

IMAGING PEROVSKITE MATERIALS AT THE ATOMIC SCALE USING SYNCHROTRON X-RAY SCANNING TUNNELING MICROSCOPY

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ABSTRACT

- Perovskites are considered to be promising candidate materials for photovoltaic cells for many reasons, including cost and ease of manufacture relative to silicon. However, the main drawback of using perovskites for this purpose is the long-term stability of the material. This experiment attempts to understand the degradation of formamidinium–methylammonium lead iodide perovskite ($\text{MA}_x\text{FA}_y\text{PbI}_3$) by observing the chemical bonding state of iodine using x-ray absorption spectroscopy. In this experiment, two different perovskite compositions were analyzed using synchrotron x-ray scanning tunneling microscopy to determine if an applied voltage led to a movement of iodine ions in the sample. A horizontal shift in the peaks or intensity of the peaks would indicate such a shift in ions. This investigation would reveal which composition was more durable, allowing us to design a more efficient, longer-lasting perovskite cell. It was observed that there were shifts in both the energy and peak height of the M_4 and M_5 absorption edge of iodine, indicating a potential change in the bonding state of iodine in our samples.

MOTIVATION

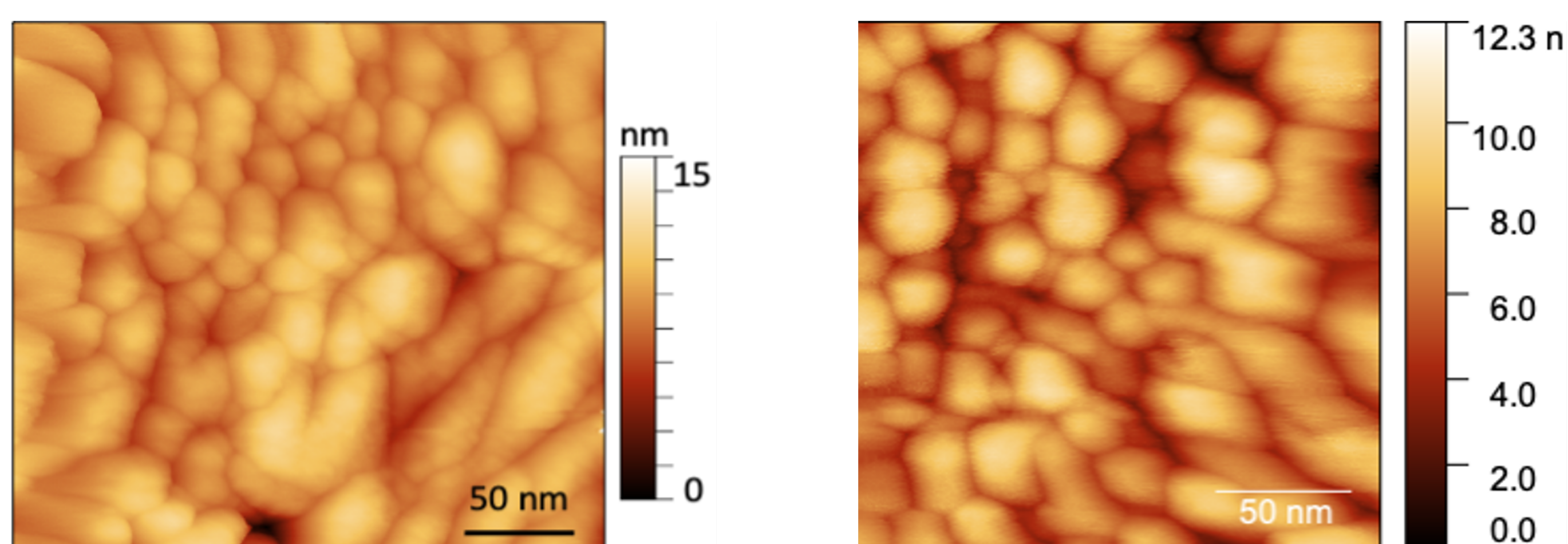
The purpose of this experiment is to explore the voltage-induced ion movement in perovskite photovoltaics (PV), and the degradation of lead iodide perovskite in two different compositions of PV cells. The samples analyzed by the synchrotron x-ray scanning tunneling microscopy (SX-STM) attempt to prove the perovskite's lifetime and stability to be a more effective material for solar cells than silicon.

METHODS

- Synchrotron X-ray Scanning Tunneling Microscopy combines the elemental sensitivity of X-ray microscopy and the spatial resolution of scanning tunneling microscopy to examine both the chemical makeup and electromagnetic configuration of materials at the nanoscale.
- This experiment used the x-ray spectroscopy capabilities of the beamline to probe the M_4 and M_5 absorption edges in the iodine atoms of two different perovskite solar cell compositions. Using SX-STM, we monitored the electromagnetic configurations of these atoms to detect any potential degradation.

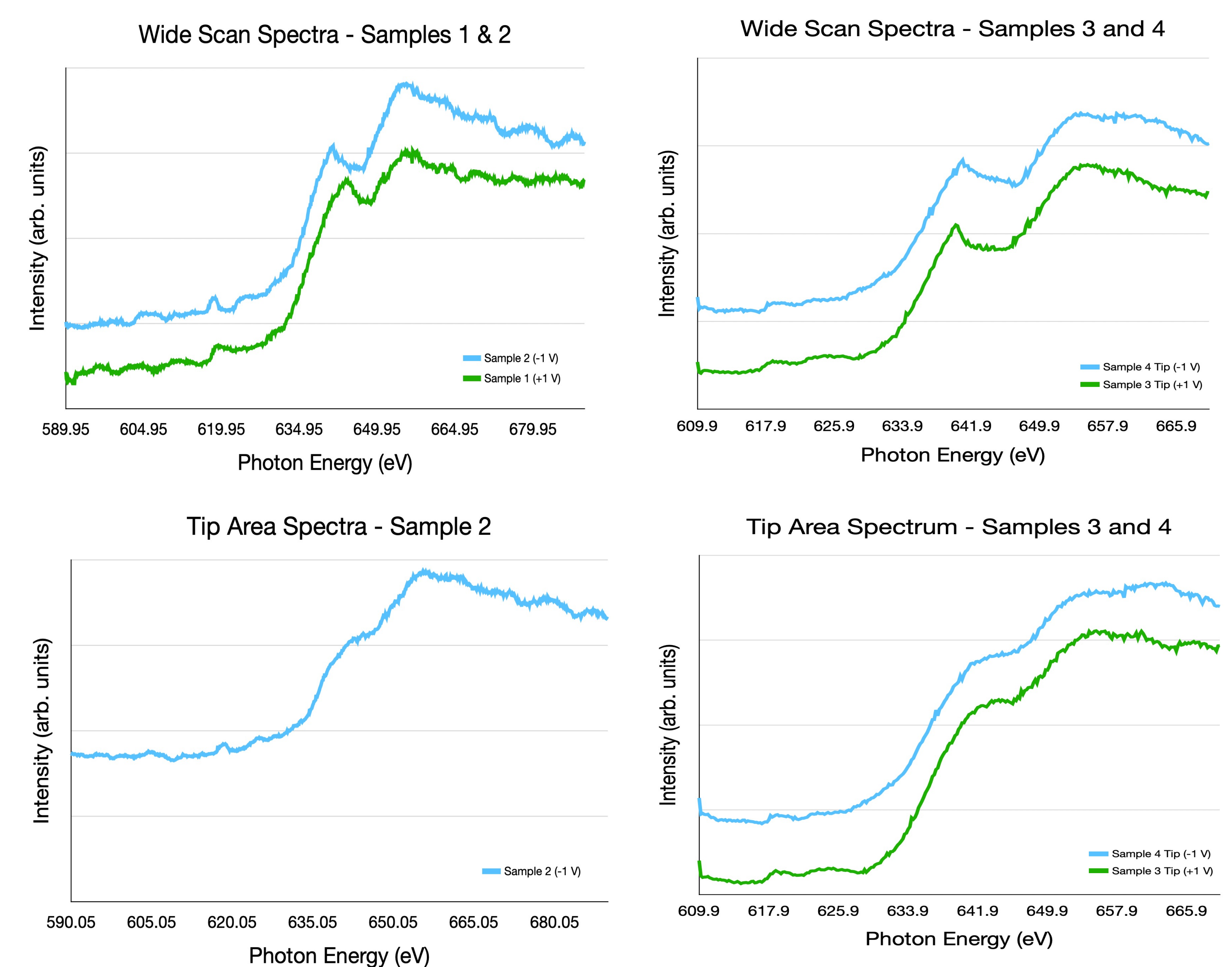
Discussion: X-Ray Absorption Spectra

- This experiment compares two different types of perovskite materials. Both materials are $\text{MA}_x\text{FA}_y\text{PbI}_3$ (methylammonium_x formamidinium_y) with different formulations.
- Each sample was measured at two different length scales. The “sample” spectra current is collected from a $100 \times 100 \mu\text{m}^2$ area. The tip current is collected by the tip detector over a much smaller area, approximately $0.25 \mu\text{m}^2$ area.
- Comparing samples 1 and 2, there is a slight energy shift in 1 and intensity shift in 2. Negative voltage may have caused the increased energy for the sample and positive voltage increased intensity through shifting the bonding state of iodine.
- The applied voltages to samples 3 and 4 showed a smaller effect on peak height and energy than in sample 1 and 2. The different perovskite composition being affected with voltages may indicate less of a shift in iodine for samples 3 and 4.
- Tip samples 3 and 4 show an intensity shift, indicating some instability in the iodine. The -1 V applied to tip 3, contrasting sample 2, showed an intensity change rather than energy, which may be a result of a different material, or a different effect on the iodine inside the perovskite.
- Below are 2 AFM scans of the perovskite samples examined in this experiment. Sample 1&2 is on the left, and sample 3 & 4 is on the right.



Data: X-Ray Absorption Spectra

- Samples 1 & 2 represent the same perovskite formulation, scanned with different applied voltages.
- Samples 3 & 4 represent a different perovskite formulation, scanned with different applied voltages



CONCLUSIONS

In this experiment, we observed that both the energy and peak height of the M_4 and M_5 absorption edge of iodine shifted under an applied voltage. We interpret this shift as a change in the bonding structure of iodine under an applied voltage, and as evidence of degradation of the perovskite crystal structure under applied voltage.

This experiment is also the first time that this instability of a perovskite material was observed in experimental conditions and demonstrates the viability of SX-STM as a method to investigate perovskite stability under external applied voltages.

NEXT STEPS

The next step following our experiment would be to conduct further testing of the degradation of formamidinium–methylammonium lead iodide, as well as other possible perovskite formulations.

The goal would be to identify a perovskite photovoltaic with minimal ion movement under applied voltages, which has the possibility of creating a more stable and efficient solar cell.

REFERENCES

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