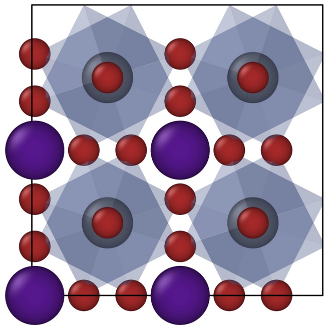
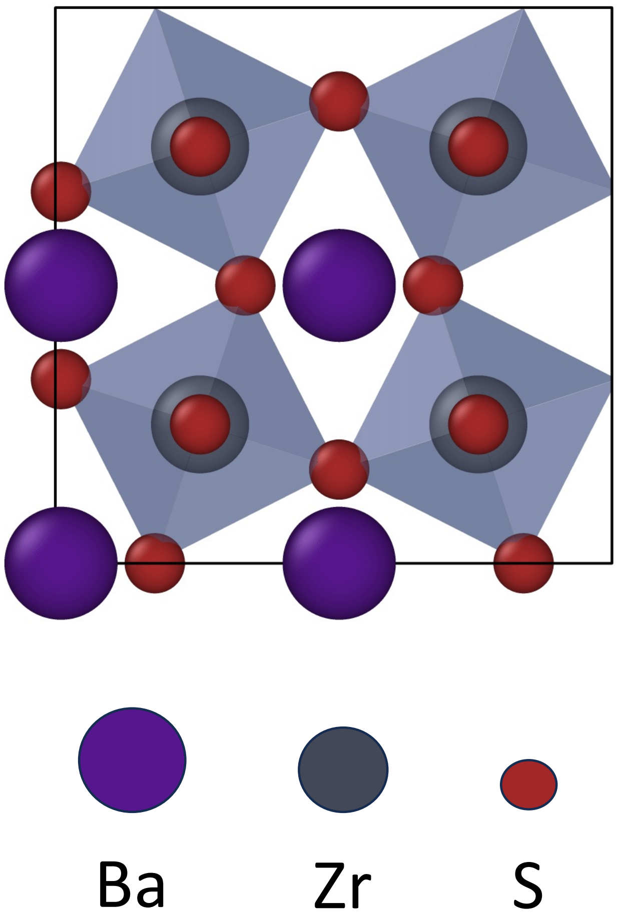
Phase stability of chalcogenide perovskite $BaZrS_3$



Dr Lucy Whalley
Assistant Professor in Physics
Northumbria University, United Kingdom

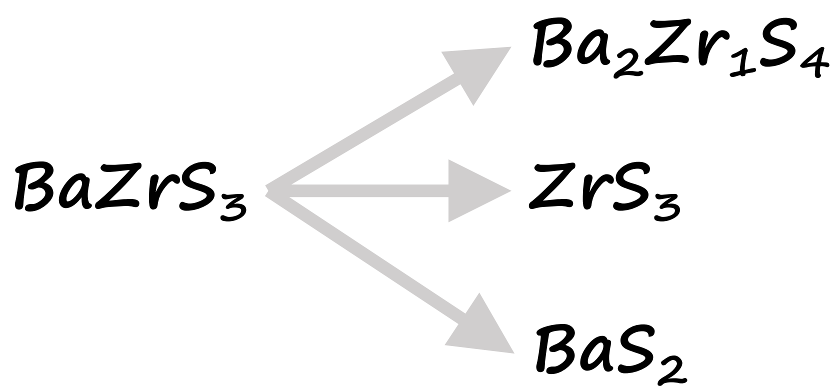
Motivation for $BaZrS_3$ (BZS)

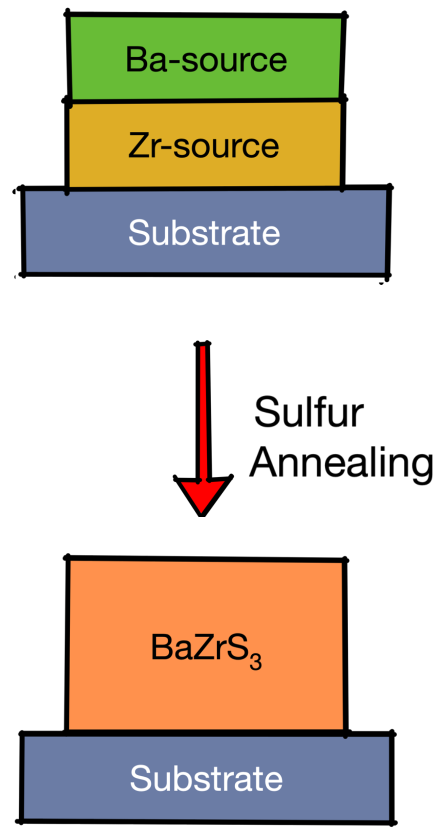


- Abundant and non-toxic
- Stable in air to 400°C
- Strong light absorption
- 1.8eV band gap → tandem PV
- Tunable E_g through S/Se or Zr/Hf mixing
- Low thermal conductivity (for thermoelectric applications)

Challenge: Phase Stability

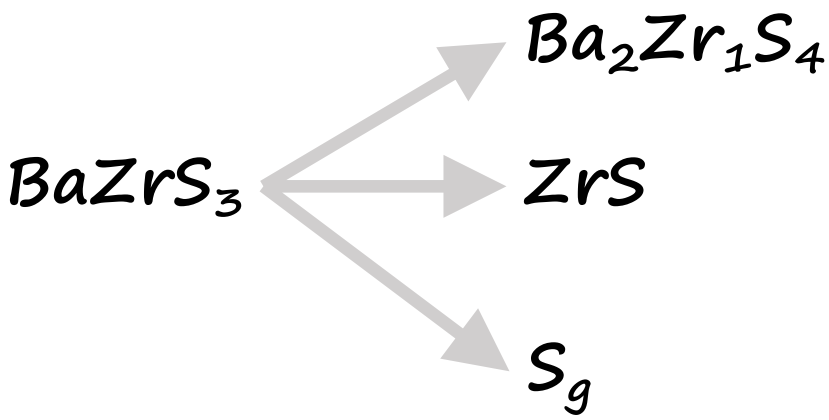
Stability against multiple phases



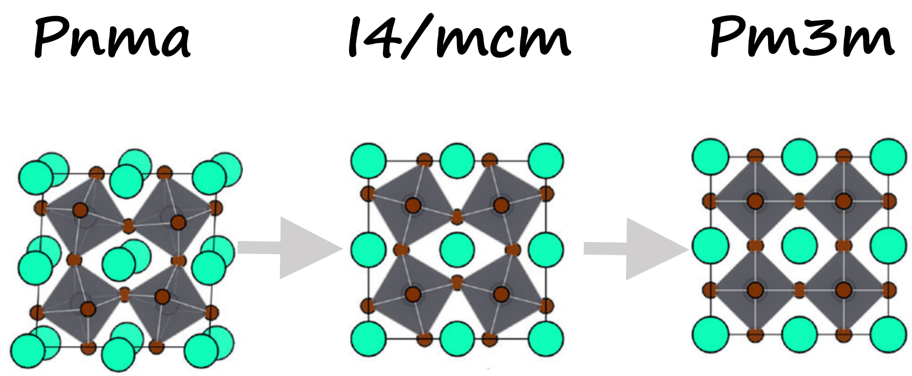


Challenge: Phase Stability

Stability against multiple phases



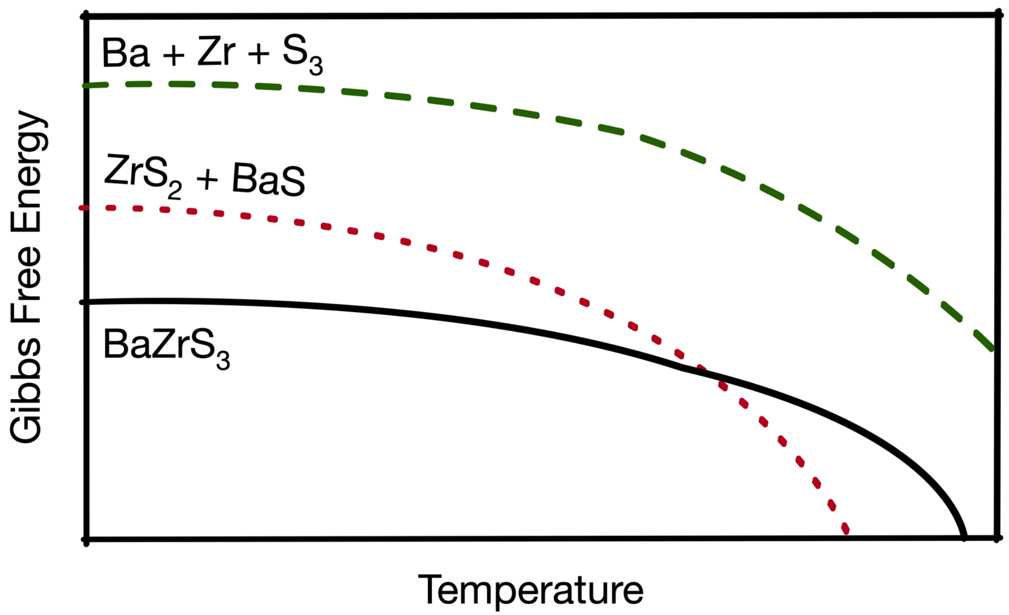
Stability against polymorphs



Thermodynamic stability

A material is thermodynamically stable if, for a given set of conditions, it is the global minimum of the Gibbs Free Energy.

$$BaZrS_3 \rightarrow Ba + Zr + 3S(s)$$
$$BaZrS_3 \rightarrow BaS + ZrS_2$$
$$3BaZrS_3 \rightarrow Ba_3Zr_2S_7 + ZrS_2$$
$$BaZrS_3 + 2S(g) \rightarrow BaS_2 + ZrS_3$$



DFT

$$\mu_i(T,P) = E^{\mathrm{DFT}} + E^{\mathrm{ZP}} + \int_0^T C_p(T)\mathrm{d}T + PV - TS_{\mathrm{vib.}}(T)$$

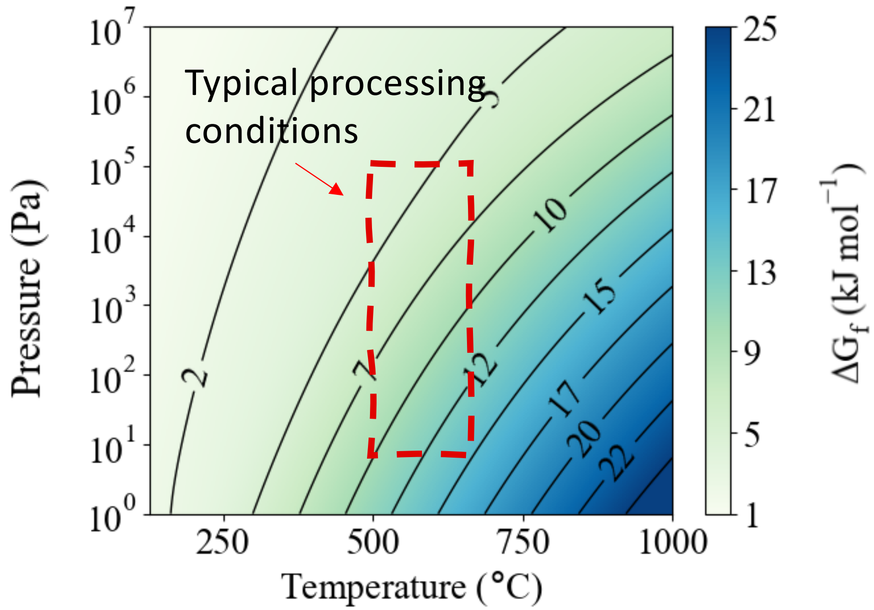
Lattice dynamics

Stability against ZrS_3 formation

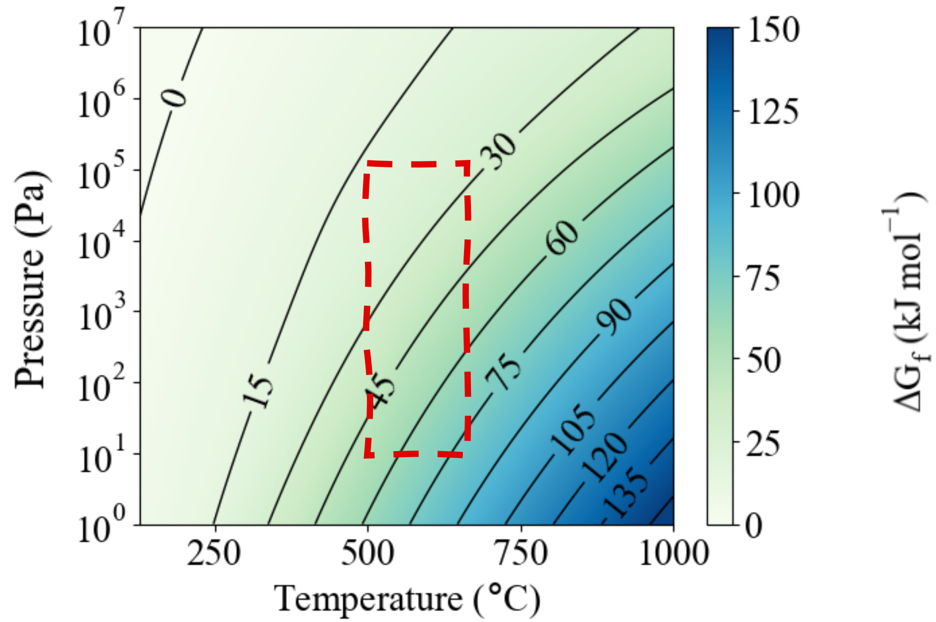
Is ZrS_3 growth favored at high sulfur pressure?

P. Kayastha, G. Longo, L. Whalley
ACS Applied Energy Materials, **2024**
10.1021/acsaem.3c03208

$BaZrS_3 + 2S(g) \rightarrow BaS_2 + ZrS_3$



$BaZrS_3 + 3S(g) \rightarrow BaS_3 + ZrS_3$

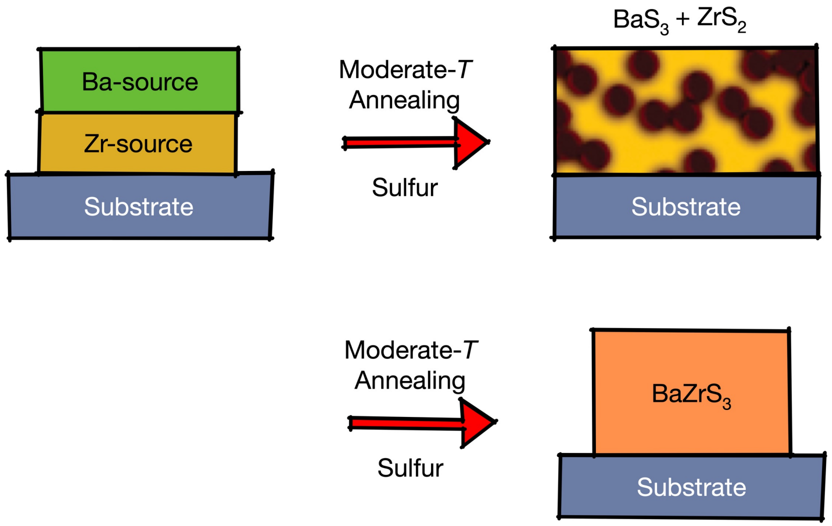


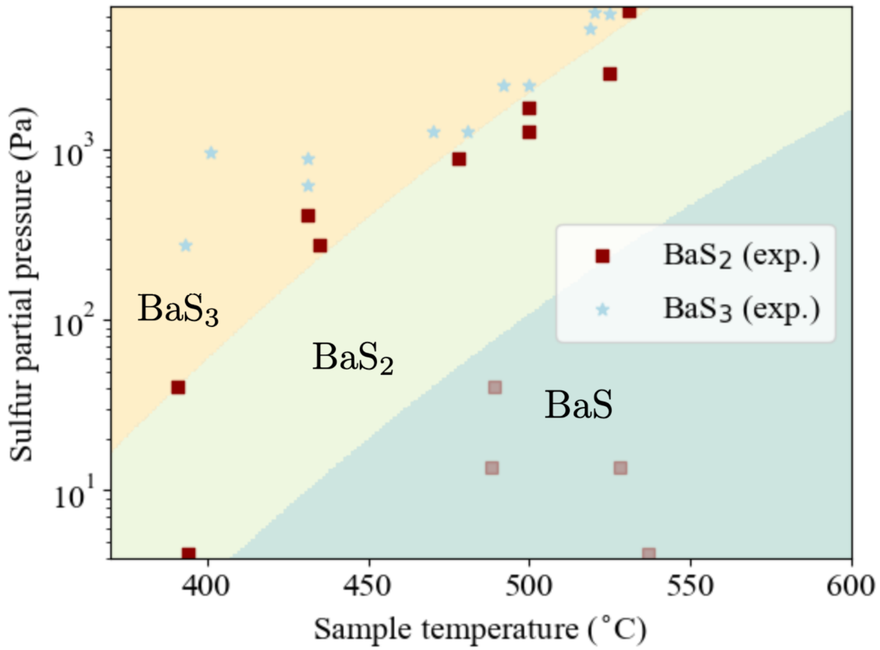
$BaZrS_3$ is more stable than all BaS_x and ZrS_x precursors
(there may still be kinetic limitations)

Paper in prep.

BaS_3 phase stability

What sulfur partial pressure is required to form BaS_3?





Experimental measurements from Scragg group at Uppsala.

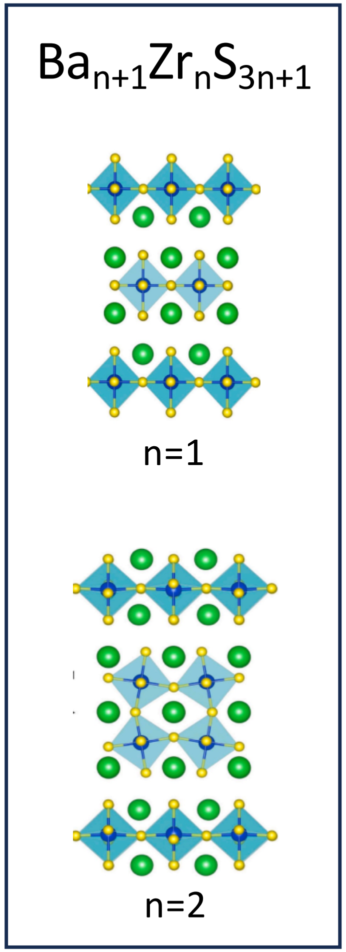
Assumption: Sulfur reaches saturated vapour pressure.

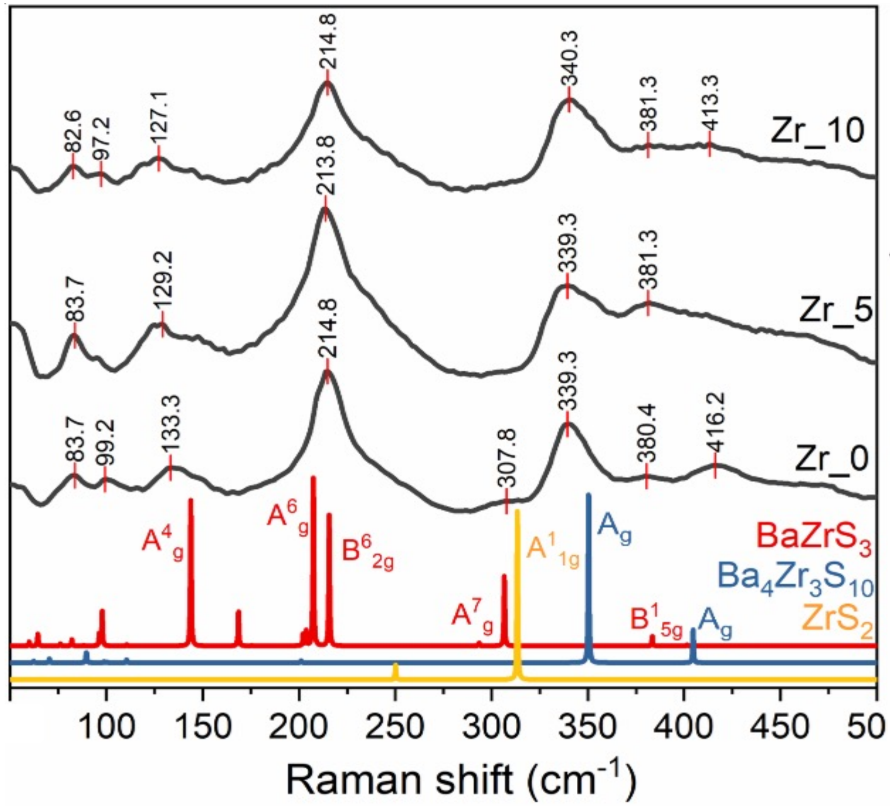
High sulfur pressures (>10^3 Pa at 500 °C) are required to form BaS_3.

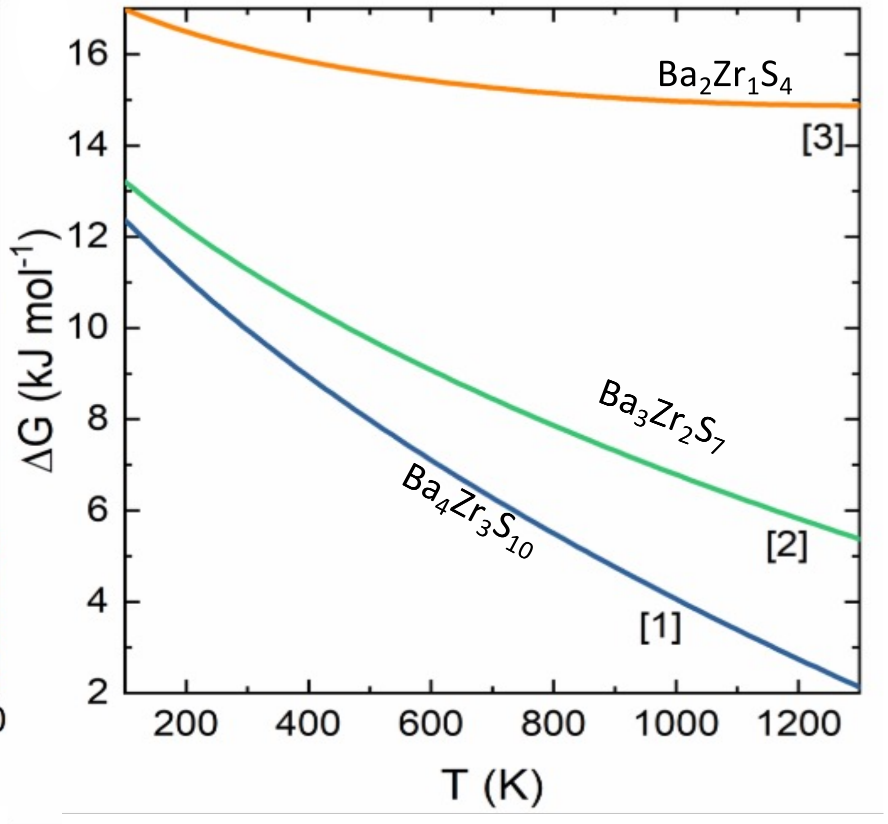
P. Kayastha, L. Whalley, G. Longo *et al*
Solar RRL, **2023**, 7, 2201078

Stability against <u>ternary</u> phases

Do Ruddlesden-Popper phases form?



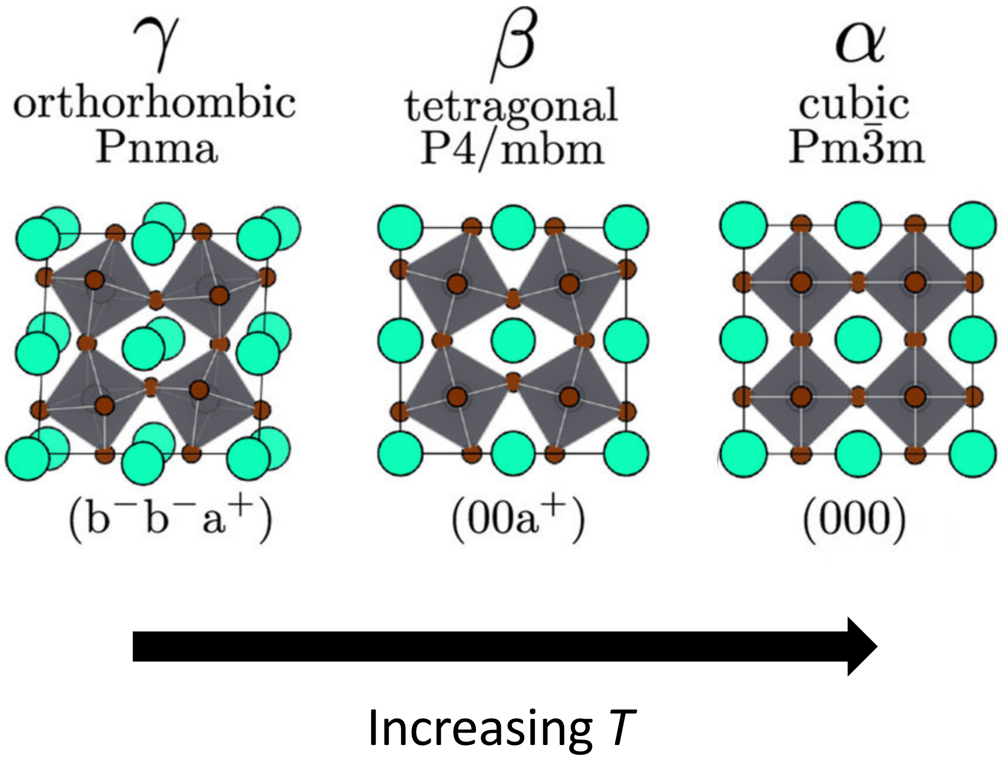


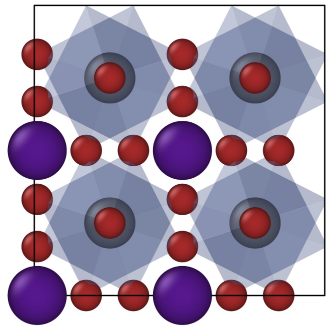


RP phases form during synthesis at high-*T*.

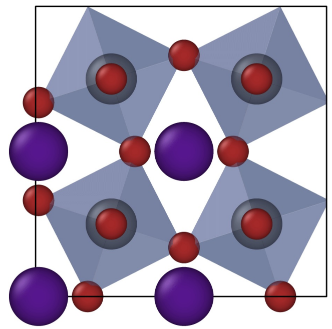
Stability against perovskite polymorphs

Are there phase transitions to other perovskite structures?





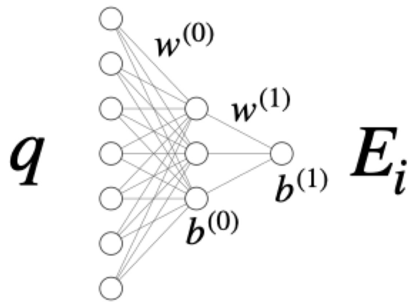
R-point phonon mode



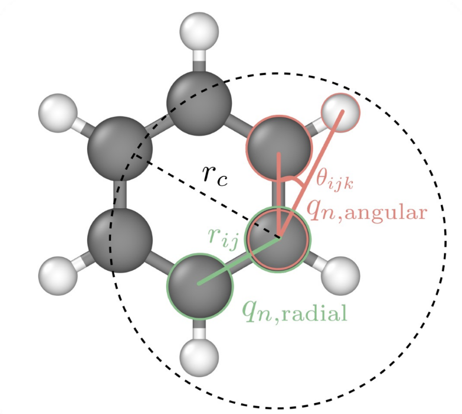
M-point phonon mode

Neuroevolution Potential (NEP)

Fan *et al* Phys. Rev. B **2021**, 104, 104309



Input features



Output

$$E_i = \sum_{\mu=1}^{N_{neu}} w_{\mu}^{(1)} \tanh\left(\sum_{\nu=1}^{N_{des}} w_{\mu\nu}^{(0)} q_{\nu}^{i} - b_{\mu}^{(0)} \right) - b^{(1)}$$

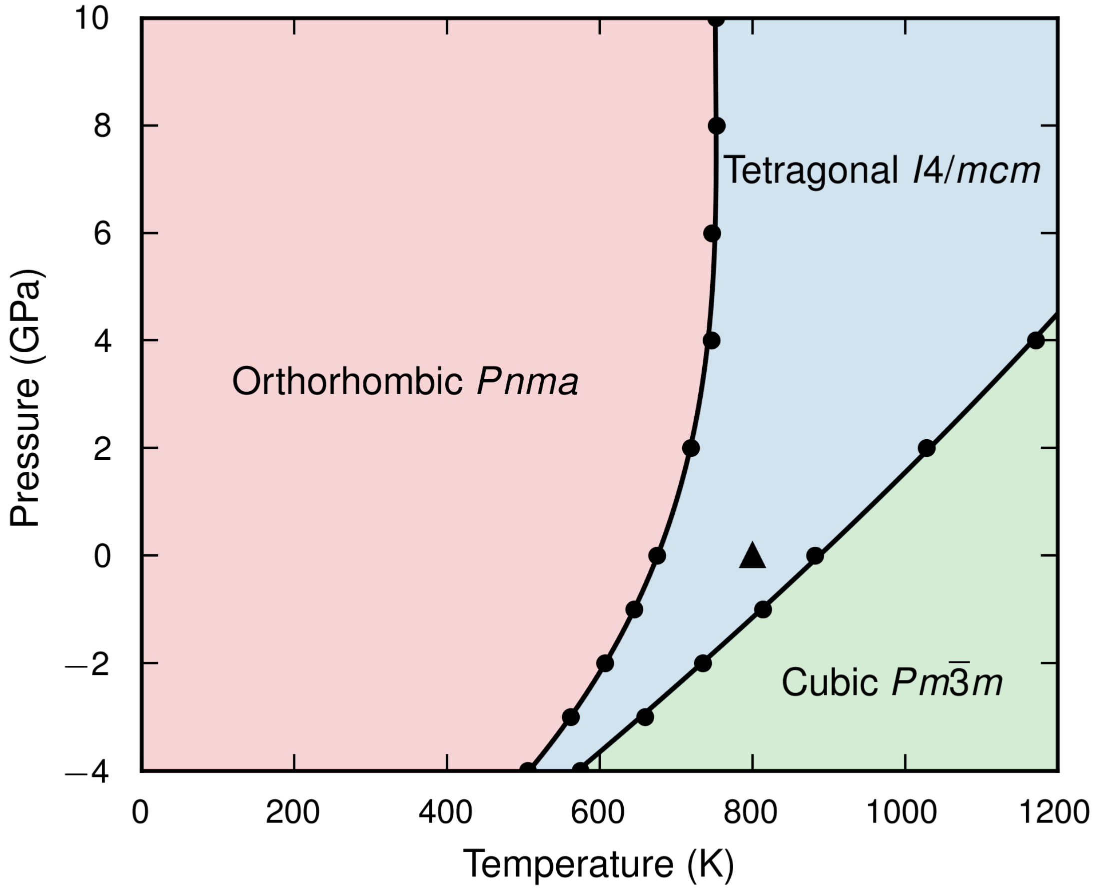
$$F_i = \sum_{i \neq j} \frac{\partial E_i}{\partial r_{ij}} - \frac{\partial E_j}{\partial r_{ji}}$$

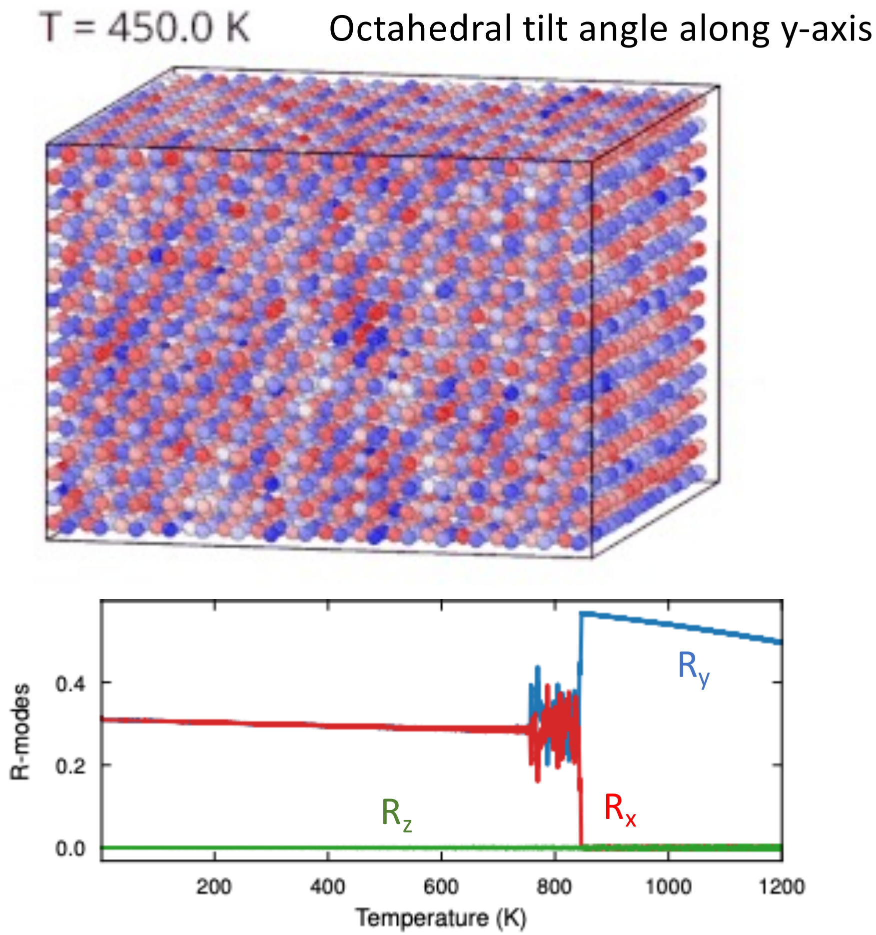
$$\mathbf{W}_i = \sum_{j \neq i} \mathbf{r}_{ij} \otimes \frac{\partial E_j}{\partial \mathbf{r}_{ji}}$$

Paper in prep.

Stability against perovskite polymorphs

Are there phase transitions to other perovskite structures?





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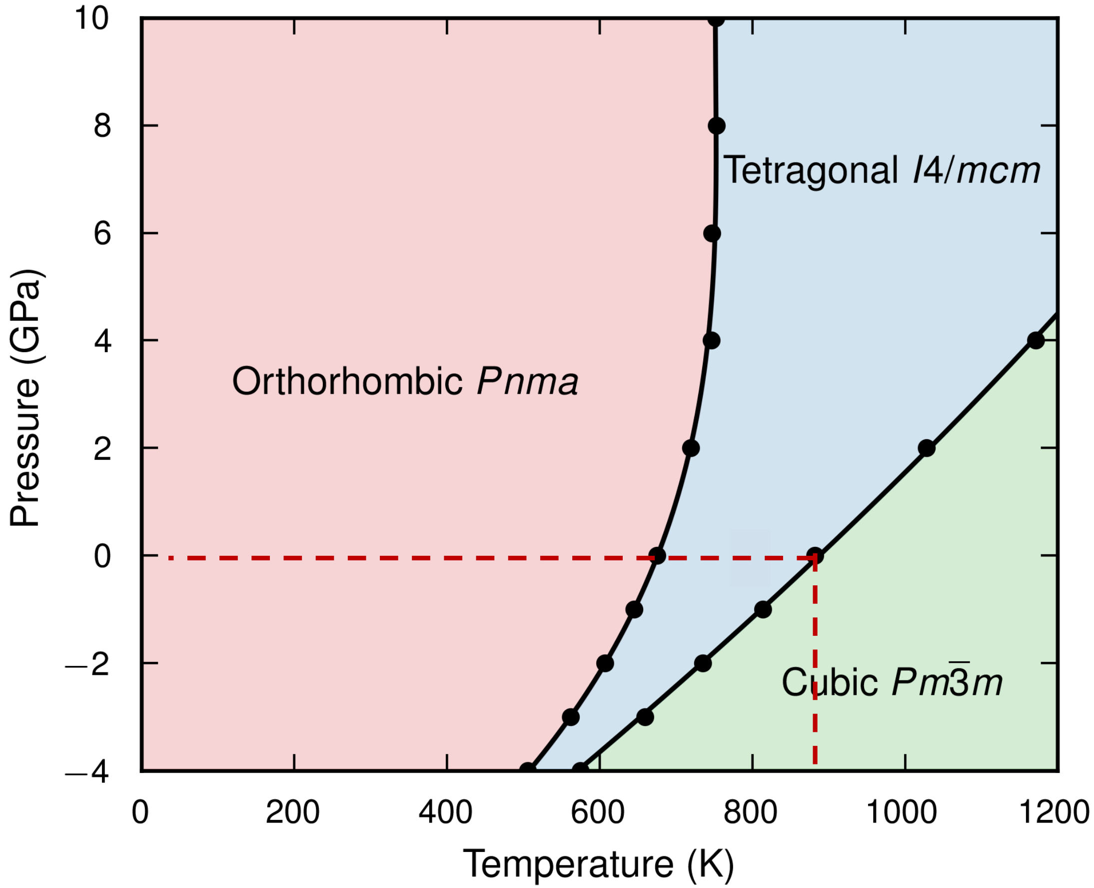

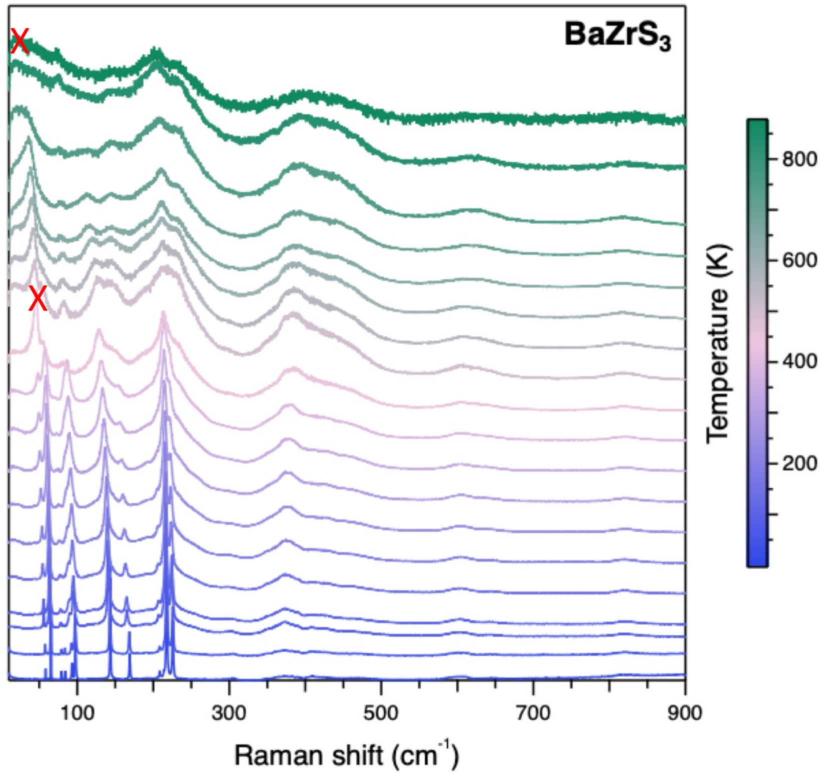

K. Ye, M. Menahem, T. Salzillo *et al*
Phys. Rev. Materials, **2024**, 8, 085402

Summary

1) $BaZrS_3$ is a promising PV material

2) Challenge: Thin-film synthesis at moderate *T*

3) $BaZrS_3$ formation from BaS_x + ZrS_x is possible

4) High partial pressures of sulfur required to form BaS_3

5) Ruddlesden-Popper phases compete at high-*T*

6) Octahedral-tilt phase transitions: Pnma $\xrightarrow[610K]{}$ I4/mcm $\xrightarrow[900K]{}$ Pm3m

Outstanding challenges

1) Characterisation and control of sulfur vapour

2) Formation of ZrO_x phases acting as Zr-sink?

3) Phase purity: RP-phase formation and characterisation

3) Lack of PL: what are the recombination pathways?

4) What is the impact of octahedral tilt patterns on thermal transport?

Collaborators

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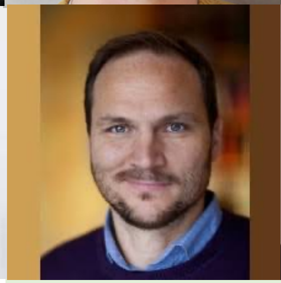
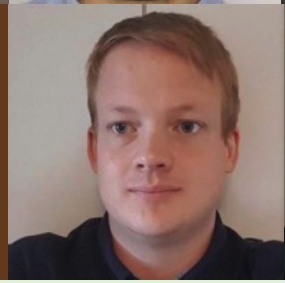
Northumbria University NEWCASTLE

Prakriti Kayastha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UNIVERSITAT POLITÈCNICA DE VALÈNCIA

Thank you

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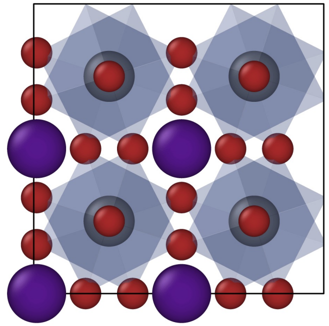

TURING SCHEME

ReNU Renewable Energy Northeast Universities

EPSRC Centre for Doctoral Training in Renewable Energy Northeast Universities

HEC MCC UK

Software Sustainability Institute