An Insight into Halide Ordering in Mixed-Halide 2D Perovskites via Global Structure Optimization

Juraj Ovčar[1], Ivor Lončarić[1], Luca Grisanti[1], Bruno Mladineo[1], Jasminka Popović[1], Aleksandra Djurišić[2]

[1] *Ruđer Bošković Institute, Zagreb, Croatia*
[2] *The University of Hong Kong, Hong Kong*
Juraj.Ovcar@irb.hr

HRZZ Croatian Science Foundation
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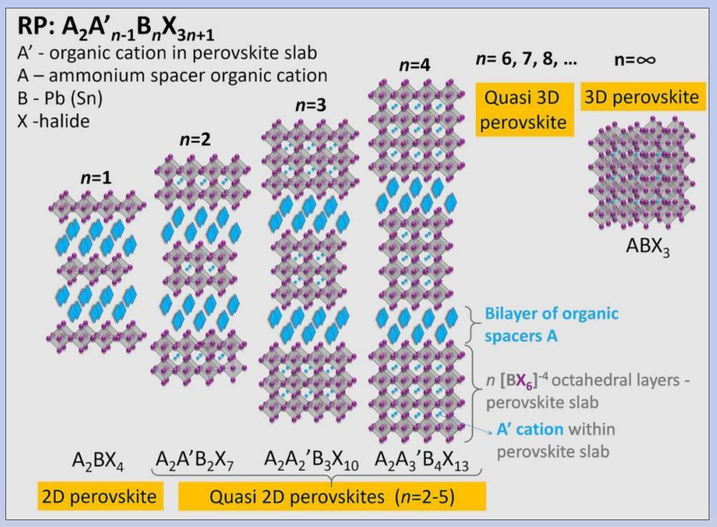
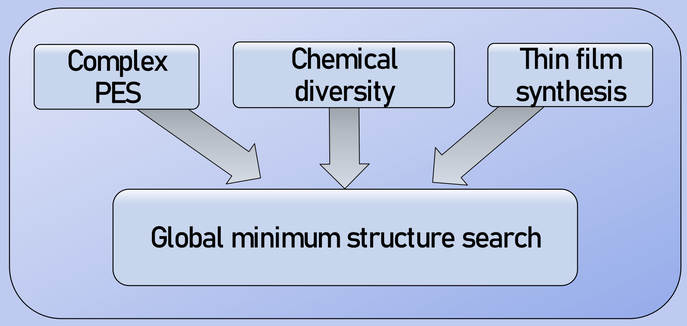
INTRODUCTION

Hybrid (quasi-)2D perovskites [1]

- 2D perovskite-like slabs interleaved with large organic cations
- Quantum and dielectric confinement
  - ➢ High exciton binding energy (~100 meV)
- Efficient and versatile LEDs and solar cells
- Stability issues

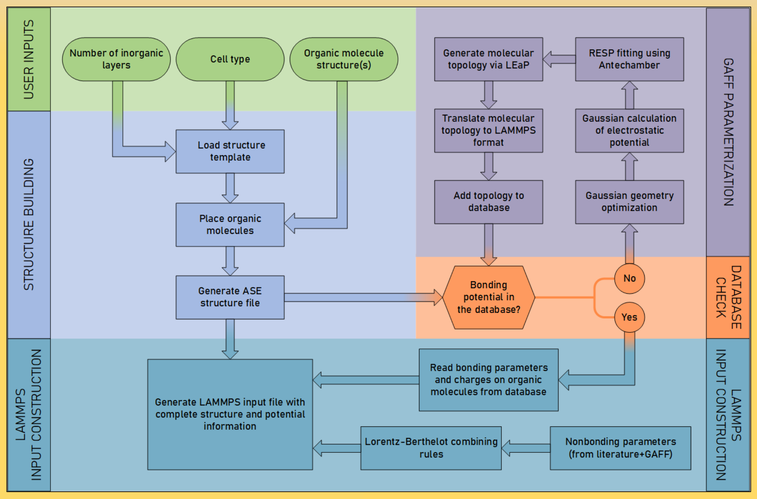


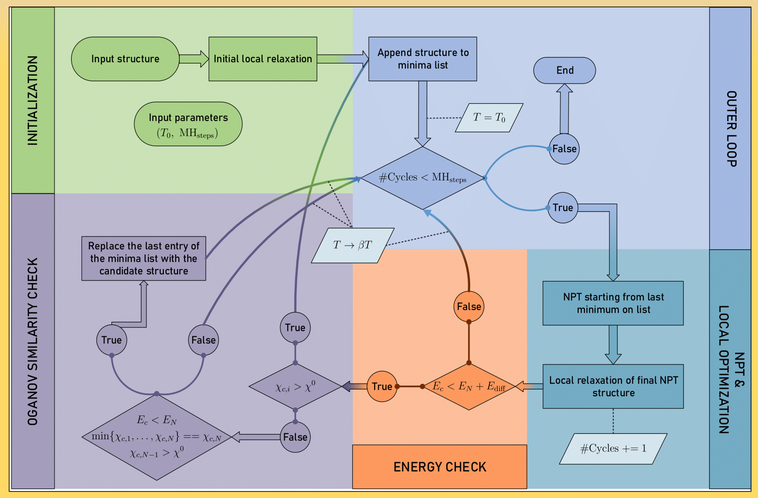


METHODOLOGY

Global optimization via Minima Hopping for Layered Perovskites (GO-MHALP) [7]

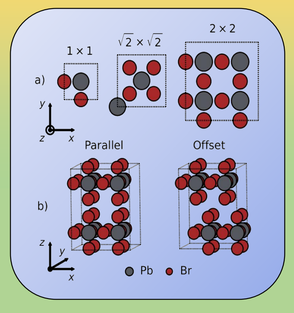
- Alternating MD and local structural optimizations [2, 3]
- Varying both cell & atomic positions during dynamics and relaxations
- Local minima acceptance criteria based on Oganov fingerprints [4]
  - ➢ Detailed exploration of local potential basins
- Based on previous ASE minima hopping implementation [5]

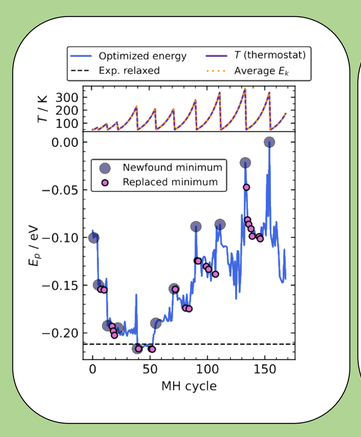


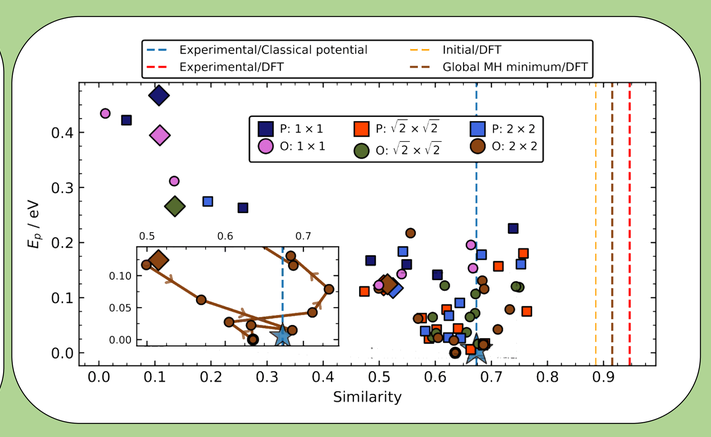


VALIDATION

- Six types of input cell geometries
- PXRDs from found local minima compared with experiment [6]





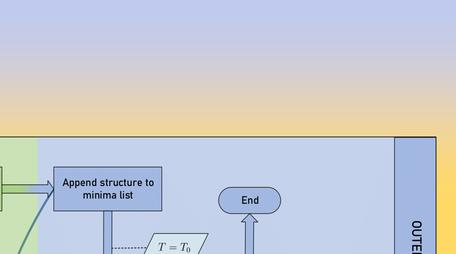


- BA_2PbBr_4 GO-MHALP run
- Similar tests successfully performed on $BA_2MAPbBr_7$ and $(4AMP)PbBr_4$ Dion-Jacobson perovskite

PREDICTION

Mixed Halide Ordering as a Tool for Stabilization of RPP Structures [8]

- t-BA forms a 2D perovskite only if Br and I halides are mixed in a 50-50 stoichiometry
- Specific halide ordering discovered with GO-MHALP
- Halide mixing allows the bulky t-BA to form strong hydrogen bonds at a low penetration depth



GO-MHALP + DFT

Configuration	E_f [eV]
Pure Br (a)	0.019
Pure I (b)	0.091
Axial I (c1)	0.245
Axial Br (c2)	**-0.275**
Alternating (c3)	0.024

References and acknowledgements

1. Advanced Materials 31.1 (2019): 1803514.
2. The Journal of Chemical Physics 120.21 (2004): 9911-9917.
3. The Journal of Phemical Physics 133.22 (2010): 224104.
4. Journal of Chemical Physics 130.10 (2009): 104504.
5. Topics in Catalysis 57.1-4 (2014): 40-53.
6. Journal of Computational Chemistry 22.3 (2001): 273-289.
7. Submitted, arXiv:2204.09763
8. Chemistry of Materials 2022, 34, 10, 4286-4297
9. Chemical Reviews 121.4 (2021): 2230-2291
10. The Journal of Physical Chemistry C 121.7 (2017): 3724-3733.

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