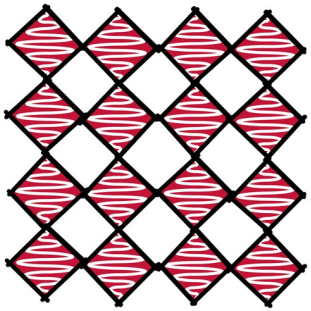
Northumbria University NEWCASTLE

Predicting $BaZrS_3$ phase stability: from harmonic lattice dynamics to the neuroevolution-potential framework

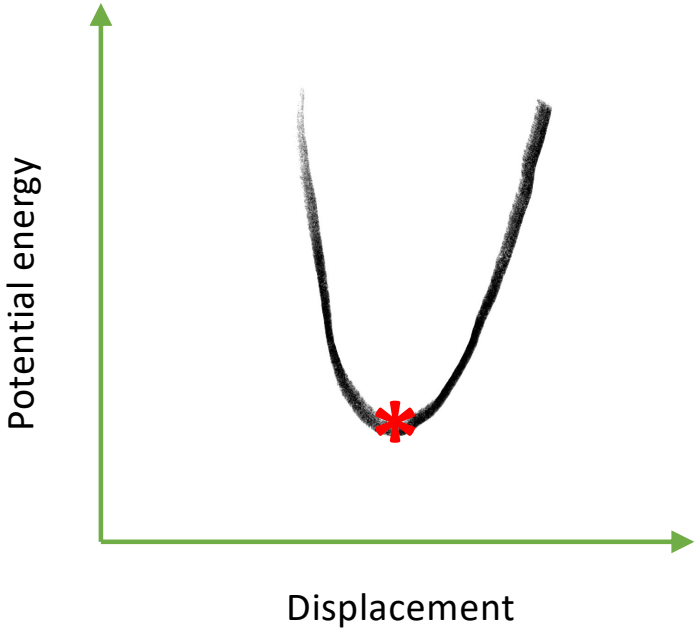


Dr Lucy Whalley
Assistant Professor in Physics
Northumbria University, United Kingdom

"A crystal is like a class of children arranged for drill, but standing at ease, so that while the class as a whole has regularity both in time and space, each individual child is a little fidgety!"

Dame Kathleen Lonsdale FRS

Small displacements from average position

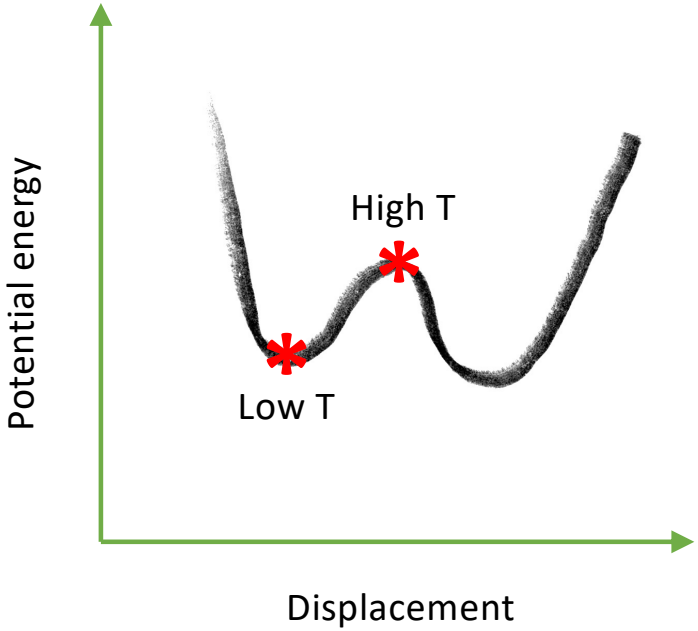


Well behaved children

Harmonic approximation

Larger displacements from average position

Naughty children



Anharmonicity

Taylor expanding the potential energy surface

Crystal Potential
Static model

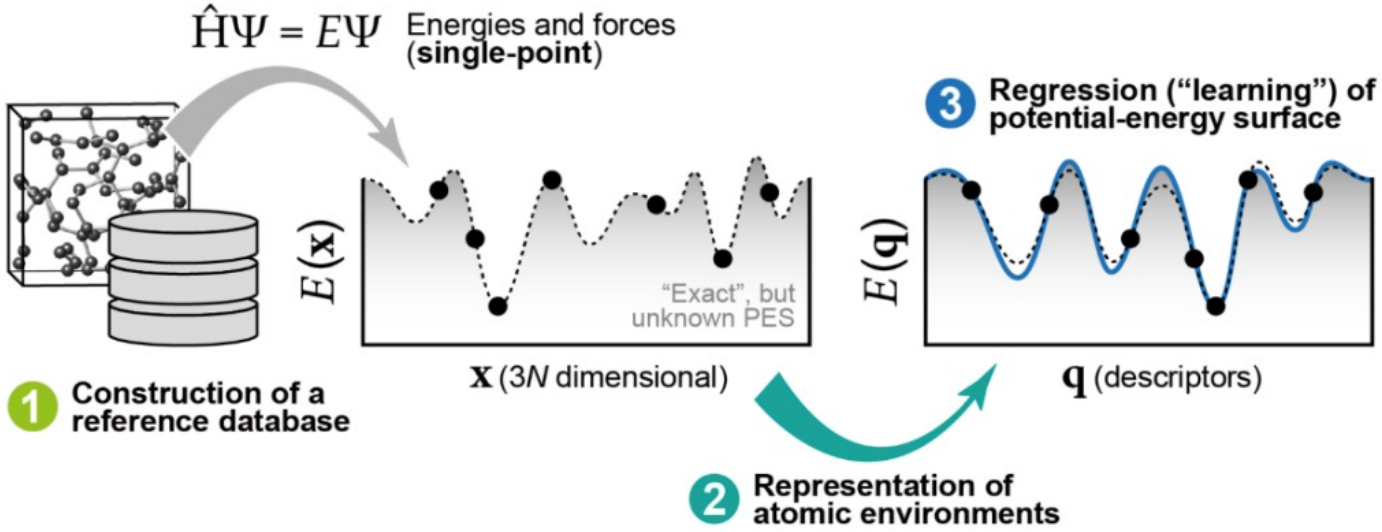
Harmonic Phonons
Non-interacting phonons
"Infinite lifetimes"

$$H = H_0 + \Phi_i^{\alpha} u_i^{\alpha} + \frac{1}{2}\Phi_{ij}^{\alpha\beta} u_i^{\alpha} u_j^{\beta} + \frac{1}{6}\Phi_{ijk}^{\alpha\beta\gamma} u_i^{\alpha} u_j^{\beta} u_k^{\gamma} + \dots$$

Ionic Forces
= 0 at equilibrium

Anharmonicity
Phonon scattering
Required for e.g. thermal conductivity

Machine-learning the potential energy surface



Machine Learning Interatomic Potentials as Emerging Tools for Materials Science
Volker L. Deringer, Miguel A. Caro, Gábor Csányi
Adv. Mater. 2019, 31, 1902765

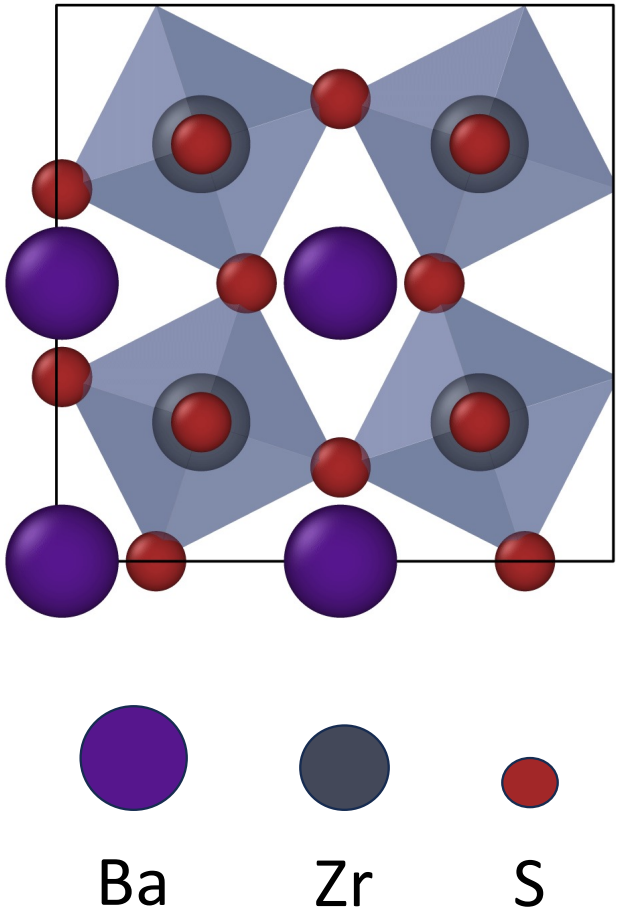
Outline

1. BaZrS3 motivation

2. Harmonic approximation
   - Lattice dynamics
   - Degradation to multiple phases

3. Anharmonicity
   - Molecular dynamics
   - Phase transitions between perovskite polymorphs

$BaZrS_3$ (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)

$BaZrS_3$ (BZS): an early stage material

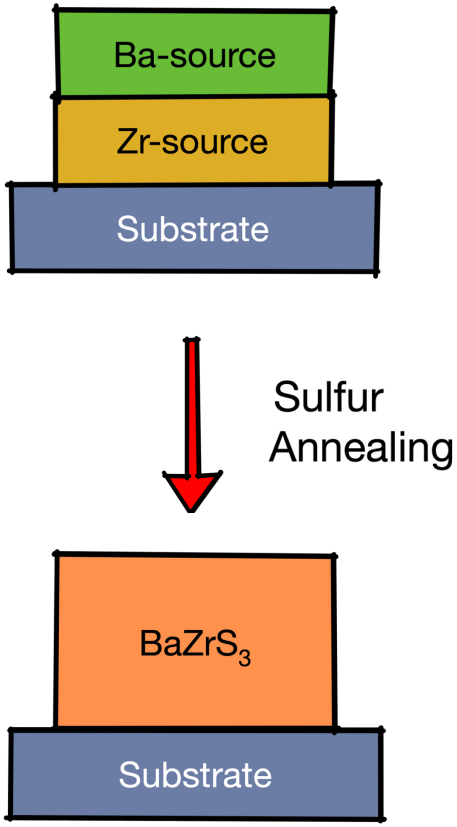
Volume 39, June 2024, 108608

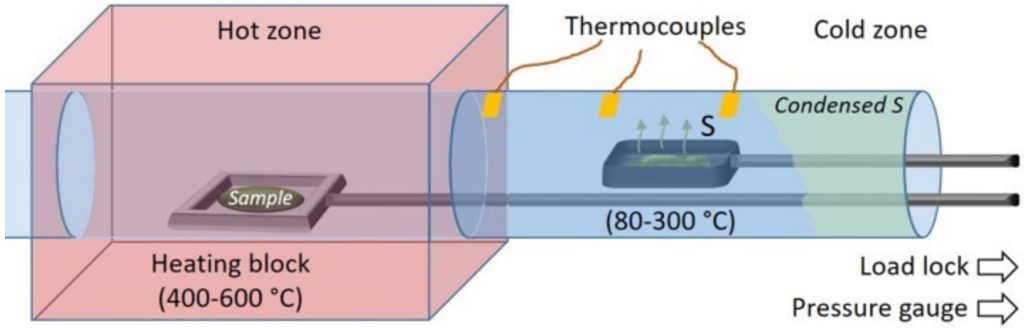
Exploring the potential of powder-to-film processing for proof-of-concept $BaZrS_3$ perovskite solar cells

P. Dallas [a], K. Gkini [a], A. Kaltzoglou [c], L. Givalou [a], M. Konstantakou [a], S. Orfanoudakis [a d], N. Boukos [a], E. Sakellis [a], P. Tsipas [a], A. Kalafatis [a], A.G. Karydas [b], A. Lagogiannis [b], P. Falaras [a], V. Psycharis [a], T. Stergiopoulos [a]

PCE: 0.11%

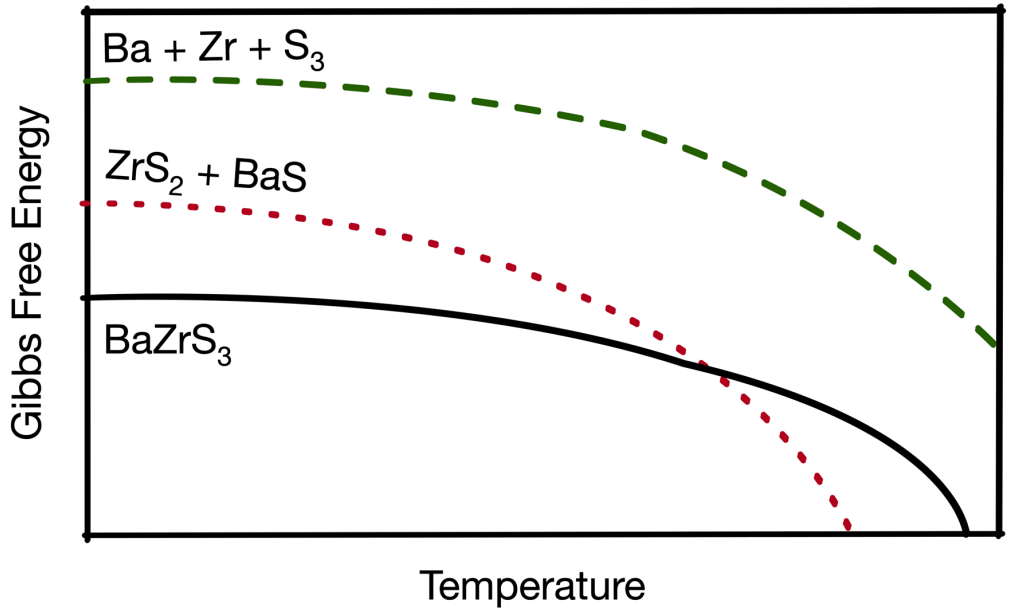
Challenge: moderate temperature synthesis





Schematic of custom furnace. From Corrado Comparotto and Jonathan Scragg at Uppsala.

Free energy predictions: DFT + harmonic lattice dynamics



e.g.

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

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

DFT

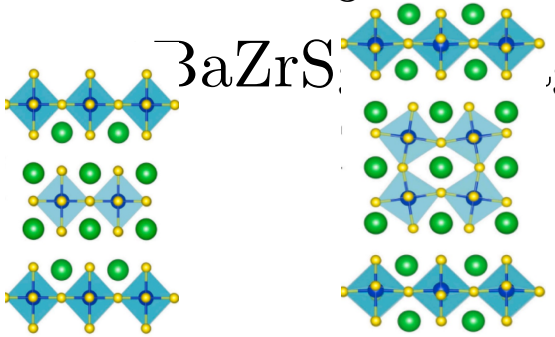
Harmonic lattice dynamics

Free energy predictions: DFT + harmonic lattice dynamics

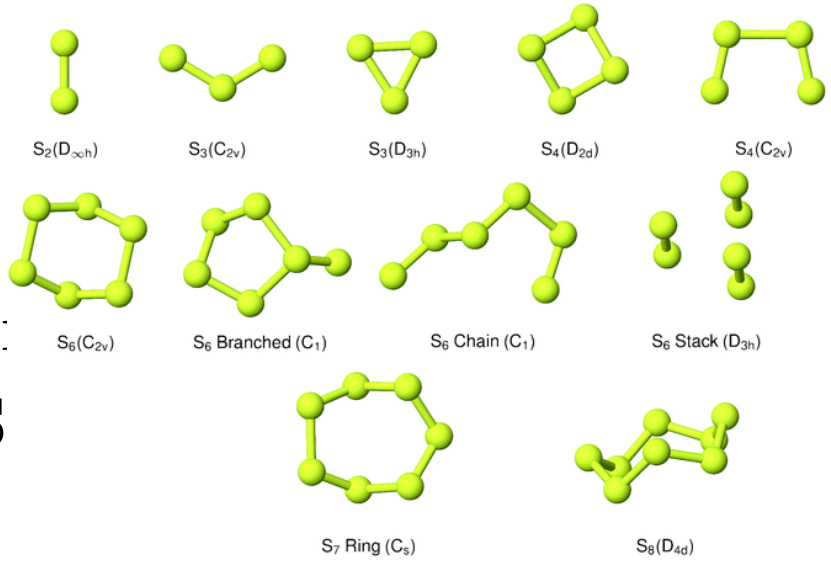
$$BaZrS_3 \rightarrow Ba + Zr$$

$$BaZrS_3 \rightarrow BaS + Z$$

$$BaZrS_3 \rightarrow {}_3Zr_2S$$



$Ba_{n+1}Zr_nS_{3n+1}$

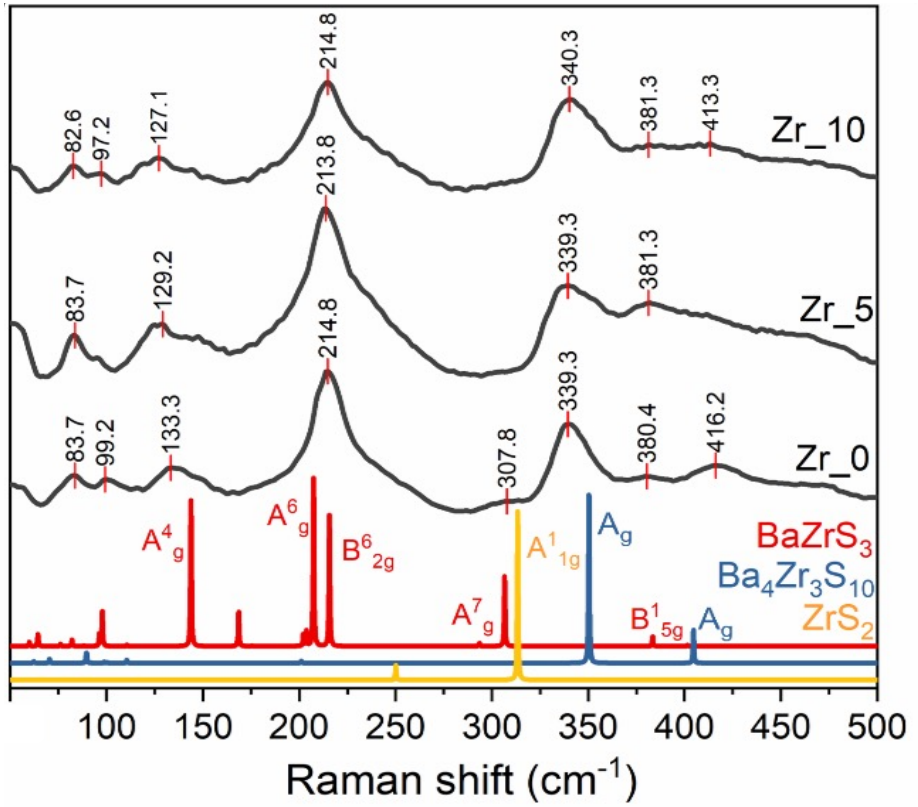


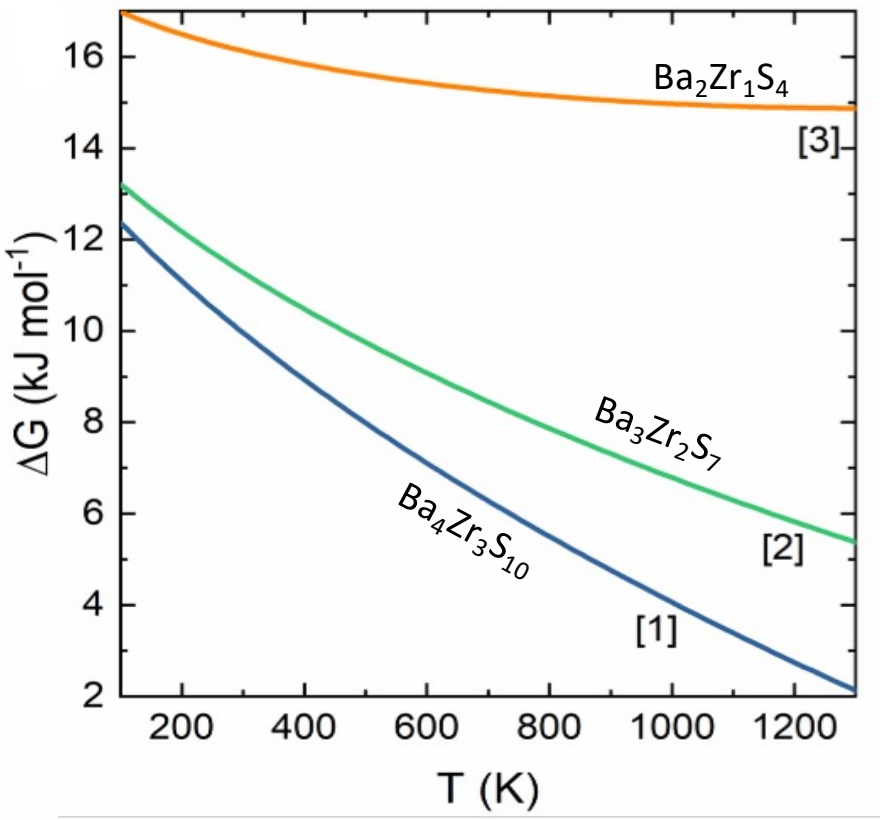
Jackson, Tiana and Walsh
Chem. Sci., 2016,7, 1082-1092

We need to be comprehensive in our approach: consider all Ba-Zr-S competing phases

Formation of Ruddlesden Popper phases

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





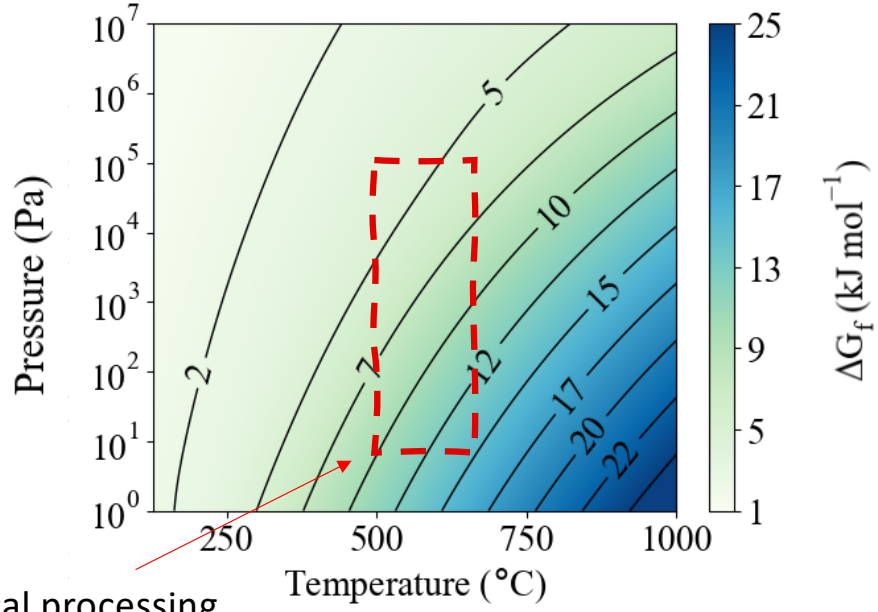
Ruddlesden Popper phases form during high-temperature synthesis

$BaZrS_3$ formation from ZrS_3

Is ZrS_3 kinetically or thermodynamically limiting?

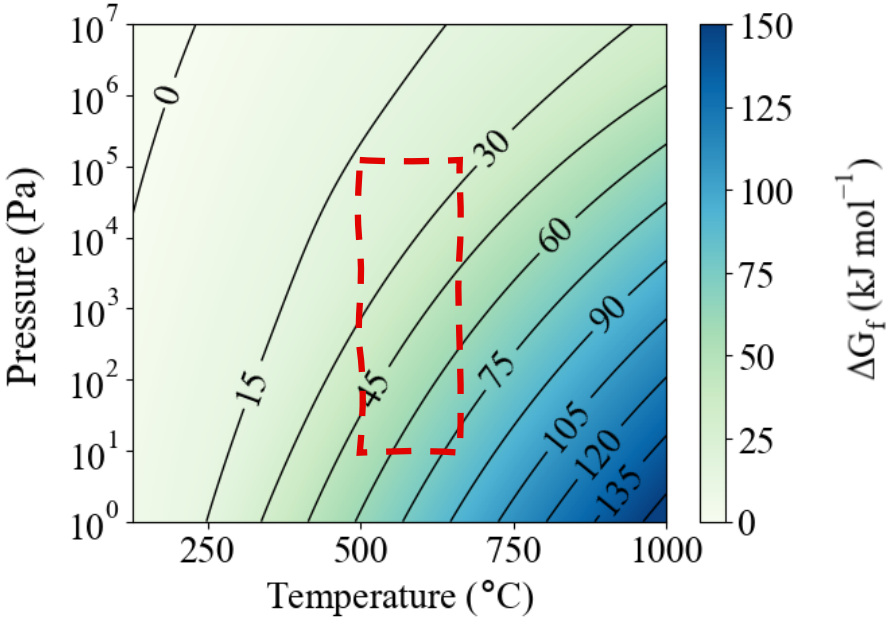
P. Kayastha, G. Longo, L. Whalley
ACS Applied Energy Materials, **2024**
10.1021/acsaem.3c03208

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



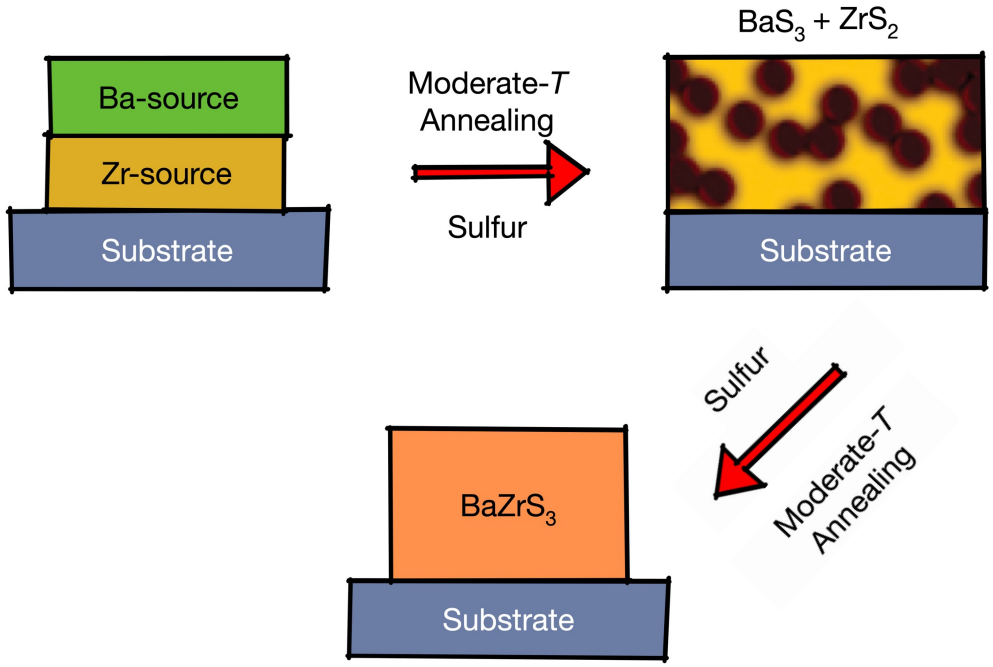
Typical processing conditions

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



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

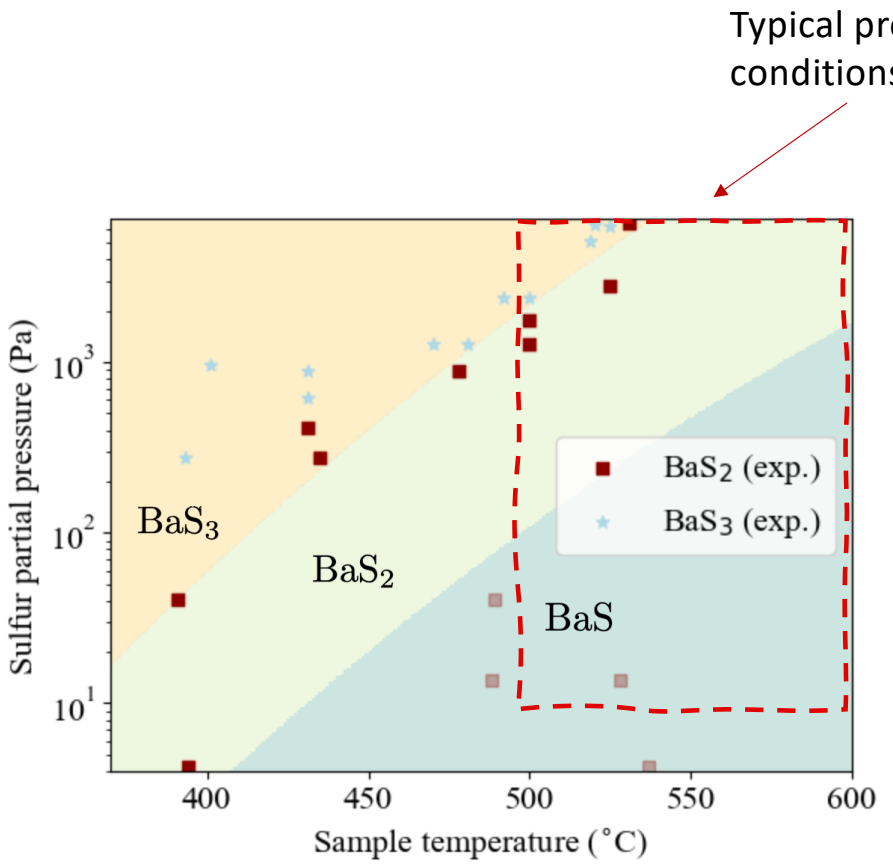
Phase diagram for Ba-S system



BaS_3 intermediate forms a liquid flux which overcomes kinetic barriers

Phase diagram for Ba-S system

C. Comparotto, L. Whalley, J. Scragg *et al*
Paper in prep.



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

Outline

1. BaZrS3 motivation

2. Harmonic approximation
   - Lattice dynamics
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3. Anharmonicity
   - Molecular dynamics
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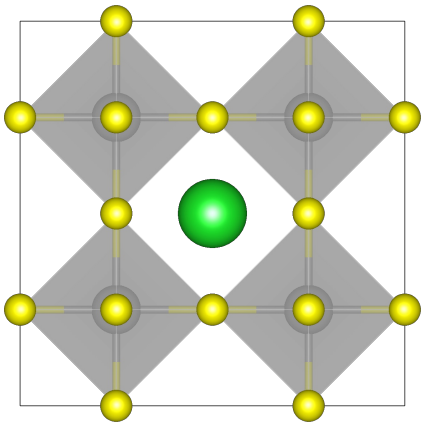
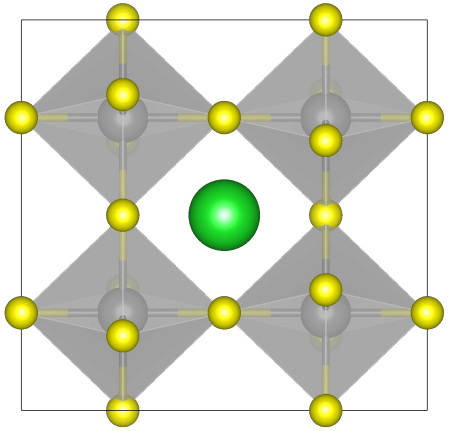
Polymorphic phase transitions in perovskites

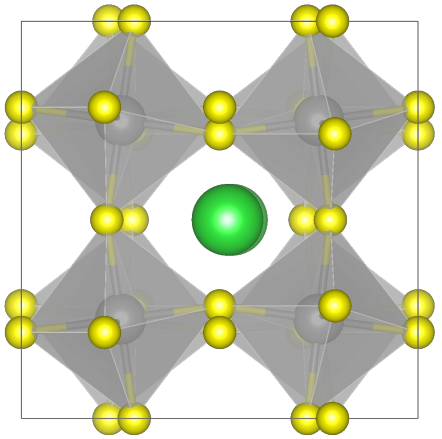
Cubic



Tetragonal



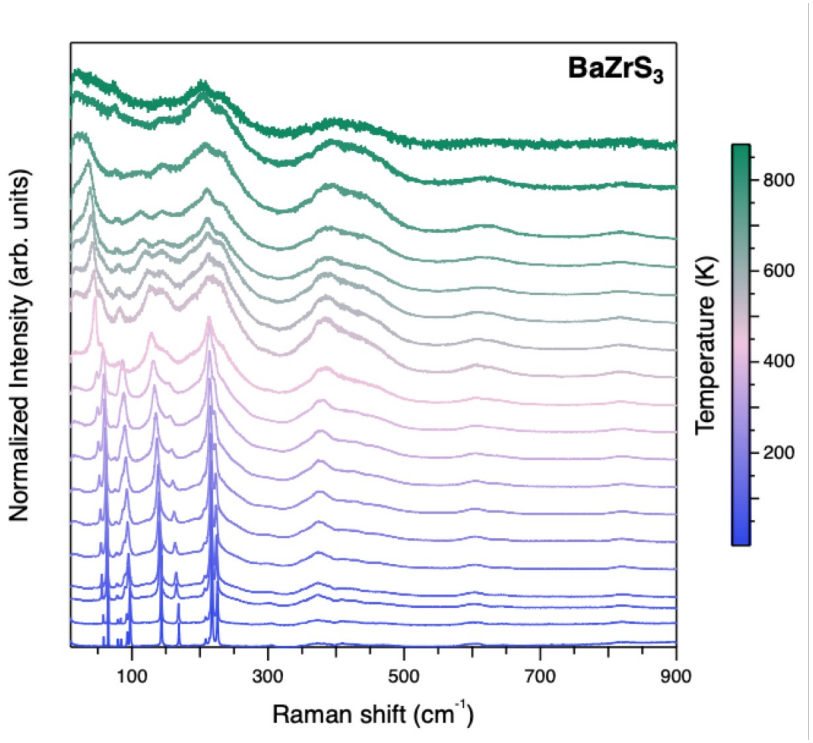
Orthorhombic



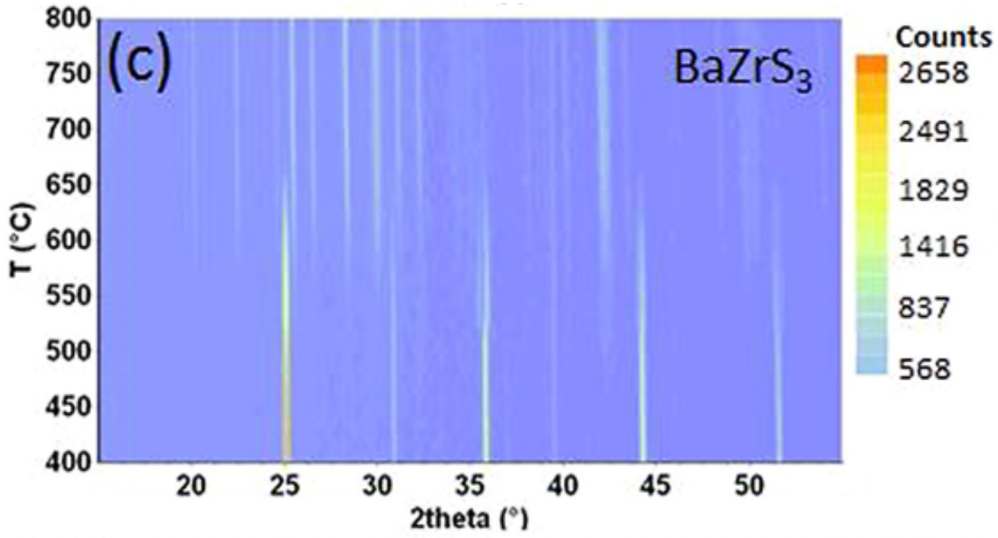
Decreasing temperature
Decreasing symmetry

Polymorphic phase transitions in $BaZrS_3$

Uncertainty in the experimental literature

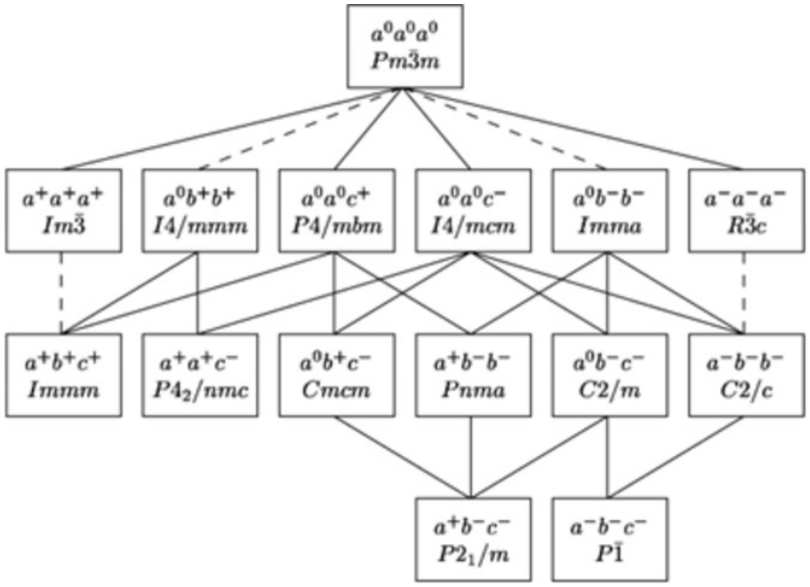


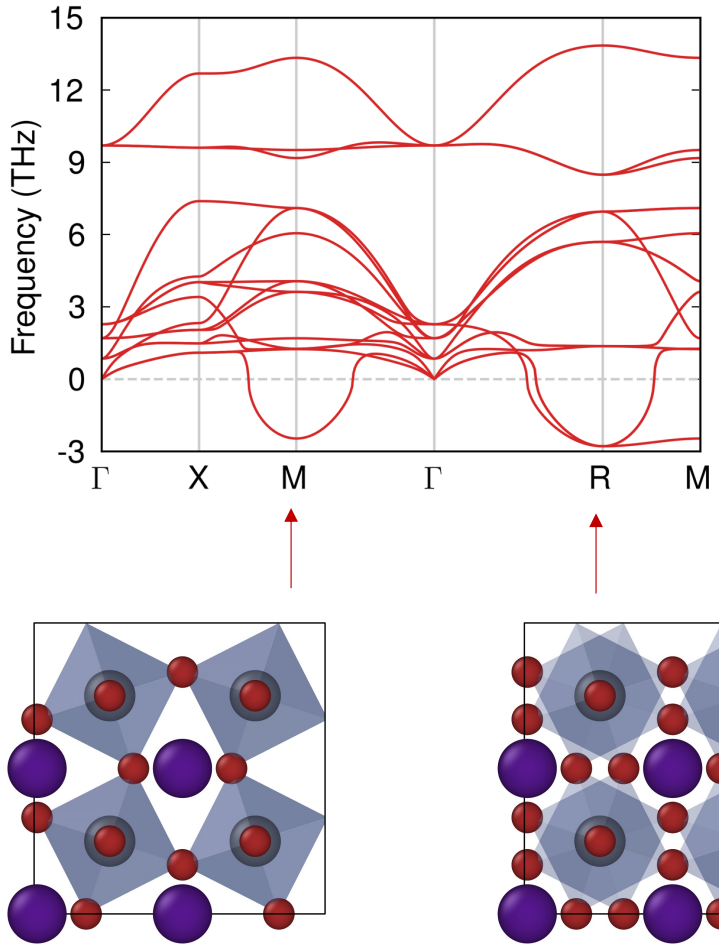
Ye et al, Phys. Rev. Materials (2024) **8**, 085402



Bystricky et al, Inorg. Chem. (2024) **63** 12826

Polymorphic phase transitions in perovskites

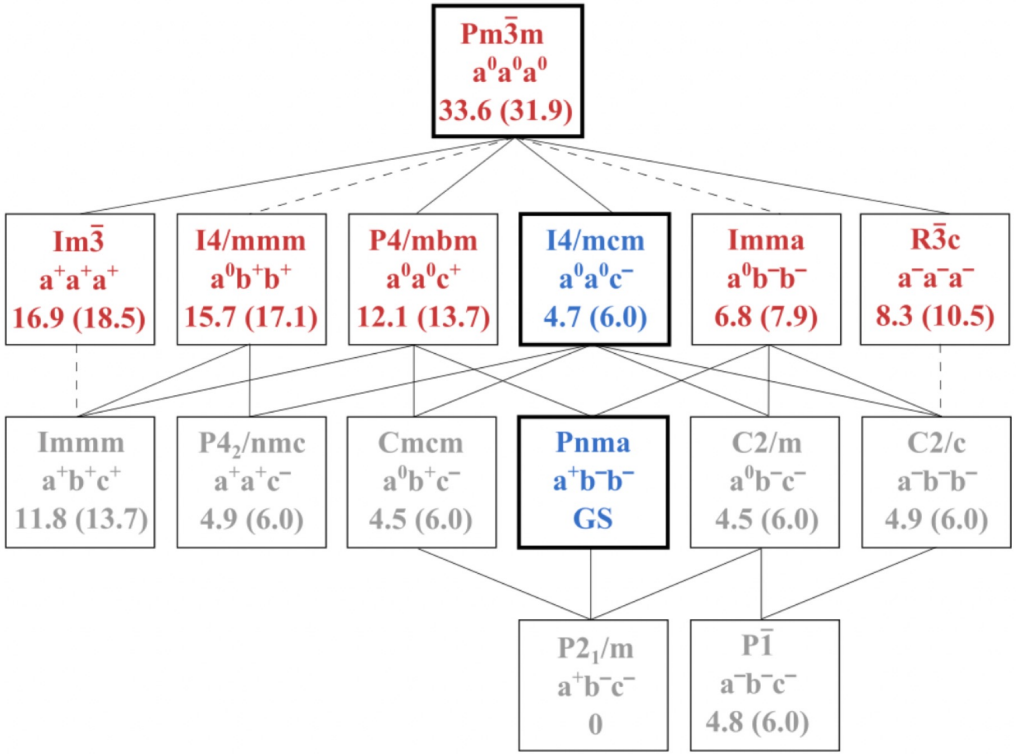


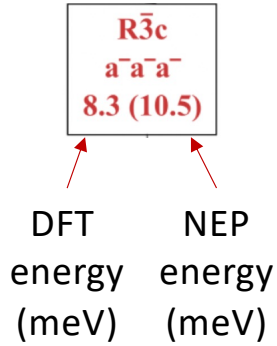


Group-Theoretical Analysis of Octahedral Tilting in Perovskites
C. J. Howard and H. T. Stokes

DFT total energies of $BaZrS_3$ polymorphs

P. Kayastha, E. Fransson, P. Erhart, L. Whalley
ArXiv pre-print, **2024**
10.48550/arXiv.2411.14289





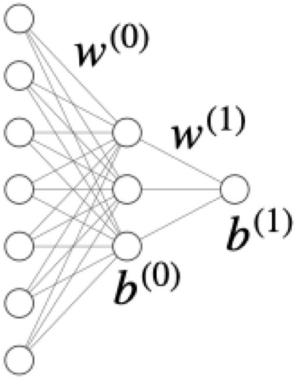
Dynamically unstable @ 0K

Dynamically stable @0K

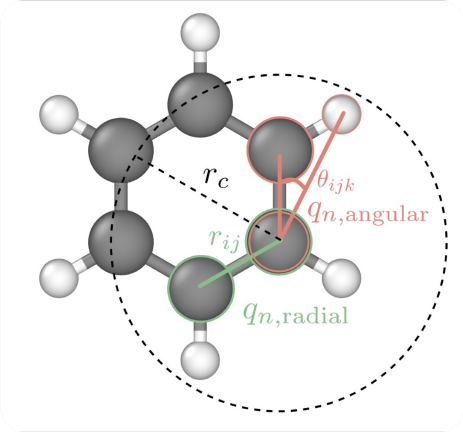
Higher symmetry structure preferred

Neuroevolution Potential (NEP)

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



Input features



Output

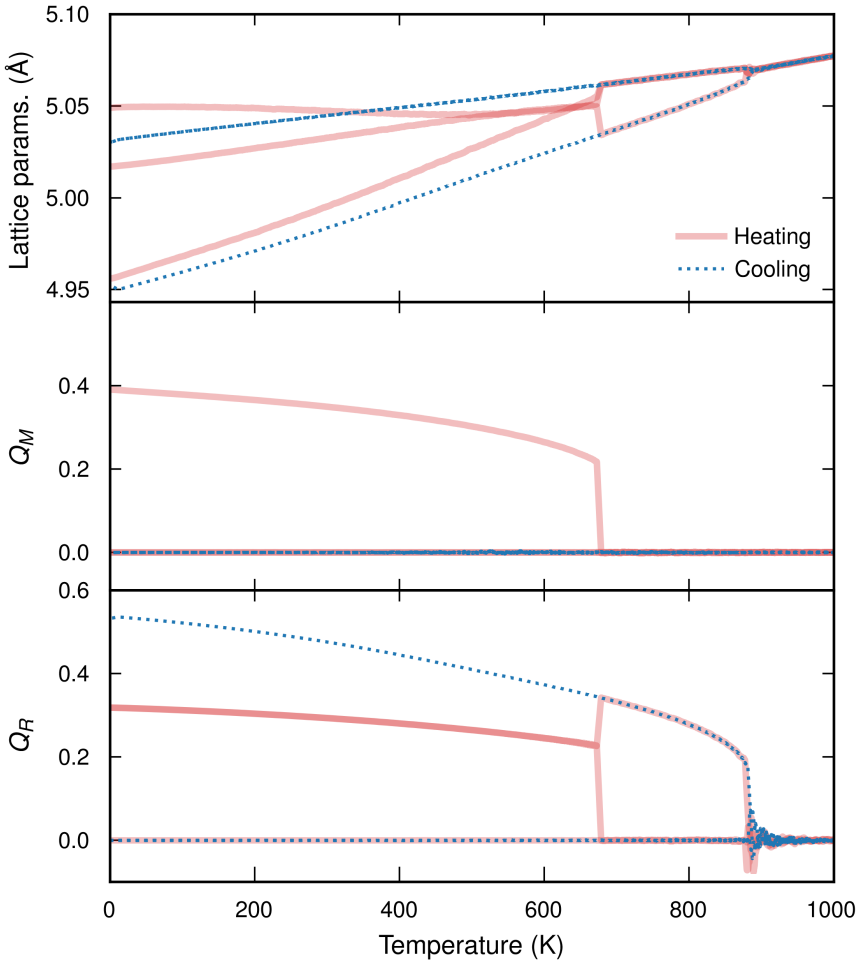
$$E_i = \sum_{\mu=1}^{N_{neu}} w_\mu^{(1)} \tanh\left(\sum_{\nu=1}^{N_{des}} w_{\mu\nu}^{(0)} q_\nu^i - b_\mu^{(0)}\right) - b^{(1)}$$

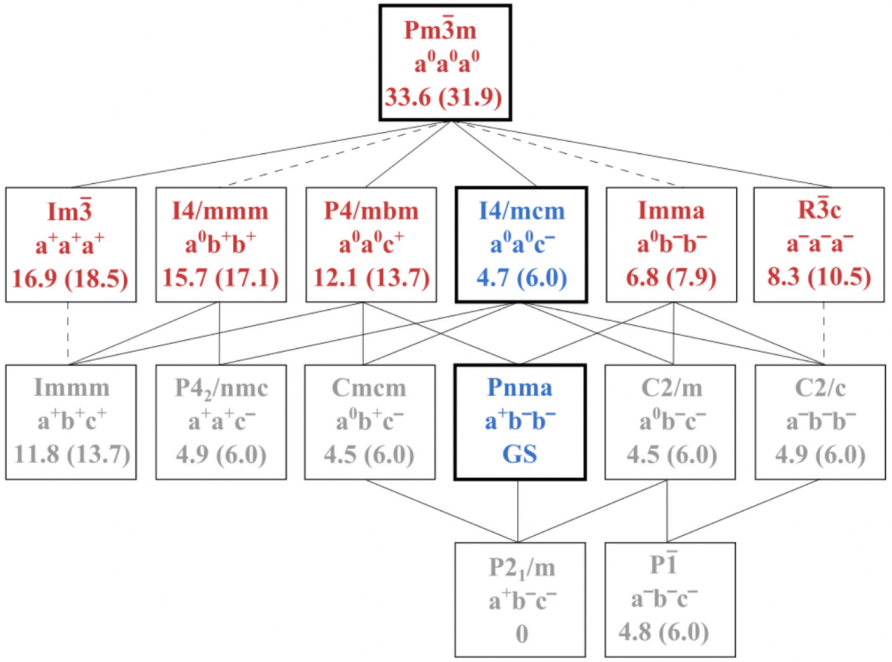
$$F_i = \sum_{i \neq j} \frac{\partial E_i}{\partial r_{ij}} - \frac{\partial E_j}{\partial r_{ji}} \qquad \mathbf{W}_i = \sum_{j \neq i} \mathbf{r}_{ij} \otimes \frac{\partial E_j}{\partial \mathbf{r}_{ji}}$$

$BaZrS_3$ phase transitions

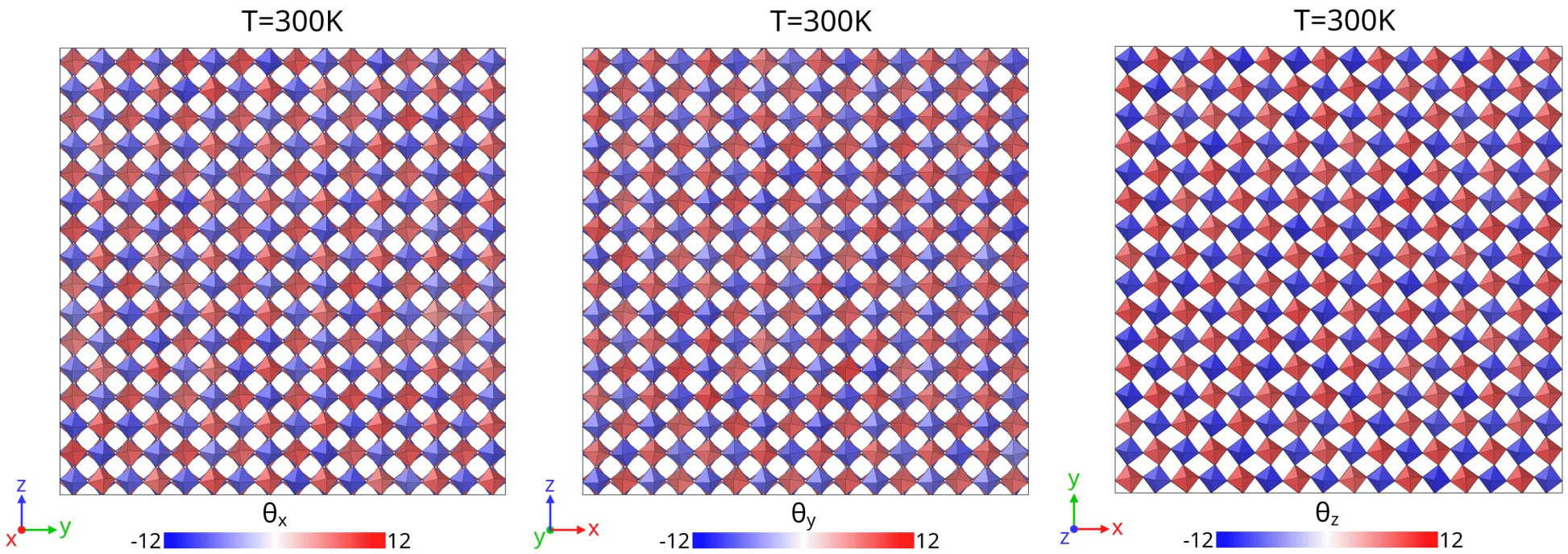
Calculated through NEP-MD

P. Kayastha, E. Fransson, P. Erhart, L. Whalley
ArXiv pre-print, 2024
10.48550/arXiv.2411.14289





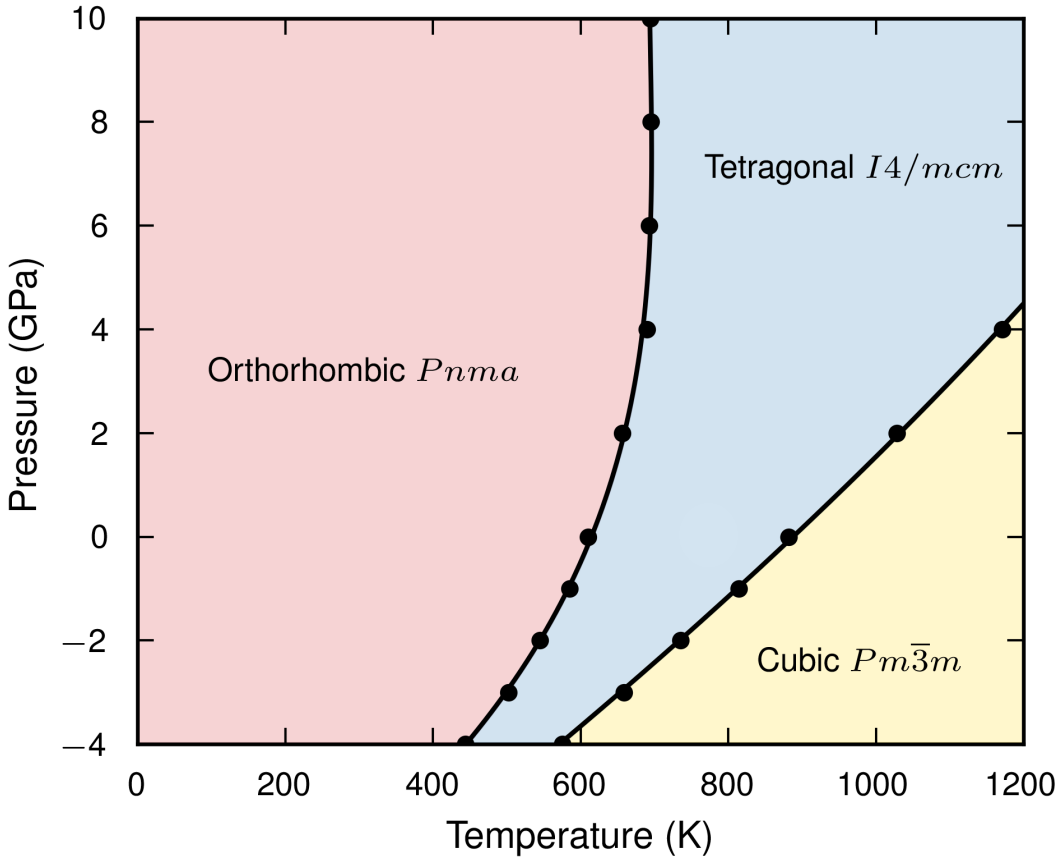
50,000 atoms


T=300K
z
y
x
θx
-12
12
T=300K
z
x
y
θy
-12
12
T=300K
y
x
z
θz
-12
12

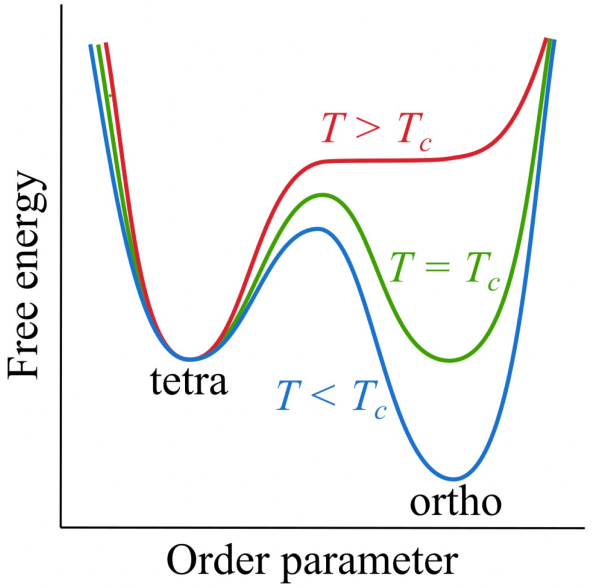
$BaZrS_3$ T- P- phase diagram

Calculated through NEP-MD and thermodynamic integration

P. Kayastha, E. Fransson, P. Erhart, L. Whalley
ArXiv pre-print, 2024
10.48550/arXiv.2411.14289



Thermodynamic Integration
required for 1st order ortho → tet



Comparison against experiment

P. Kayastha, E. Fransson, P. Erhart, L. Whalley
ArXiv pre-print, 2024
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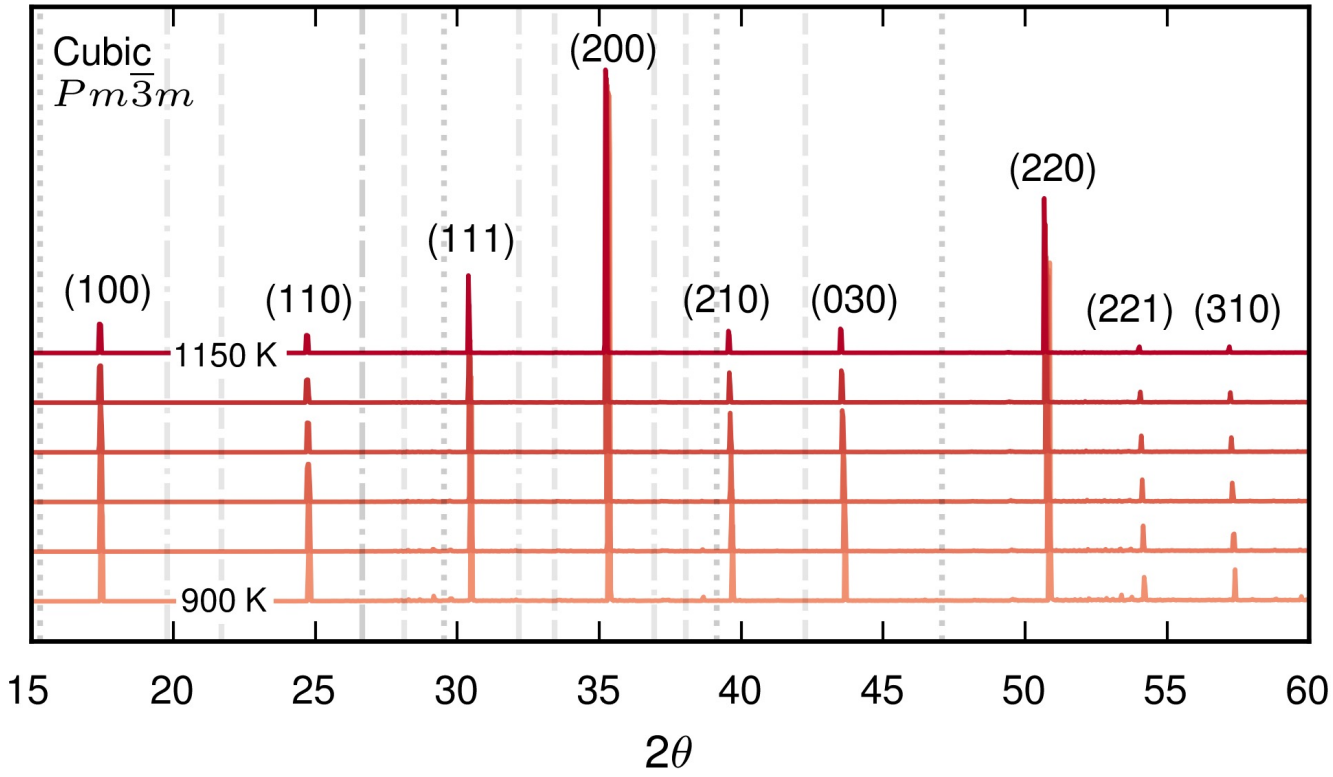

dynasor

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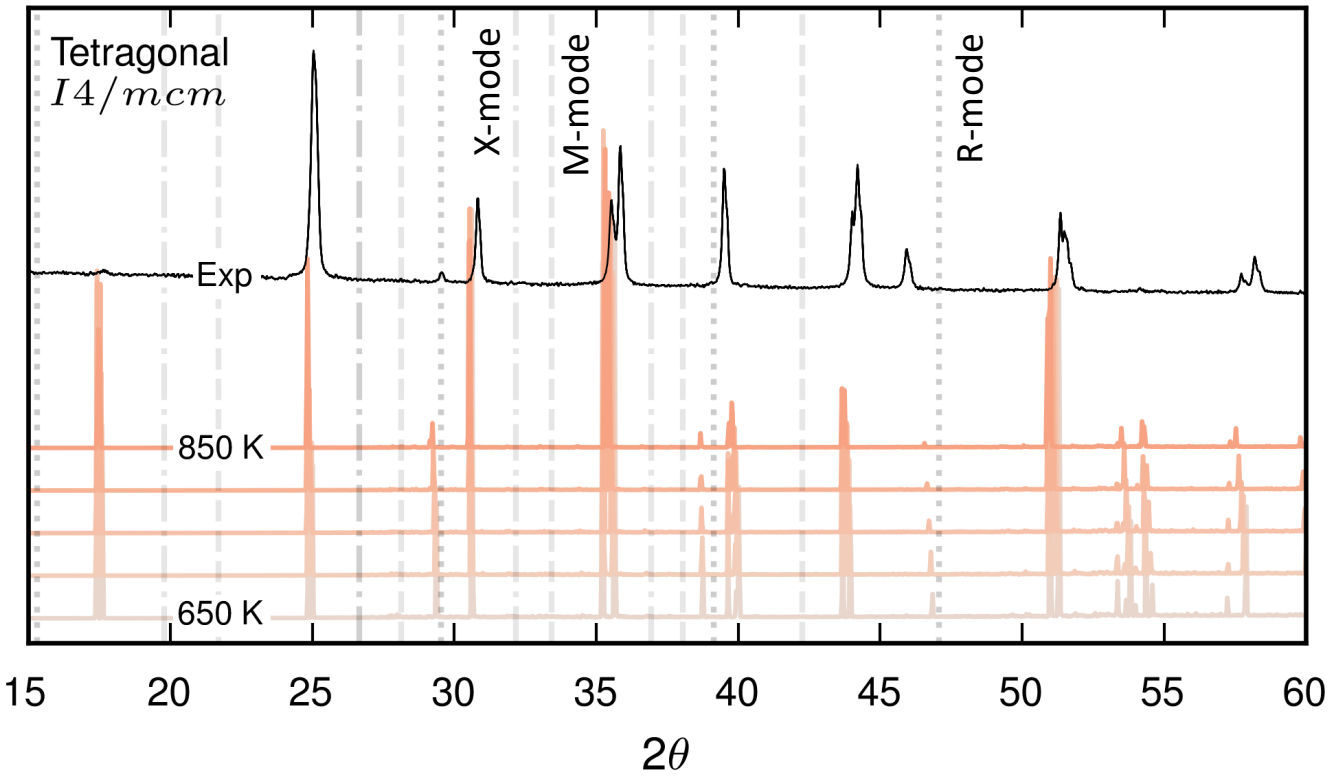

dynasor

Experimental data from Bystricky et al, Inorg. Chem. (2024) **63** 12826

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ArXiv pre-print, 2024
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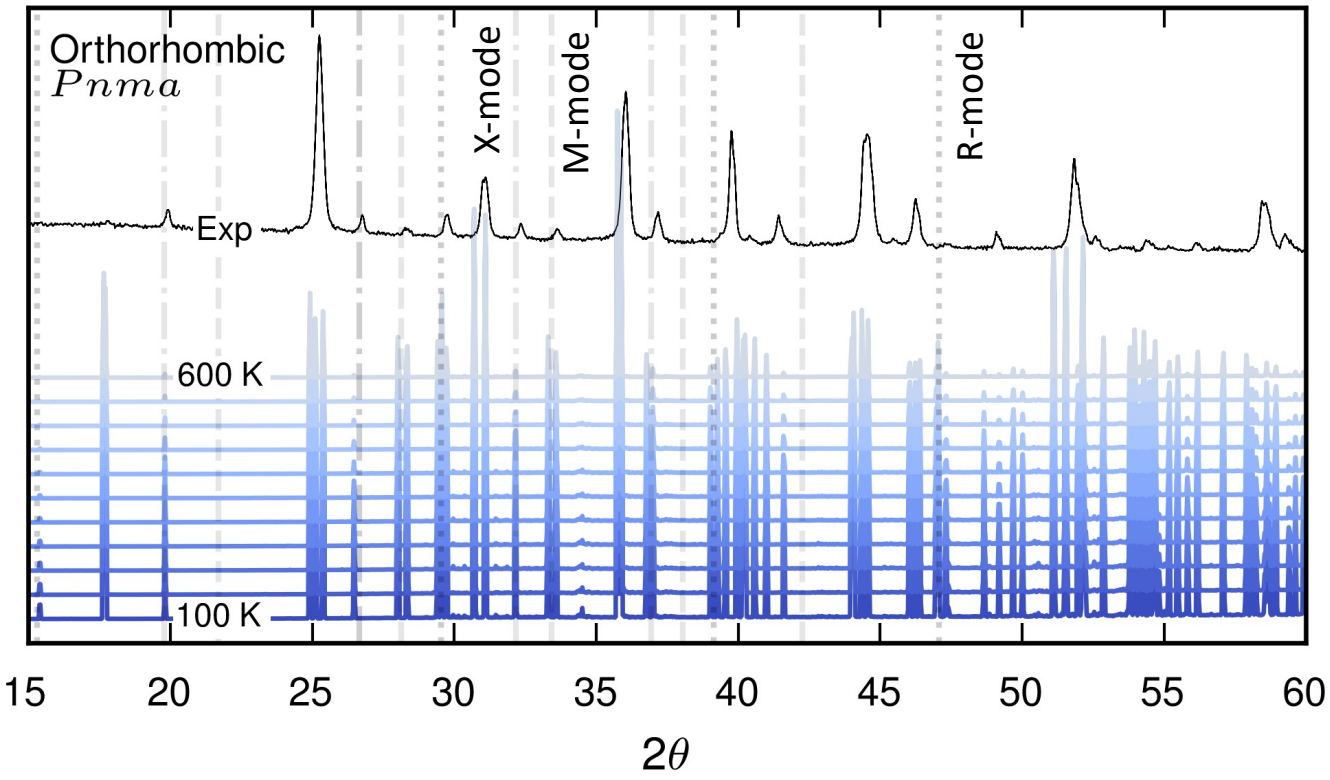
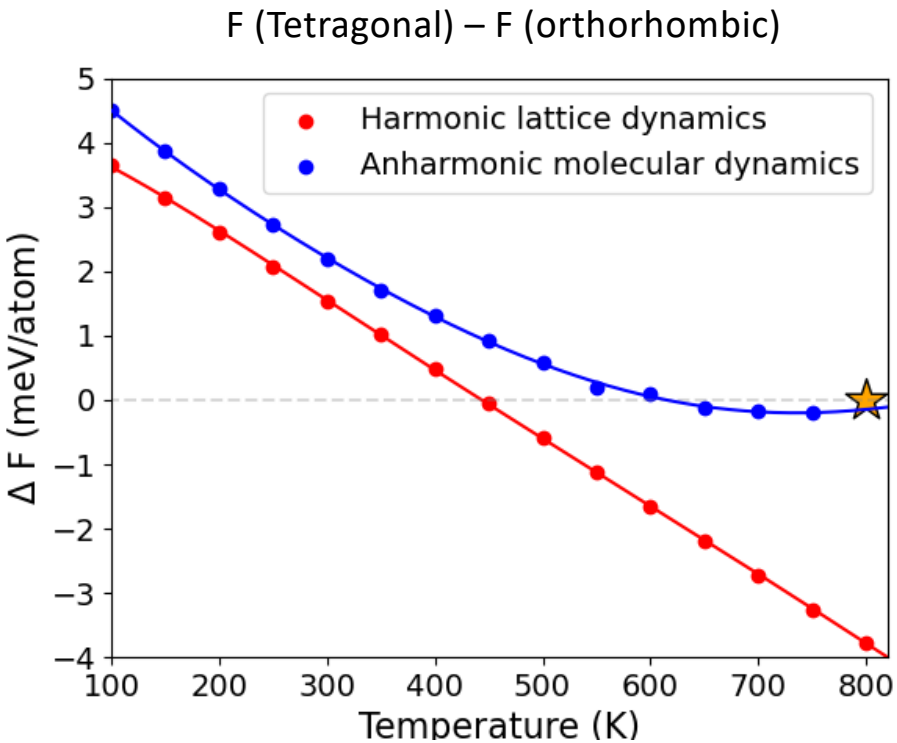


dynasor

Experimental data from Bystricky et al, Inorg. Chem. (2024) **63** 12826

Phase transition temperatures:
Harmonic vs Anharmonic vs Experiment



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

Recommended Reading:

K. V. Sopiha, C. Comparotto, J. A. Márquez, J. J. S. Scragg,
Chalcogenide Perovskites: Tantalizing Prospects, Challenging Materials. *Adv. Optical Mater.* 2022, 10, 2101704. https://doi.org/10.1002/adom.202101704

$BaZrS_3$ Collaborators

Prakriti Kayastha

Jonathan Scragg

Corrado Comparotto

Erik Fransson

Paul Erhart

Giulia Longo

Thank you

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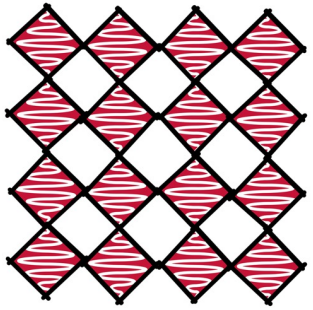

TURING SCHEME

ReNU Renewable Energy Northeast Universities

EPSRC Centre for Doctoral Training in Renewable Energy Northeast Universities

HEC MCC UK

nu research PV