

# Following the reaction of chalcogenide perovskite $\text{BaZrS}_3$

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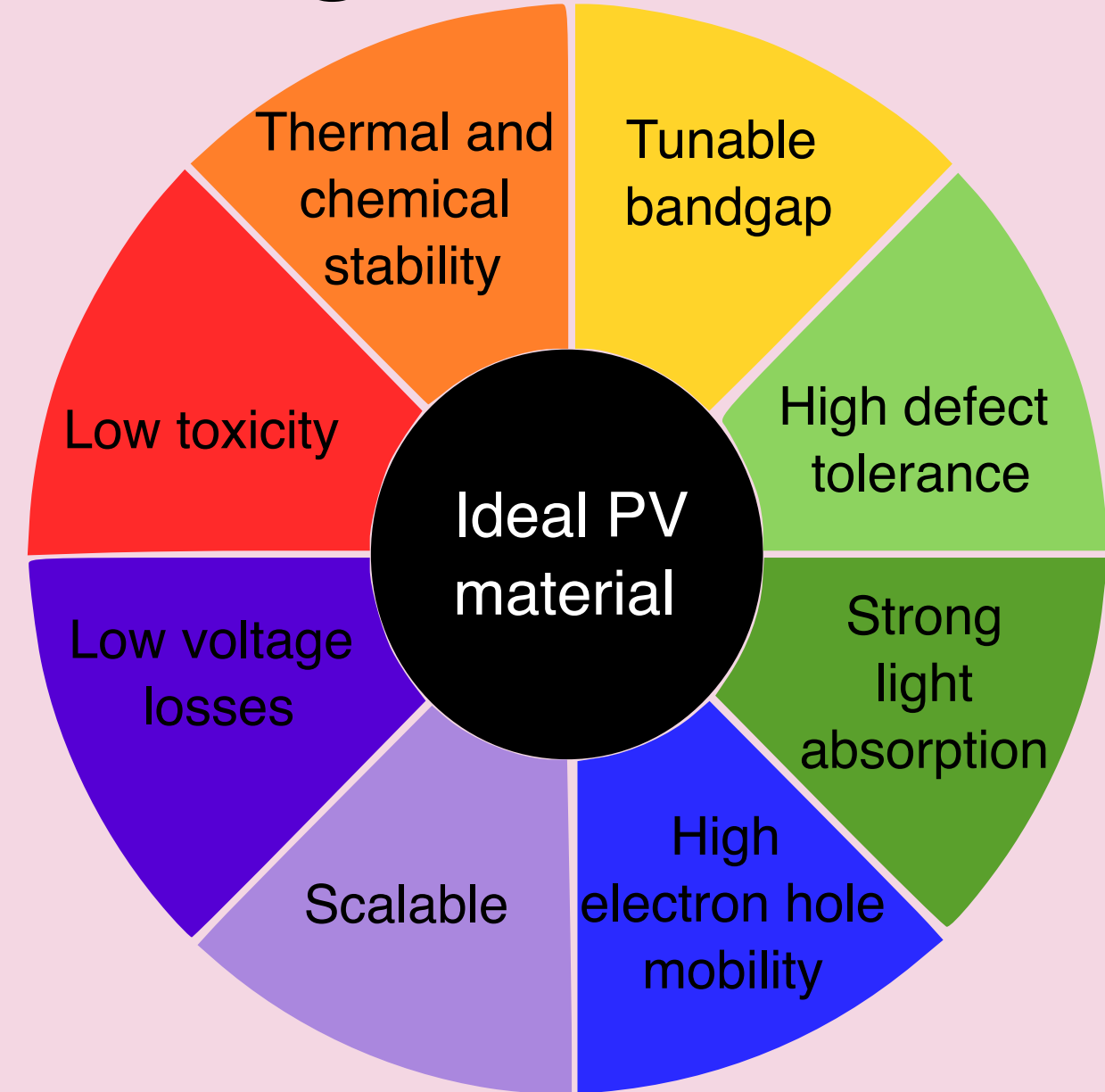


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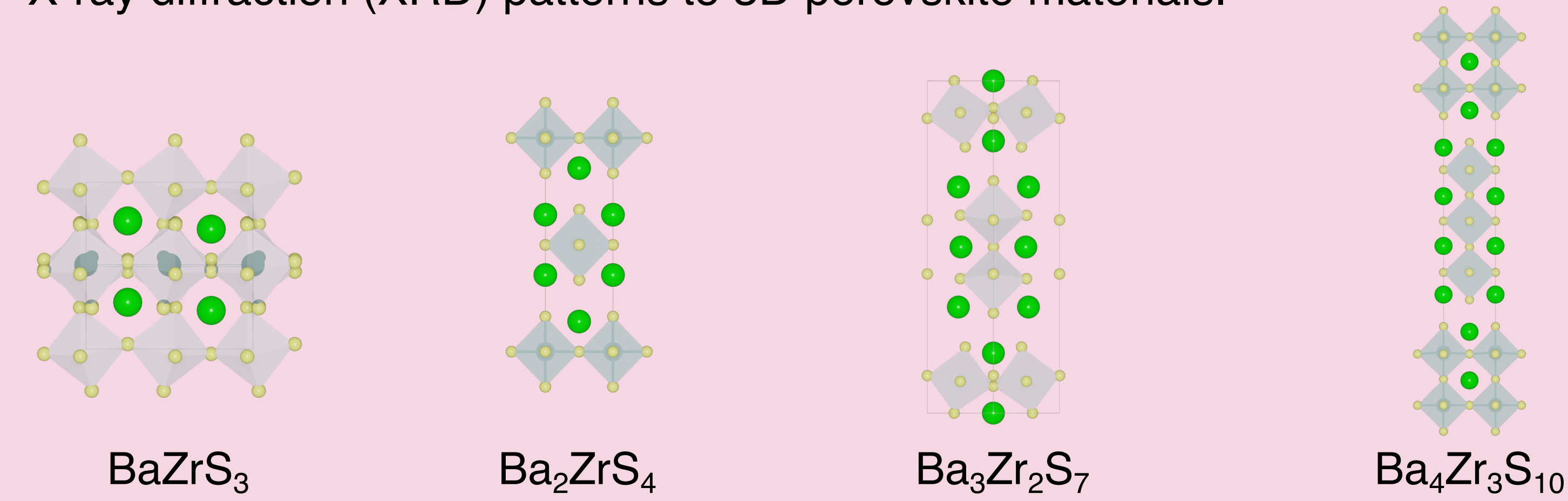
## Background



Chalcogenide perovskite  $\text{BaZrS}_3$  is a candidate material for high-efficiency Si/perovskite tandem photovoltaics.<sup>1</sup>

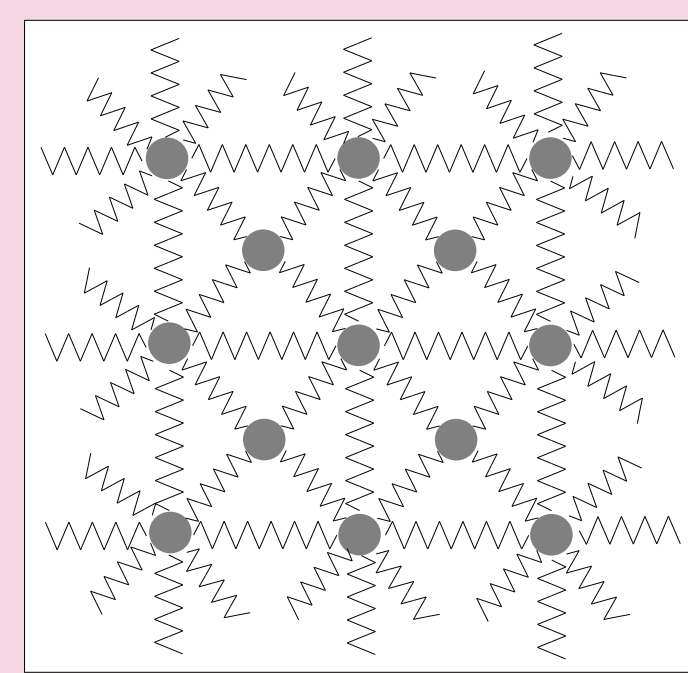
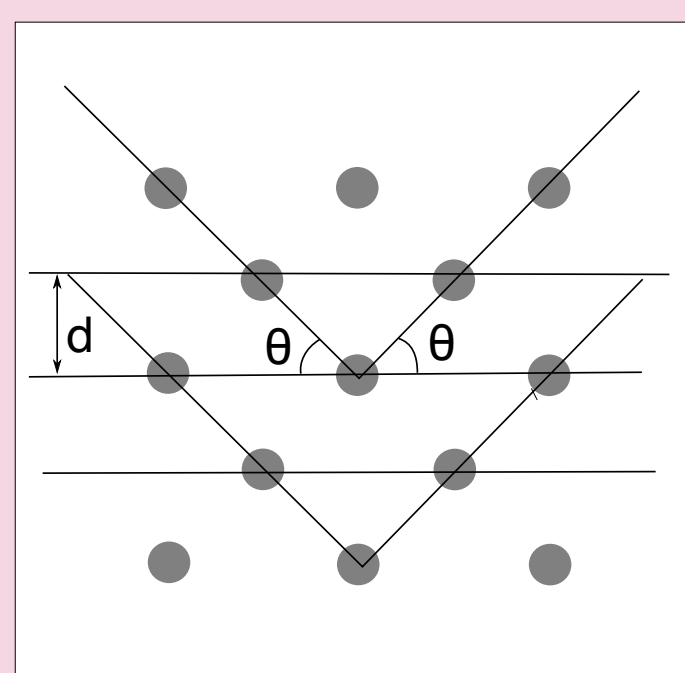
Competing binary and ternary phases can form during synthesis. Tuning precursor stoichiometry, temperature, and chalcogenide partial pressure can determine which phases are thermodynamically accessible.

Ruddlesden-Popper phases (RP)  $\text{A}_{n+1}\text{B}_n\text{X}_{3n+1}$  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.

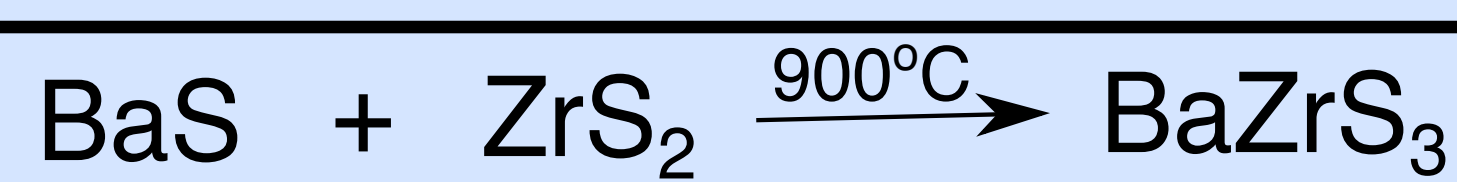
## Objectives

- Synthesis and characterization of  $\text{BaZrS}_3$  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  $\text{Cu K}\alpha_1$  (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 potentials evaluated using our package: ThermoPot
- Force constant matrix and dielectric tensors were post-processed to obtain Raman peak positions as implemented in Phonopy-Spectroscopy

## References

<sup>1</sup> Tiwari et al, 2021 J Phys. Energy **3** 034010.

<sup>2</sup> Skelton et al, 2017 Phys. Chem. Chem. Phys. **19** 12452.

<sup>3</sup> Ye et al, 2022 Phys. Rev. B **105** 195203.

<sup>4</sup> Chem et al, 1993 J Solid State Chem. **103** 75

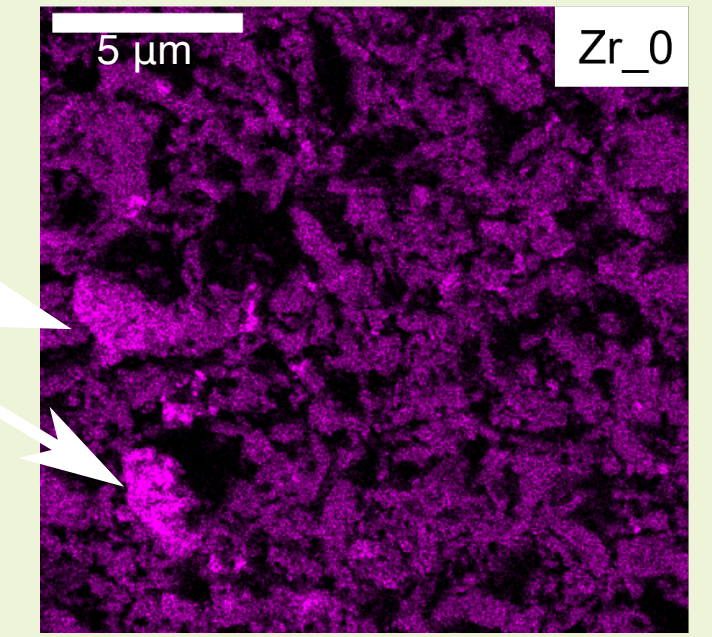
<sup>5</sup> Pallikara et al, 2022 Electron. Struc. **4** 033022.

<sup>6</sup> Gross et al, 2017 Phys. Rev. Appl. **8** 044014.

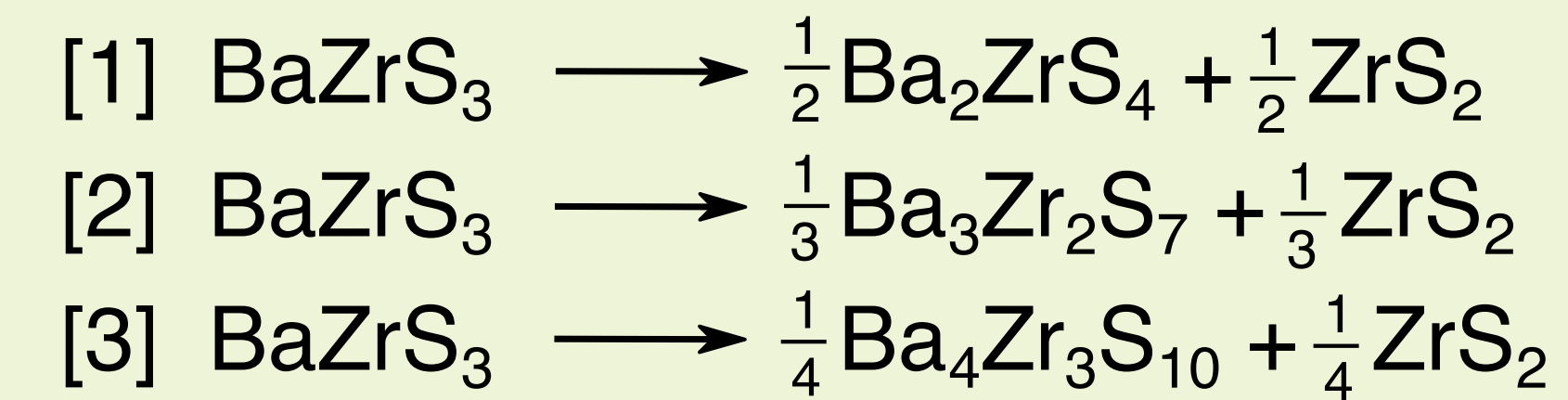
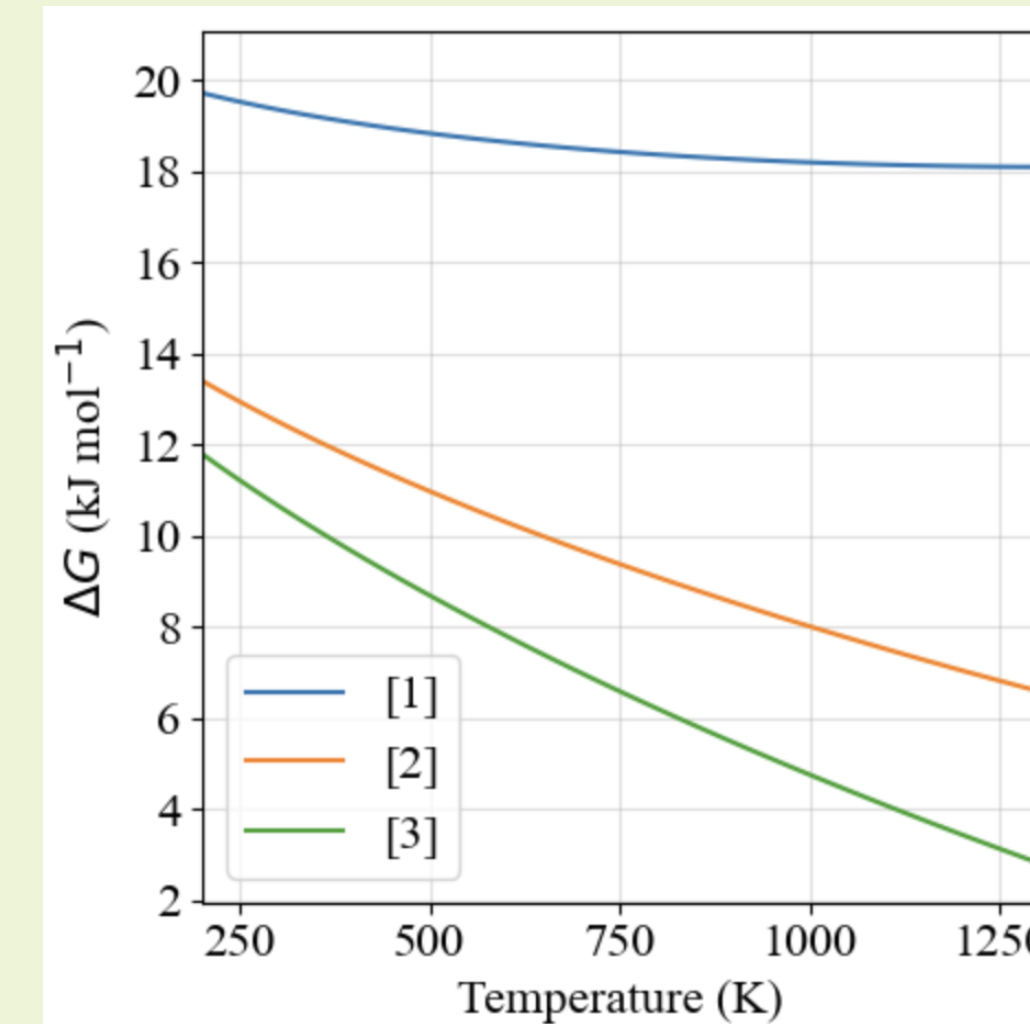
<sup>7</sup> Crovetto et al, 2020 ACS Appl. Mater. Interfaces **12** 50446

## 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).



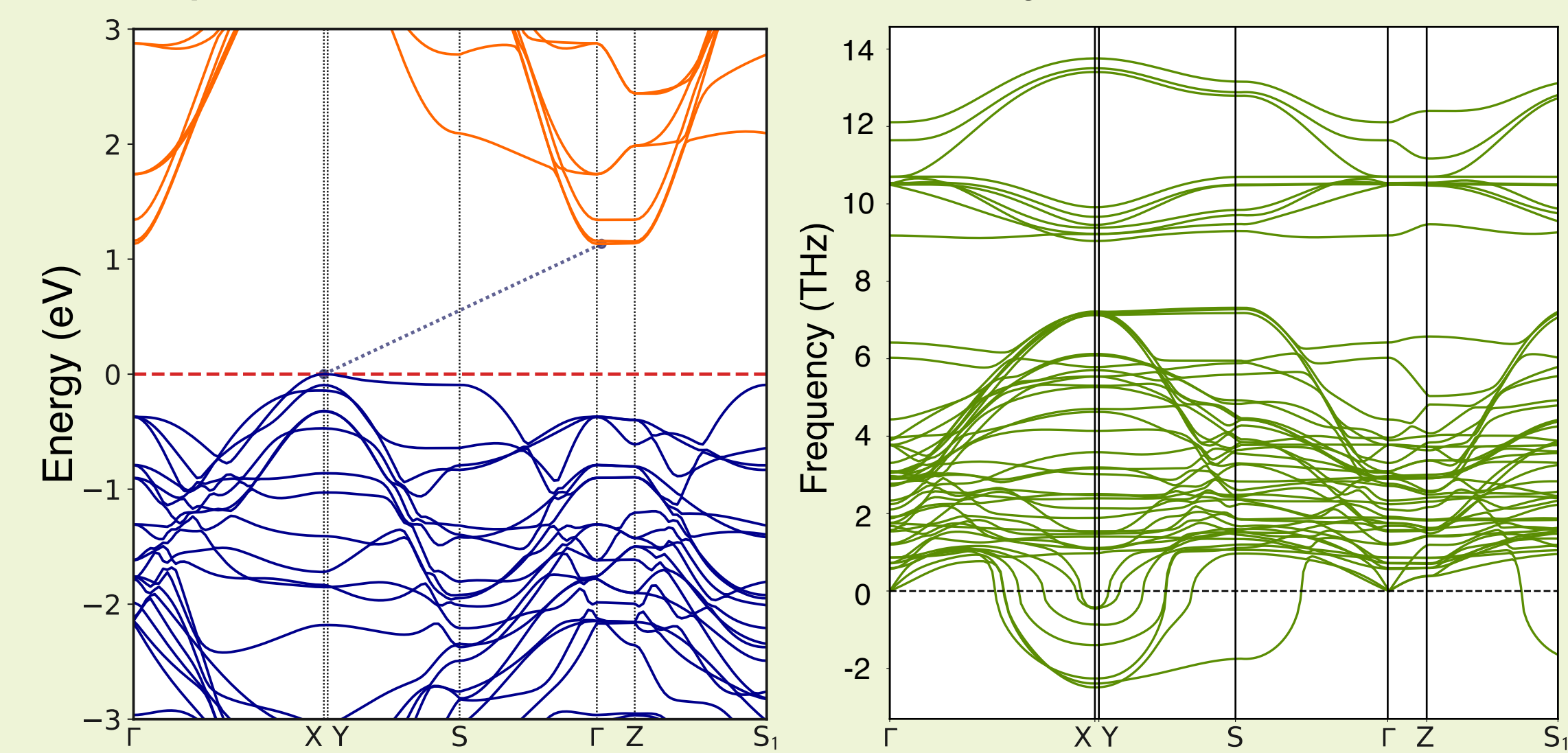
We predict the Gibbs free energies ( $\Delta G$ ) of degradation for the three RP phases:



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

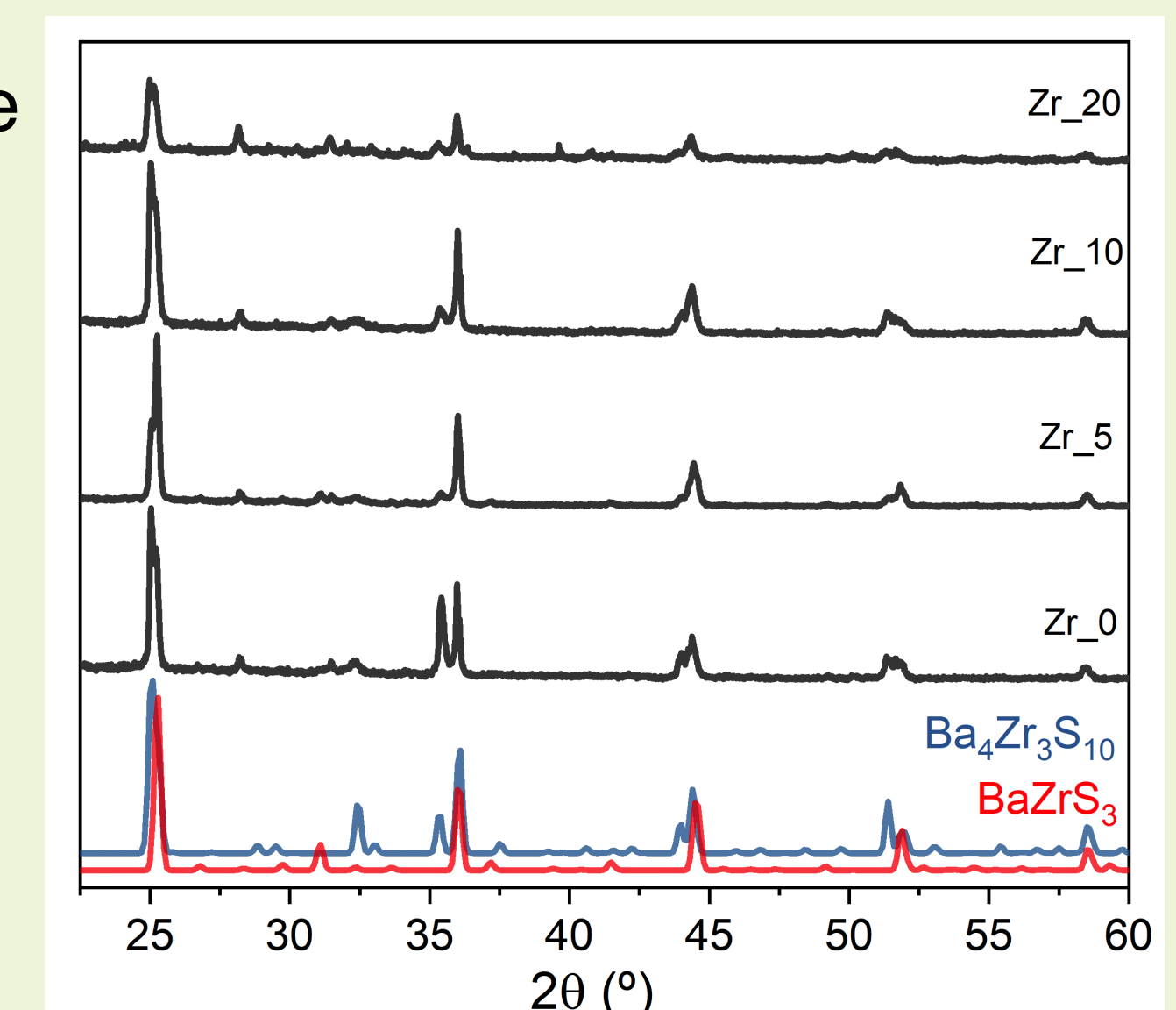
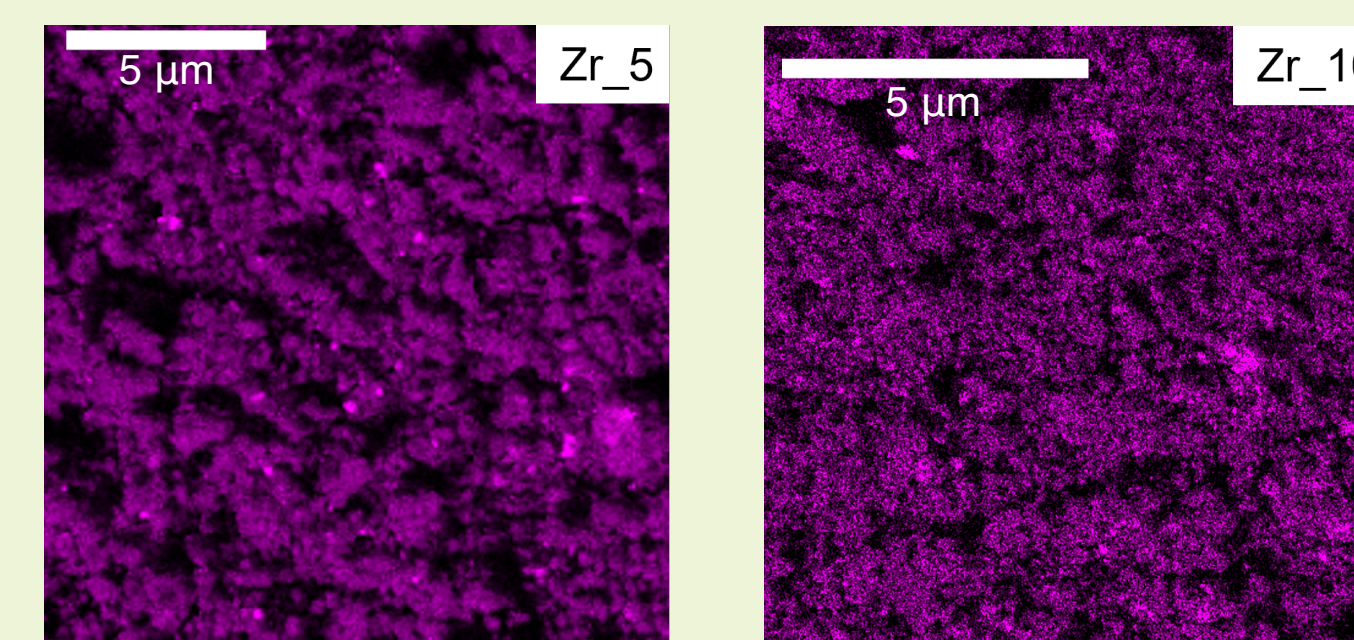
Our predictions show that the RP family of materials are likely to form alongside  $\text{BaZrS}_3$ , especially when there is a deficiency in Zr-S.

The  $\text{Ba}_4\text{Zr}_3\text{S}_{10}$  phase<sup>4</sup> is not widely studied yet. In this work, we predict the electronic and phonon band structures of this system.



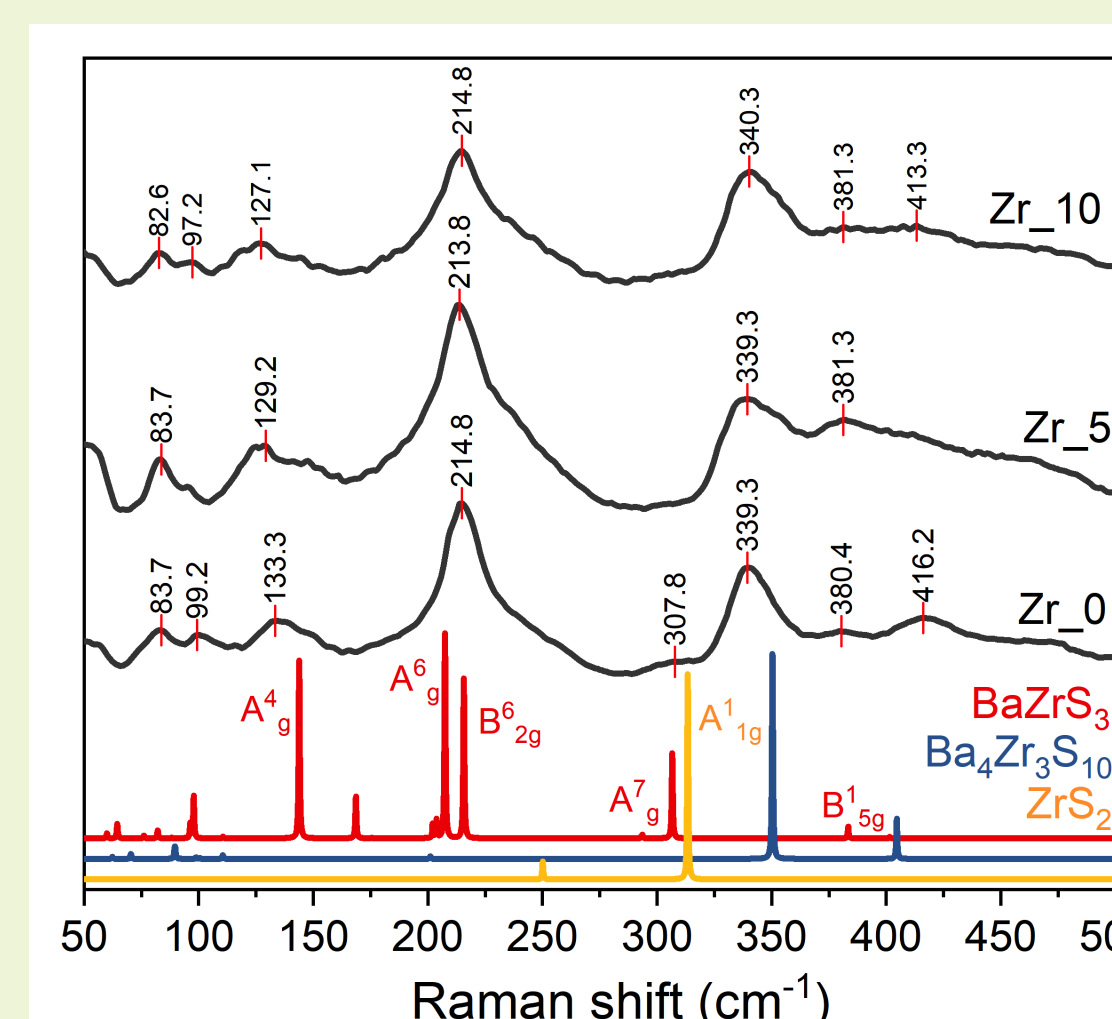
An indirect electronic bandgap of 1.13 eV is predicted with a dispersive in-plane conduction band. A phonon zone boundary (X) instability indicates that there is a lower symmetry phase that is dynamically stable.<sup>5</sup>

Adding an excess molar ratio of  $\text{ZrS}_2$  reduces the Zr-S deficit and aids in formation of a more homogeneous  $\text{BaZrS}_3$  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  $\text{ZrS}_2$  molar ratio in the sample

Our predicted Raman spectra for  $\text{BaZrS}_3$  and  $\text{Ba}_3\text{Zr}_2\text{S}_7$  are in agreement with other reports.<sup>6</sup> 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  $214 \text{ cm}^{-1}$  confirms the formation of  $\text{BaZrS}_3$ . The  $\text{Ba}_4\text{Zr}_3\text{S}_{10}$  peak at  $339 \text{ cm}^{-1}$  is suppressed in the 5% excess  $\text{ZrS}_2$  sample. This supports our hypothesis that excess  $\text{ZrS}_2$  favours the reaction to be more  $\text{BaZrS}_3$  phase pure.

The red shift in the predicted spectra compared to the experiment is due to the overpolarization of S atoms.<sup>7</sup> 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  $\text{BaZrS}_3$  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.

Phonopy-Spectroscopy  
GitHub link:



ThermoPot  
GitHub link:



Raman spectra database  
GitHub link:

