Dynamics of Hybrid Vacancy-Ordered Double Halide Perovskites \((\text{FA})_2\text{PtI}_6\) and \((\text{GUA})_2\text{PtI}_6\)

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Hybrid Halide Perovskite Materials as Optoelectronics

- MAPbI$_3$ and FAPbI$_3$: high performance photovoltaic absorbers
  - MA = methylammonium (CH$_3$NH$_3^+$)
  - 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://www.cam.ac.uk/research/news/leds-made-from-wonder-material-perovskite
Hybrid Halide Perovskite Structure

- Perovskite: $\text{ABX}_3$
  - A site organic cation
  - $\text{BX}_6$ 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

- $\text{A}_2\text{B} \square \text{I}_6$
  - $\text{A}$ is an organic cation, $\square$ 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

- \((\text{FA})_2\text{PtI}_6\) and \((\text{GUA})_2\text{PtI}_6\) in literature
  - GUA = guanidinium \((\text{C(NH}_2)_3^+)\)
  - 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?

Hydrogen Bonding and Structure

- \((\text{FA})_2\text{Sn} \square \text{I}_6\): 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 \((\text{FA})_2\text{Pt} \square \text{I}_6\) and familial compound \((\text{GUA})_2\text{Pt} \square \text{I}_6\)

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
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

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.
Indexing process

The mass percentage of the elements are as follows:
Al (16.65%) C (32.24%) O (59.29%) 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

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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References

Questions?