Dynamics of Hybrid Vacancy-Ordered Double Halide Perovskites $(FA)_2PtI_6$ and $(GUA)_2PtI_6$

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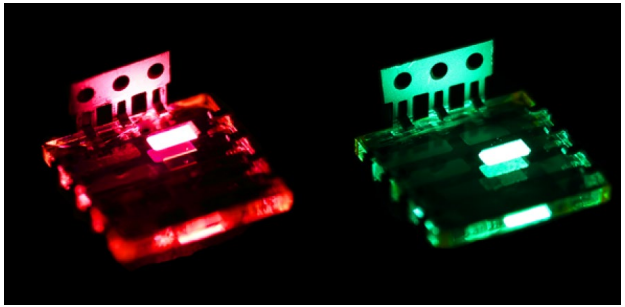
Hybrid Halide Perovskite Materials as Optoelectronics

- $MAPbI_3$ and $FAPbI_3$: high performance photovoltaic absorbers
  - MA = methylammonium ($CH_3NH_3^+$)
  - FA = formamidinium ($CH(NH_2)_2^+$)
- Why are they attractive?
  - Cheap, easy to make, easily compositionally tunable
- But…
  - Unstable (air, humidity), possible lead leaching into environment

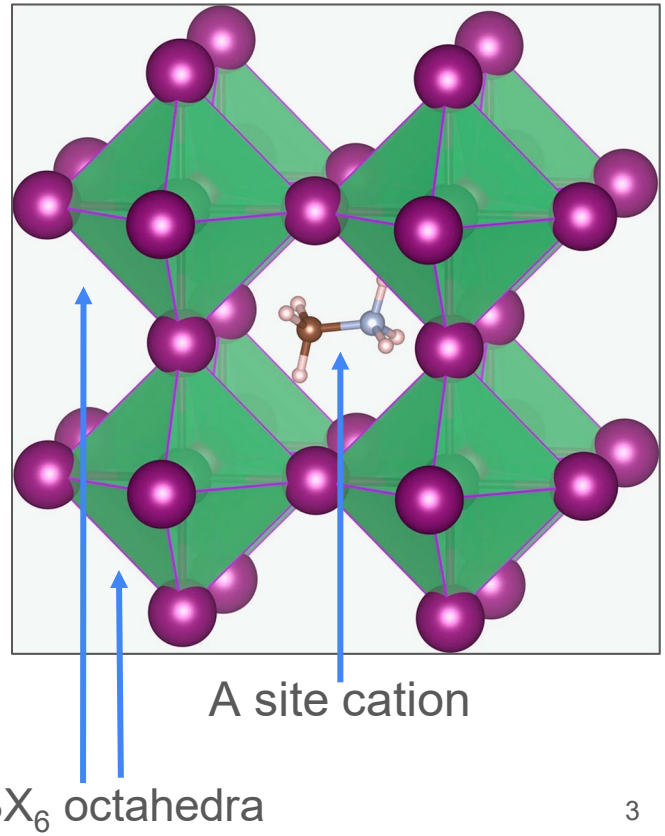
https://cns.utexas.edu/news/physicists-offer-insight-into-improving-perovskite-solar-cells



https://www.cam.ac.uk/research/news/leds-made-from-wonder-material-perovskite

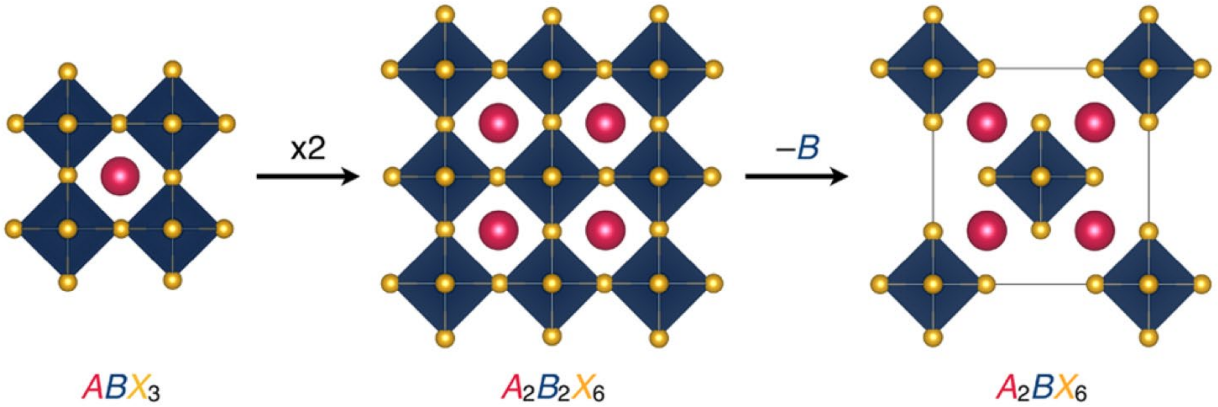
Hybrid Halide Perovskite Structure

- Perovskite: ABX_3
  - *A* site organic cation
  - BX_6 octahedra
- Why hybrid?
  - Small organic cations enable formation of the compound (tolerance factor)
- Organic cation is dynamic
  - Complexity of crystallography



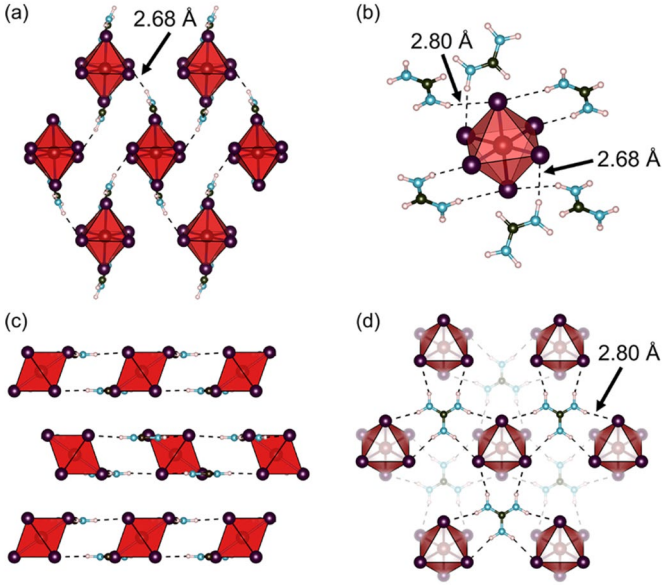
In Search of More Stable Variants

- $A_2B\square I_6$
  - A is an organic cation, ☐ is a vacancy
- It has been shown that though they lack 3-D connectivity, vacancy ordered iodides demonstrate attractive optoelectronic properties
  - Iodine-iodine interaction despite lack of 3D connected bond (valence band dispersion)
  - Much more stable, but less efficient



Hydrogen Bonding Directs Structures at Low Temperatures

- $(FA)_2Pt\square I_6$ and $(GUA)_2Pt\square I_6$ in literature
  - GUA = guanidinium ($C(NH_2)_3^+$)
  - Organic cation/iodide hydrogen bonding controls structural evolution
  - Cation is static at low temperatures (NMR, X-ray single crystal)
- Dynamics change at higher temperatures
  - Change in dynamics, single crystal destruction, twinning
- **How does temperature affect the dynamics of the organic cation, which controls the structure of the material?**



Evans, H. A., Fabini, D. H., Andrews, J. L., Koerner, M., Preefer, M. B., Wu, G., ... & Seshadri, R. (2018). Hydrogen bonding controls the structural evolution in perovskite-related hybrid platinum (IV) iodides. *Inorganic chemistry*, *57*(16), 10375-10382.

Hydrogen Bonding and Structure

- $(FA)_2Sn\square I_6$: hydrogen bonding between the organic cation and inorganic framework causes ferroelastic phase transition (hysteresis)
  - Directly related to the organic cation's dynamic behavior
- Are these ferroelastic phase transitions universal in vacancy-ordered double hybrid halide perovskites?
  - Isostructural compound $(FA)_2Pt\square I_6$ and familial compound $(GUA)_2Pt\square I_6$

Maughan, A. E., Mozur, E. M., Candia, A. M., & Neilson, J. R. (2020). Ferroelastic Phase Transition in Formamidinium Tin (IV) Iodide Driven by Organic–Inorganic Coupling. *Inorganic Chemistry*, *59*(19), 14399-14406.

Approaching Our Question

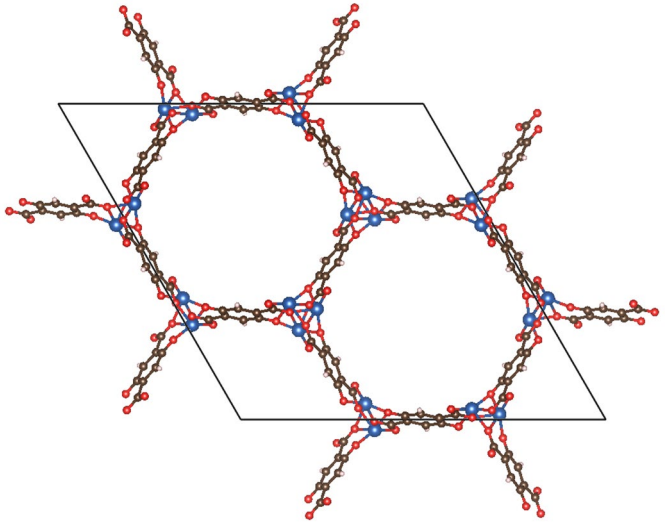
- We will use X-ray diffraction and quasi-elastic neutron scattering (QENS) to monitor the dynamics of the organic cation
  - Crystallography of a dynamic organic cation inside of a static inorganic cage requires a careful treatment
  - QENS allows us to look for crystallographically silent dynamics of the organic *A* site cation
    - Changes in cation dynamics impact photoconductivity in hybrid perovskite photovoltaic cells

https://www.aps.anl.gov/About/Welcome

https://neutrons.ornl.gov/basis

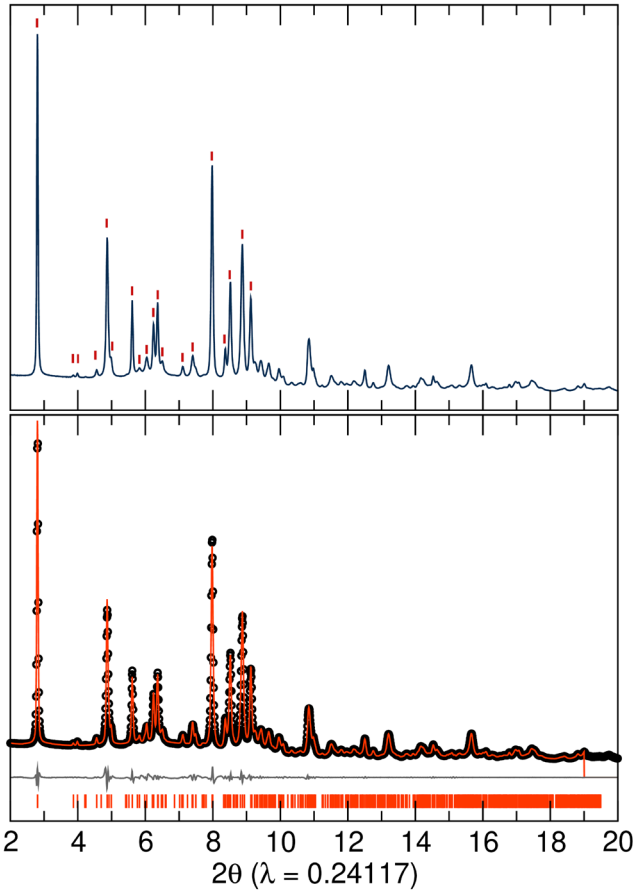
Preparation for Incoming Data

- Crystallography bootcamp
  - Understanding of crystallographic nomenclature, multiplicity, atom sites, space group symbols
- Refinement practice
  - Diffraction analysis of various complex hybrid structures
    - Metal-organic-framework (MOFs)
  - Rigid bodies
  - Peak indexing and finding a structure solution

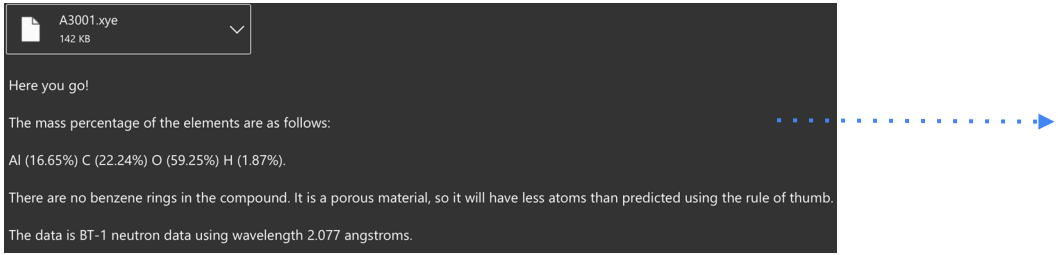


Solving a material's structure

- Indexing our sample's diffraction pattern
  - Peak location (orange ticks)
  - Match our data against hundreds of suggested space groups and unit cell combinations
- If ticks line up, Pawley refinement
  - Peak intensity (height)
  - Peak shape/width
  - Highest symmetry possible
- If Pawley successful, Rietveld refinement
  - Incorporates multiplicity, type, location of atoms on the unit cell



Indexing process



Indexing process

A3001.xye
142 KB

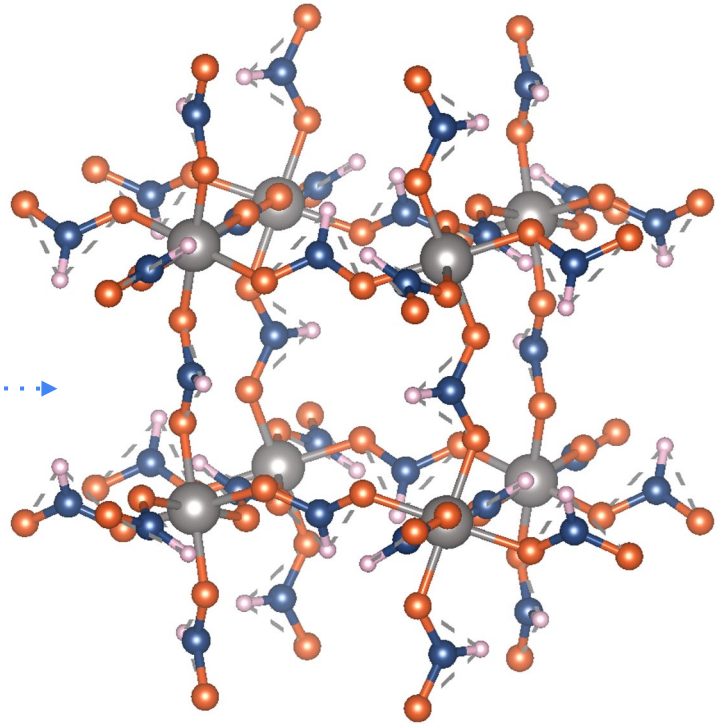
Here you go!

The mass percentage of the elements are as follows:

Al (16.65%) C (22.24%) O (59.25%) H (1.87%).

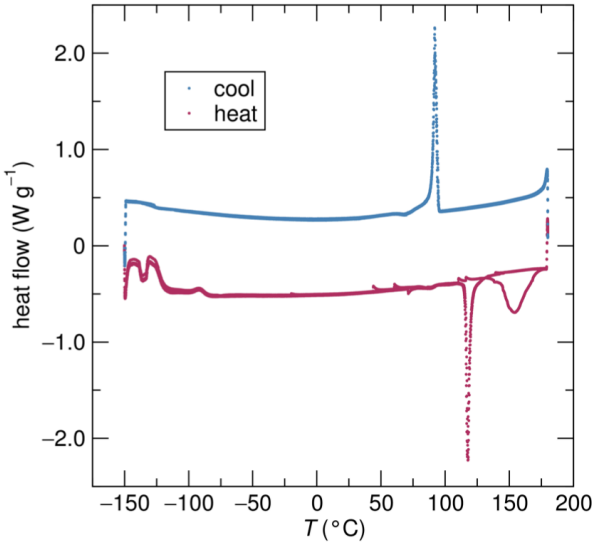
There are no benzene rings in the compound. It is a porous material, so it will have less atoms than predicted using the rule of thumb.

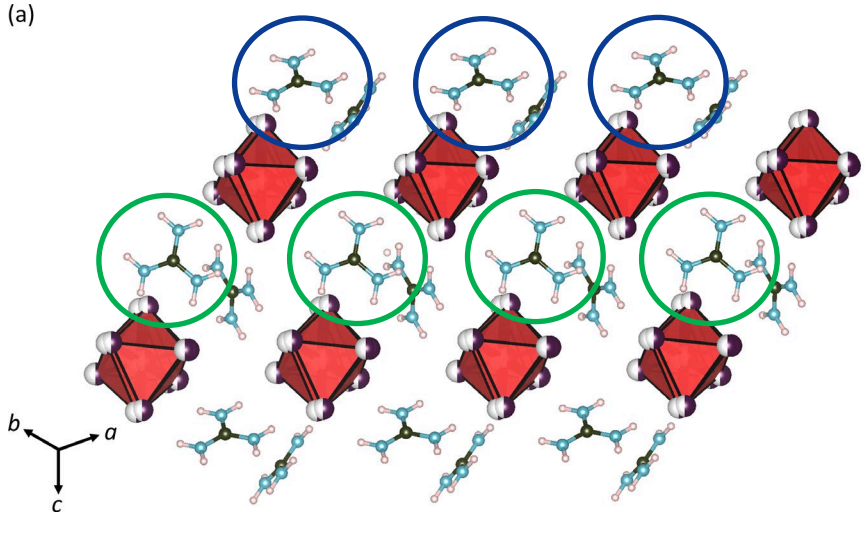
The data is BT-1 neutron data using wavelength 2.077 angstroms.

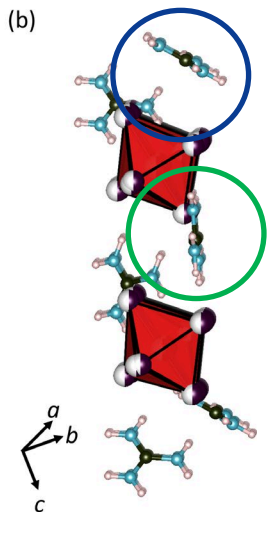


H-Bonding Dictates Structure Through Phase Transition

- Sluggish phase transition is observed (first heating)
- High temperature phase is related to original phase
  - Original phase is metastable (never recovered)
  - Guanidinium is still hydrogen bonded and stable







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Future Plans

- Analyze our X-ray data, receive and analyze QENS data
  - X-ray will now inform the QENS experiment
  - QENS data by the end of August
- Eventual publication
- Add to the growing understanding of perovskite-related compounds
  - Achieve compositional control of these materials

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Questions?