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Halide Perovskites Under Repeated Light Exposure Using Confocal Microscopy

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Introduction

Halide perovskites are semiconductor crystals that have the potential to be used in solar cells. Perovskites have an ABX_3 structure. A and B are both positively charged cations, and X is an anion such as iodine. The bandgap of these semiconductor perovskites varies depending on the composition of the anion.

Mixed halide perovskites are perovskites which have a mixed composition of this anion. In our case, this is a composition of iodine, bromine, and chlorine.

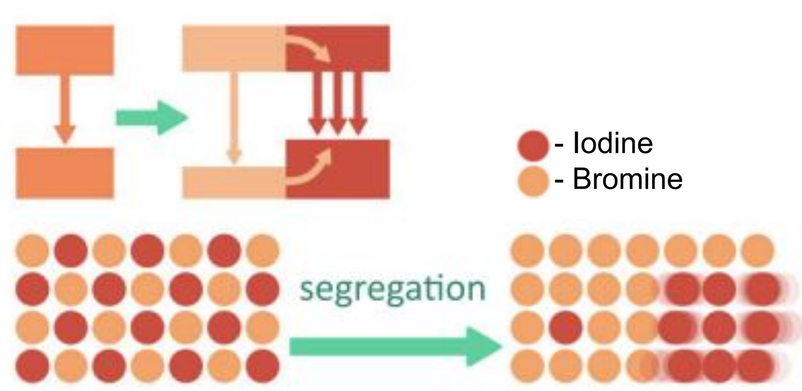


Fig 1. As segregation occurs, iodide-rich regions form, which have a lower bandgap energy. This means more light is emitted at that wavelength. [1]

Under exposure to light, however, mixed halide perovskites segregate, a process where iodine groups together to form distinct regions with a lower-wavelength band gap (about 730-740 nm). If they are then left to rest without light, they will desegregate, a process where the material remixes to its original state.

We use confocal microscopy to measure the intensity of light emitted by different wavelengths over time as the sample is exposed to light. The wavelength at which the sample emits light tells us what the band gap of the sample is in that specific region, allowing us to see segregation occur.

We also use a grainsort technique to sort different regions of the sample using an intensity threshold. Black grains are defects, blue grains are initially well-mixed and do not become iodide-rich, red grains are initially defects and become iodide-rich, and white grains are initially well-mixed and become iodide-rich.

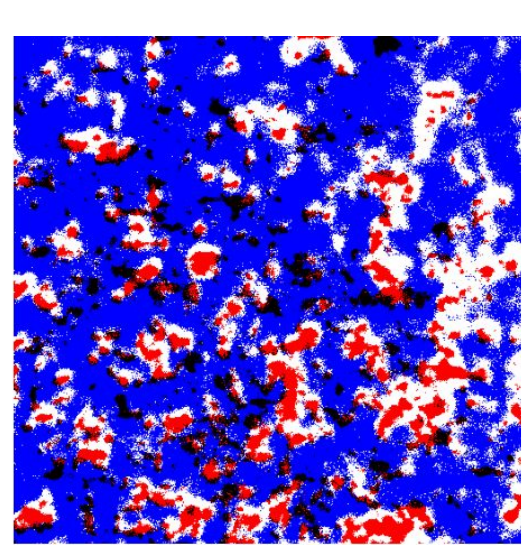


Fig 2. Example of grainsort of $MAPb(IBr_2)_3$ from Kevin's thesis. [2]

Studying these microscopic changes in the material could give insight into why it behaves the way it does, and why on a small scale different regions react differently to light exposure. Understanding this would be a step towards engineering a more stable material that could be used in solar cells.

Experiment

Samples used (both on glass and on quartz substrate):
$MAPb(IBr_2)$ (0% Cl)
$MAPb(I_{0.35}Br_{0.6}Cl_{0.05})_3$ (5% Cl)
$MAPb(I_{0.4}Br_{0.5}Cl_{0.1})_3$ (10% Cl)

Data was collected over a period of several minutes using confocal microscopy, to observe how the sample changes under light. We test for any changes in segregation and sample homogeneity with varying levels of chlorine in the sample, and how desegregation occurs as samples are given intervals between light exposure.

Examples of images from confocal microscope:

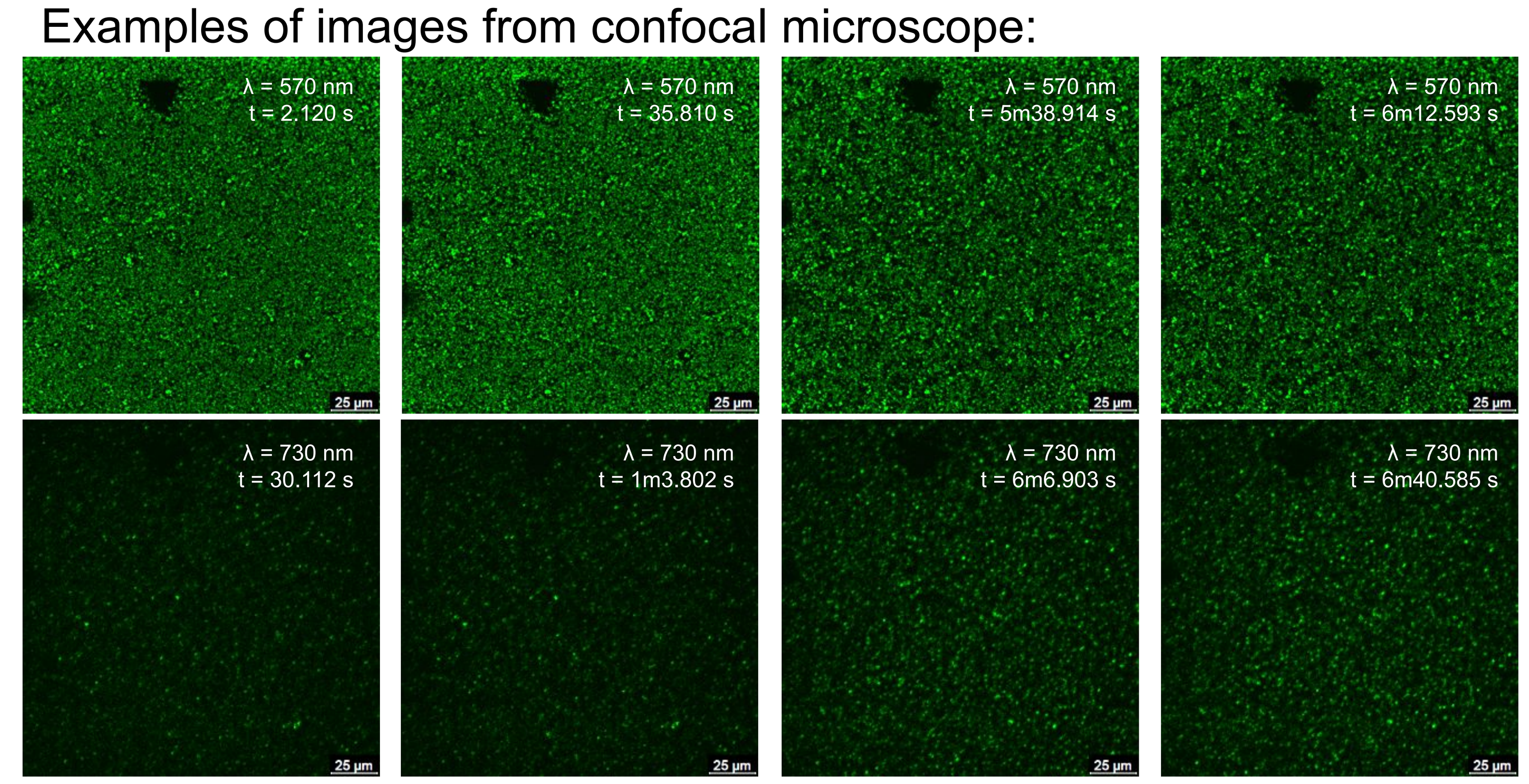


Fig 3. Results from light exposure at low intensity on 0% Cl sample on glass. As time progresses, the 570 nm emissions dim out (not very noticeably here, but this varies depending on the sample), and the 730 nm emission increases as iodine-rich regions form.

These quartz samples exhibited bimodal behavior, where some areas were already iodide-rich as shown:

Therefore, the data used in results was taken from samples on glass.

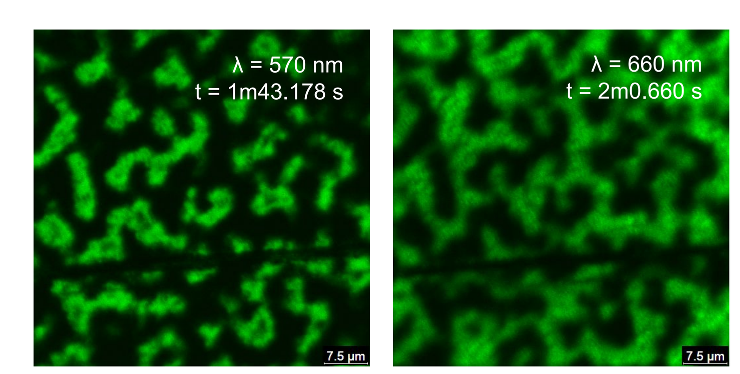


Fig 4. Results from 5% Cl sample on quartz, at approximately the same time. The sample is emitting clear peaks at both wavelengths, in distinct areas.

Results

Comparing results for different Cl compositions:

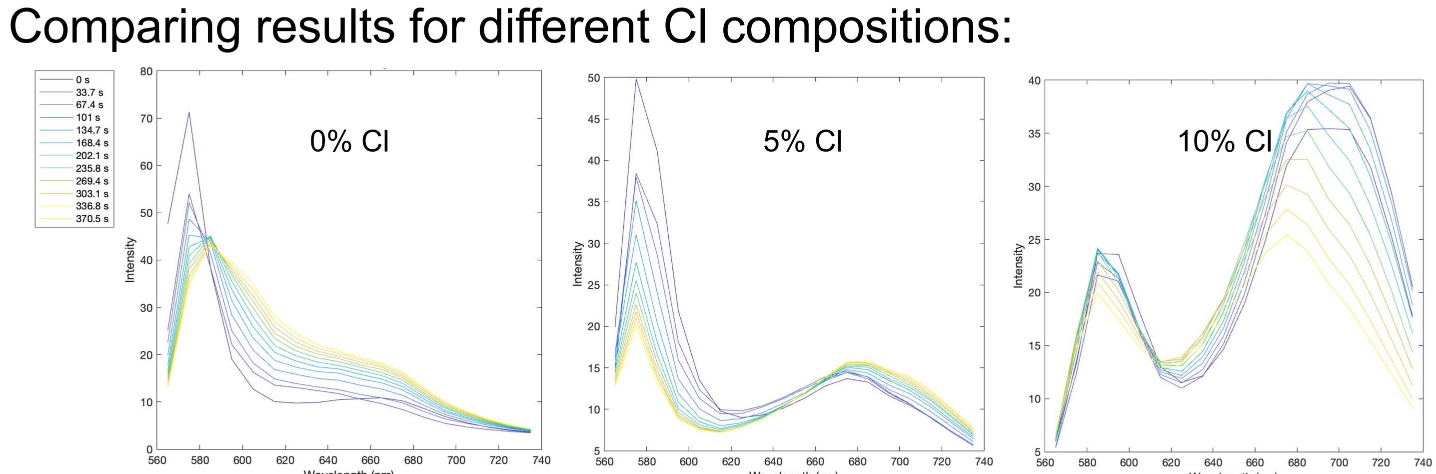


Fig 5. Intensity vs. wavelength for different Cl content in samples. Darker purple indicates initial time, moving in a gradient to yellow as time progresses.

Generally, the higher the Cl content, the faster the sample segregates.

Results

Results for exposing the same 0% Cl sample to light multiple times:

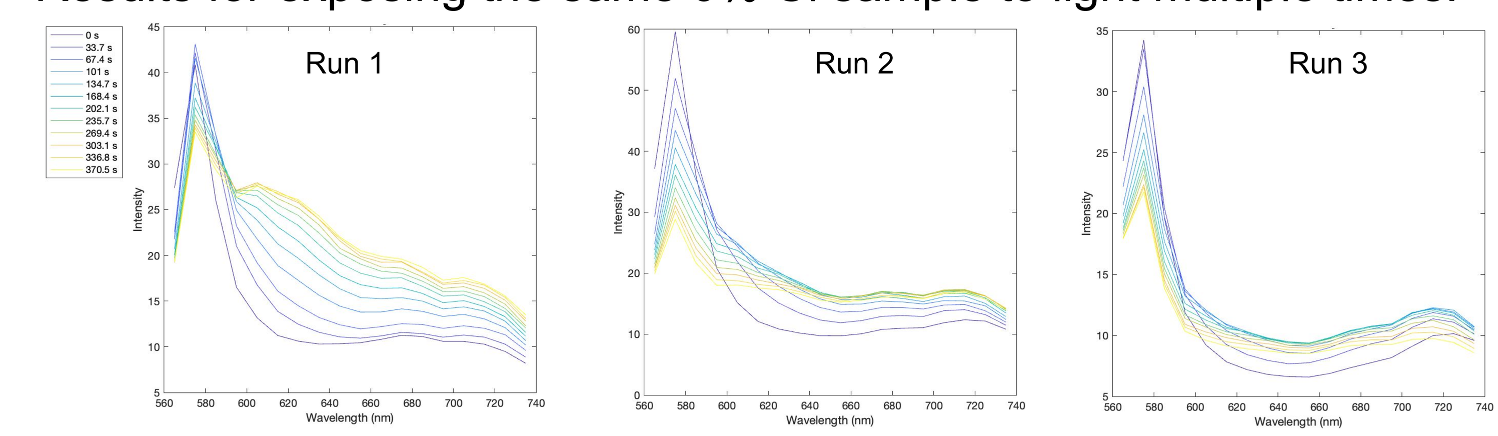


Fig 6. Plots show intensity vs. wavelength for different time steps. Samples were exposed to low-intensity light for about 6 minutes, then given a 12-minute break between each run.

Samples appear to segregate faster upon second exposure. However, they are also very likely to burn out – by the third time they're exposed, the 740 nm channel briefly increases in intensity, then dies out. We can see this in the grain sort as well.

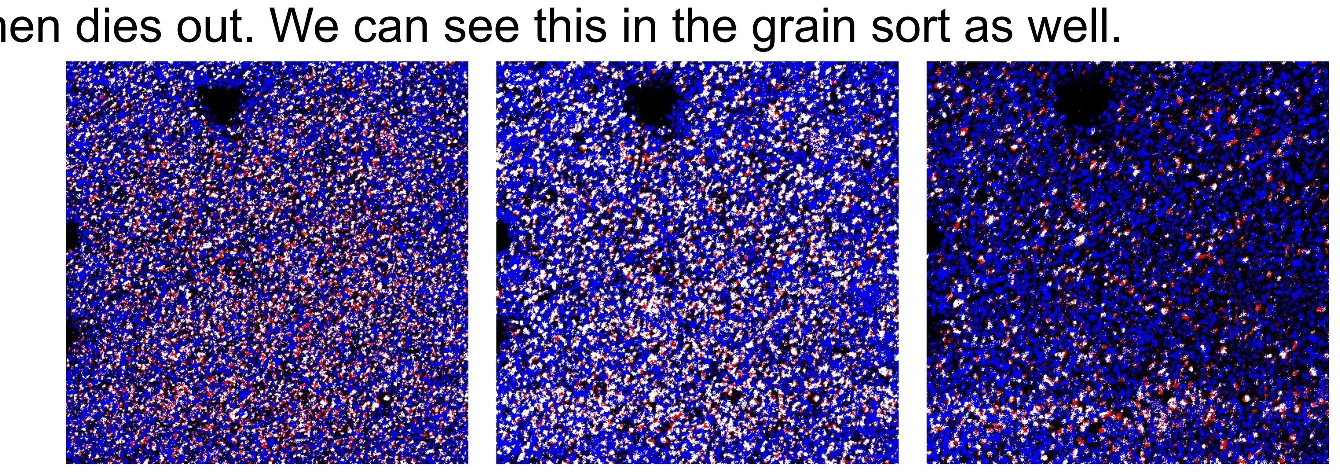
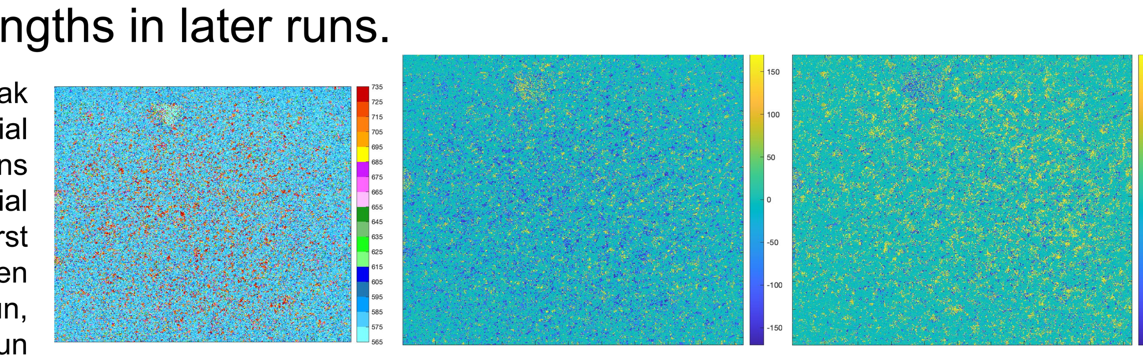


Fig 7. From left to right: 0% Cl first run, second run after 12 minute rest, and third run after 12 minute rest

We can also measure the wavelength value with the highest intensity at each point, for a given time. At the initial timestamp for each run, the change in these values between runs tells us how a sample desegregates. These wavelength values tend to increase between the first and second runs, as shown in the figures below. However, there are also some areas where there is more emission at lower wavelengths in later runs.

Fig 8. Changes in peak wavelength values at initial time between runs From left to right: initial wavelength values for first series; change between first and second run, second and third run



Summary & Future Work

- Samples with a higher concentration of chlorine segregate faster. Samples which are exposed to light in repeated cycles with generally segregate faster in cycles after the first one.
- After segregation, provided a sample is not overexposed, most grains return to their initial wavelength (they are initially well-mixed).
- Future plans: collect more data on cycles at lower intensity, avoiding overexposure as much as possible, and compare confocal data with SEM (scanning electron microscopy).

References

[1] Motti, S. G., Patel, J. B., Oliver, R. D. J., Snaith, H. J., Johnston, M. B., & Herz, L. M.. "Phase segregation in mixed-halide perovskites affects charge-carrier dynamics while preserving mobility." Nature Communications, 12, (2021).
[2] Liao, K.M. "Analyzing Halide Segregation in Mixed Halide Perovskites using Confocal Microscopy and Grain Type Classification" [Thesis, Wesleyan University], (2025).