Micro-scale Light Emission and Morphological Properties of Double Halide Perovskites

Rebecca Schechter, Kevin Liao, Renee Sher
Physics Department, Wesleyan University

Perovskites and Halide Segregation

Mixed halide perovskites (MHPs) are semiconductors with the unit cell structure ABX_3 where A is a large cation (MA^+, Cs^+, FA^+), B is a small metal cation (Pb^{2+}, Sn^{2+}), and X is a halide anion (I^-, Br^-, Cl^-). MHPs are a promising multi-junction solar cell candidate due to their tunable band gap (1.5-3.2 eV), caused by adjusting the ratio of halides. However, MHPs under illumination halide segregation occurs, which demixes the halide ions and forms I- and Br-rich regions. Charges are funneled through the I-rich regions due to their lower band gap, which reduces the voltage.

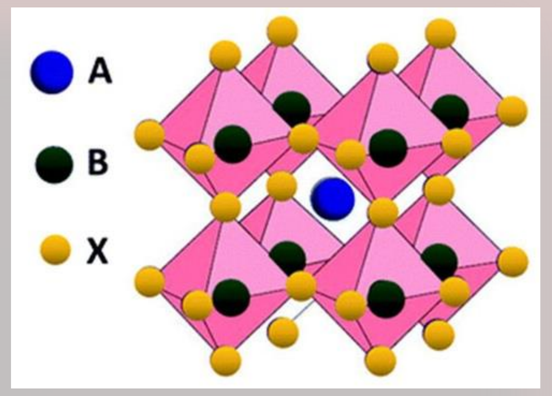

Fig. 1. Perovskite crystal.

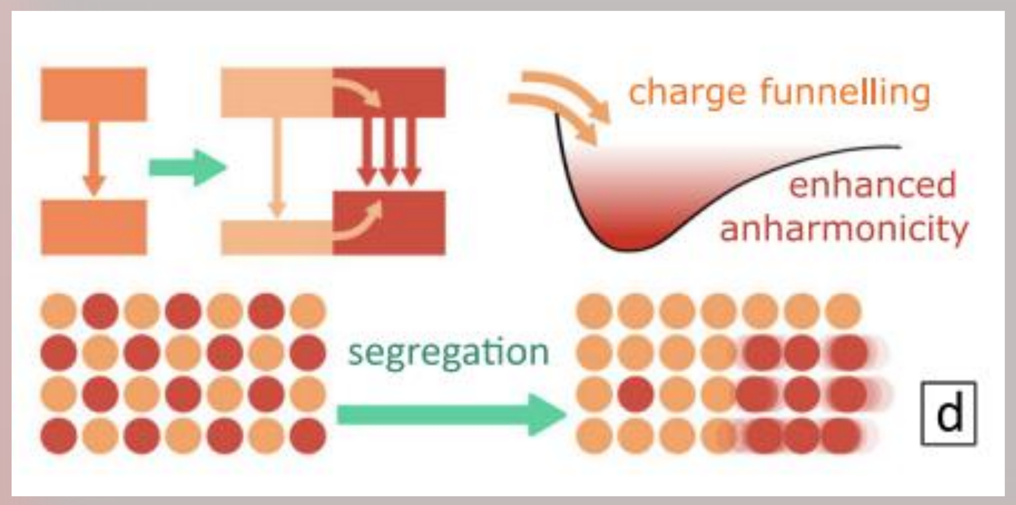

Fig. 2. Top Right: Diagram of energy well formed in I-rich region causing charge funneling. **Top Left:** Diagram of the homogenously mixed halide band gap segregating into higher and lower bandgap regions, corresponding to Br-rich (orange) and I-rich (red) domains. **Bottom:** Diagram of halides segregating. [1]

Confocal Microscopy

Samples:

- $MAPb(I_{1-X}Br_X)_3$ X=0.5
- $MAPb(I_{1-X-Y}Br_XCl_Y)_3$ Y=0.05

We obtain light emission data using confocal microscopy and do lifetime and regional. The ion segregation causes the light emission to shift from λ_1=600nm to λ_2=740nm.

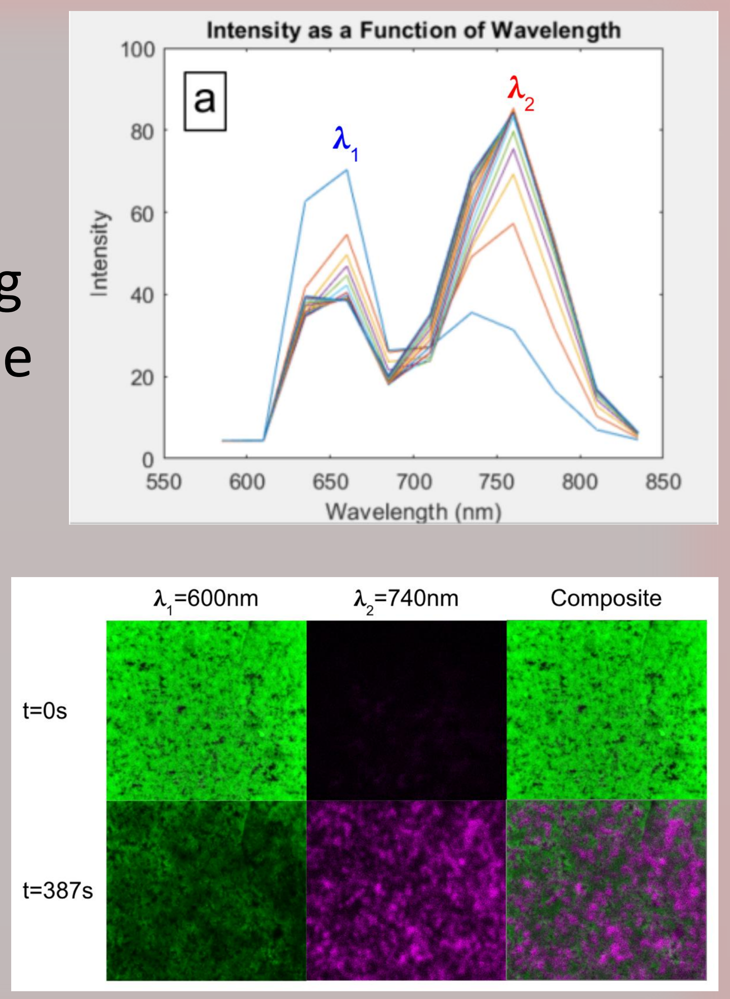

Fig. 3. Top: Characteristic confocal photoluminescence (PL) vs wavelength graph of an MHP showing halide segregation, causing a second PL peak to form at a higher wavelength. [2] **Bottom:** Confocal scans of $MAPb(I_{1-X}Br_X)_3$ x=0.5 sample at λ_1, λ_2, and a composite image at the initial and final times.

Grain Type Analysis

When we look at different regions we see three different grain behaviors:

- Type 1: grains emit relatively strongly at λ_1 and weakly at λ_2 for all times: initially well mixed but does not become I-rich during segregation
- Type 2: grain emission at λ_1 stays dim, while λ_2 grows to be strong: initially defects which become I-rich during segregation
- Type 3: grain emission at λ_1 starts strong then dims and λ_2 starts dim and grows strong: initially well-mixed that become I-rich during segregation

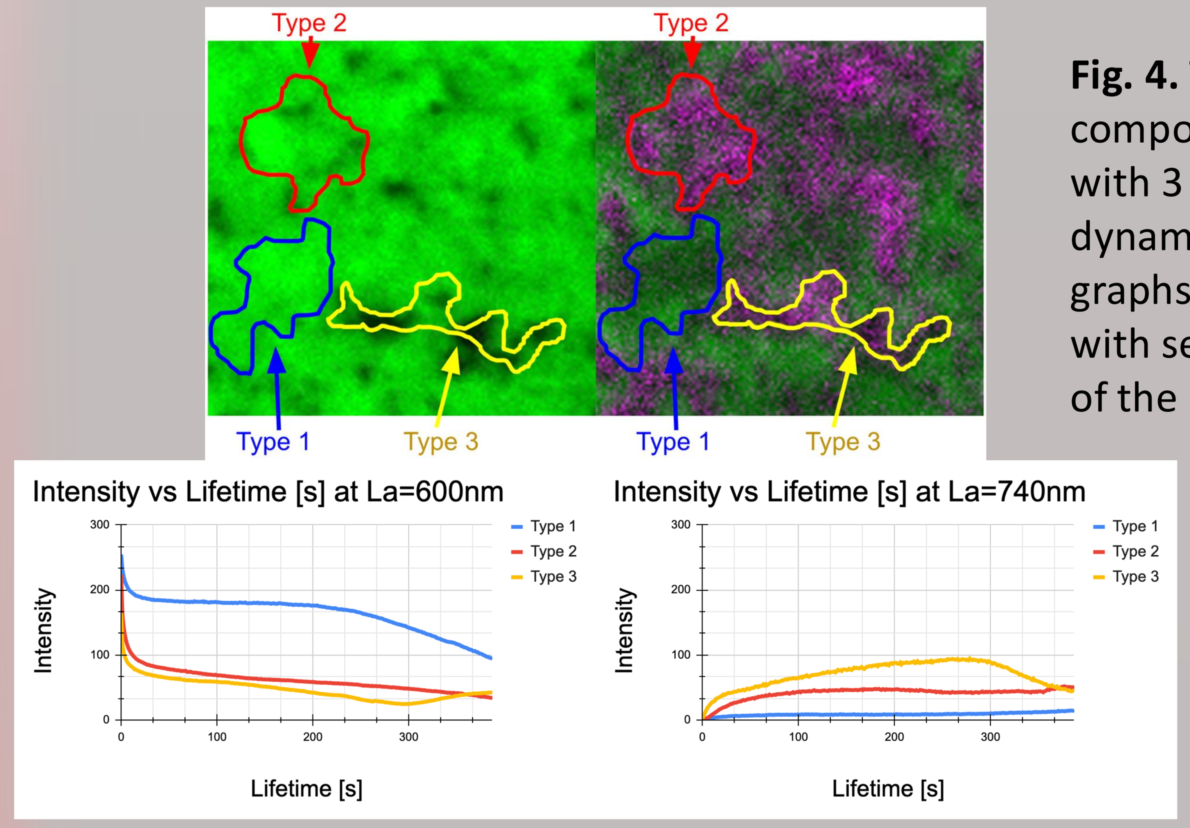

Fig. 4. Top: t=0 and t=6.3min composite confocal images with 3 regions of different dynamics. **Bottom:** λ_1 and λ_2 graphs of intensity over time with separate lines for each of the 3 grain types.

We coded these grain types to map grain types in a more systematic way. The types were decided based on if the λ_1 or λ_2 intensity crossed a certain threshold.

- Blue: Type 1
- Red: Type 2
- White: Type 3
- Black: fully defected regions that have no strong emission

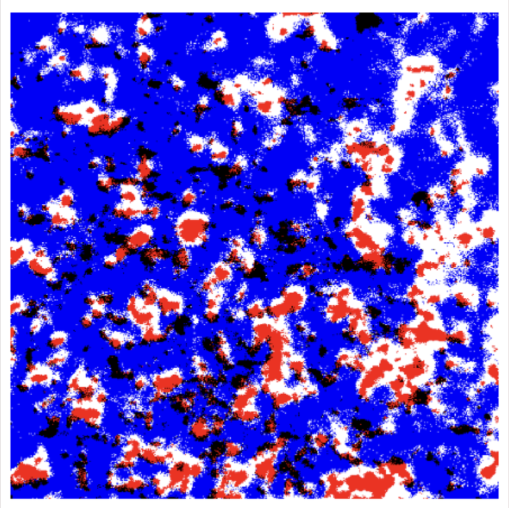

Fig. 5. The grain type map for with selected thresholds I_1 = 200, I_2 = 60. [2]

The grain sort analysis can be applied to cycles of confocal scans of the same location with time to desegregate. The preliminary results showed that the segregation time shortens and that the samples do not fully desegregate after 15 minutes.

Inclusion of Chlorine (Cl)

We studied the effects of including 5% Cl in the samples. In the Cl sample, the percentages of Br and I were tuned so that the λ_1 and λ_2 are the same as that of the double halide perovskites. We found that the 5% Cl sample does not segregate as much in the same amount of time as the 0% Cl sample, as expected. [3] However, the lifetime dynamics of the 0% and 5% Cl samples are different. The 5% sample immediately starts decaying and then plateaus, as expected, while 0% only starts decaying after a longer amount of time.

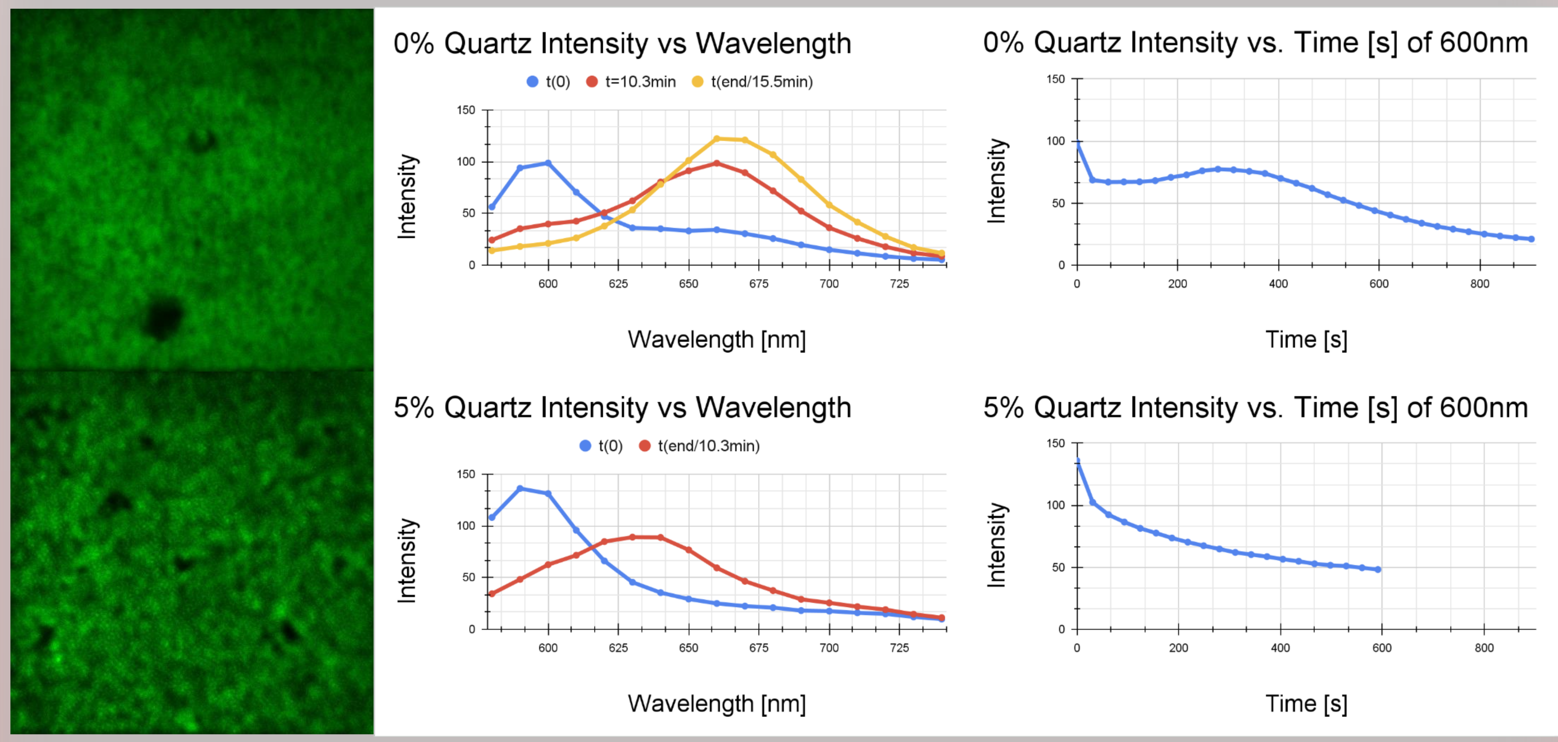

Fig. 7. Right: 0% on top of 5% Cl samples. **Middle:** 0% and 5% Cl intensity vs wavelength graphs with curves corresponding to a different timestep. **Right:** 0% and 5% Cl lifetime graphs, both at λ_1 =600nm.

Future Work

- Comparing SEM and confocal grain sizes in samples with fiducial markers
- Fourier analysis of images to analyze homogeneity
- Further testing on effects of Cl on halide segregation

References

[1] Motti, S. G., *et al.*, "Phase segregation in mixed-halide perovskites affects charge-carrier dynamics while preserving mobility." *Nature Communications*, *12*, (2021).
[2] Liao, Kevin. *Analyzing Halide Segregation in Mixed Halide Perovskites using Confocal Microscopy and Grain Type Classification*. April, 2025. Wesleyan University, BA Thesis.
[3] Xu, Jixian, *et al.*, "Triple-halide wide–band gap perovskites with suppressed phase segregation for efficient tandems." *Science* **367**, 1097-1104 (2020).