Following the reaction: Computational spectroscopy of the $BaZrS_3$ perovskite

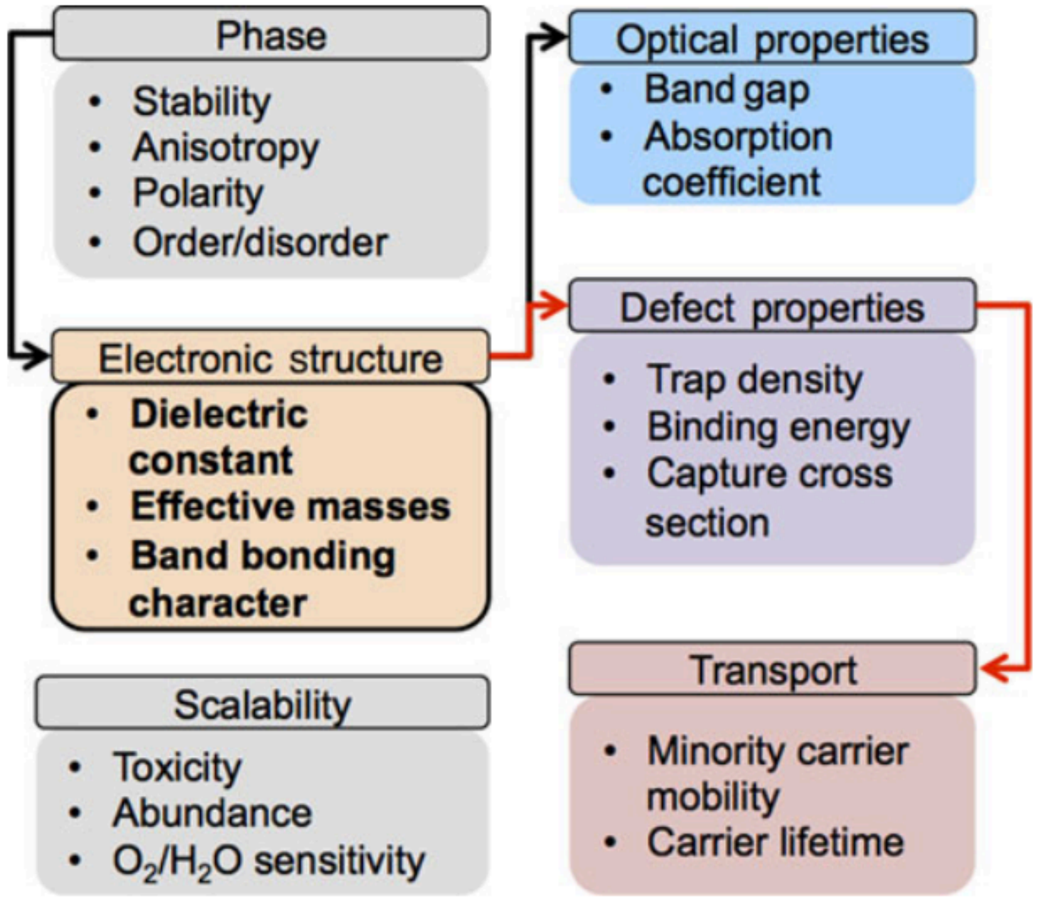
NUPV Group Meeting

Prakriti Kayastha, 2nd March 2022

Overview

- Why chalcogenide perovskites, why IR spectroscopy?
- Combining theory and experiment to understand synthesis
- DFT workflow and results
- Comparisons with other semiconductors

PV wishlist



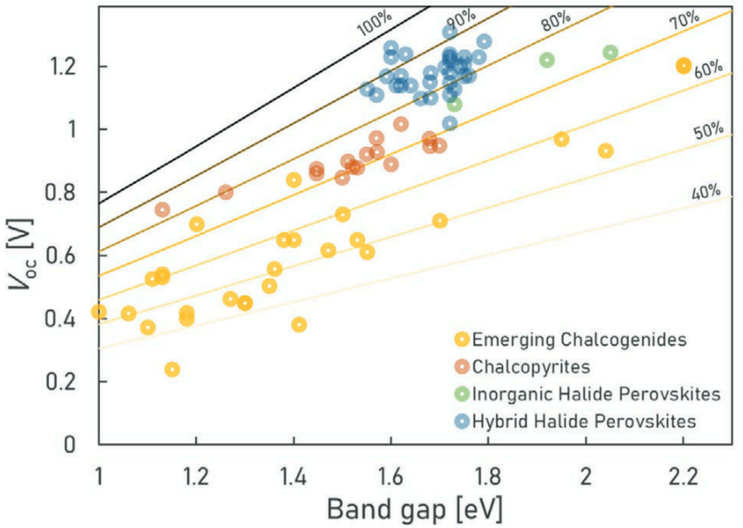
Brandt et al, MRS Comm. (2015)

Background

Chalcogenide Perovskites

- Alternative to lead based perovskites which are toxic
- Long term stability compared to other perovskites
- Tunable bandgaps
- Efficient transport properties

- But, show high voltage losses
- Have low defect tolerance

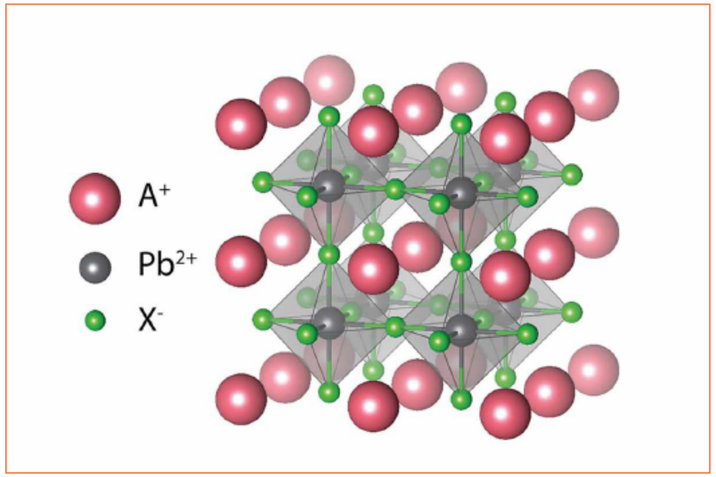


Tiwari et al, J Phys. Energy (2021)
Sophia et al, Adv. Optical Mater. (2022)

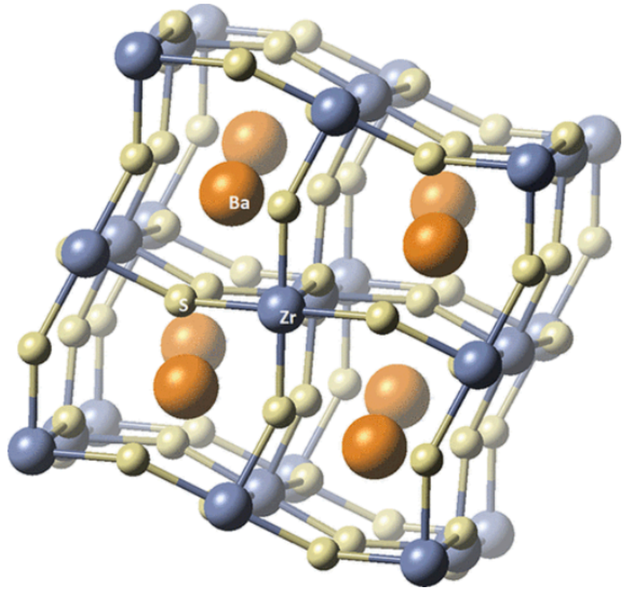
Background

Chalcogenide Perovskites

Traditional cubic perovskite structure



Orthorhombic chalcogenide perovskite structure



- $BaS + ZrS_2 \longrightarrow BaZrS_3$
- Following the reaction to find possible stable structures

Huang et al, Nanotech. (2021)

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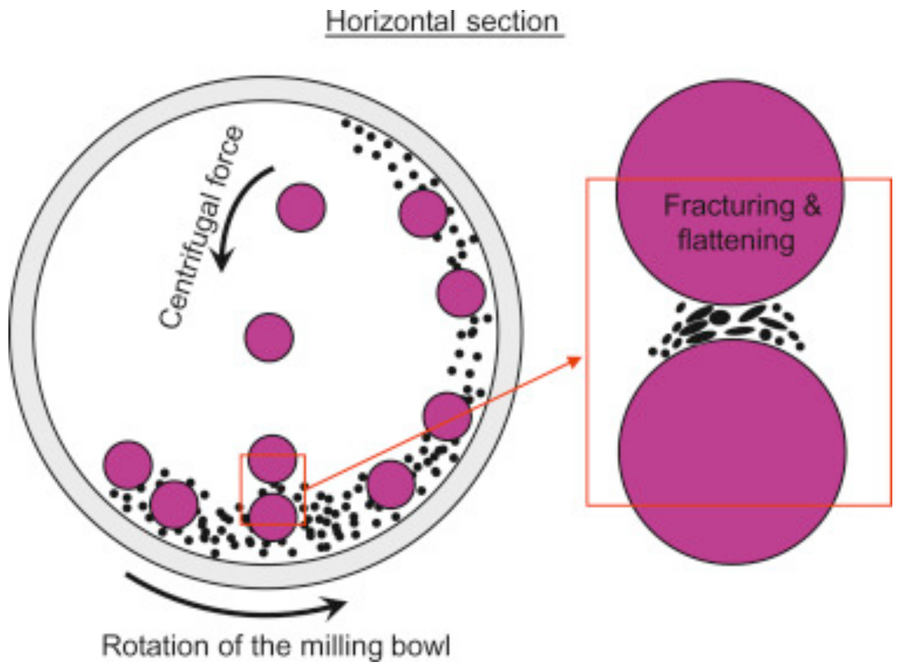
Ball milling synthesis

Wishlist and Process

- Thin film devices
- Low temp synthesis - presence of Zr increases temp requirements
- $BaS + ZrS_2 \xrightarrow{BM} \text{“}BaZrS_3\text{”} \xrightarrow{PC} BaZrS_3$
- Precursor shows signs of perovskite formation (Giulia’s preliminary result)
- Use photonic curing for a crystalline film deposition



Faraji et al, Severe Plastic Deformation 2018

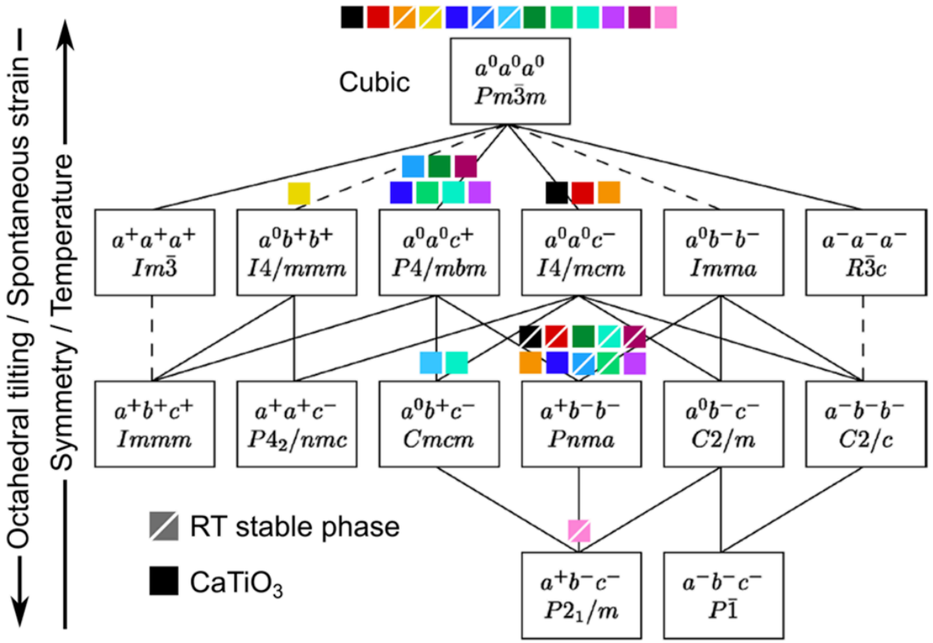
Why an IR spectra is needed?

- Ball milling produces irregular nanoparticles
- Mechanical forces produces crystal defects
- Nanoparticles need to be stabilised by organic chains
- Not suitable for XRD analysis
- IR spectra characterisation - irrespective of synthesis method
- IR is fast, needs small sample sizes and can be done in situ

Smock et al, Acc. Chem. Res. (2021)

Potential materials during the reaction

Metastable materials



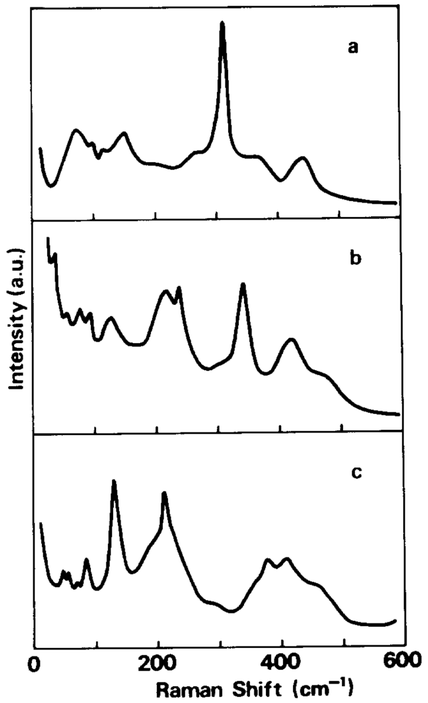


FIG.1
Raman spectra of Ba_2ZrS_4 (a), $Ba_3Zr_2S_7$(b) and $BaZrS_3$(c) at 300K with 647.1nm excitation.

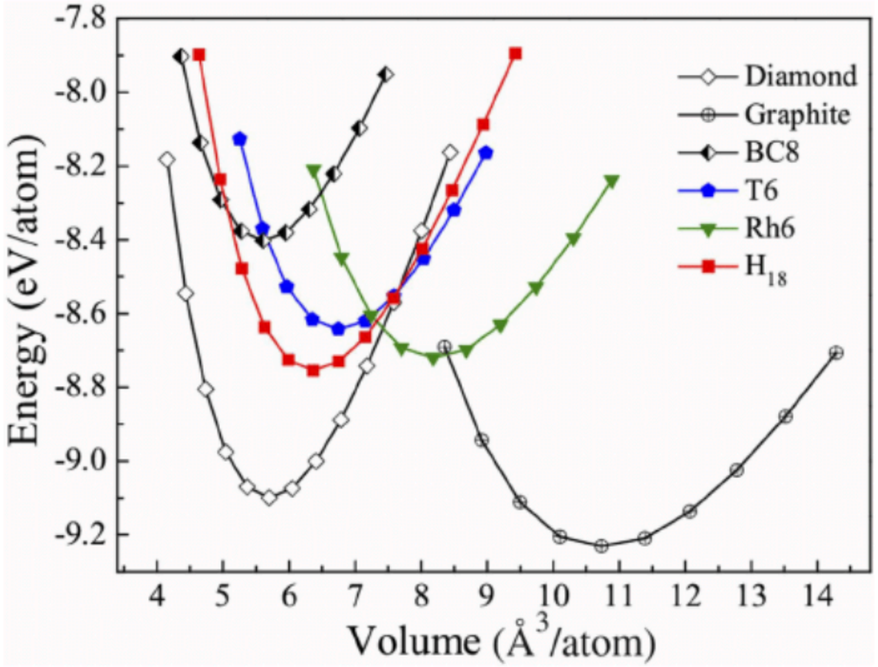
- BaS ($Fm\bar{3}m$), BaS_2 ($C2/c$), BaS_3 ($P\bar{4}2_1m$)
- ZrS_2 ($P\bar{3}m1$), ZrS ($P4/nmm$), ZrS_3 ($P2_1/m$), ZrS ($Fm\bar{3}m$)
- $BaZrS_3$ ($Pnma$), $Ba_3Zr_2S_7$ ($P4_2/mnm$), $Ba_3Zr_2S_7$ ($I4/mmm$), Ba_2ZrS_4 ($I4/mmm$)

Steele et al, Acc. Chem. Res. (2020)

Ishii et al, Mat. Res. Bull. (1993)

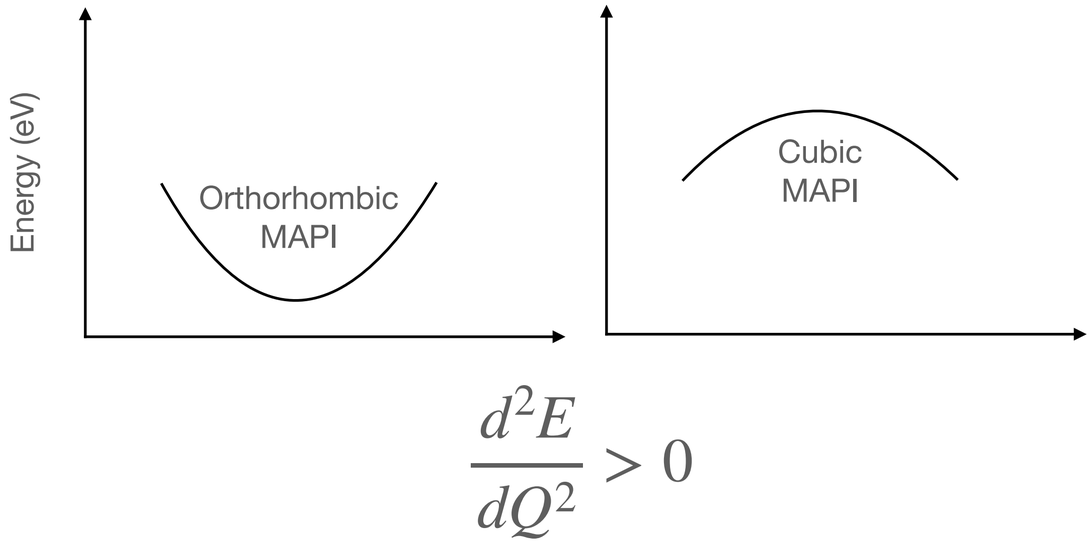
Thermodynamic vs dynamic stability

Global Potential Energy Surface



Thermodynamic Stability: depth in the PES

Graphite phase more
stable than diamond



Dynamical Stability: curvature of the PES

Orthorhombic MAPI phase
is dynamically stable

Zhao et al, Sci. Rep. (2016)
Whalley et al, Phys. Rev. B (2016)

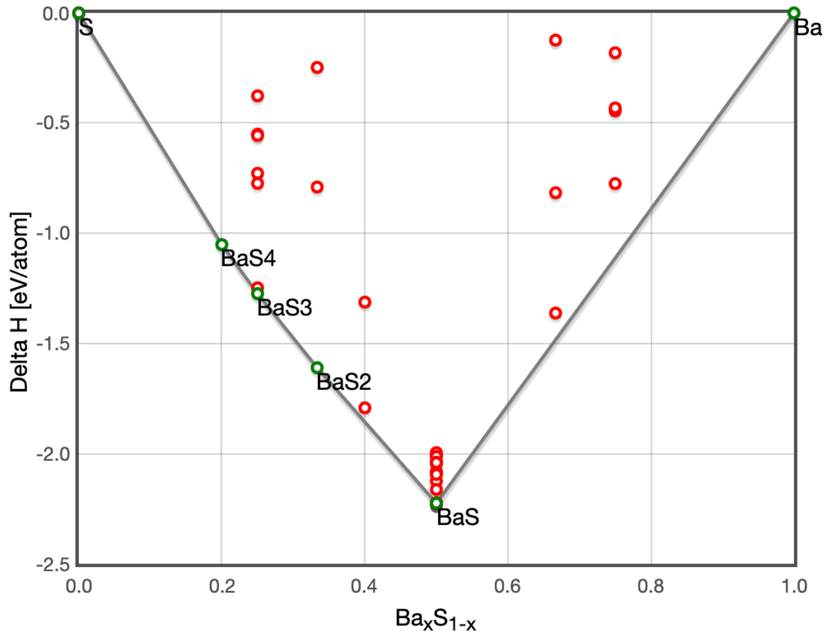
Thermodynamic Stability

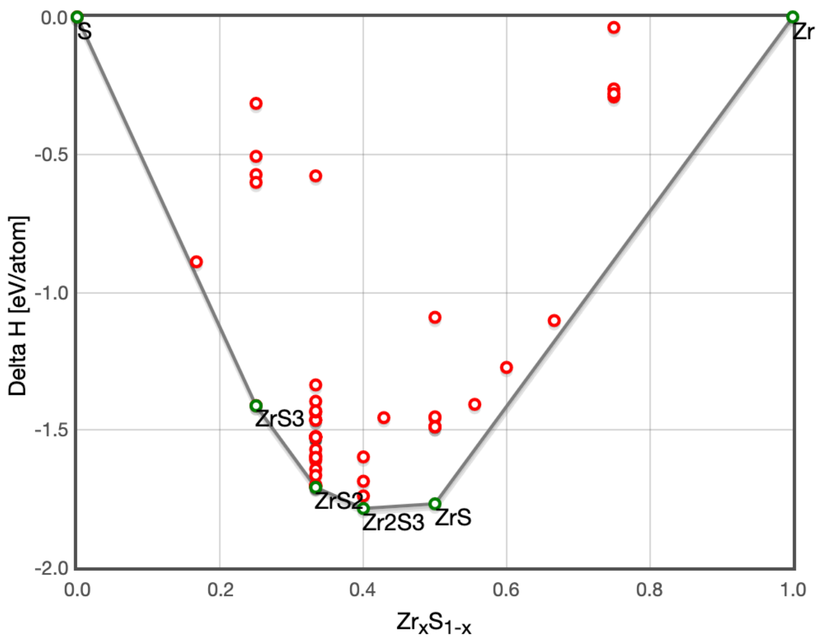
Formation energy

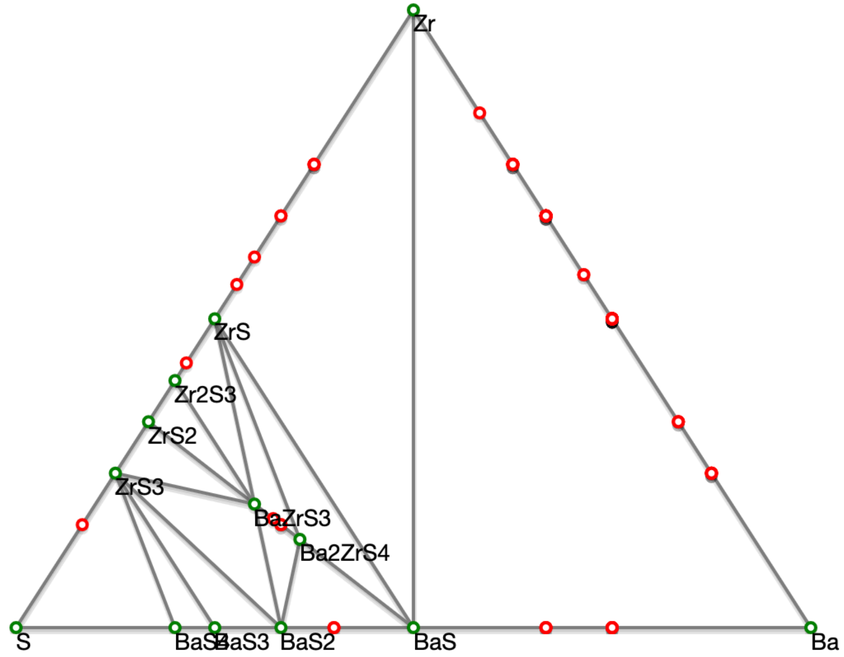
- $$E_F(BaZrS_3) = \frac{E(BaZrS_3) - E(Ba) - E(Zr) - 3E(S)}{5}$$
- Constituents in their elemental form
- Measure in an eV/atom
- Relative energy to the most stable phase

Convex hull and Gibbs' triangle

From online databases







http://oqmd.org/analysis/phase_diagram/

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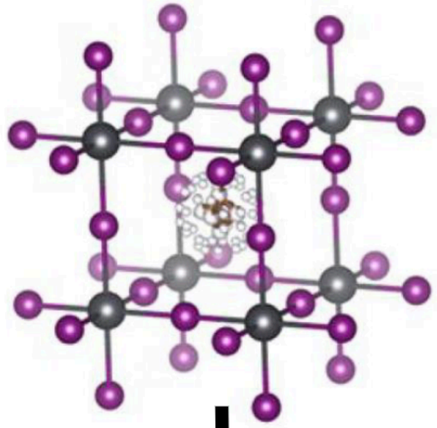
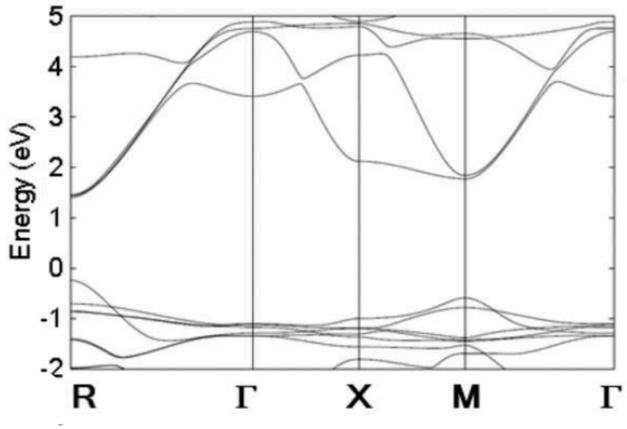
DFT in a nutshell



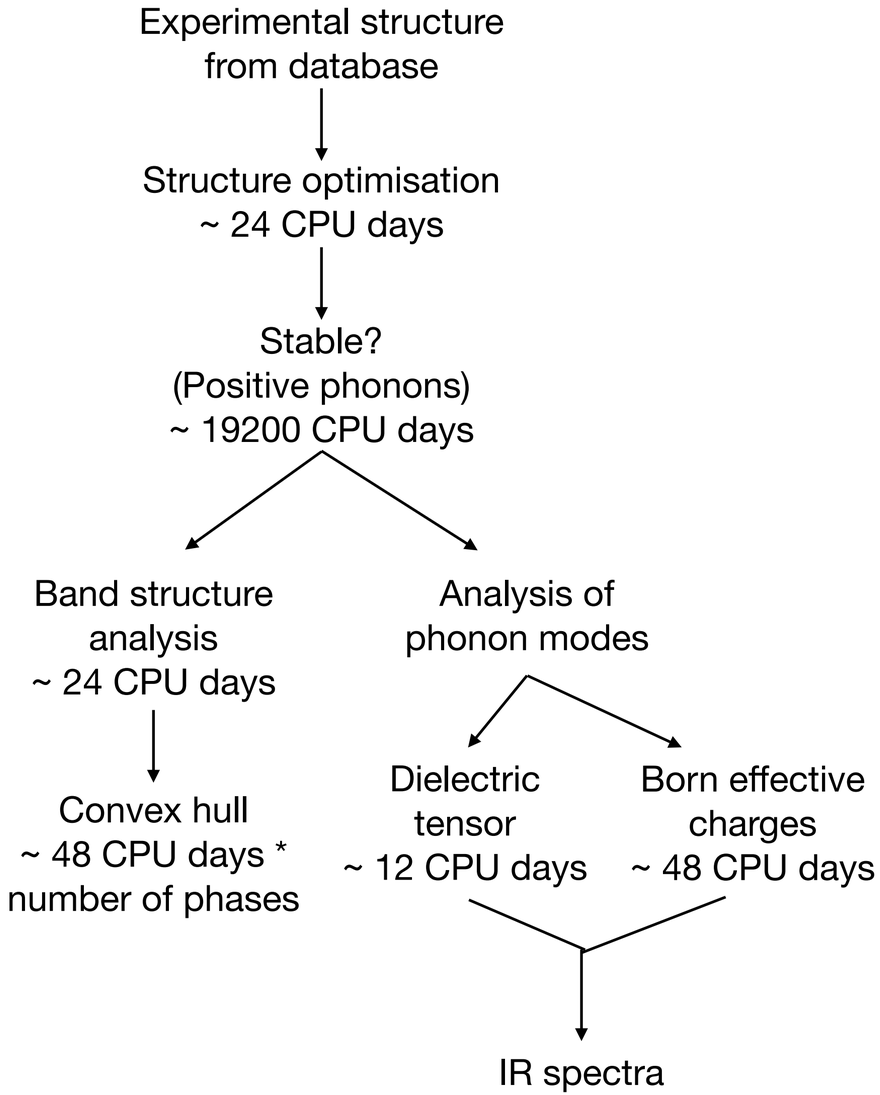
Structure (Cubic MAPI)

DFT



Property

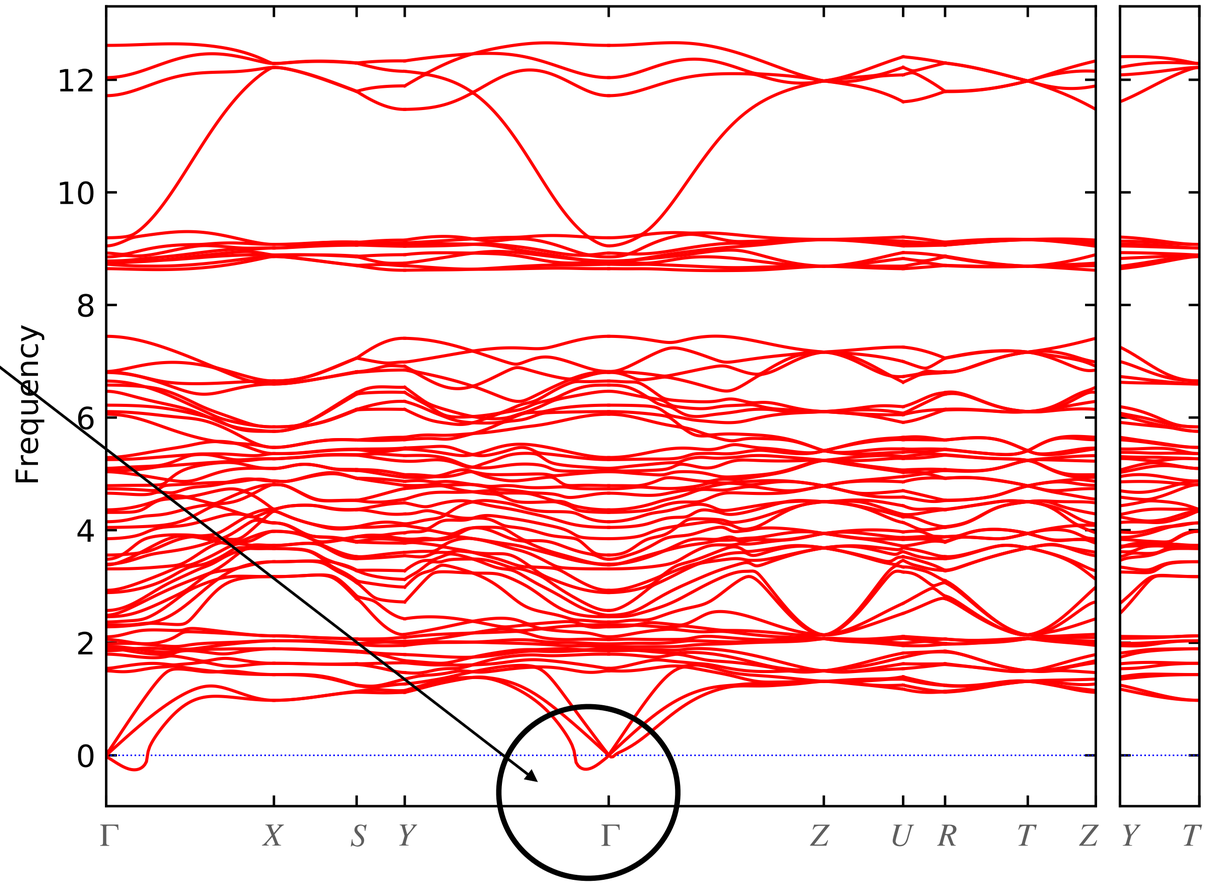
General DFT workflow



Dynamic Stability

Phonons

- Supercell $2 \times 2 \times 2$
- Found a small soft mode
- Use a larger supercell $3 \times 3 \times 2$ (also part of literature) to cure the soft mode
- Not too concerning, IR spectra only extracts information at Γ point



F A Alowa, Masters Thesis, 2021

Electronic Structure

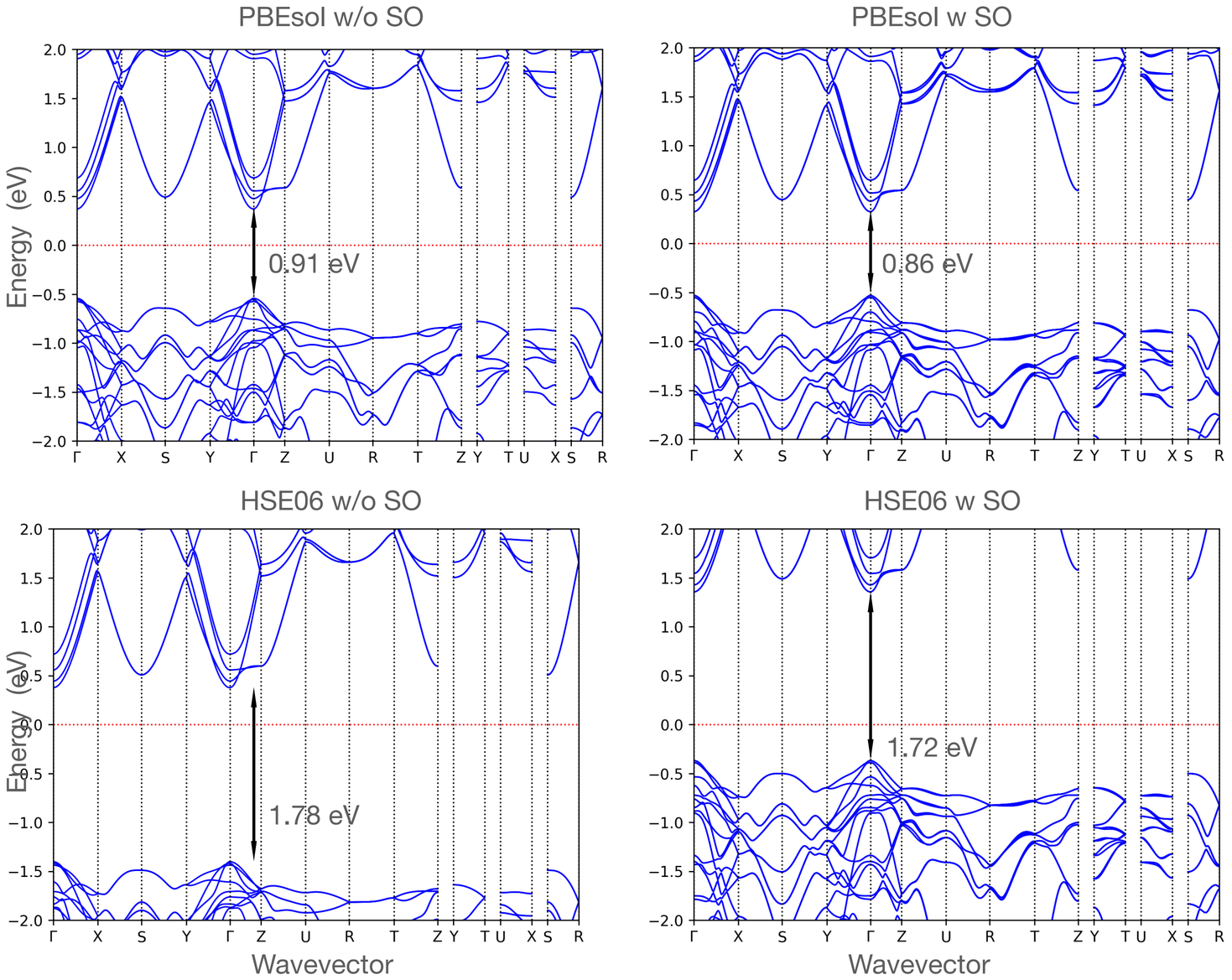
Bandgap and spin-orbit coupling

- Orthorhombic unit cell, with an initial structure from materials project
- Relaxed with a PBEsol functional with the FHI-aims code
- Lattice constants, bandgaps agree with literature
- Which elements contribute to the VBM and CBM?

Sharma et al, ACS App. Electron. Mater. (2021)

Band structure of $BaZrS_3$

- PBEsol - fast for structure optimisation, underestimation of bandgap
- HSE06 - not feasible for structure optimisation, good agreement with experimental bandgap of 1.81 eV
- SO - splitting of bands in momentum space



Nishigaki et al, RRL Solar (2020)

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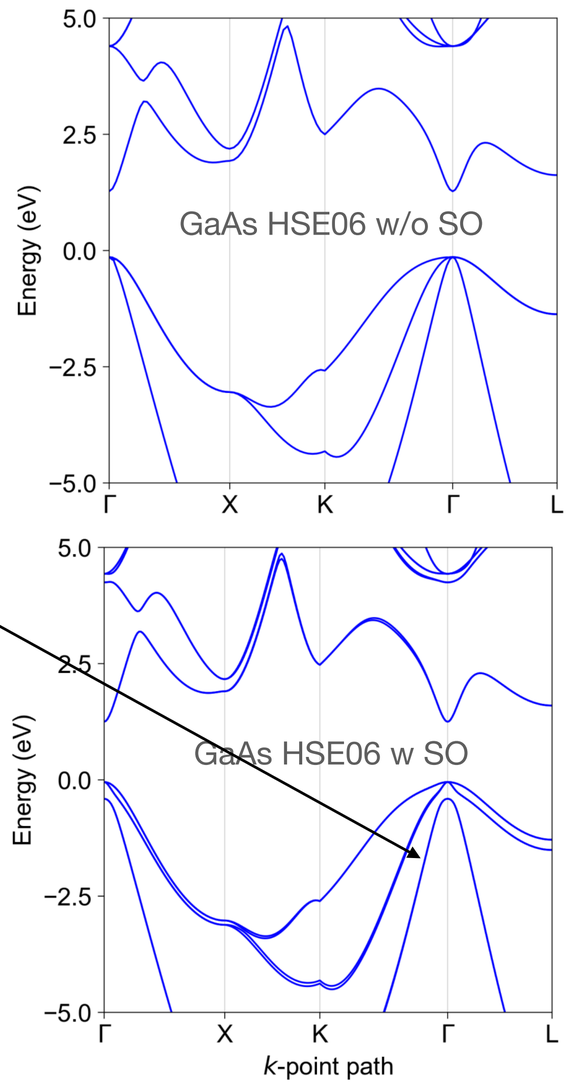
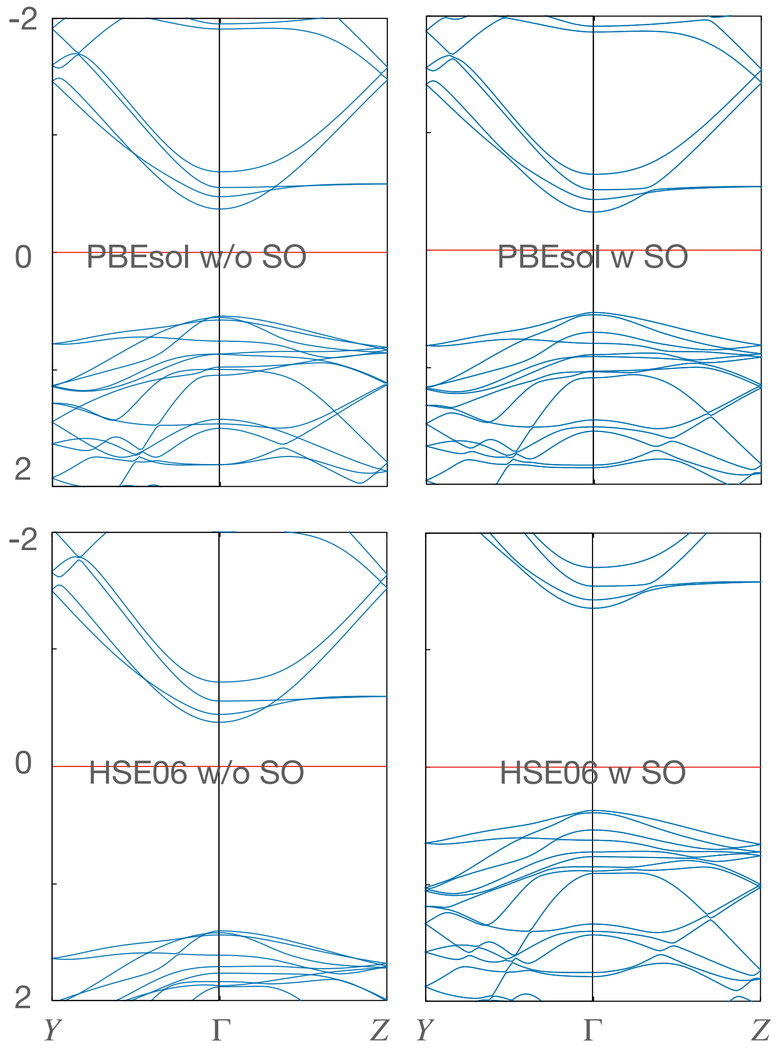
Band Structure

Split-off bands as in traditional semiconductors

- Heavy hole band
- Light hole band
- Split-off band





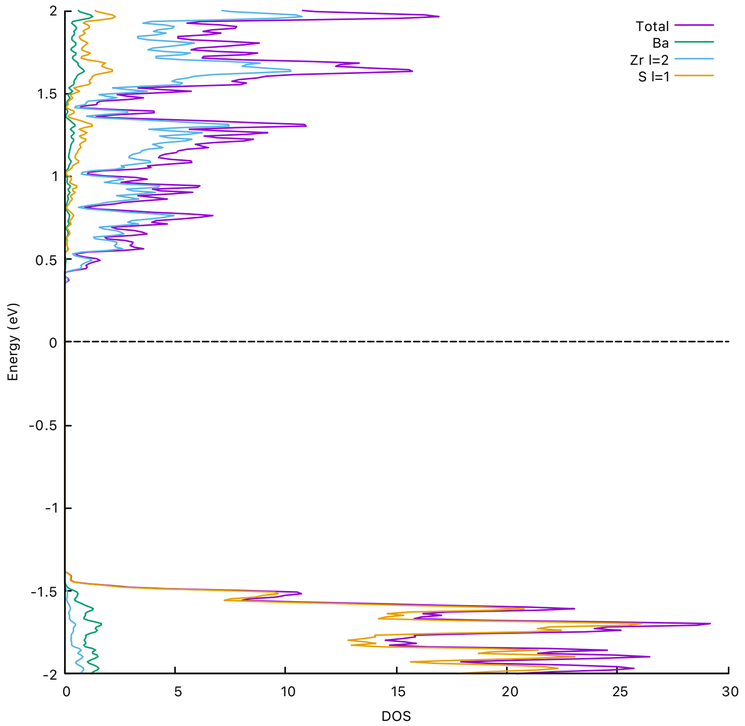
L Whalley, PhD Thesis, 2019

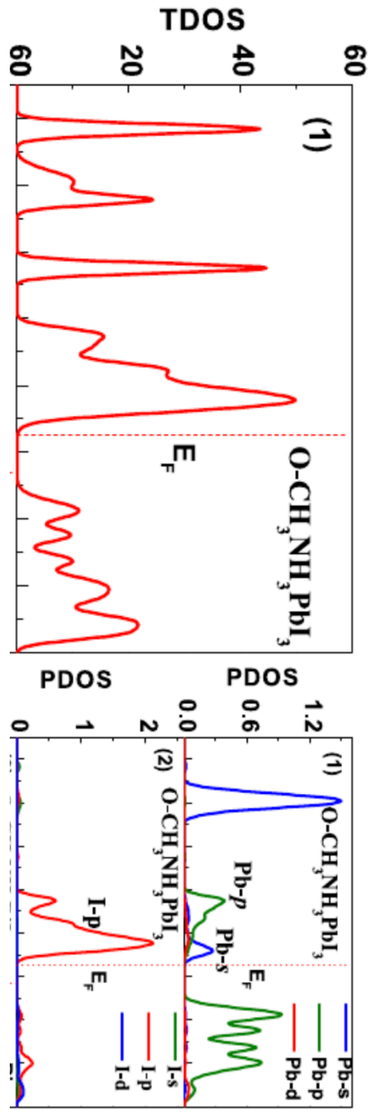
Electronic Structure

DOS: Which bands contribute to VBM and CBM?

- For $BaZrS_3$
  - Zr d-bands in the CBM
  - S p-bands in the VBM
- In contrast with MAPI where:
  - Pb s-bands + I p-bands in the VBM
  - Pb p-bands in the CBM

From HSE06





Zhu et al, Sci. Rep. (2016)

Next steps

- Fix small dynamical instability in current calculation (IR modes only from Γ)
- Parallel work to code FHI-aims interface with Phonopy-Spectroscopy
- Identifying IR/Raman active modes
- Convex hulls and Gibbs' triangle calculations

Take home messages

- With DFT, materials can be modelled to give an accurate prediction of observation in the labs
- DFT predicted energies and structures give more insight into the global PES
- IR spectra will aid in following the reaction in $BaZrS_3$ synthesis

Thank you for listening!