Following the reaction: Computational spectroscopy of perovskite $BaZrS_3$

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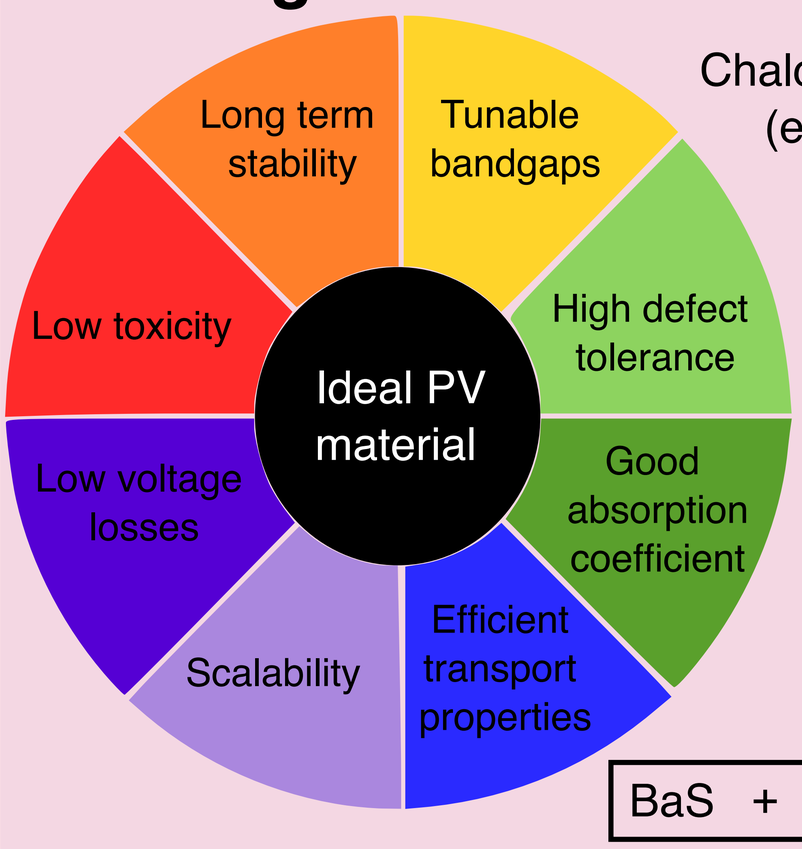
1. Background

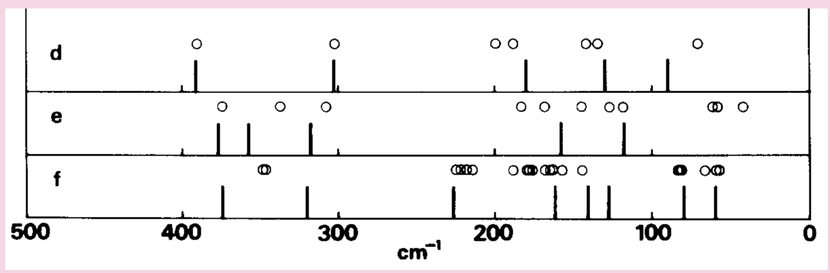


Chalcogenide perovskites (e.g. $BaZrS_3$) fit the bill for high efficiency photovoltaics (PV)

Zr has a high boiling point, which typically requires high temperature synthesis conditions

$$BaS + ZrS_2 \longrightarrow BaZrS_3$$

LDA-DFT vs experimental IR spectra for competing ternary phases[2]



Ba_2ZrS_4 (*I4/mmm*)

$Ba_3Zr_2S_7$ (*I4/mmm*)

$BaZrS_3$ (*Pnma*)

Competing phases form during the reaction which have similar vibrational signatures, hence IR/Raman spectra for each material is needed

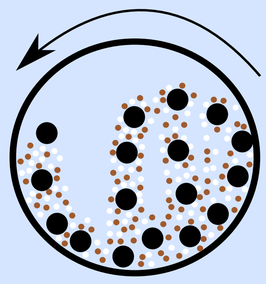
2. Objectives

- Thin film synthesis at low temperature
- Monitor reaction using computational and experimental spectroscopy
- Follow the reaction with a library of IR/Raman spectra of the perovskite and competing phases of Ba, Zr and S

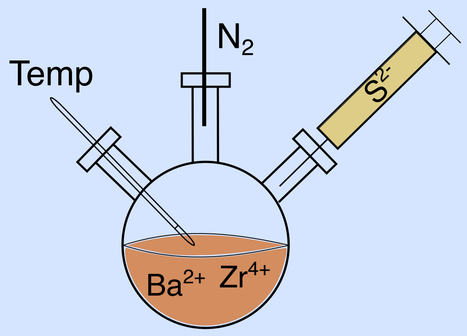
3. Methodology

Experimental setup:

Solid state synthesis with ball milling BaS and ZrS_2 powders



Solution based reaction with hot injection method for nanoparticle synthesis



Computational setup:

- Density functional theory with FHI-aims with PBEsol for geometries and phonons and HSE06 for bandgaps
- IR/Raman spectral lines with Phonopy-Spectroscopy
- Spin-orbit (SO) coupling is applied to check for relativistic effects
- Further Phono3py calculation for spectral widths and thermal transport properties

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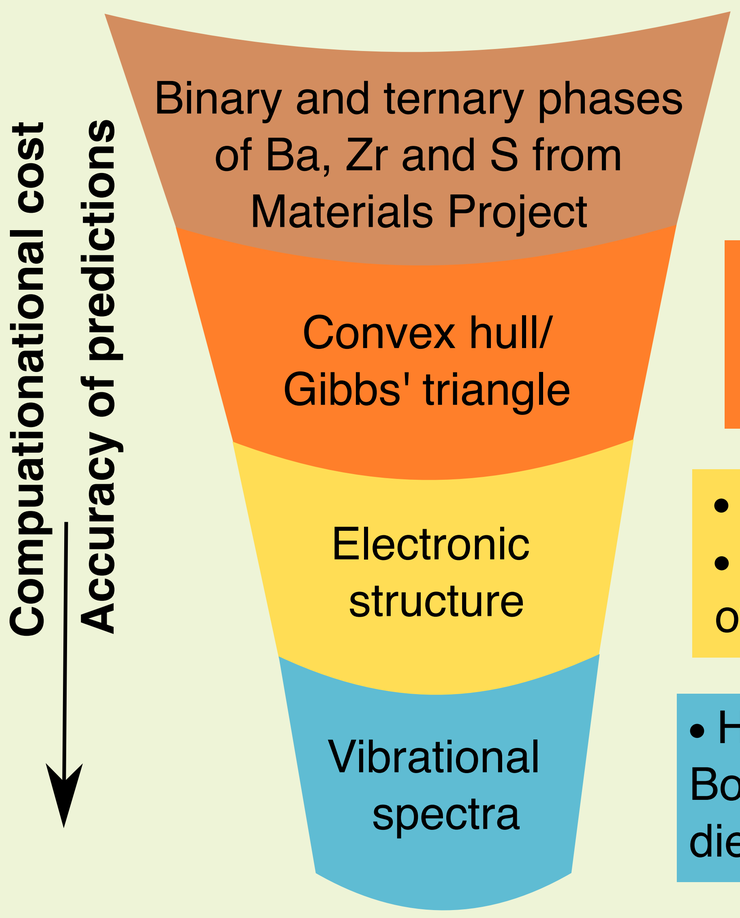
3. Results

Identify possible materials that form during synthesis



- Online databases are a goldmine for experimentally reported materials
- Exploration of phases 0.5 eV above the reported thermodynamically stable phase
- Band gaps, density of states
- Formation energy, reconstruction of the convex hull/Gibbs' triangle
- Harmonic phonon bandstructure, Born effective charges, dielectric tensor

More results here

- The phases we explore are:
BaS ($Fm\bar{3}m$), BaS_2 ($C2/c$), BaS_3 ($P42_1m$)
ZrS_2 ($P\bar{3}m1$), ZrS ($P4/nmm$), ZrS_3 ($P2_1/m$),
ZrS ($Fm\bar{3}m$), Ba_3Zr2S_7 ($P4_2/mnm$), $BaZrS_3$ (*Pnma*),
$Ba_3Zr_2S_7$ (*I4/mmm*), Ba_2ZrS_4 (*I4/mmm*)

- Hybrid DFT on $BaZrS_3$ has a bandgap 1.78 eV, agrees well with experimental bandgap 1.81 eV [4]

- Zr d-bands in CBM, S p-bands in VBM
Split-off band observed with SO coupling

- Imaginary modes found in the phonon bandstructure away from the Γ point, but these do not necessarily mean the structure is unstable [5]

4. Next steps

- Non-analytical corrections to phonon bandstructure with Born effective charges
- Phonopy-Spectroscopy with FHI-aims to predict IR/Raman peak positions of competing phases during the reaction
- Peak widths with Phono3py calculations

5. References

[1] Tiwari *et al*, 2021 J Phys. Energy **3** 034010.
[2] Ishii *et al*, 1993 Mater. Res. Bull. **28** 493.
[3] Skelton *et al,* 2017 PCCP **19** 12452.
[4] Niskigaki *et al*, 2020 Solar RRL **4** 1900555.
[5] Pallikara *et al*, 2022 arXiv:2203.01244

6. More at: