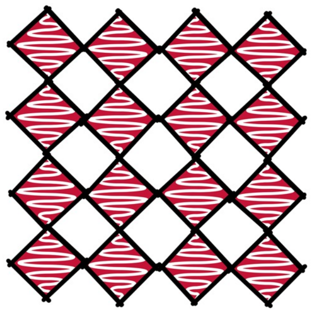
Perovskite materials: defects and dynamics



Dr Lucy Whalley

Assistant Professor in Physics

Northumbria University, United Kingdom

Materials Modelling: what role can it play?

"Theoretical materials science and technology has several levels, and also several roles. It provides a framework in which to organize empirical results. It can be used to scope a new field. It can be used to separate out the components of some complex system, where experiment alone still confuses. And one can imagine cases—especially for the shortest or the longest timescales—where theory can outreach experiment."

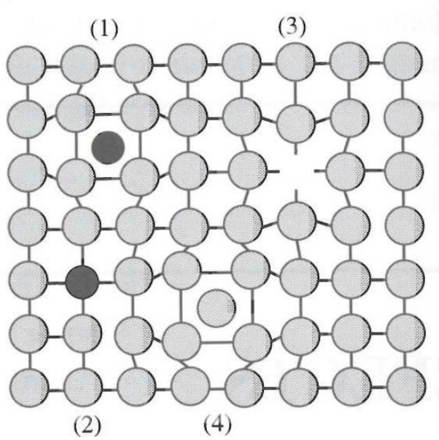
Marshall Stoneham
Defects in semiconductors and oxides: where are the gaps in first principles theory? (2009)

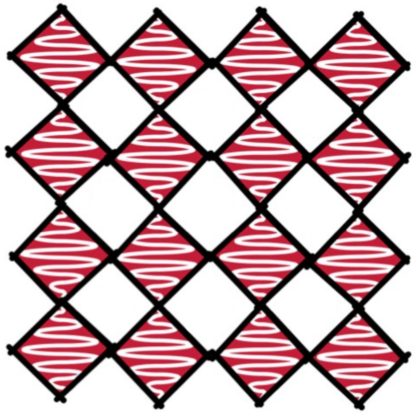
Components in a complex system

Defects

Dynamics

carrier concentration
carrier mobility
phase stability
ion transport
...





phase stability
carrier mobility
thermal transport
light absorption
....

Non-radiative carrier capture

electronic excitation → thermal energy

1. Halide perovskites

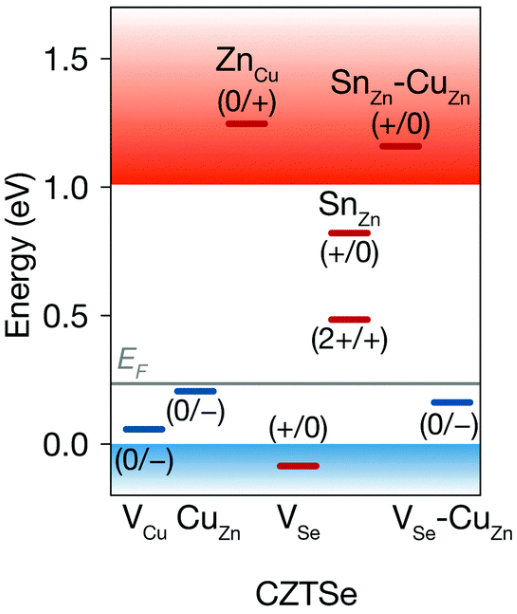
defects and dynamics → non-radiative processes

2. Chalcogenide perovskites –

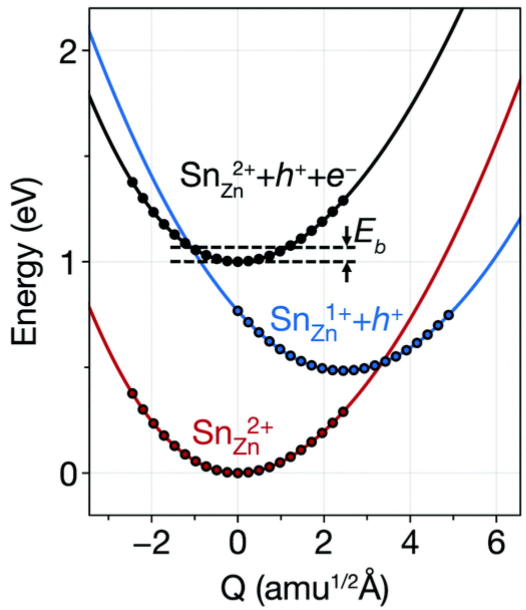
lattice and molecular dynamics → phase stability

Predicting PV device performance

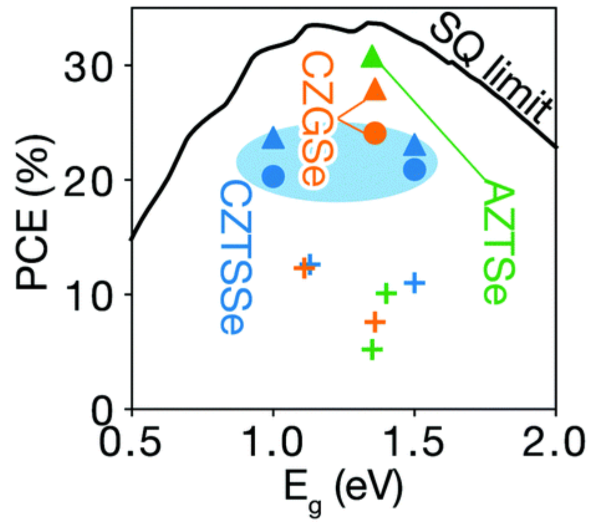
Charge transition level diagram



Configuration co-ordinate diagram

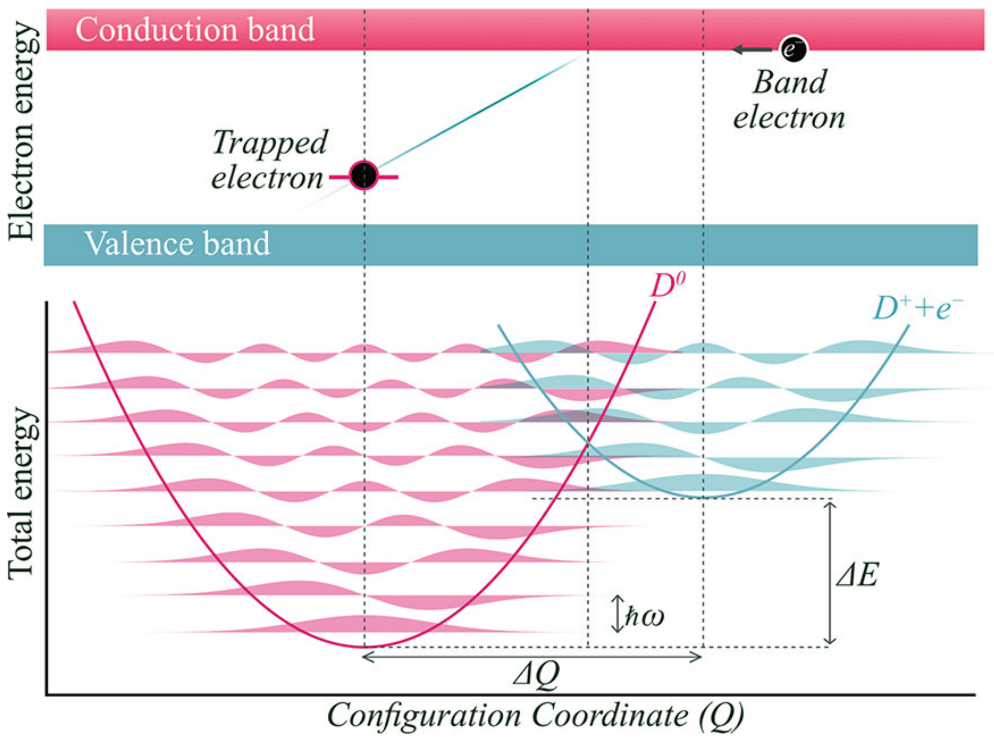


Defect-limited photovoltaic efficiency



Kim, Marquez, Unold and Walsh, *Energy Environ. Sci.,* 2020,13, 1481-1491

Quantum mechanical prediction of the capture coefficient C



Whalley et al., *J. Am. Chem. Soc.* 2021, 143, 9123−9128

Semi-classical

C determined by energy barrier (ΔQ, ΔE, PES curvature)

↓

Quantum mechanical

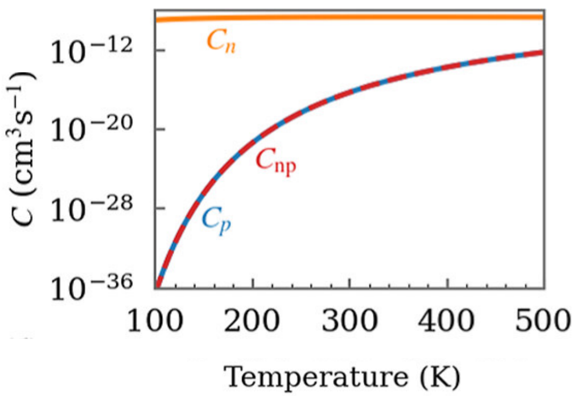
C determined by Fermi's golden rule

$$C = V\frac{2\pi}{\hbar}gW_{\mathrm{if}}^2\sum_m \Theta_m \sum_n |\langle \chi_{im}|\Delta Q|\chi_{fn}\rangle|^2 \times \delta(\Delta E + m\hbar\omega_{\mathrm{i}} - n\hbar\omega_{\mathrm{f}})$$

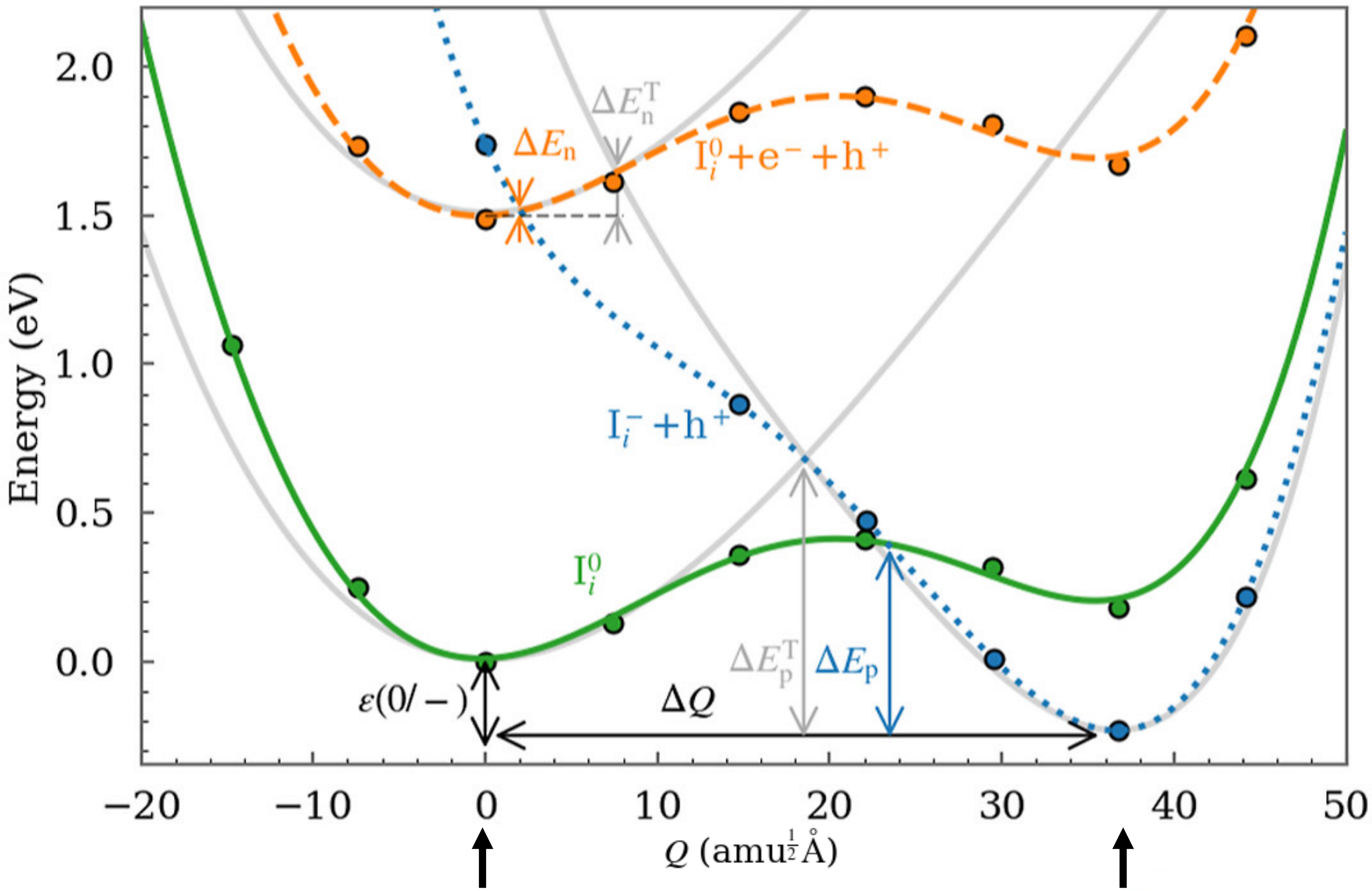
Large lattice relaxation leads to benign defects

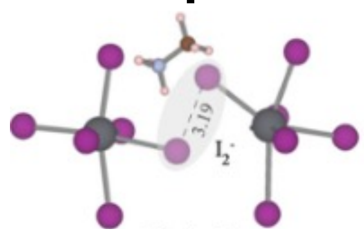
Whalley et al., *J. Am. Chem. Soc.* 2021, 143, 9123−9128

Cf. radiative coefficient 1x10^{-10} cm^{3}s^{-1} at 300K

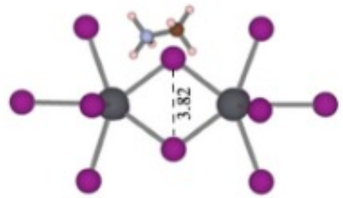


Iodine interstitial in $MAPbI_3$, DFT w/ HSE06 functional + SoC





Neutral interstitial

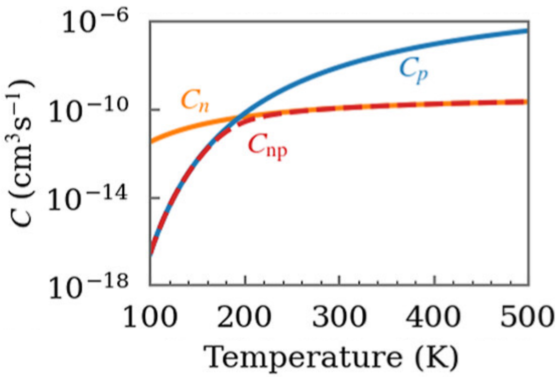


Negative interstitial

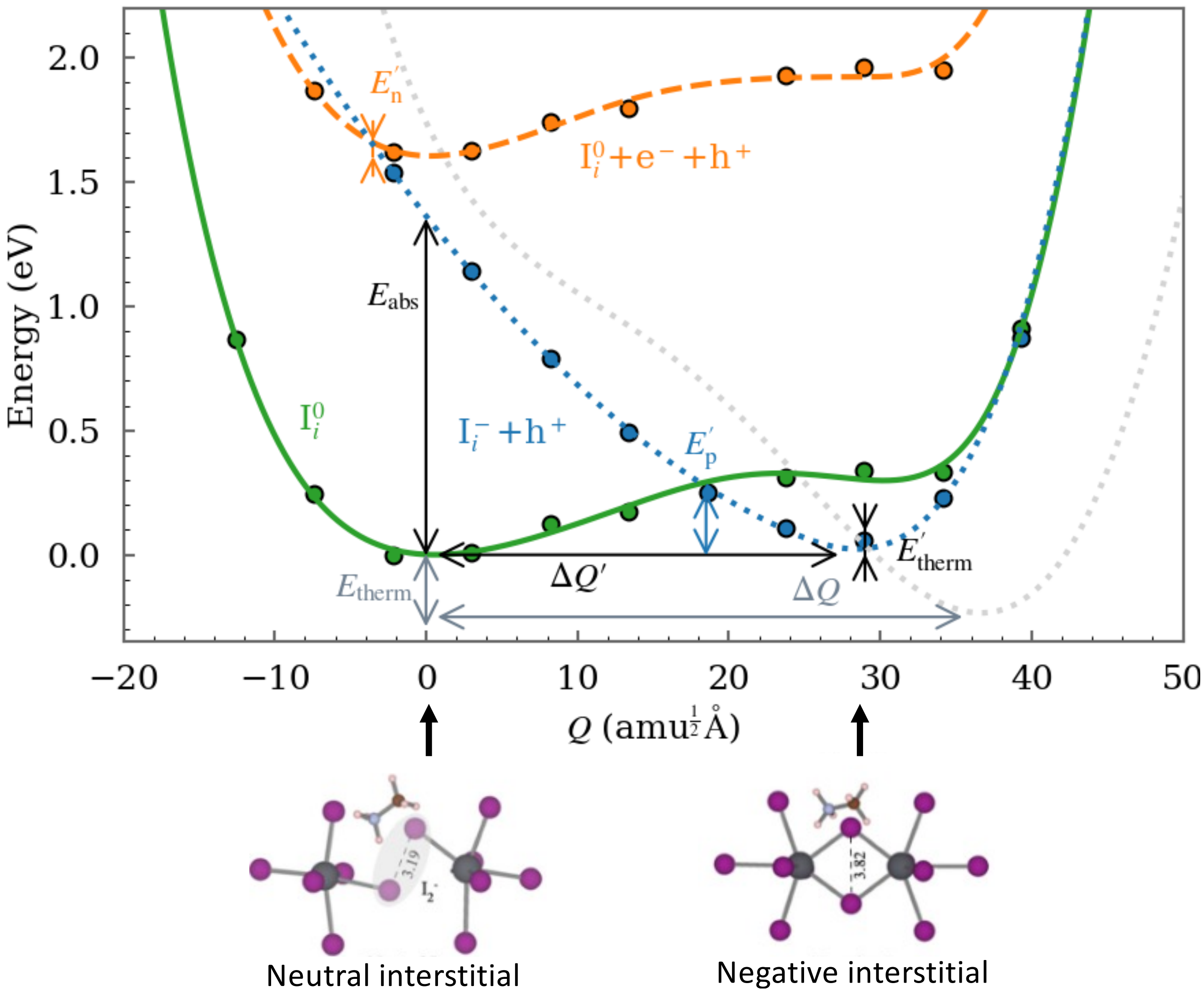
Cs incorporation suppresses lattice relaxation

Whalley, *J. Chem. Phys. C* 2023, 127 (32), 15738−15746

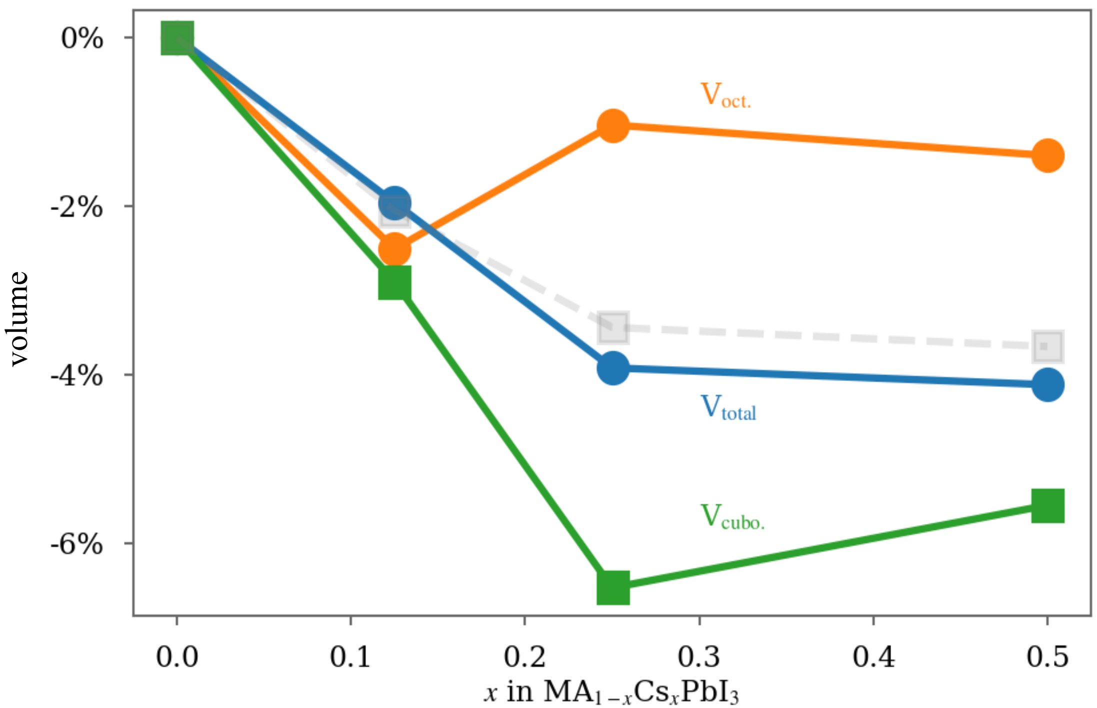
Cf. radiative coefficient 1x10^{-10} cm^{3}s^{-1} at 300K

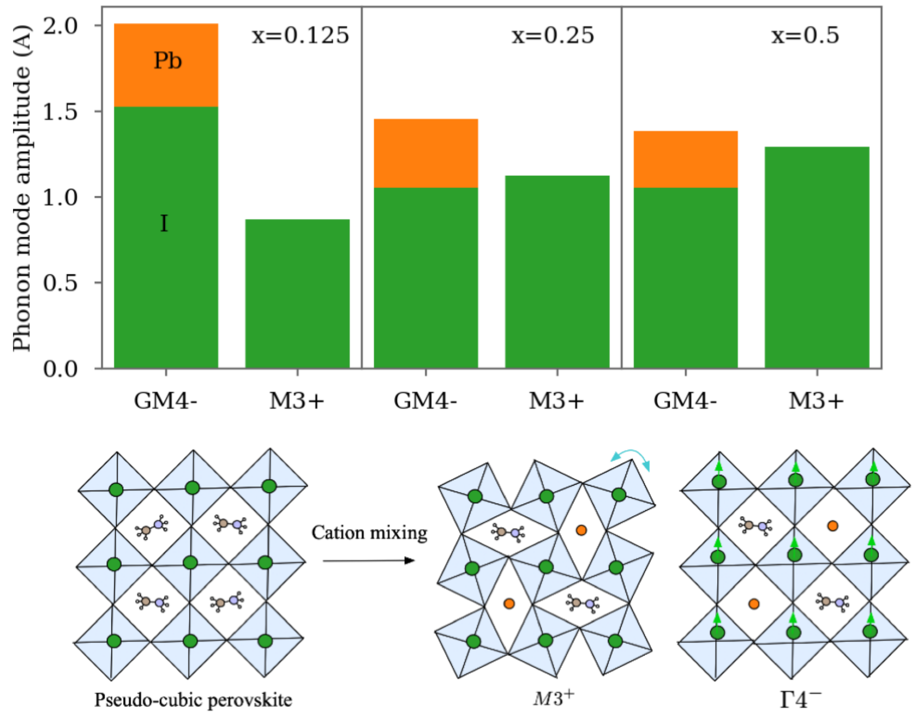


Iodine interstitial in $MA_{0.875}Cs_{0.125}PbI_3$, DFT w/ HSE06 functional + SoC



$MA_{1-x}Cs_xPbI$: Volume reduction through octahedral tilting



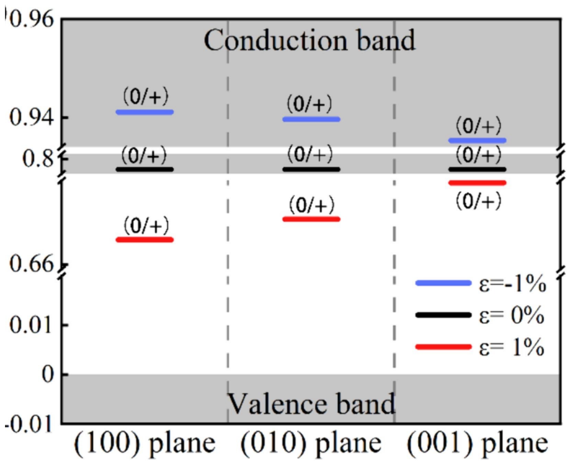


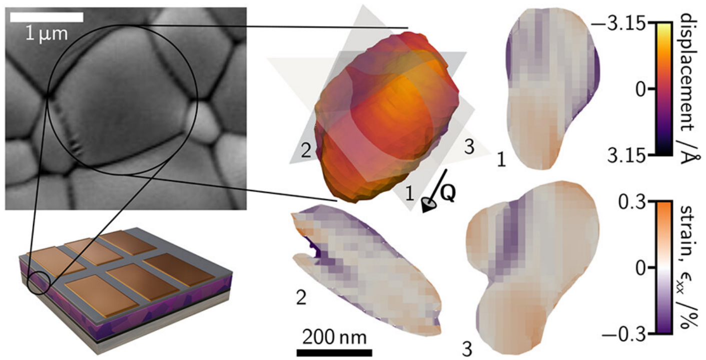
Whalley, *J. Chem. Phys. C* 2023, 127 (32), 15738−15746

The iodine interstitial can display a range of defect activity

Strain effects defect properties $CsPbI_3$

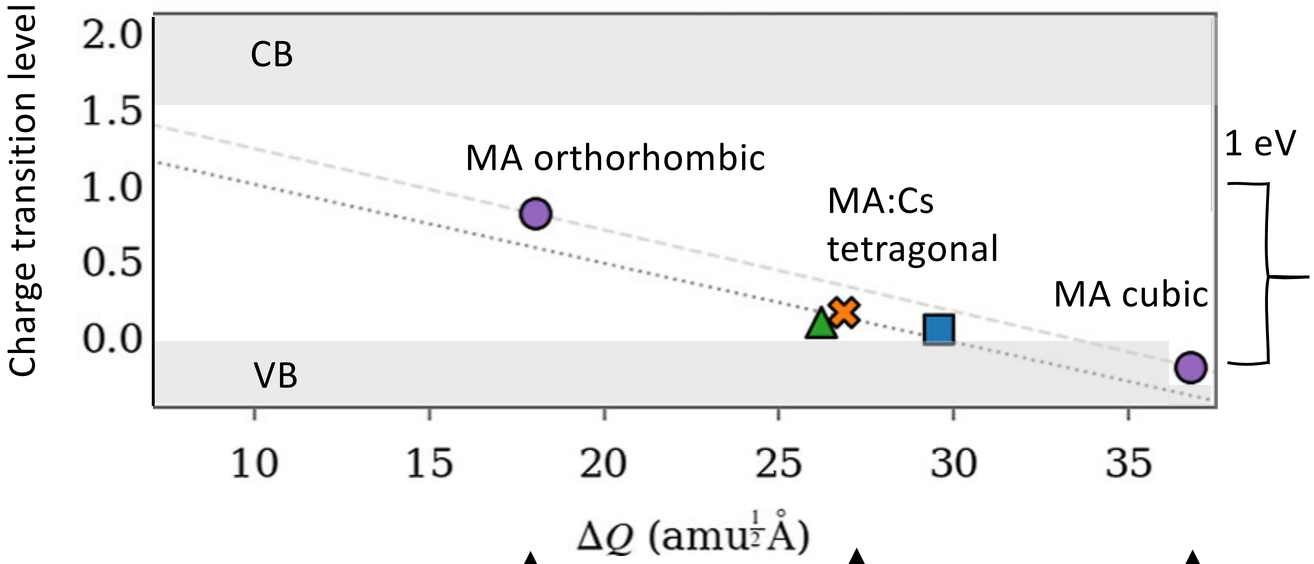
Applied Surface Science 2025, 679, 161235

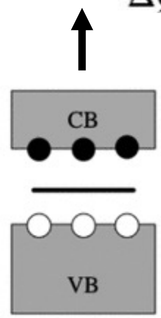




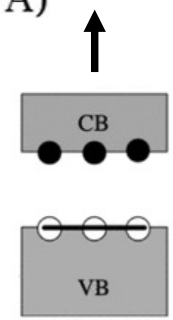
Strain heterogeneity in halide perovskite devices

ACS Energy Lett. 2024, 9, 6, 3001–3011

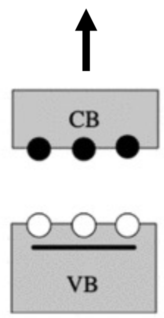




electron-hole recombination



fast hole trap and release



long lived electron trap

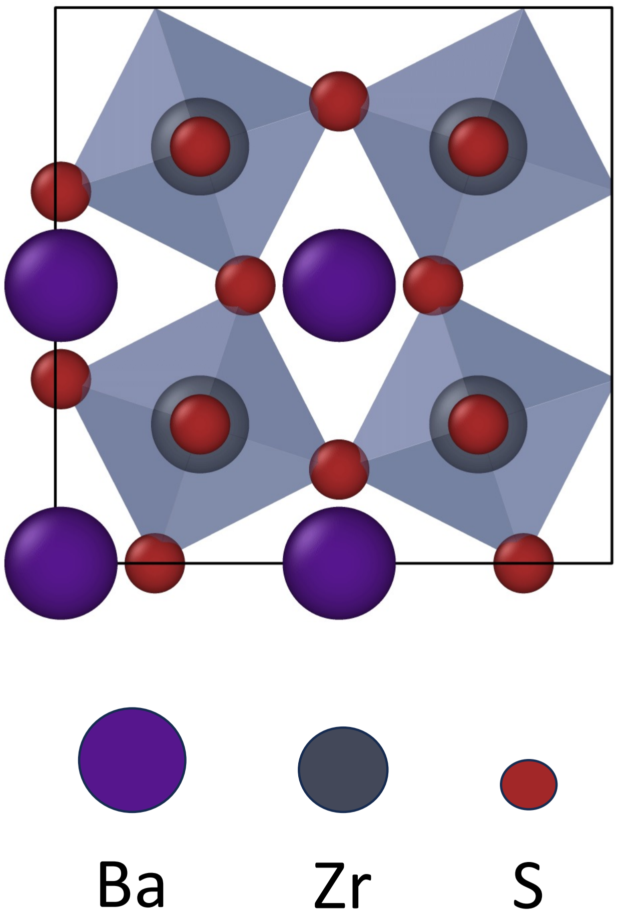
1. Halide perovskites

defects and dynamics → non-radiative processes

2. Chalcogenide perovskites

lattice and molecular dynamics → phase stability

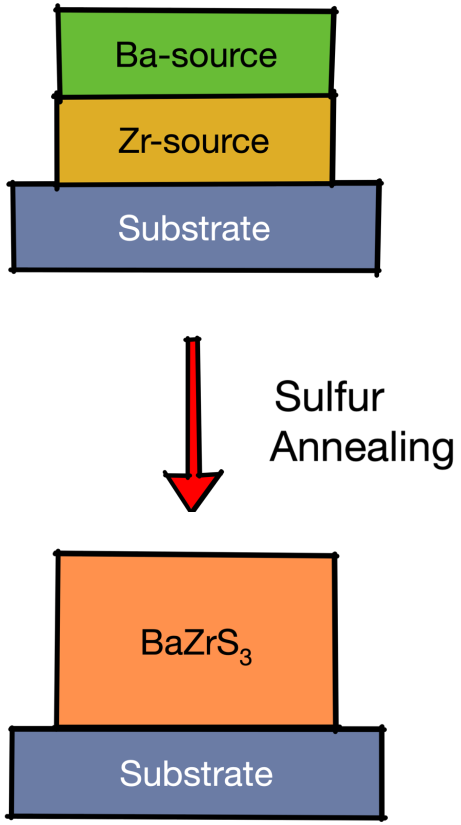
$BaZrS_3$ (BZS): a tantalizing material

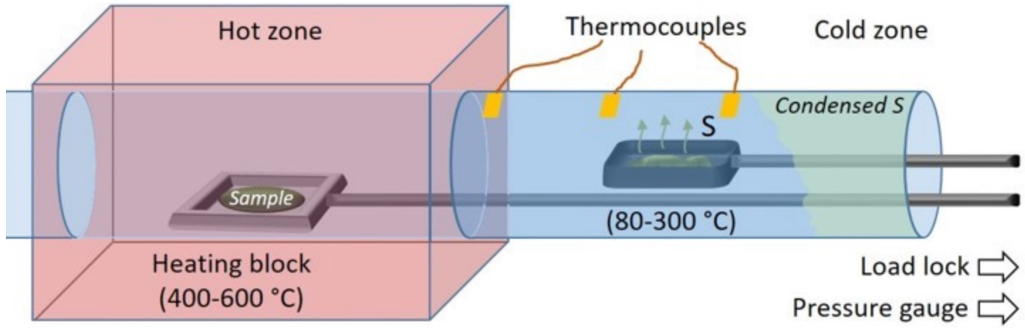


- Abundant and non-toxic
- Stable in air to 400°C
- Strong light absorption
- 1.8eV band gap → tandem PV
- Tunable E_g through S/Se or Zr/Hf mixing
- Low thermal conductivity

  (1.84 W/mK @ 300 K)

Challenge: moderate temperature synthesis

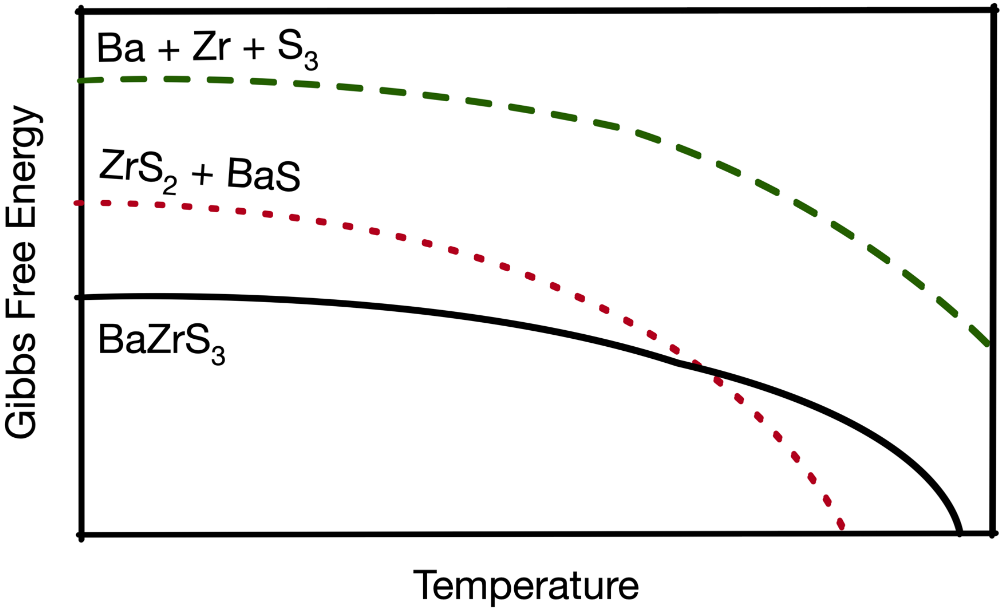




Schematic from Corrado Comparotto and Jonathan Scragg at Uppsala University

Free energy predictions

1. DFT + harmonic lattice dynamics



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

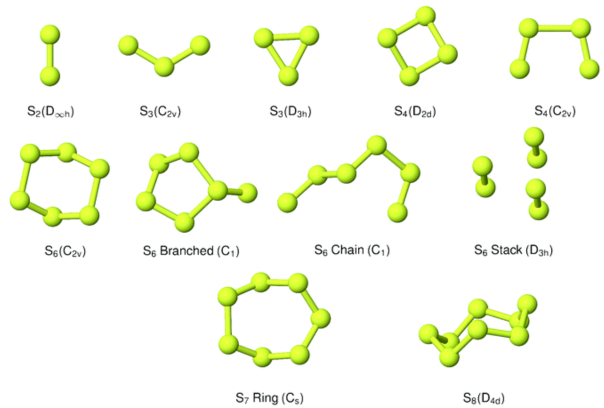
2. Comprehensive approach

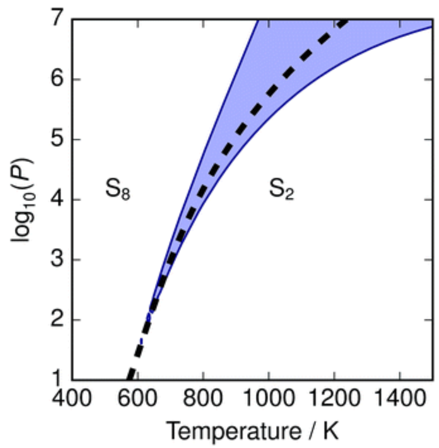
$$\mathrm{BaZrS_3} \rightarrow \mathrm{Ba} + \mathrm{Zr} + 3\mathrm{S(s)}$$

$$\mathrm{BaZrS_3} \rightarrow \mathrm{BaS} + \mathrm{ZrS_2}$$

$$3\mathrm{BaZrS_3} \rightarrow \mathrm{Ba_3Zr_2S_7} + \mathrm{ZrS_2}$$

3. Analytic chemical potential for S_x vapour



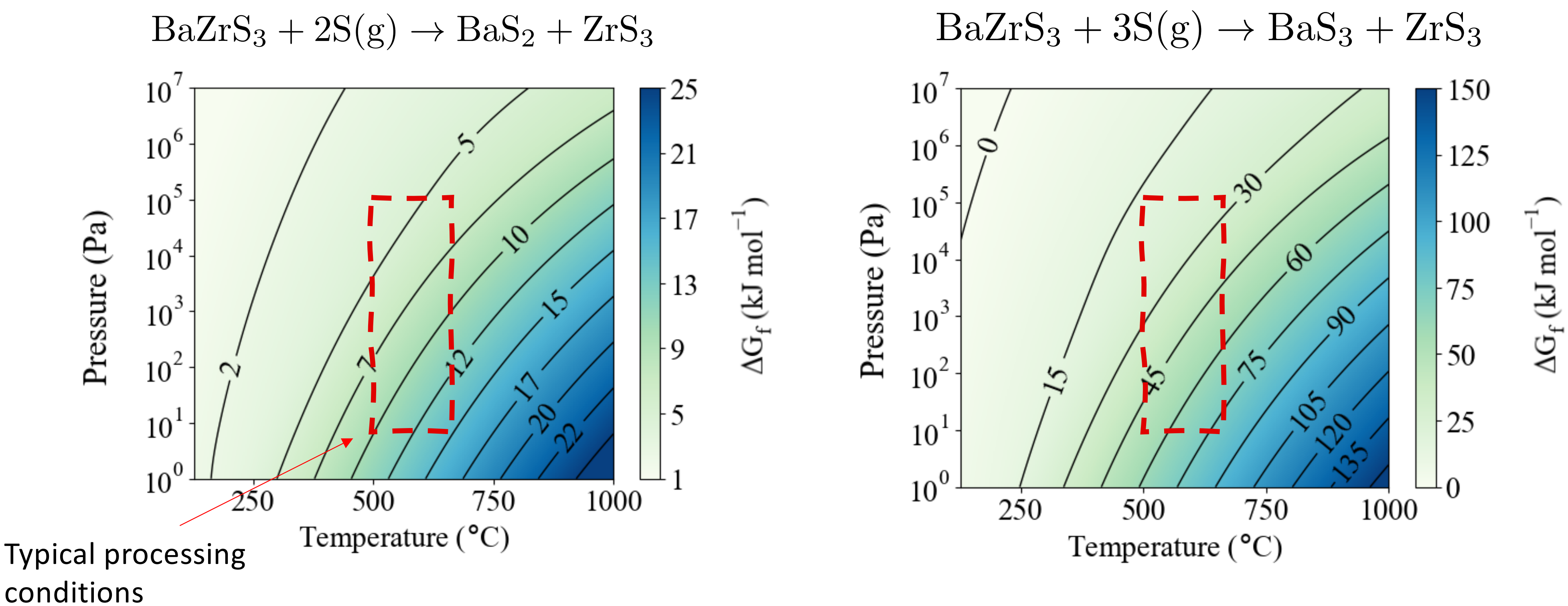


Jackson, Tiana and Walsh, *Chem. Sci.*, 2016,7, 1082-1092

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

$BaZrS_3$ formation from ZrS_3

Problem: If the partial pressure of sulfur is too high during annealing, ZrS_3 forms and limits perovskite formation.

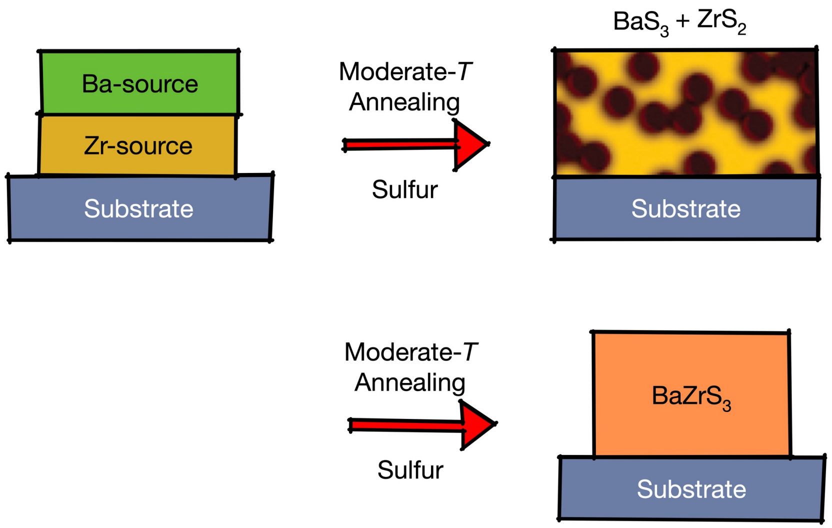


Conclusion: $BaZrS_3$ is stable relative to ZrS_3. Any limitations are kinetic.

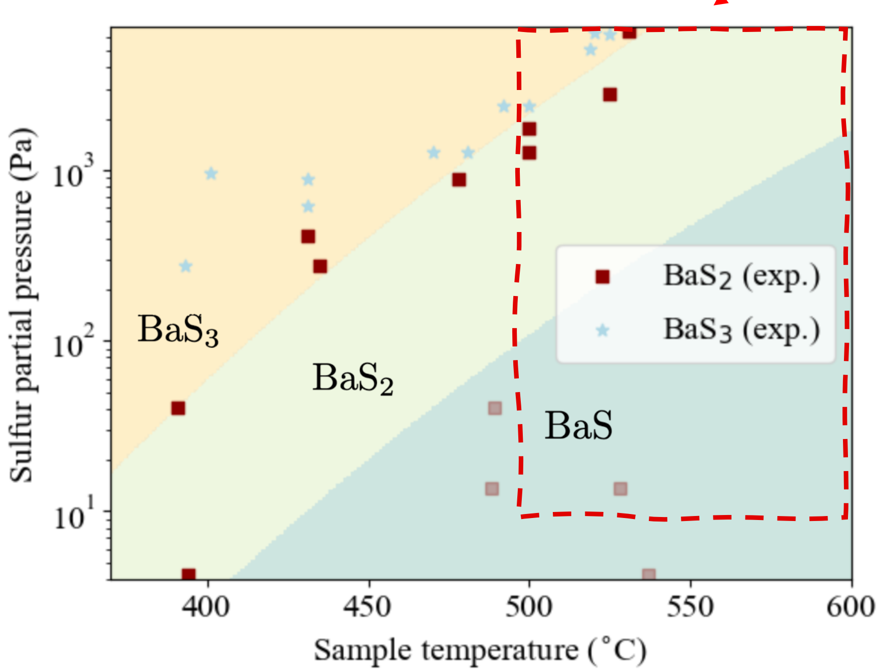
Paper in prep.

Phase diagram for Ba-S system

BaS_3 intermediate forms a liquid flux which overcomes kinetic barriers



Typical processing conditions

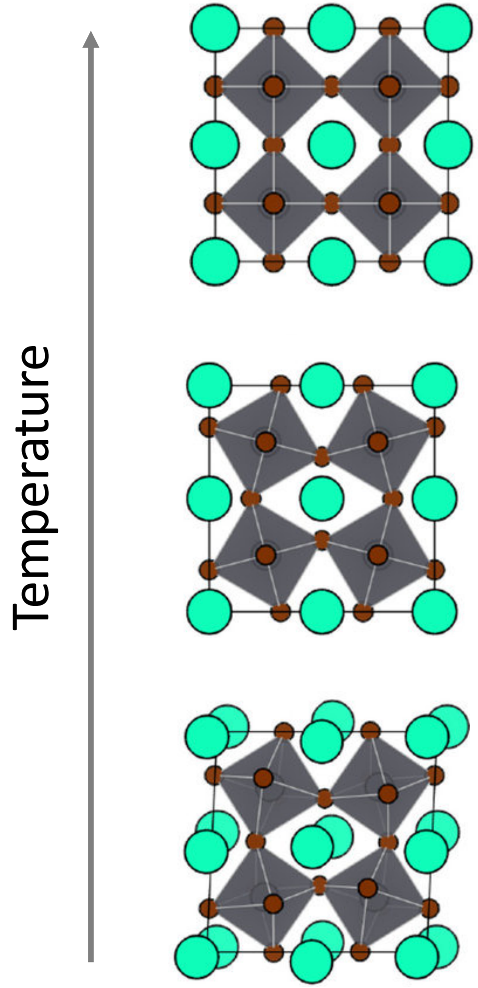


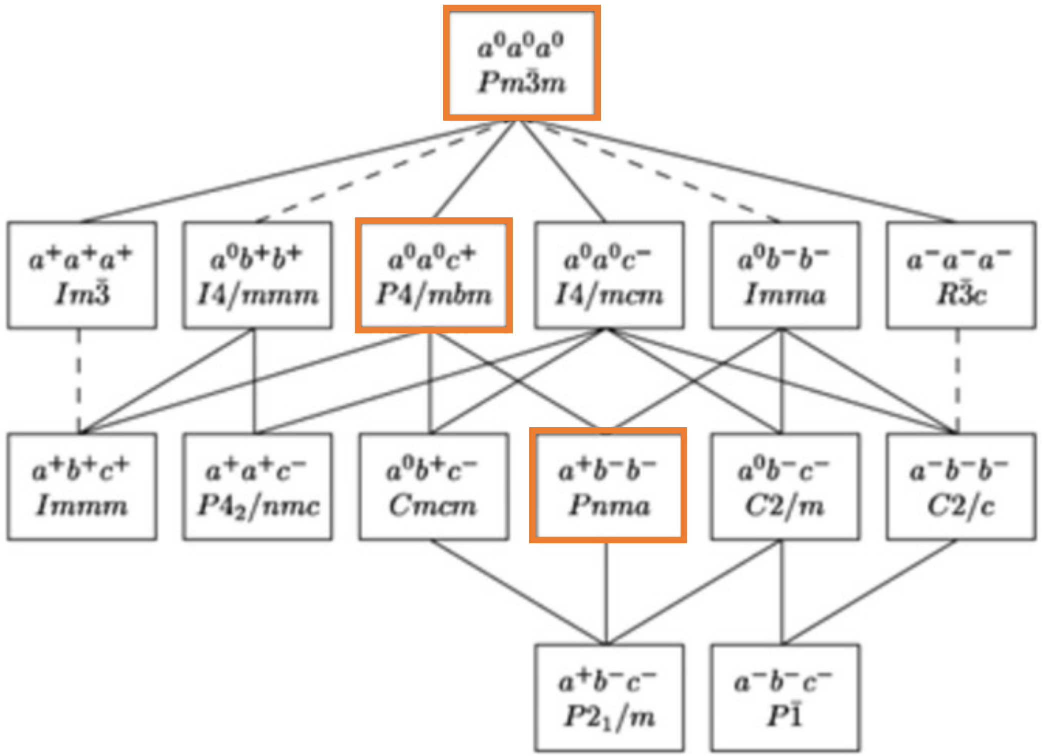
Experimental measurements from Scragg group at Uppsala.

Assumption: Sulfur reaches saturated vapour pressure.

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

Perovskite polymorphs

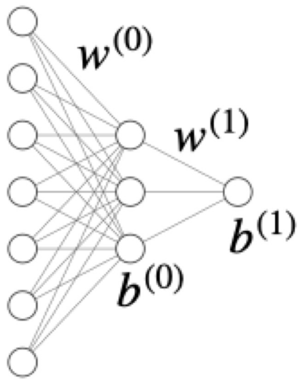




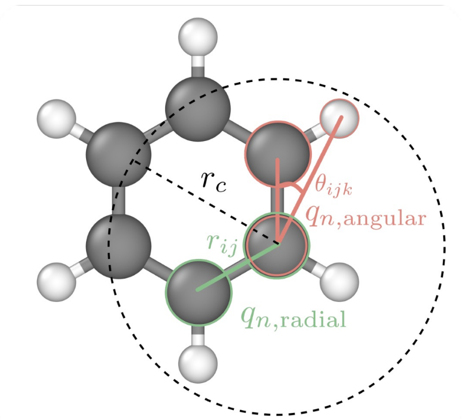
Group-Theoretical Analysis of Octahedral Tilting in Perovskites
C. J. Howard and H. T. Stokes

Neuroevolution Potential (NEP)

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



Input features



Output

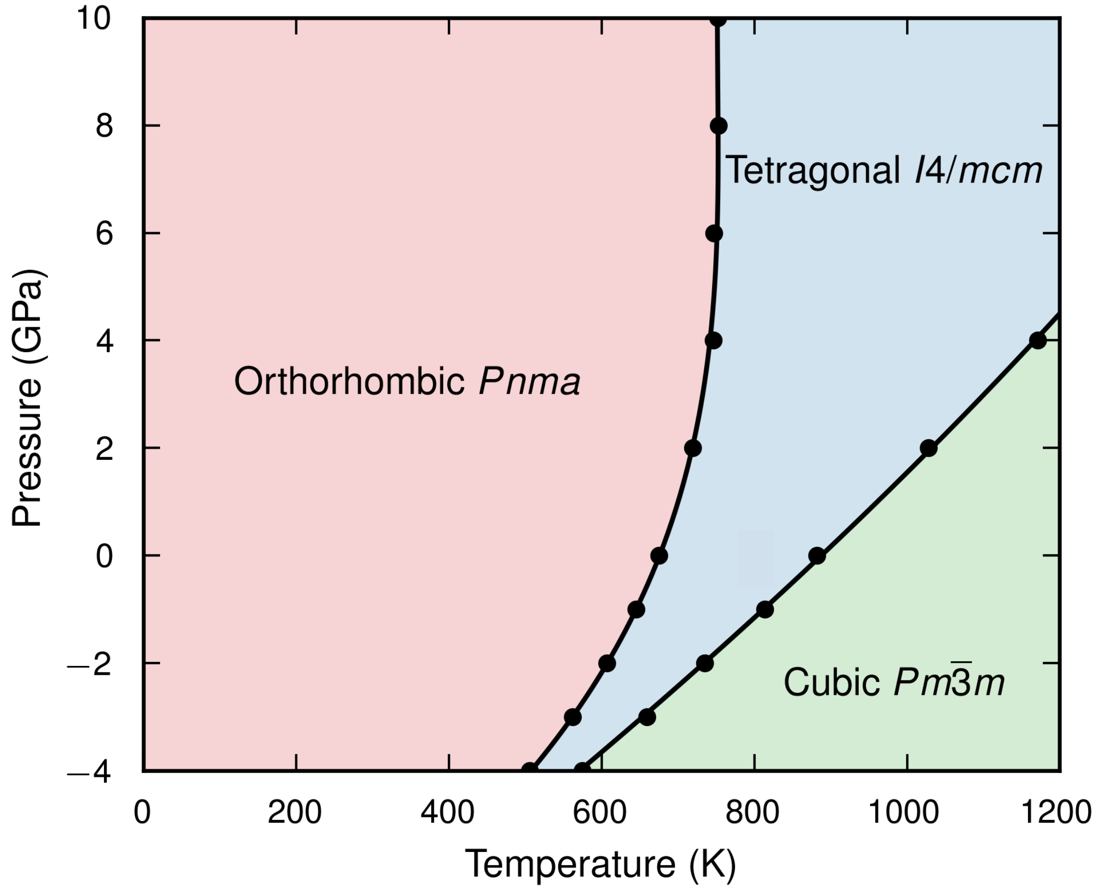
$$E_i = \sum_{\mu=1}^{N_{neu}} w_\mu^{(1)} \tanh\left(\sum_{\nu=1}^{N_{des}} w_{\mu\nu}^{(0)} q_\nu^i - b_\mu^{(0)} \right) - b^{(1)}$$

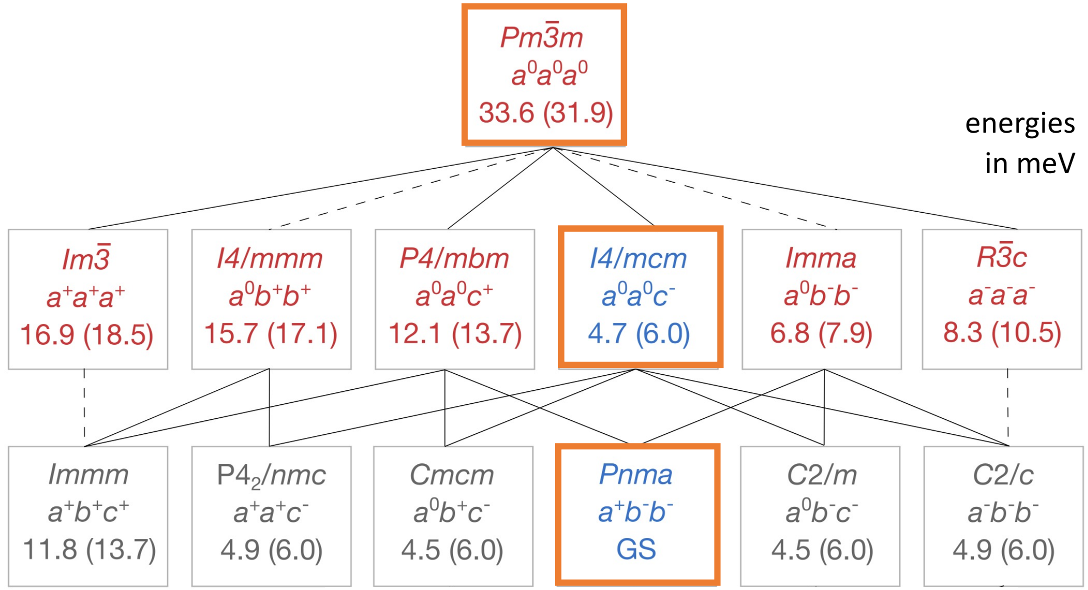
$$F_i = \sum_{i \neq j} \frac{\partial E_i}{\partial r_{ij}} - \frac{\partial E_j}{\partial r_{ji}} \qquad \mathbf{W}_i = \sum_{j \neq i} \mathbf{r}_{ij} \otimes \frac{\partial E_j}{\partial \mathbf{r}_{ji}}$$

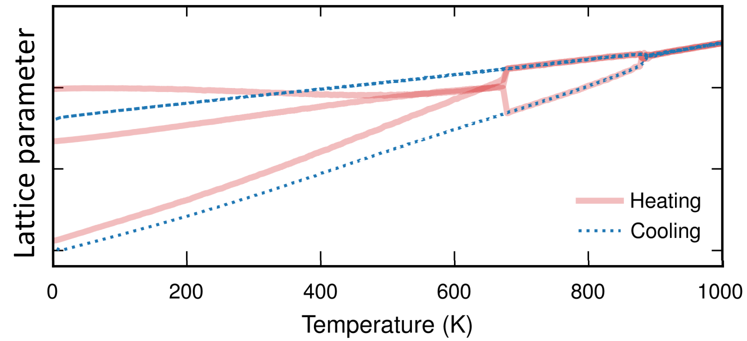
Paper in prep.

$BaZrS_3$ phase diagram

Calculated through NEP-MD and thermodynamic integration







Outstanding challenges for $BaZrS_3$ development

1) Formation of ZrO_x phases during synthesis
2) Ruddlesden Popper phase formation
3) Lack of PL: identifying recombination pathways
4) Impact of perovskite polymorphs on thermal transport
5) Characterization and control of sulfur vapour

Collaborators

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UPPSALA UNIVERSITET

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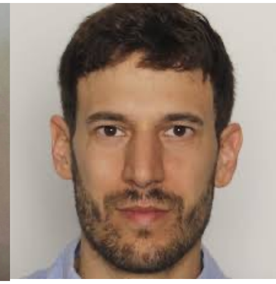
Paul Erhart

Erik Fransson

Jonathan Scragg



Corrado Comparotto

Kostya Sopiha

Giulia Longo

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

cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY