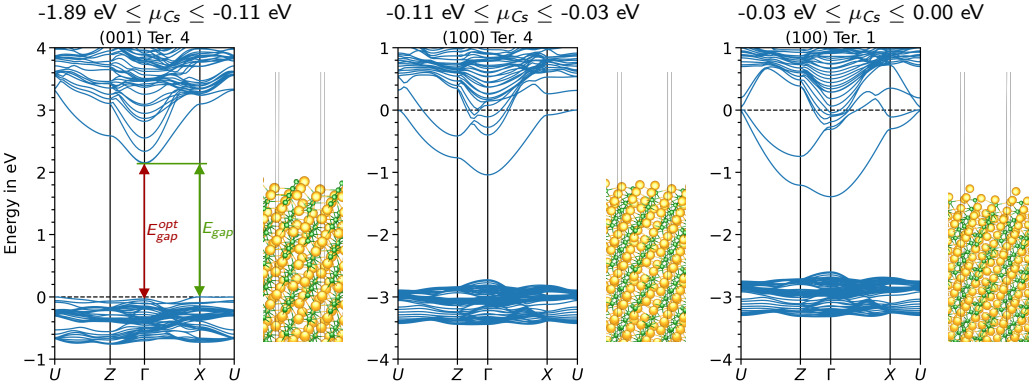



| | (001) Ter. 4 | (001) Ter. 4 | (001) Ter. 4 |
|---|---|---|---|
| $E_{gap}$ in eV | 2.14 ($X \rightarrow \Gamma$) | 0.00 | 0.00 |
| $E_{gap}^{opt}$ in eV | 2.18 ($\Gamma$) | 0.00 | 0.01 ($U$) |
| Ionization potential in eV | 3.03 | 1.39 | 1.37 |

0 eV is set to the valence band maximum (VBM).
Saßnick and Cocchi, *in preparation*.

# Surface properties of the $Cs_8Te_4$ [62] *Pmna* phase

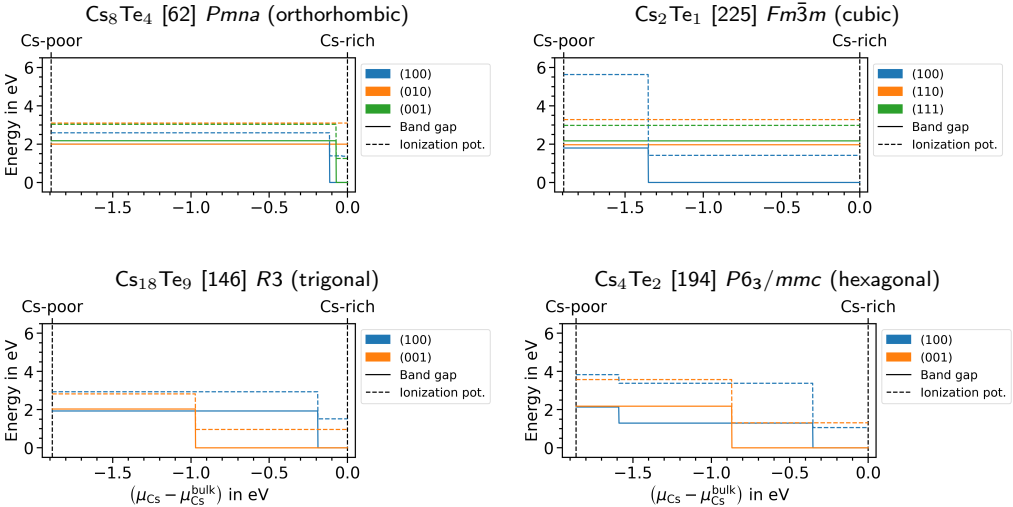
Cs-poor ⟶ Cs-rich




| | (001) Ter. 4 | (001) Ter. 4 | (001) Ter. 4 |
|---|---|---|---|
| $E_{gap}$ in eV | 2.14 ($X \rightarrow \Gamma$) | 0.00 | 0.00 |
| $E_{gap}^{opt}$ in eV | 2.18 ($\Gamma$) | 0.00 | 0.01 ($U$) |
| Ionization potential in eV | 3.03 | 1.39 | 1.37 |

0 eV is set to the valence band maximum (VBM).
Saßnick and Cocchi, *in preparation*.

# Overview of the electronic properties of all surface facets




Saßnick and Cocchi, *in preparation*.

# Conclusions

- First approximation of the stability of different bulk phases and surface facets.
- Analysis of relationship between compositional changes and electronic properties.
- Additional (theoretically) stable structures found at experimentally relevant compositions.
- The largest band gap is reached at a composition of 2:1 due to fully occupied Te p-states for Cs-Te.
- Surface facets tend towards metallic properties in Cs-rich environments accompanied with a reduction in the ionization potential.
- The routine can be applied to any material-system and we are planning to publish the source code soon.