Predicting Alloyed Mixed-Valence Perovskite Structures

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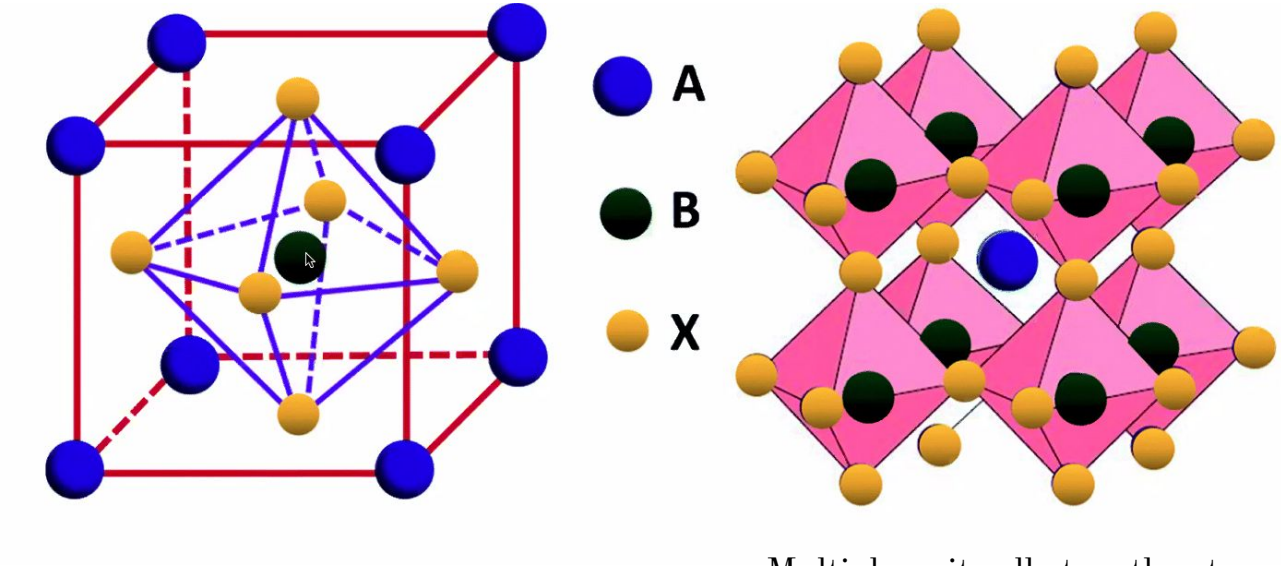
What Are Perovskites?

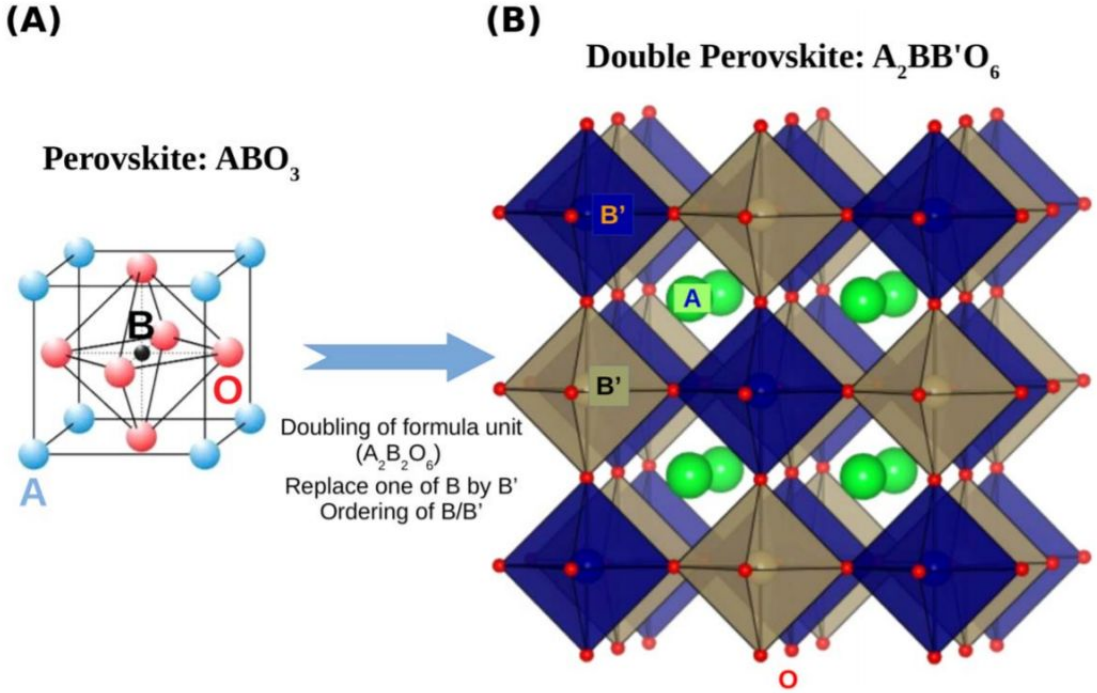
Cubic Perovskites: Have the general formula ABX_3 where A and B are cations, and X is an anion



One unit cell (repeating unit)

Multiple unit cells together to make up one crystal structure

- **Double Perovskites**: Variation of the cubic perovskite - has the general formula of $A_2BB'X_6$.
  - Note: the B (central) sites are not the same in each repeating unit - they alternate between B and B'!

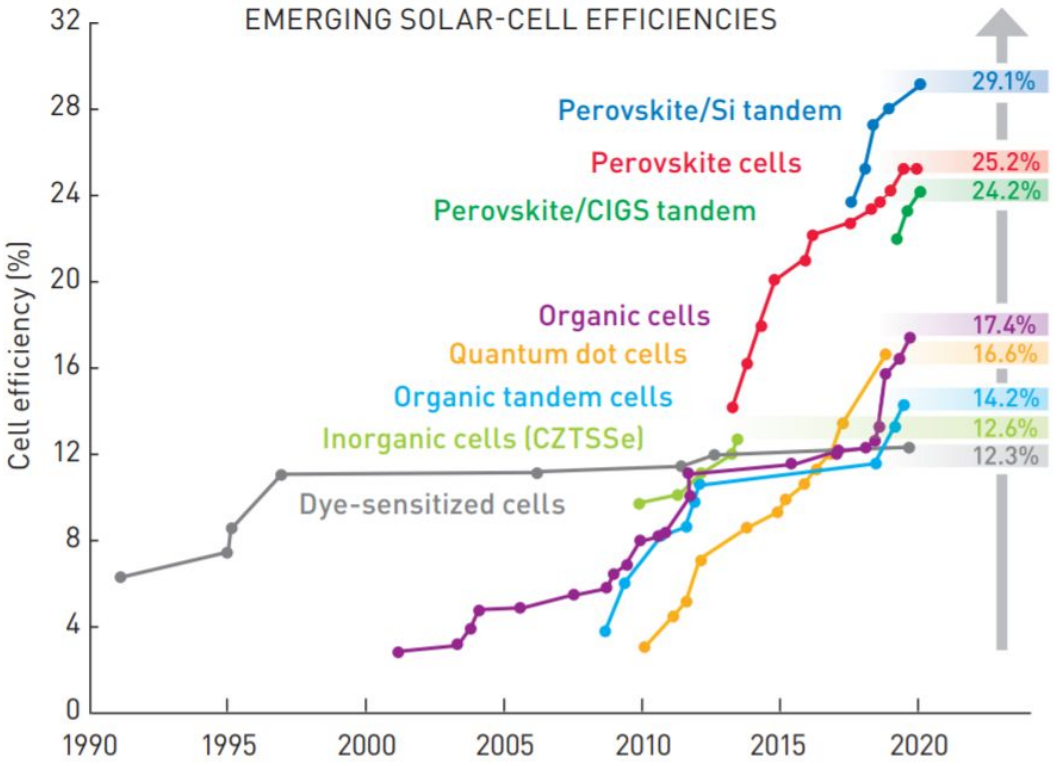


(Single Perovskite)
B site: 4+

(Double Perovskite)
B Site: 3+ B' Site: 1+

Mixed Valence means the ions in the B sites can have different charges!

Why Do We Study Perovskites?



- Used in solar-cells, fuel cells, and other sustainable energy applications
- More efficient
- Relatively cheap

Mixing Double and Single Perovskites

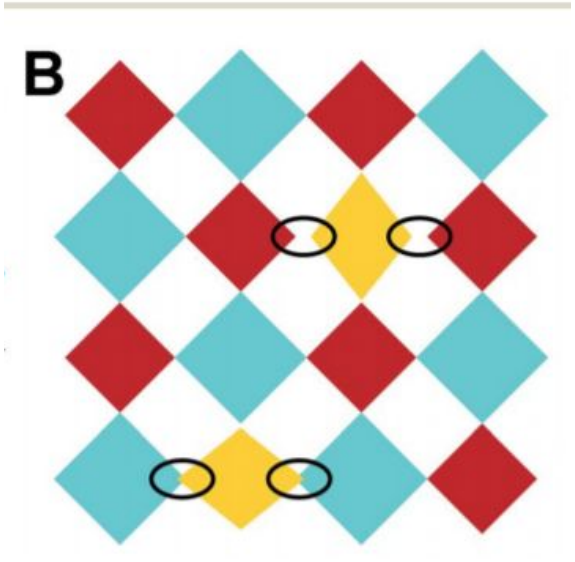
Double Perovskite **before** mixing

All ions aligned perfectly

Key:

- Red = In3+
- Blue = Cu+
- Yellow = Cu2+

Double Perovskite **after** mixing



Less stable because of the mismatches (gaps and overlaps between ions)!

The perovskite materials with the top-down view of the B sites only

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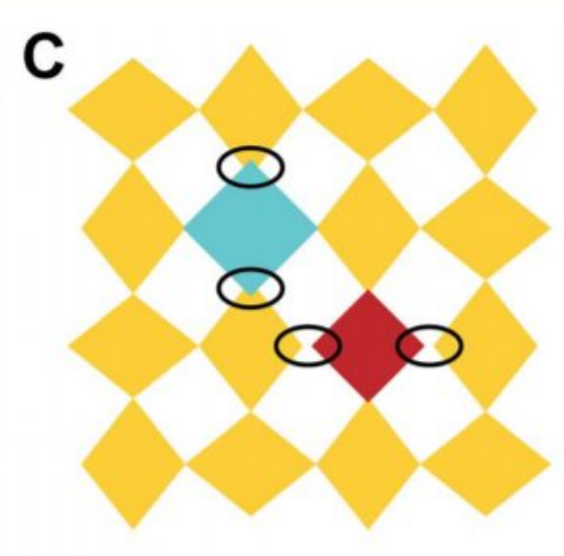

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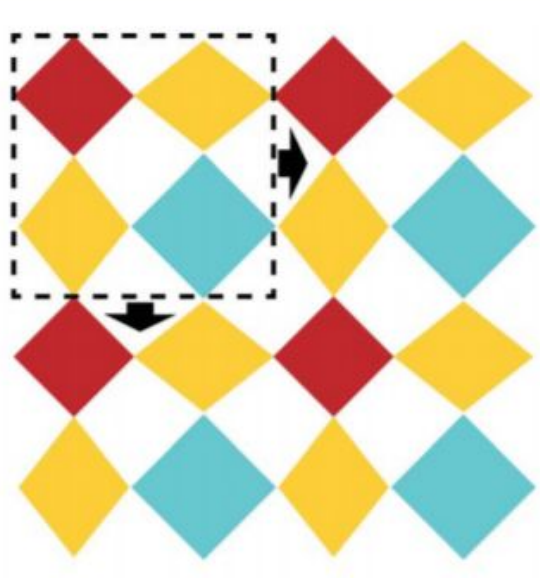
Mixing Double and Single Perovskites

Now.. we need to find a stable arrangement with less mismatches for our mixed perovskite....

Mixing Double and Single Perovskites



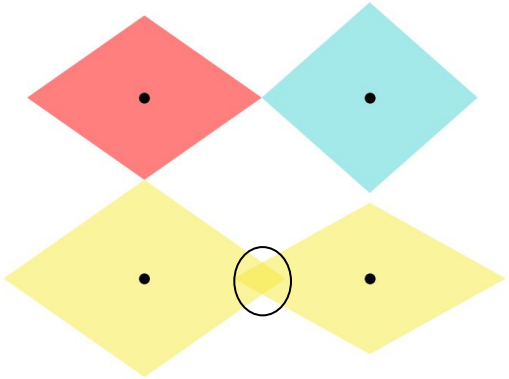
No mismatches - finally, something stable!

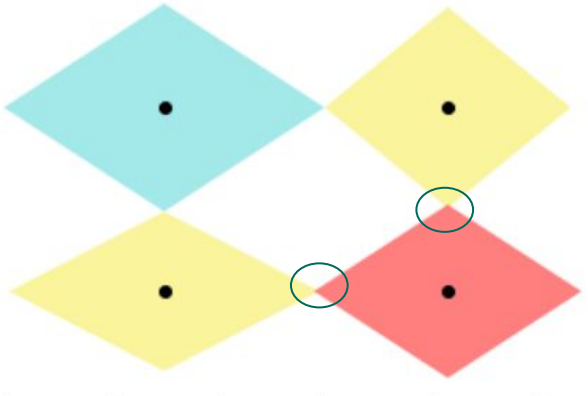
Objective

- Develop a program using Python to predict possible stable structures with minimal mismatches using different combinations of ions at the B/B’ sites

Results:

- Program predicts all possible structural arrangements with various sets of ions (can specify with ions you want to use to form a perovskite crystal)
- Calculates the total mismatch for each arrangement using the length of each bond in the material
- Ex: these are considered different “combinations”/arrangements and have different mismatches





Results

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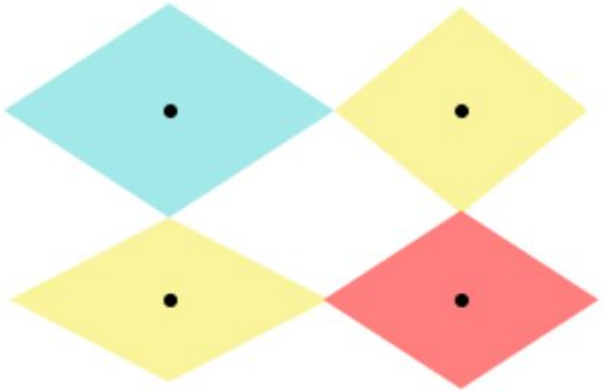
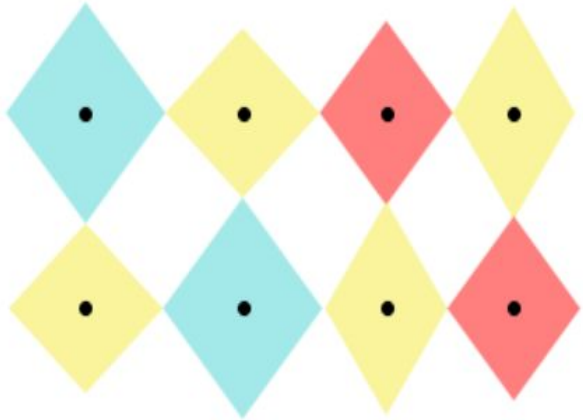
2x2 Arrangements:



Optimal arrangement for a 2x2 structure

- 48 possible arrangements

2x4 Arrangements:

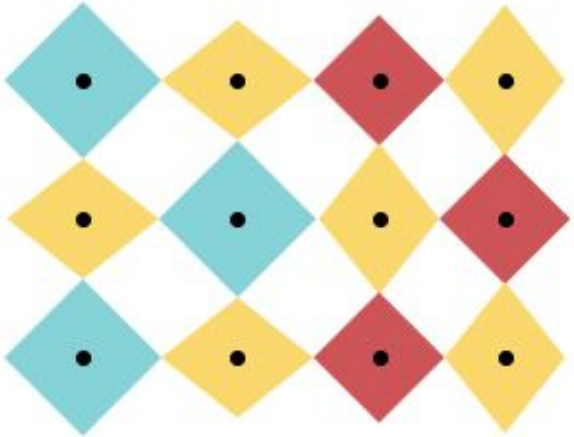


Optimal arrangement for a 2x4 structure

- 6720 possible arrangements

Results

3x4 Combinations:



Optimal combination for a 3x4

- 1,182,720 possible arrangements

Takeaways:

- MANY possible combinations with just 1 set of 3 ions - imagine the possibilities when we start to also generate combinations for other sets of ions!

- Computers can save us A LOT of time when planning synthesis reactions

Future Directions:

Long-Term Goal:

- Add more parameters to make sure materials are stable in experimental conditions
- Account for edge conditions (far right column and bottom row) in geometric calculations
    - Sometimes, the bond lengths are distorted from bonds across multiple unit cells

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