

Following the reaction of chalcogenide perovskite BaZrS_3

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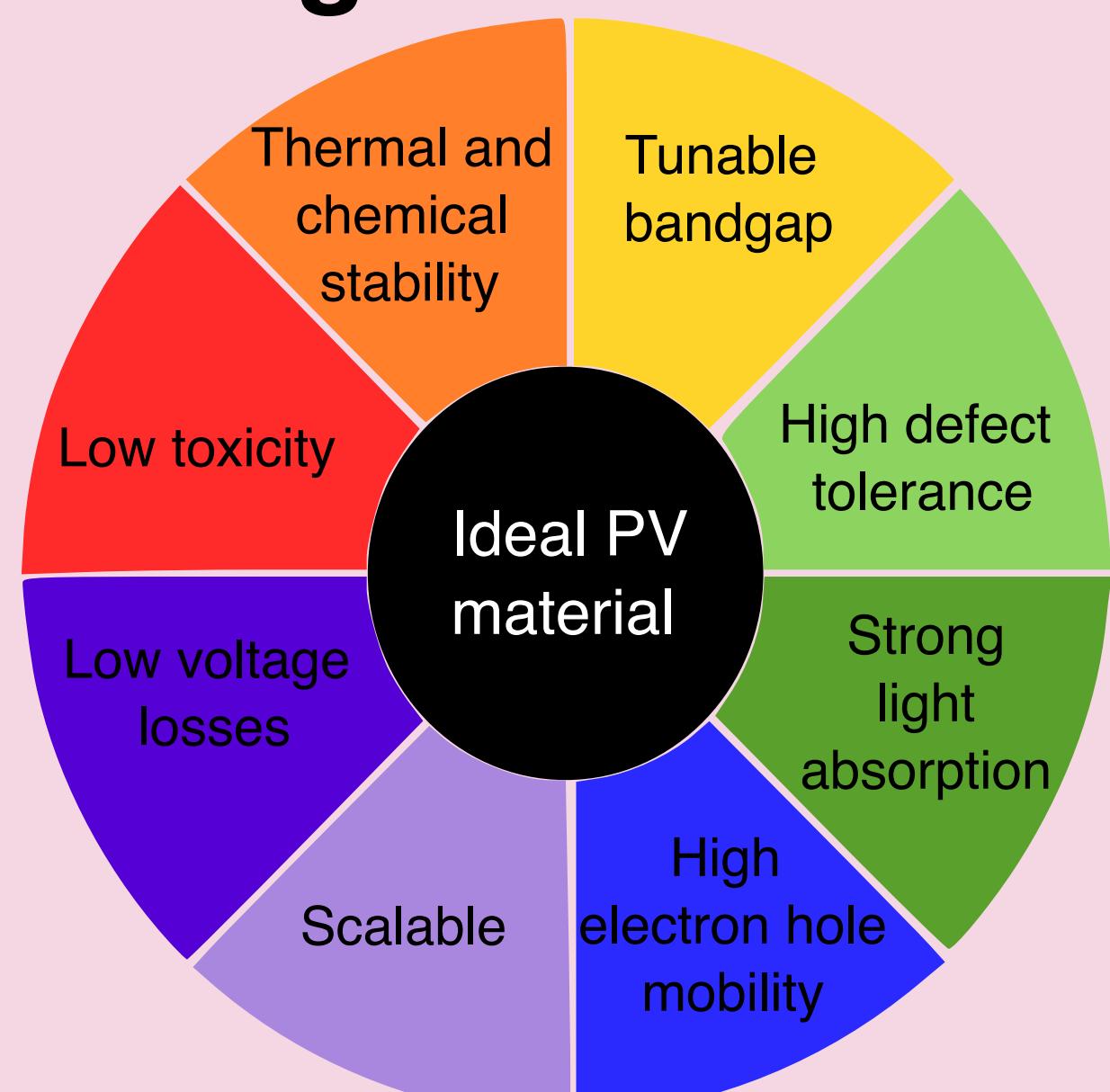


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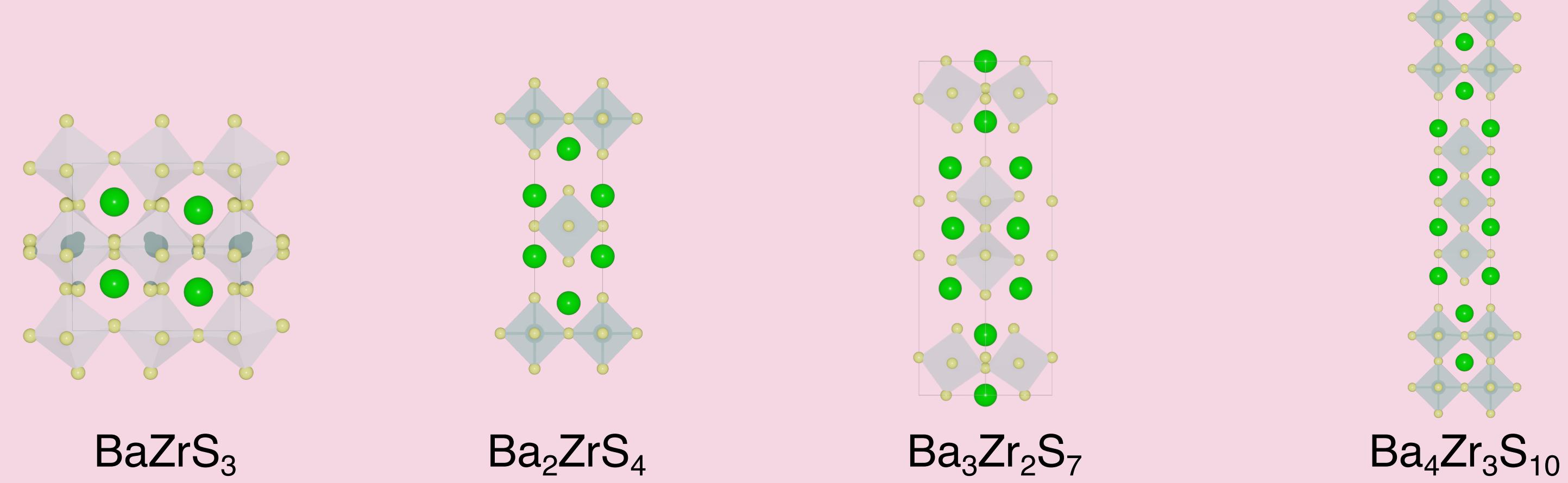
Background



Chalcogenide perovskite BaZrS_3 is a candidate material for high-efficiency Si/perovskite tandem photovoltaics.¹

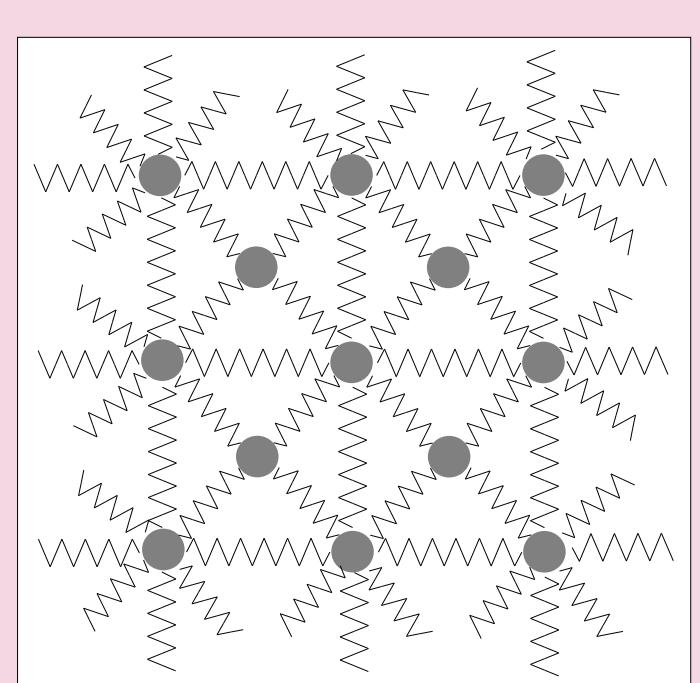
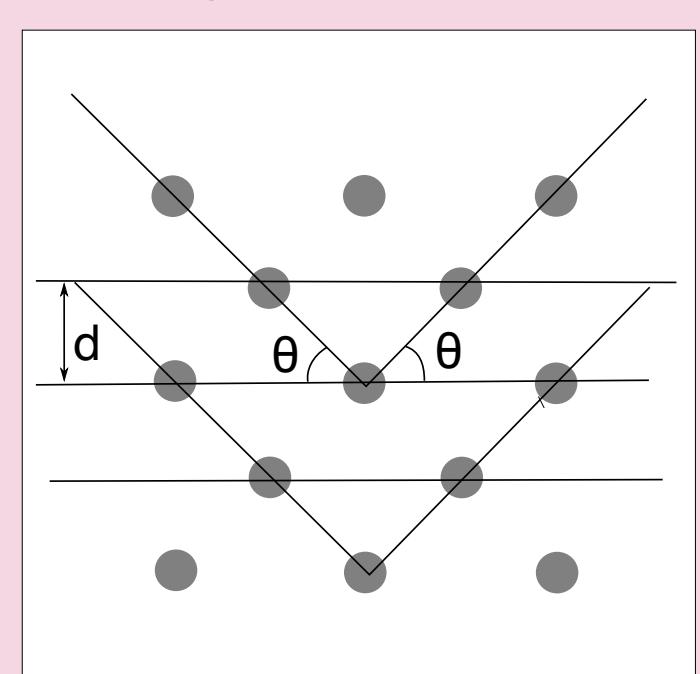
Competing binary and ternary phases can form during synthesis. Tuning precursor stoichiometry, temperature, and chalcogenide partial pressure can determine which phases are thermodynamically accessible.

Ruddlesden-Popper phases (RP) $A_{n+1}B_nX_{3n+1}$ can form during solid-state synthesis. They have a layered 2D perovskite structure and hence similar X-ray diffraction (XRD) patterns to 3D perovskite materials.



XRD probes the average long range order of crystalline materials

Raman spectroscopy is a more sensitive probe of local structural changes



Peak assignments in both methods can be made with higher certainty when they are considered in a conjunction with each other.

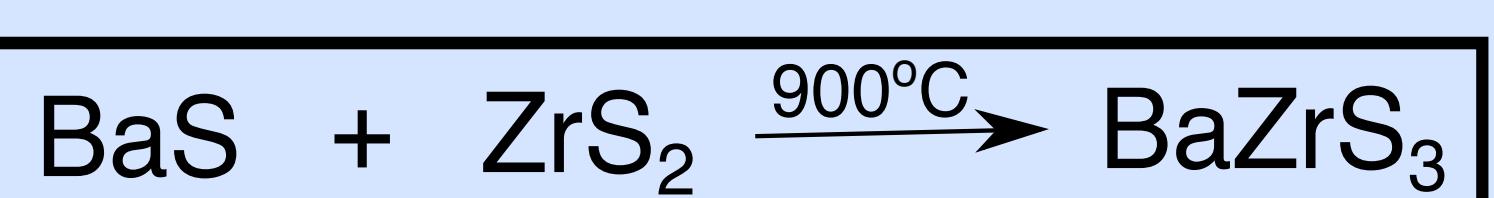
Objectives

- Synthesis and characterization of BaZrS_3 and competing phases
- X-ray diffraction based analysis for bulk crystal structure evaluation
- Computational predictions and experimental measurements of Raman spectra
- *Ab-initio* predictions of energetically accessible phases across synthesis temperatures

Methodology

Material synthesis:

Solid state synthesis by grinding varying molar mixtures of the binary powders. Powders were kept in a closed ampule in a furnace for 5 days and then quenched.



Material characterisation:

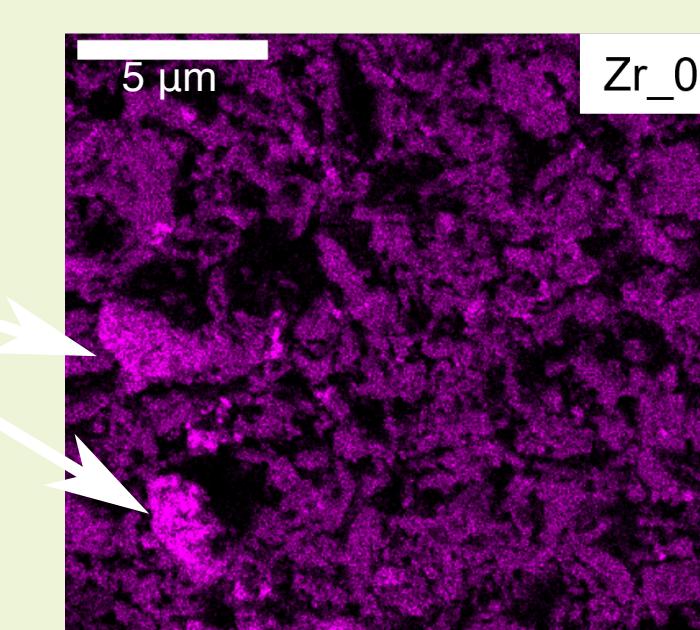
- Powder XRD patterns were acquired at room temperature using Cu $\text{K}\alpha_1$ (1.54056 Å) radiation.
- EDS and elemental mapping were collected using 20kV electron acceleration.
- Raman spectra were collected at room temperature using a 785 nm laser. The power at the sample was measured to be 4.7 mW.

Computational setup:

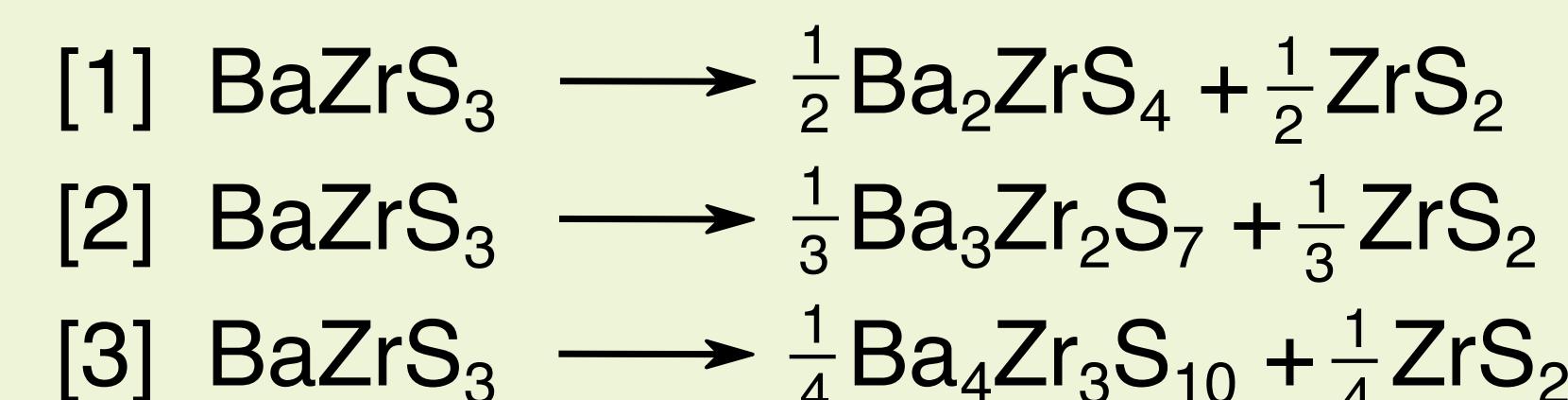
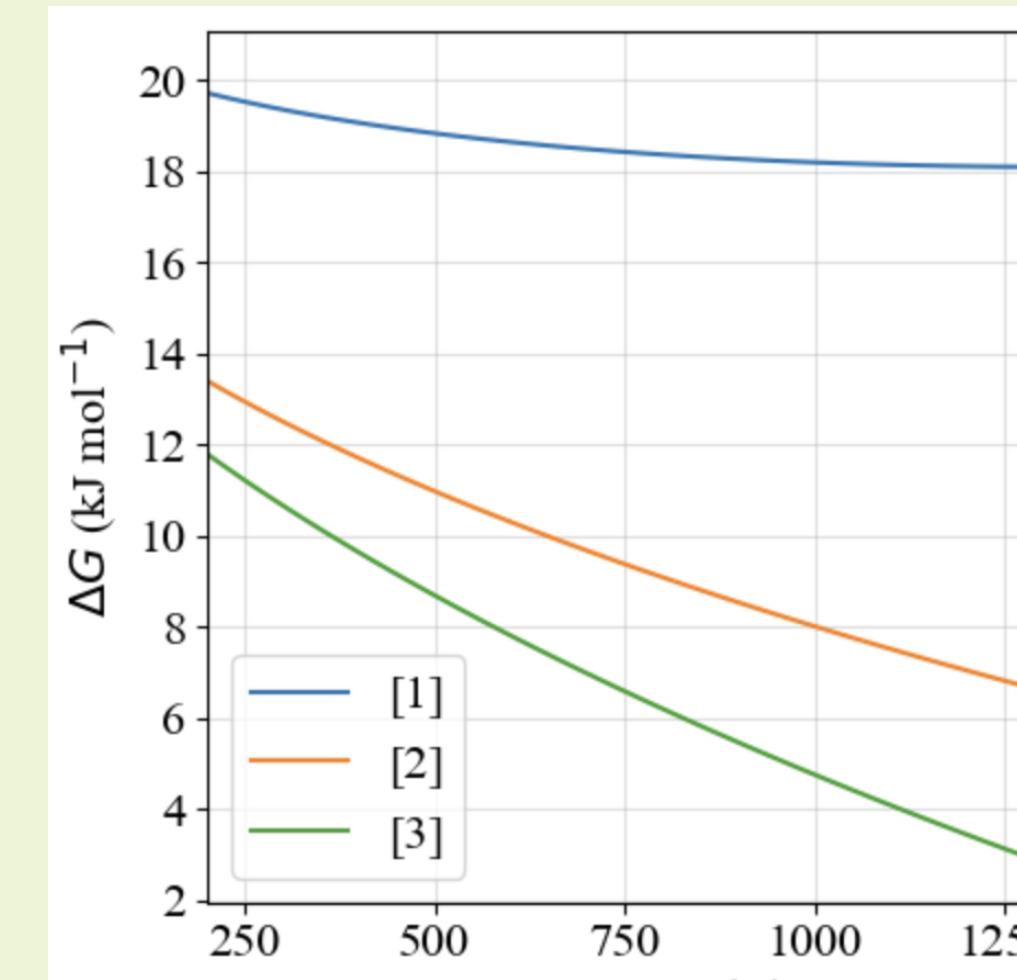
- Density functional theory calculations with FHI-aims for 15 materials in the Ba-Zr-S phase space. The selected phases are <0.5 eV/atom above the convex hull as reported on Materials Project.
- XC: Lattice relaxation and phonons using PBEsol, accurate thermodynamic potentials using SCAN, accurate electronic band dispersions using HSE06.
- Vibrational properties and phonon band structures evaluated with Phonopy.
- Thermodynamics evaluated using our package: ThermoPot
- Force constant matrix and dielectric tensors were post-processed to obtain Raman peak positions as implemented in Phonopy-Spectroscopy

Results

In stoichiometric conditions, Zr rich regions are formed leading to the formation Zr-deficit RP phases. This is verified through Energy dispersive X-ray spectroscopy (EDS).

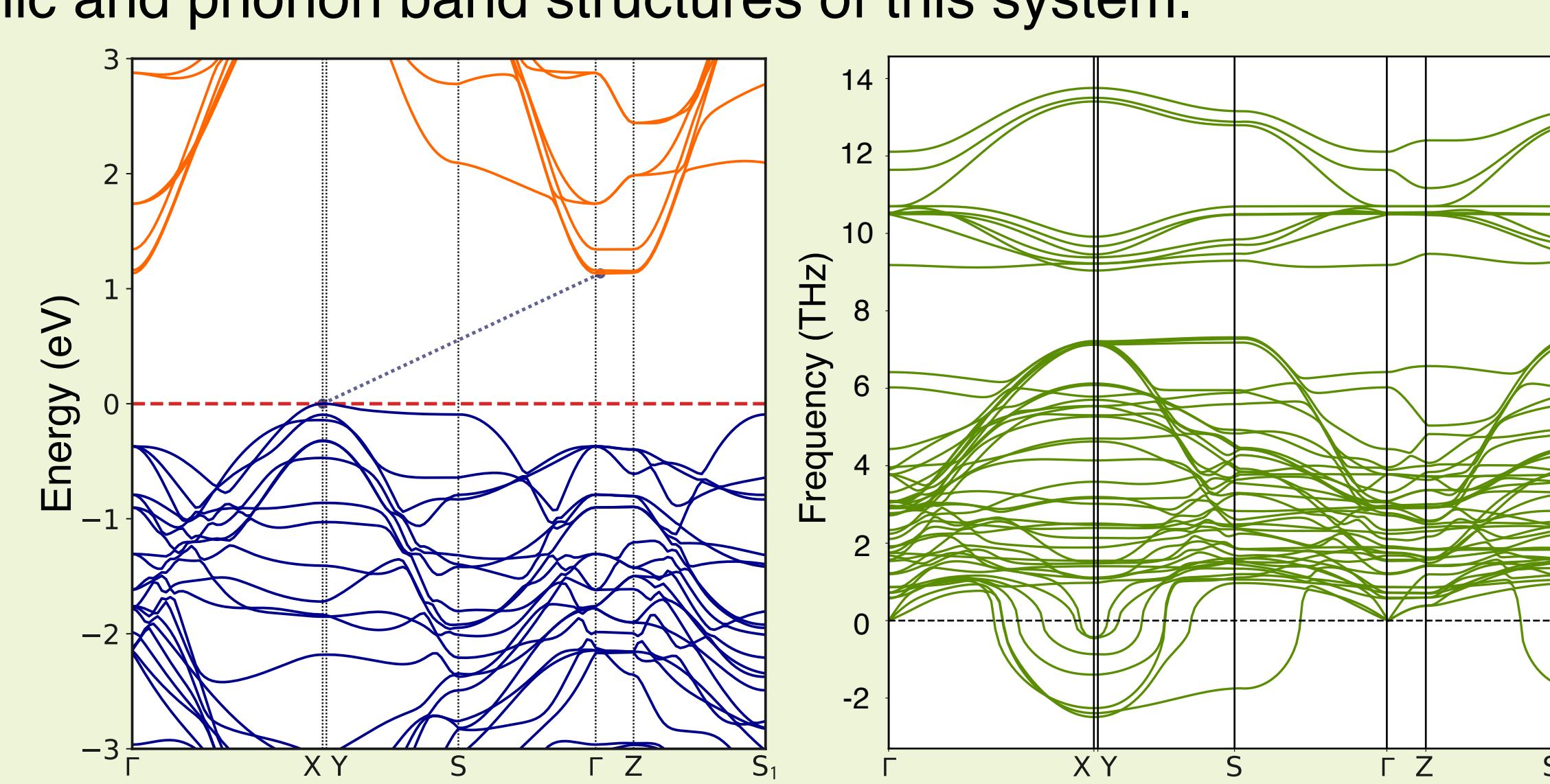


We predict the Gibbs free energies (ΔG) of degradation for the three RP phases:



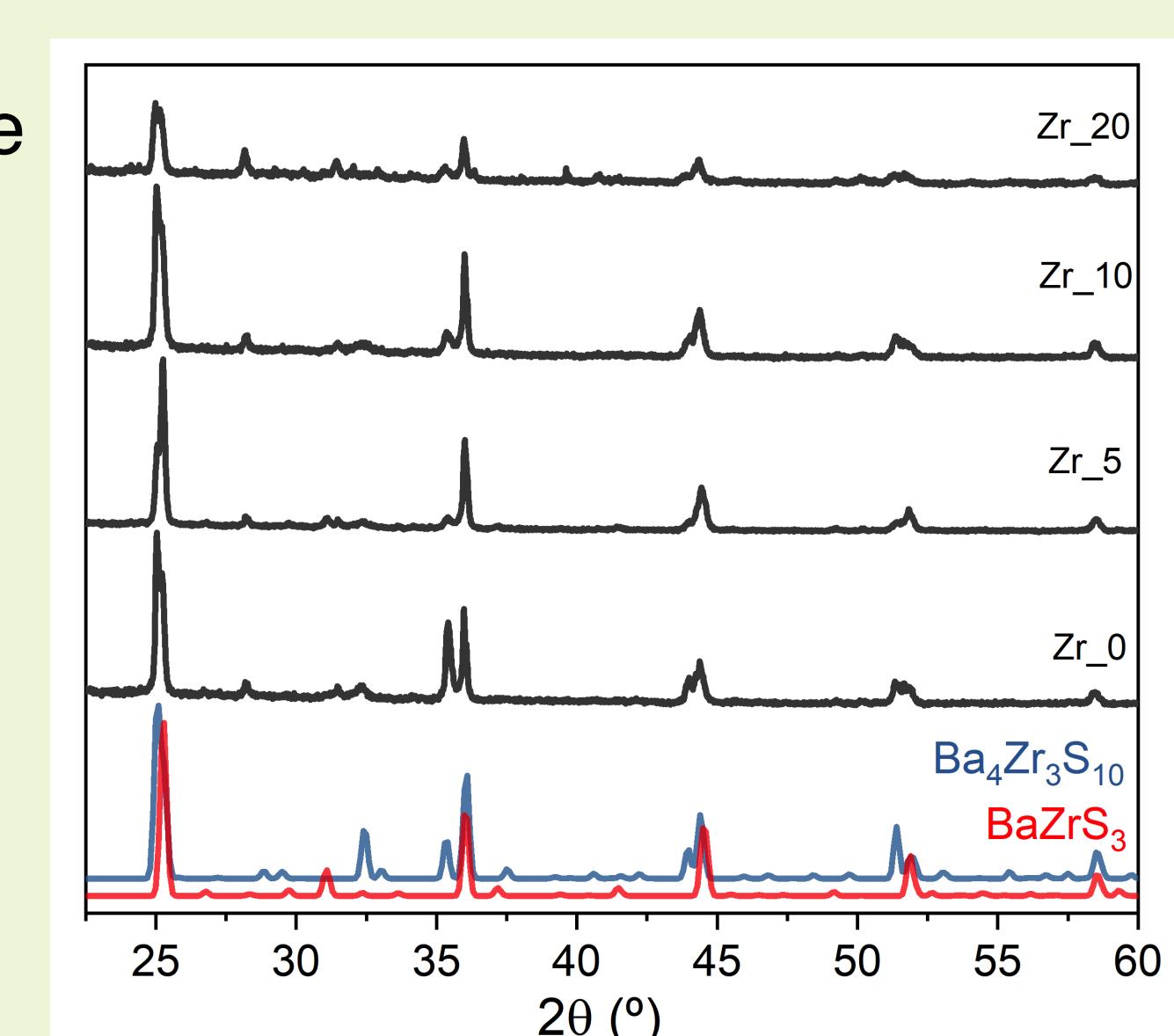
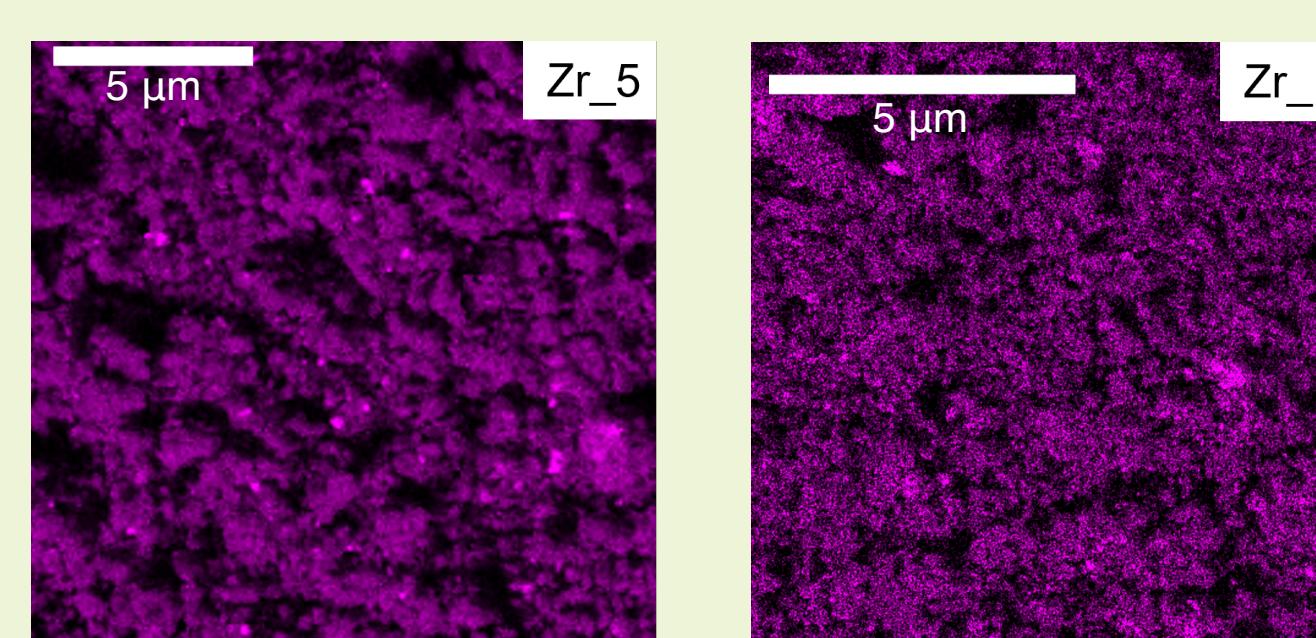
Near 1200 K, the temperature used for solid state synthesis, reaction [3] has $\Delta G = 3.42 \text{ kJ/mol}$ and reaction [2] has $\Delta G = 7.03 \text{ kJ/mol}$. Low ΔG values explain the formation of $\text{Ba}_3\text{Zr}_2\text{S}_7$ in previous reports³ and $\text{Ba}_4\text{Zr}_3\text{S}_{10}$ in our work.

Our predictions show that the RP family of materials are likely to form alongside BaZrS_3 , especially when there is a deficiency in Zr-S. The $\text{Ba}_4\text{Zr}_3\text{S}_{10}$ phase⁴ is not widely studied yet. In this work, we predict the electronic and phonon band structures of this system.



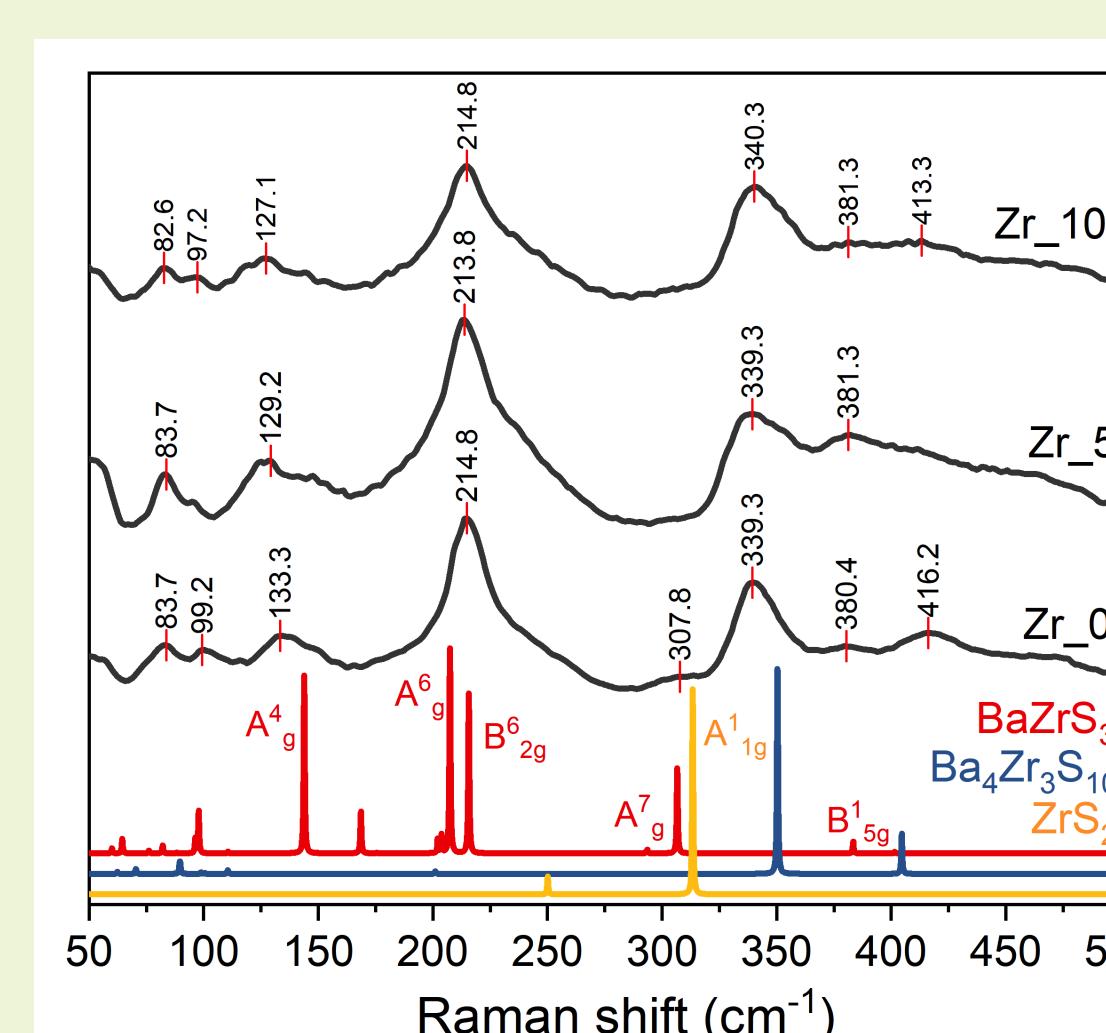
An indirect electronic bandgap of 1.13 eV is predicted with a dispersive in-plane conduction band. A phonon zone boundary (X) instability indicates that there is a lower symmetry phase that is dynamically stable.⁵

Adding an excess molar ratio of ZrS_2 reduces the Zr-S deficit and aids in formation of a more homogeneous BaZrS_3 sample. An excess 5% molar ratio reduces the XRD intensity of peaks associated with the $\text{Ba}_4\text{Zr}_3\text{S}_{10}$ phase. This is also verified with EDS measurements.



Zr labels correspond to excess ZrS_2 molar ratio in the sample

Our predicted Raman spectra for BaZrS_3 and $\text{Ba}_3\text{Zr}_2\text{S}_7$ are in agreement with other reports.⁶ In this work, we report Raman spectra of 8 additional materials including the $\text{Ba}_4\text{Zr}_3\text{S}_{10}$ phase.



A characteristic peak at 214 cm^{-1} confirms the formation of BaZrS_3 . The $\text{Ba}_4\text{Zr}_3\text{S}_{10}$ peak at 339 cm^{-1} is suppressed in the 5% excess ZrS_2 sample. This supports our hypothesis that excess ZrS_2 favours the reaction to be more BaZrS_3 phase pure.

The red shift in the predicted spectra compared to the experiment is due to the overpolarization of S atoms.⁷ Preliminary results show that phonon calculations with HSE06 gives a more accurate prediction of peak positions.

We postulate that the formation of RP phases during BaZrS_3 synthesis may be responsible for the large variation in experimentally reported bandgaps. Without multi-modal characterisation, it can be possible to mis-identify the closely related RP and perovskite phases.

We have published a database of Raman spectra for competing phases in the Ba-Zr-S phases so that our approach can be adopted by others.

References

¹ Tiwari et al, 2021 J Phys. Energy **3** 034010.

² Skelton et al, 2017 Phys. Chem. Chem. Phys. **19** 12452.

³ Ye et al, 2022 Phys. Rev. B **105** 195203.

⁴ Chem et al, 1993 J Solid State Chem. **103** 75

⁵ Pallikara et al, 2022 Electron. Struc. **4** 033022.

⁶ Gross et al, 2017 Phys. Rev. Appl. **8** 044014.

⁷ Crovetto et al, 2020 ACS Appl. Mater. Interfaces **12** 50446

Phonopy-Spectroscopy
GitHub link:



ThermoPot
GitHub link:



Raman spectra database
GitHub link:

