Following the reaction: Computational spectroscopy of perovskite $BaZrS_3$

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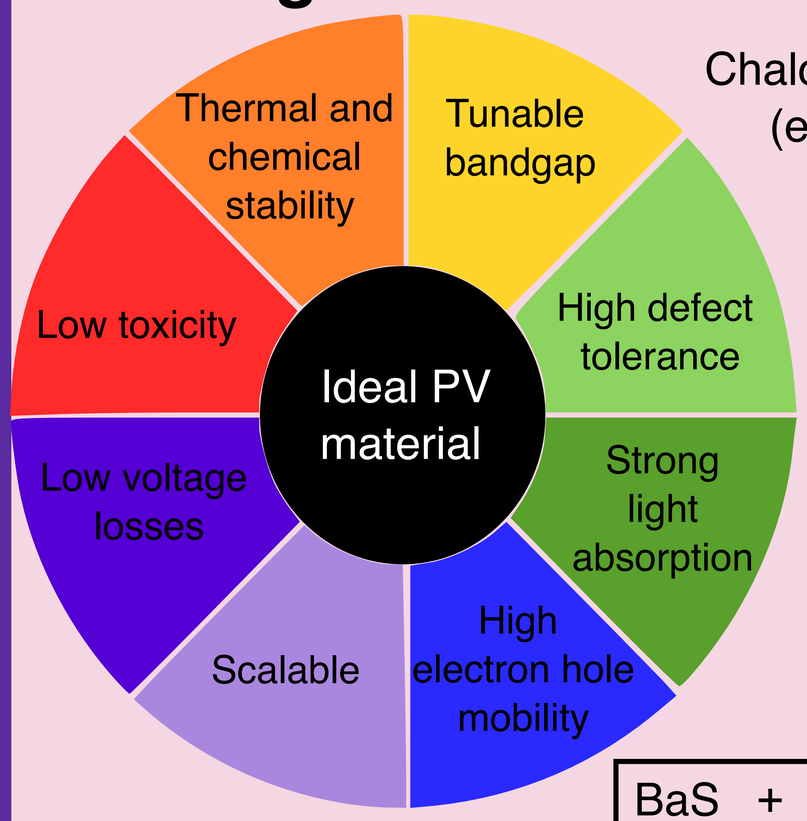
1. Background

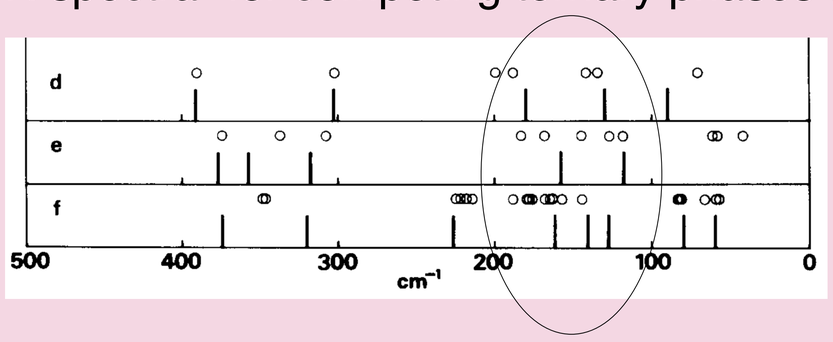


Chalcogenide perovskites (e.g. $BaZrS_3$) fit the bill for high efficiency photovoltaics (PV). [1]

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

$$BaS + ZrS_2 \longrightarrow BaZrS_3$$

IR spectra[2] for competing ternary phases of $BaZrS_3$:



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 the full IR/Raman spectra for each material is needed.

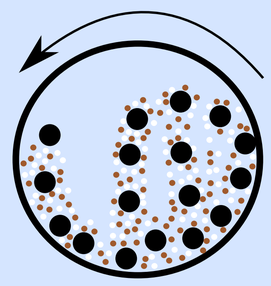
2. Objectives

- Synthesize $BaZrS_3$ thin-films at low temperature (< 500^0c)
- Monitor reactions:
  - using experimental and computational IR/Raman spectra
  - perovskite and energetically accessible competing phases of Ba, Zr and S.

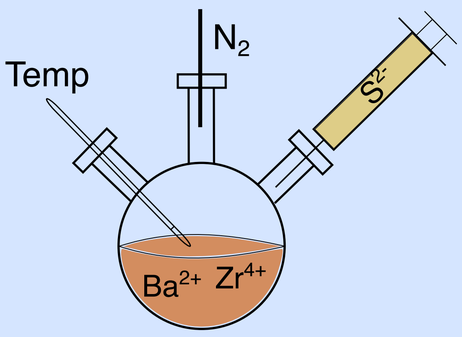
3. Methodology

Experimental setup - two approaches:

Solid state synthesis by ball milling BaS and ZrS_2 powders.



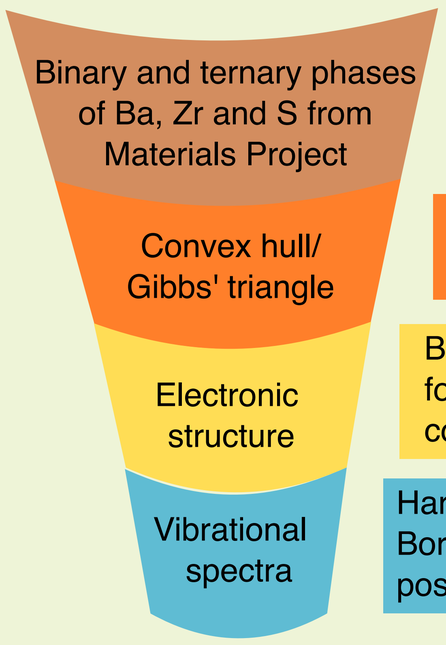
Nanoparticle synthesis using hot-injection solution processing.



Computational setup:

- Density functional theory with FHI-aims:
  - PBEsol for lattice relaxation and phonons.
  - HSE06 hybrid functional for electronic band structures.
- IR/Raman peak positions using lattice dynamics with finite differences Phonopy-Spectroscopy.[3]
- Spin-orbit (SO) coupling is applied to check for relativistic effects.

4. Results



Online databases are a goldmine of experimentally reported materials

Exploration of phases < 0.5 eV above the reported thermodynamically stable phase

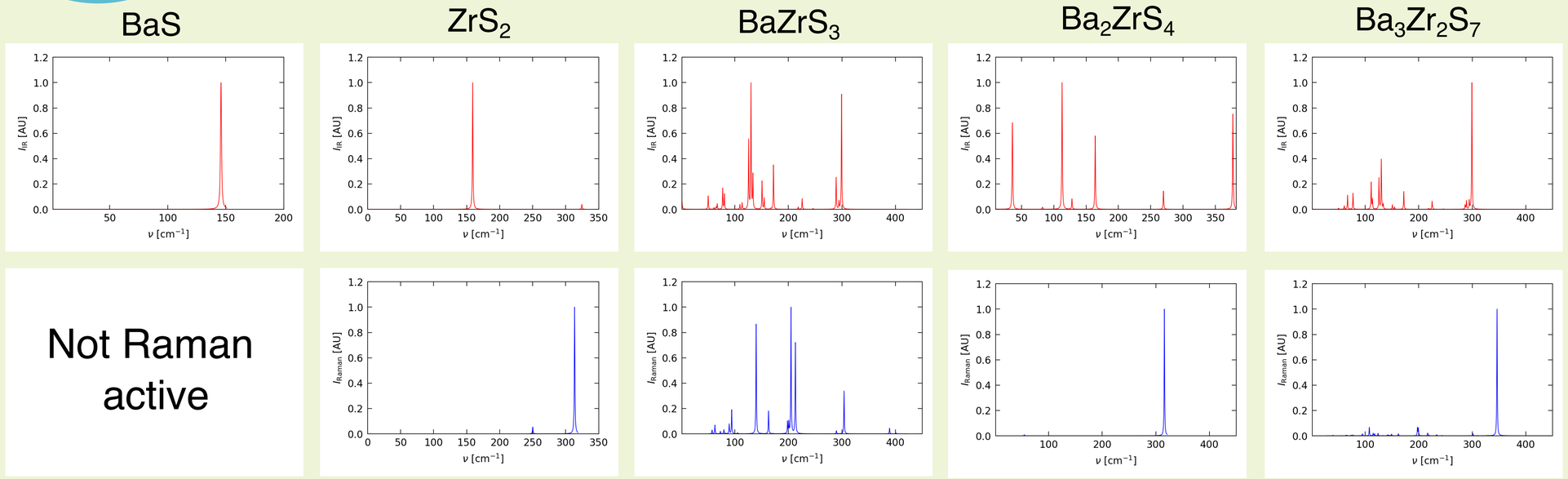
Band gaps, density of states, formation energies, reconstruction of convex hull/Gibbs' triangle with HSE06

Harmonic phonon band structure + Born effective charges + dielectric tensor + postprocessing = IR/Raman spectra

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

Hybrid DFT on $BaZrS_3$ has a bandgap 1.78 eV, which agrees well with experimental bandgap 1.81 eV.[4]
We reconstruct the convex hull by including temperture

Imaginary modes found away from the Γ-point, but this does not imply an unstable structure.[5]



$BaZrS_3$ and $Ba_3Zr_2S_7$ Raman spectra is in agreement with previously reported results.[6,7]

Using complementary IR/Raman techniques can help to identify compounds in a complex phase space.

5. Next steps

- Predict IR/Raman spectra of competing ternary phases and comparison to experimental data.
- 3rd-order force constants to evaluate IR/Raman linewidths and thermal conductivity.
- Predict Gibbs free energies as a functions of temperature and pressure.

6. 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 Electron. Struc. (in press)
[6] Gross *et al*, 2017 Phys. Rev. Appl. **8** 044014
[7] Ye *et al*, 2022 Phys. Rev. B **105** 195203

7. More at: