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How Interplay between Photo and Thermal Activation Dictates Halide Ion Segregation in Mixed Halide Perovskites

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Abstract

The halide ion mobility in mixed halide perovskite exhibits two opposite trends in response to photo and thermal activation. While halides prefer to remain as Br-rich and I-rich domains under steady state light irradiation of MAPbBr_{1.5}I_{1.5} films, they prefer to remain in their stable mixed composition when kept in the dark. The activation energies as determined from the temperature-dependent rate constants are $E_{a,\text{forward}}=28.9 \text{ kJ mol}^{-1}$ for photoinduced segregation and $E_{a,\text{reverse}}=53.5 \text{ kJ mol}^{-1}$ for remixing of halides in dark respectively. The energy input from photoexcitation assists to overcome the dark (thermally activated) mixing to induce Br-rich and I-rich domains. This segregated state is maintained as long as the mixed halide film is irradiated continuously with visible light. The excitation intensity threshold above which segregation occurs follows a linear temperature dependence, such that phase separation occurs above $I_{\text{exc}}=30 \text{ } \mu\text{W/cm}^2$ white light at 23 °C. The threshold at 90 °C becomes higher with minimum intensity requirement of 100 $\mu\text{W/cm}^2$ to induce segregation. The thermodynamic rationale behind this unusual halide mobility under photo and thermal excitation discussed here can aid in understanding the stability issues of perovskite solar cells.

TOC Graphics

Significant strides have been made in recent years to boost the efficiency of metal halide perovskite solar cells.¹⁻⁴ However, challenges remain to develop solar cells that can exhibit operational stability comparable to existing photovoltaic devices. In addition to intrinsic and surface defects, several other properties contribute to their operational instability.⁵ Efforts have been made to employ tri-cation (Cesium (Cs), methyl ammonium (MA) and formamidium (FA)) based perovskite films^{6,7} or surface treatments to improve the stability of perovskite solar cells.⁷⁻¹³

However, an intriguing aspect that influences the solar cell performance is the mobility of halide ions within the perovskite film.¹⁴⁻²¹ In fact, the crystalline liquid like property²² of these materials enables the movement of ions with relative ease. For example, we have recently shown that two different colloidal solutions or physically paired MAPbBr₃ and MAPbI₃ films, when combined, undergo quick exchange of halide ions driven through thermal activation.²³⁻²⁵ The difference in spectral features of bromide and iodide perovskite films enables tracking of the movement of halide ions. The rate of remixing (or homogenization) process increases with increasing temperature, thus suggesting thermally activated process dictating the mixing/exchange of halide ions. Techniques such as emission, impedance spectroscopy, transient capacitance and infrared imaging have proven useful to track the ion mobility in perovskite films.^{16,26-30}

Whereas entropy of mixing explains the thermally activated mixing of halide ions to yield mixed halide perovskite,^{26,31,32} an opposite trend is observed when the mixed halide film is subjected to photoirradiation. This process commonly referred to as *photoinduced phase segregation* or *halide segregation* yields Br-rich and I-rich perovskite domains.³³⁻³⁵ As the mixed halide perovskite phase segregates, the I-rich domains act as recombination sites for the photogenerated charge carriers. The formation of these recombination sites has been shown to limit the performance of halide perovskite-based solar cells.^{15,36,37}

The interesting aspect of halide segregation is its reversibility. We see a total recovery when the film is left in the dark as thermal activation drives the segregated domains back to the original homogenized composition. Several models have been proposed to explain photoinduced segregation of halides. These include; two state model in the excited state, polaron-induced lattice strain, defect-driven halide ion movement and overcoming the thermal activation of mixing with bandgap excitation.^{8,26,34,38-43}

The two different types of halide ion movement, *viz.*, the photoinduced phase segregation and the subsequent recovery process under dark conditions, are summarized through the expressions (reactions 1 and 2):

In other words, the stable geometry without irradiation (i.e. in the dark) is the mixed or homogeneous state while the halide ions prefer to remain segregated under continuous photoirradiation. Note that Reactions 1 and 2 are idealized expressions since the Br:I ratio can vary to create Br-rich and I-rich domains. Since the entropically driven remixing and segregation processes compete under photoirradiation, it is important to establish how photoexcitation overcomes the entropy of mixing and

the driving force behind such unusual activity. In order to obtain insight into these two processes we have now undertaken temperature-dependent studies of segregation and dark recovery kinetics. The kinetic and thermodynamic arguments that explain the photoinduced halide segregation and dark recovery are discussed.

Mixed halide films of $\text{MAPbBr}_{1.5}\text{I}_{1.5}$ were cast on $0.5\ \mu\text{m}$ FTO covered glass slides using static drop casting. A 0.9M solution of 0.45M PbI_2 , 0.45M MAI, 0.45M PbBr_2 and 0.45M MABr was dissolved in 0.9M dimethyl sulfoxide (DMSO), such that a molar ratio of (1:1:1:1) was obtained, which was then mixed with dimethylformamide (DMF) to obtain the precursor solution. The spin coated films on glass slides were subsequently annealed at $65\ ^\circ\text{C}$ on a hotplate for 1 minute followed by immediate annealing at $100\ ^\circ\text{C}$ for 2 minutes to facilitate the nucleation process of adjacent grains. Through XPS analysis it was confirmed that the films had a 1:1 composition of Br and I (See Supporting Information **Figure S1**). A film thickness of 235 nm was determined through cross-sectional SEM (See Supporting Information **Figure S2**). To suppress the atmospheric degradation at elevated temperatures these films were covered with a blank glass slide and clamped with binder clips. The directly synthesized $\text{MAPbBr}_{1.5}\text{I}_{1.5}$ films were found to have somewhat of a segregated composition. To homogenize the films prior to any experiments, the films were left on a hotplate at $100\ ^\circ\text{C}$ for 4 hours. The films were then placed in a spectrophotometer with a Peltier thermal setup and subjected to light/heat treatment. The steady state UV-VIS absorption spectra were recorded to track the photoactivated and thermally activated mobility of halide ions. All experiments where the photoactivated halide ion mobility was probed, a white light source was used to simulate operating conditions. A spectrum of the tungsten halogen lamp employed for photoirradiation can be found in the Supporting Information **Figure S3**.

Photoactivated mobility of halide ions. When the mixed halide perovskite film is subjected to visible light irradiation, we observed a loss of the excitonic peak and increased absorbance in the red region (**Figure 1A**). The difference absorption spectra recorded in **Figure 1B** show these changes with an isosbestic point around 630 nm. This further shows the photoinduced conversion of $\text{MAPbBr}_{1.5}\text{I}_{1.5}$ into Br-rich and I-rich regions confirming the observations as reported in earlier studies.^{26,34,38,39,42} The presence of an isosbestic point between the depletion of mixed halide absorption and iodide rich domain absorption shows the existence of two different forms. With increasing irradiation time, the concentration of segregated forms increases.

The prominent bleach at 616 nm and the induced absorption at 642 nm was tracked to determine the rate of halide segregation (**Reaction 1**). To determine how the light intensity (I_{exc}) changes the segregation rate, a study was carried out where the illumination intensity was varied (**Figure 1C**). Absorption spectra for the additional intensities can be found in Supporting Information **Figure S4**. All kinetic traces were fitted with monoexponential fittings to determine the rate constants.

Figure 1D shows that first order rate constants increase with increasing intensity of excitation. The rate constant increases from $k_{\text{forward}}=0.3\times 10^{-3}\ \text{s}^{-1}$ at $I_{\text{exc}}=20\ \text{mW}/\text{cm}^2$ to $k_{\text{forward}}=1.2\times 10^{-3}\ \text{s}^{-1}$ when the intensity is increased to $I_{\text{exc}}=60\ \text{mW}/\text{cm}^2$. More relevantly, linear behavior of $\ln(k_{\text{forward}})$ versus I_{exc} immediately suggests an exponential dependence of the rate constant with photogenerated carrier density. We can express the forward rate constant for the halide segregation in the form of **Equation 3**,

$$k_{\text{forward}} \propto Ae^{-\left[\frac{-|\Delta E_{\text{light}}| + E_{a,\text{reverse}}}{kT}\right]} \quad (3)$$

where A is a proportionality constant, $E_{a,\text{reverse}}$ is the native activation energy for anion migration and $\Delta E_{\text{light}} \propto I_{\text{exc}}$. ΔE_{light} is ultimately related to carrier density dependent energetic differences in band gaps between iodide rich domains and the parent mixed halide.^{26,43} This energy input (ΔE_{light}) assists in overcoming the energy barrier of remixing ($E_{a,\text{reverse}}$). At a given temperature $\ln(k_{\text{forward}})$ should therefore exhibit a linear dependency with I_{exc} , as corroborated by the data in **Figure 1D**.

Figure 1: Absorbance spectra of MAPbBr_{1.5}I_{1.5} mixed halide perovskite films recorded at different times during the segregation process. All films were held at constant room temperature (23 °C). (A) Segregation of film when photoirradiated with an intensity of $I_{\text{exc}}=40$ mW/cm². (B) Difference absorbance spectra obtained from spectra b-j in (A) with 0 minute spectrum (a) being used as a reference. (C) Tracking of the difference absorption spectra for different intensities ($I_{\text{exc}}=30, 40, 50$ mW/cm²) at the bleach (616 nm) and the induced absorption at 642 nm and monoexponential kinetic fits (solid line). (D) Rate constant dependence with I_{exc} as obtained from monoexponential fits to the data. The solid line is a linear fit to the data.

Many different models have been proposed to explain the halide ion mobility under light irradiation. The defects arising from halide ion vacancies seems to play a role in driving the halide ions away from each other.^{34,40,43-49} The trapping of holes by iodide also plays a role in inducing the halide ion mobility.⁵⁰ As discussed in earlier studies, the intensity threshold observed for photosegregation shows the requirement to overcome the thermodynamic activation barrier for making halide ions move away from each other.^{26,43}

Thermally activated remixing of halide ions. When previously photoirradiated mixed halide films (i.e. halide ion segregated films) were stored in the dark the original mixed halide form was restored thus confirming the mobility of halide ions in the opposite direction (**Reaction 2**). This bidirectional movement of halide ions was similar to our earlier study showing the exchange of Br and I in paired films of MAPbBr₃ and MAPbI₃ films with thermal activation.²⁵ The aim was therefore to study the thermal effect on recovery, using films that had been fully segregated under the same conditions ($I_{\text{exc}}=30 \text{ mW/cm}^2$ at 23 °C). At room temperature, it took 14 hours for pre-segregated mixed halide ion film to recover fully, thus showing the slow mobility of halide ions. However, with increasing temperature one can significantly increase the rate of dark recovery (viz., mixing of halide ions to original mixed halide composition). For example, when the photosegregated halide film was kept in the dark at 80 °C, it took just 20 minutes for the film to recover and attain the original mixed halide composition. **Figures 2 (A-D)**

Figure 2: Absorbance spectra of MAPbBr_{1.5}I_{1.5} mixed halide perovskite films recorded at different timepoints of the recovery process. (A, B) Recovery of pre-segregated films when recovered at room temperature (23 °C) and when subjected to 80 °C. (C, D) Difference absorbance spectra obtained from (A, B) showing the reversible recovery process until their initial position is attained. The absorbance spectra of the original MAPbBr_{1.5}I_{1.5} film (before subjecting it to photoirradiation) is used as reference.

show dark recovery of the pre-photo-segregated films at 23 °C and 80 °C.

The difference spectra were recorded using the absorbance spectra of the original MAPbBr_{1.5}I_{1.5} film (before subjecting it to photoirradiation) as reference. Thus, the spectra *a* in **Figures 2C** and **2D** correspond to the segregated halide ion state (i.e. immediately after stopping the photoirradiation). With increasing time, the recovery shows a trend that is opposite to the one observed during the photoirradiation. The presence of an isosbestic point (**Figures 2C** and **2D**) at both these temperatures confirm that the recovery represents the existence of two states (viz: segregated and mixed halide composition) and the concentration of these domains are decreased with increasing time of dark recovery.

To study the thermal effect on the rate of dark recovery, difference absorbance spectra for all the recorded temperatures were monitored at the two peak positions. **Figure 3A** shows the tracked recovery of the absorption at 620 nm and induced absorption at 650 nm for 23 °C, 70 °C and 80 °C. It is evident that rate of recovery significantly increases as the temperature is increased. The time required for the films to fully recover is shown in **Figure 3B**. This temperature dependent dark recovery shows the importance of thermal activation in inducing the mobility of halide ions, thus reversing the trend observed during photoirradiation. All traces in **Figure 3A** together with the additional temperatures (See Supporting Information **Figure S5**), were fit to monoexponential decays to determine pseudo first order rate constants for the dark recovery. This dependence on temperature was further analyzed through the Arrhenius expression

$$\ln(k_{\text{reverse}}) = -E_{\text{a,reverse}}/RT + \ln(A) \quad (4)$$

where A is a preexponential constant. The plot of $\ln(k_{\text{reverse}})$ versus inverse temperature shown in **Figure 3C** exhibits a linear relationship. The activation energy corresponding to **Reaction 2**, as determined from

the slope of the plot, is $E_{a, \text{reverse}} = 53.5 \pm 3.8 \text{ kJ mol}^{-1}$. This value is similar to the activation energy ($E_a = 50.7 \text{ kJ mol}^{-1}$) that was determined from the exchange of halide ions between physically paired of MAPbBr_3 and MAPbI_3 films, which we recently showed.²⁵

These results show the thermodynamic activation barrier for observing mobility of halide ions in perovskite films. As discussed earlier, the entropy of mixing plays an important role in attaining the mixed halide composition with an energy of activation of $E_{a, \text{reverse}} = 53.5 \text{ kJ mol}^{-1}$. This estimate of activation energy differs from the value 28 kJ mol^{-1} (0.29 eV) obtained for iodide diffusion from the transient capacitance measurements. The activation energy obtained in the present study is a direct estimate observed through both Br^- and I^- ion diffusion and agrees well with the estimate of 59 kJ mol^{-1} (or 0.62 eV) observed with photocurrent measurements⁵¹ and 50.7 kJ mol^{-1} obtained with halide ion exchange between two pressed films.²⁵

Halide ion mobility under combined photo and thermal activation. The experiments described above highlight the two competing reactions presented in **Reaction 1** and **2** for photoactivated and thermally activated halide ion mobility. Under photoexcitation the bromide and iodide prefer to remain separate as iodide rich and bromide rich domains, while in dark they prefer to stay together with homogenized or mixed halide composition. The obvious question is how combined photo and thermal effects influence the entropically-driven remixing. Again, mixed halide $\text{MAPbBr}_{1.5}\text{I}_{1.5}$ films were prepared as described in

the Supporting Information, and then subjected to photoirradiation (constant intensity of $I_{\text{exc}}=20$ mW/cm²) at different temperatures. The results are shown in **Figure 4**.

Figure 4A shows the difference absorption spectra recorded during photoirradiation of MAPbBr_{1.5}I_{1.5} at 100 °C. Similar experiments were carried out at different temperatures (See Supporting Information **Figure S6**), and the absorbance change monitored at 620 and 650 nm were recorded. **Figure 4B** shows kinetic traces of halide ion segregation observed at 23 °C, 60 °C, and 100 °C. Here it is evident that k_{forward} increases with increasing temperature in agreement with **Equation 3**.

Figure 4: Absorbance spectra of MAPbBr_{1.5}I_{1.5} mixed halide perovskite under constant photoirradiation ($I_{\text{exc}}=20$ mW/cm²) when held at elevated temperatures. (A) Difference absorbance spectra acquired at interval timepoints when held at 100 °C. (B) Tracking of the segregation evolution for different annealing temperatures (23 °C, 60 °C, and 100 °C) at the bleach (620 nm) and the induced absorption at 650 nm. Traces shown in solid lines are monoexponential decay kinetics fits. (C) Arrhenius plot of natural log of the rate constants versus the inverse of temperature, with the average rate constants for the bleach and induced absorption extracted from monoexponential fits of (B).

This k_{forward} dependence on temperature is attributed to the light energy that mobilizes the halide ions, which then have a lower activation barrier causing I-rich and Br-rich domains to form faster. All traces (23 °C, 60 °C, and 100 °C) in **Figure 4B**, together with 40 °C and 80 °C shown in the Supporting Information, were fitted to monoexponential decay to determine the rate constants (k_{forward}). Using these average rate constants for the bleach and induced absorption, the Arrhenius plot of $\ln(k_{\text{forward}})$ versus inverse temperature in **Figure 4C** shows a linear relationship. The effective activation energy determined from the slope of this linear fit is $E_{a,\text{forward}} = 28.9 \pm 1.1$ kJ mol⁻¹, which is lower than that determined for the homogenization of mixed halide perovskite films ($E_{a,\text{reverse}}$). This lower activation energy of photosegregation overcomes the larger activation barrier of thermal mixing and thus favors halide ion segregation. Further work is therefore required to develop effective ways of increasing the activation energy related to photosegregation at high intensities. Attempts have been made to retard the phase segregation by improving crystallinity and grain size, while surface treatments using an electron-donating ligand such as trioctylphosphine oxide have been reported to significantly reduce the onset of the halide segregation in mixed halide perovskite.^{8,17,34,43}

Excitation intensity threshold for light-induced halide segregation

As discussed above, light-induced halide segregation is not suppressed even at temperatures up to 100 °C for I_{exc} values above $I_{\text{exc}}=20 \text{ mW/cm}^2$. It was therefore necessary to significantly lower the excitation intensity to establish an equilibrium between **Reactions 1 and 2**. Here, prior studies of light-induced halide phase segregation have suggested an excitation intensity threshold ($I_{\text{exc,threshold}}$) of order $I_{\text{exc,threshold}} \sim 100 \text{ } \mu\text{W/cm}^2$ for light-induced halide segregation.^{26,43} **Figure 5** shows recorded absorption spectra of MAPbBr_{1.5}I_{1.5} films subjected to (broadband white light) I_{exc} -values of 30 $\mu\text{W/cm}^2$ and 100 $\mu\text{W/cm}^2$ at 23 °C and 90 °C respectively (**Figure 5A**: $I_{\text{exc}}=30 \text{ } \mu\text{W/cm}^2$ and 23 °C; **Figure 5B**: $I_{\text{exc}}=100 \text{ } \mu\text{W/cm}^2$ and 90 °C). Absorption spectra were recorded over 10 hours of continuous illumination to establish whether any segregation occurred at these low intensities. In both cases, the data show virtually no change of MAPbBr_{1.5}I_{1.5} absorption spectra, suggesting the suppression of halide phase segregation. **Figures 5C and 5D** show difference absorption spectra for the two cases, corroborating the claim.

Increasing I_{exc} above 30 $\mu\text{W/cm}^2$ at 23 °C, however, leads to slow phase segregation. Data acquired at $I_{\text{exc}}=40 \text{ } \mu\text{W/cm}^2$ and 80 $\mu\text{W/cm}^2$ are shown in **Figure S7**. An excitation intensity threshold of $I_{\text{exc,threshold}} \approx 30 \text{ } \mu\text{W/cm}^2$ is therefore established at 23 °C with a time of exposure of 10 hours.

Identical experiments conducted at 90 °C reveal an elevated intensity threshold value of $I_{\text{exc,threshold}} \approx 100 \text{ } \mu\text{W/cm}^2$. In fact, by conducting experiments at different temperatures between 23 °C and 90 °C (**Figure S8**), we find a linear dependency of $I_{\text{exc,threshold}}$ with T . **Figure 6** summarizes observed temperature-dependent $I_{\text{exc,threshold}}$ -values and indicates I_{exc} -values above (below) which induce (suppress) light-induced halide segregation at a given temperature. This is analogous and complementary to a photostability phase diagram linking I_{exc} and carrier diffusion lengths previously found for MAPb(Br_xI_x)₃ thin films.²⁶

The results in **Figure 6** are important to developing a microscopic understanding of light-induced halide phase segregation. Namely, existence of an excitation intensity threshold for phase segregation argues against a polaron strain model.³² Such phenomenon has no intensity threshold for observing segregation. Moreover, the linear temperature dependency of $I_{\text{exc,threshold}}$ qualitatively agrees with the microscopic model developed earlier.⁴³ The underlying concept is that the additional energy from photogenerated carriers in the perovskite film influence ion migration dynamics. By balancing phase segregation and dark recovery probabilities, one finds the following expression (**Equation 5**) for excitation intensity threshold to observe halide segregation,

Figure 5: Absorbance spectra of MAPbBr_{1.5}I_{1.5} mixed halide perovskite films held at different temperature and intensity pairs over the course of ten hours, (A) 23 °C and $I_{\text{exc}}=30 \mu\text{W}/\text{cm}^2$, and (B) 90 °C and $I_{\text{exc}}=100 \mu\text{W}/\text{cm}^2$. (C,D) Corresponding difference absorbance spectra obtained from (A,B) where the 0 minute spectrum has been subtracted from all spectra recorded at different times.

Figure 6: $I_{\text{exc, threshold}}$ as a function of temperature for observing halide ion segregation in MAPbBr_{1.5}I_{1.5} mixed halide perovskite films. Below the recorded $I_{\text{exc, threshold}}$ for each temperature, no halide ion segregation of the films could be observed.

$$I_{\text{exc,threshold}} = \left(\frac{kT^*}{\Delta E_{\text{g,domain}}} \right) \left(\frac{h\nu}{\alpha} \right) \left(\frac{1}{\tau V_{\text{e/h}}} \right) \quad (5)$$

where $\Delta E_{\text{g,domain}}$ is an energy associated with exchanging Br^- with I^- within phase segregated domains, $h\nu$ is the excitation energy, α is the perovskite absorption coefficient, τ is the carrier lifetime, and $V_{\text{e/h}}$ is a geometrical volume linked to carrier diffusion lengths. T^* is an effective temperature, which differs from the absolute system temperature T , through inclusion of attractive/repulsive interactions between I^- and Br^- underlying $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)$'s mixing enthalpy. Most relevant about **Equation 5** is that it predicts a linear T -dependency of $I_{\text{exc,threshold}}$, assuming that carrier diffusion lengths remain constant in the film. Furthermore, using nominal values of $\Delta E_{\text{g,domain}} \approx 3.6$ meV/atom,⁴³ $h\nu = 3$ eV, $kT = 25$ meV, $\alpha = 10^5$ cm⁻¹, $\tau = 100$ ns²⁶ and $V_{\text{e/h}} = 4.2 \times 10^{-12}$ cm³ (associated carrier diffusion length of $l_{\text{e/h}} \approx 1$ μm) we find a room temperature intensity threshold of 80 $\mu\text{W}/\text{cm}^2$. This value is in good agreement with the experimental values found here as well with previous emission measurements using diode laser excitation^{26,43}

To summarize, three separate sets of experiments were conducted to elucidate the kinetics and thermodynamic driving force responsible for photoinduced segregation in $\text{MAPbBr}_{1.5}\text{I}_{1.5}$ mixed halide perovskite films. First, the photoactivated halide ion mobility was probed by illuminating the samples with different intensities at 23 °C. This was done to determine k_{forward} values, which were found to increase from $k_{\text{forward}} = 0.3 \times 10^{-3}$ s⁻¹ at $I_{\text{exc}} = 20$ mW/cm² to $k_{\text{forward}} = 1.2 \times 10^{-3}$ s⁻¹ at $I_{\text{exc}} = 60$ mW/cm². Second, k_{reverse} was probed by subjecting pre-segregated films to elevated temperatures to increase the rate of dark recovery. It was found, that as the annealing temperature increased, the rate of halide diffusion increased following an Arrhenius relationship with an activation energy of $E_{\text{a,reverse}} = 53$ kJ mol⁻¹. Third, $\text{MAPbBr}_{1.5}\text{I}_{1.5}$ films were subjected to both photoexcitation and heat treatment to determine the rate of segregation. Here the illumination intensity of $I_{\text{exc}} = 20$ mW/cm² was held constant while the temperature was varied. This study found that as the temperature was increased, k_{forward} increased following an Arrhenius relationship with an effective activation energy of $E_{\text{a,forward}} = 29$ kJ mol⁻¹. This lower activation energy of the photoactivated segregation enables perovskite films to overcome the entropically driven mixing and create Br-rich and I-rich domains. The halide segregation prevails as long as the mixed halide film is irradiated continuously with visible light. When the intensity was lowered to establish equilibrium between the two competing reactions, our study found that the intensity had to be significantly decreased. Excitation intensity thresholds of $I_{\text{exc,threshold}} = 30$ $\mu\text{W}/\text{cm}^2$ and $I_{\text{exc,threshold}} = 100$ $\mu\text{W}/\text{cm}^2$ were established for $T = 23$ °C and $T = 90$ °C respectively. Moreover, $I_{\text{exc,threshold}}$ was found to follow a linear temperature dependence in qualitative agreement with a microscopic model for phase segregation, thus confirming the interplay between thermally driven mixing and photodriven segregation of bromide and iodide ions.

The results presented here provide an insight into photo and thermal activation of halide ion mobility in $\text{MAPbBr}_{3-x}\text{I}_x$ films. The study provides the foundation for new and exciting ways of studying the segregation mechanism and thus develop ways to control segregation, thus contributing to the development of high-performance mixed halide perovskites, which can be used for next generation tandem solar cells.

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Supporting Information: The supporting information contains synthetic and annealing procedures, and experimental procedures (UV-Vis absorbance, SEM, and XPS) and the detailed results on the absorption and XPS measurements.

References.

1. Ono, L. K.; Qi, Y.; Liu, S. Progress toward Stable Lead Halide Perovskite Solar Cells, *Joule* **2018**, 2, 1961-1990.
2. Nayak, P. K.; Mahesh, S.; Snaith, H. J.; Cahen, D. Photovoltaic solar cell technologies: analysing the state of the art, *Nature Reviews Materials* **2019**, 4, 269-285.
3. Jena, A. K.; Kulkarni, A.; Miyasaka, T. Halide Perovskite Photovoltaics: Background, Status, and Future Prospects, *Chemical Reviews* **2019**, 119, 3036-3103.
4. Tai, Q.; Tang, K.-C.; Yan, F. Recent progress of inorganic perovskite solar cells, *Energy & Environmental Science* **2019**, 12, 2375-2405.
5. Zhang, F.; Bi, D.; Pellet, N.; Xiao, C.; Li, Z.; Berry, J. J.; Zakeeruddin, S. M.; Zhu, K.; Grätzel, M. Suppressing defects through the synergistic effect of a Lewis base and a Lewis acid for highly efficient and stable perovskite solar cells, *Energy & Environmental Science* **2018**, 11, 3480-3490.
6. Saliba, M., et al. Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency, *Energy & Environmental Science* **2016**, 9, 1989-1997.
7. Dang, H. X., et al. Multi-cation Synergy Suppresses Phase Segregation in Mixed-Halide Perovskites, *Joule* **2019**, 3, 1746-1764.
8. Belisle, R. A.; Bush, K. A.; Bertoluzzi, L.; Gold-Parker, A.; Toney, M. F.; McGehee, M. D. Impact of Surfaces on Photoinduced Halide Segregation in Mixed-Halide Perovskites, *ACS Energy Letters* **2018**, 3, 2694-2700.
9. Luan, J.; Xu, J.; Chen, J.; Shi, X.; Zhang, B.; Dai, S.; Yao, J. Efficient Planar CH₃NH₃PbBr₃ Perovskite Solar Cells Prepared at Room Temperature with Ionic-Liquids/Fullerene as an Electron Transport Bilayer, *Journal of Solid State Chemistry* **2019**, 270, 436-442.
10. Schulz, P.; Cahen, D.; Kahn, A. Halide Perovskites: Is It All about the Interfaces?, *Chemical Reviews* **2019**, 119, 3349-3417.
11. Boyd, C. C.; Cheacharoen, R.; Leijtens, T.; McGehee, M. D. Understanding Degradation Mechanisms and Improving Stability of Perovskite Photovoltaics, *Chemical Reviews* **2019**, 119, 3418-3451.
12. Christians, J. A.; Schulz, P.; Tinkham, J. S.; Schloemer, T. H.; Harvey, S. P.; Tremolet de Villers, B. J.; Sellinger, A.; Berry, J. J.; Luther, J. M. Tailored interfaces of unencapsulated perovskite solar cells for >1,000 hour operational stability, *Nature Energy* **2018**, 3, 68-74.
13. Berhe, T. A., et al. Organometal halide perovskite solar cells: degradation and stability, *Energy & Environmental Science* **2016**, 9, 323-356.
14. Yuan, Y.; Huang, J. Ion Migration in Organometal Trihalide Perovskite and Its Impact on Photovoltaic Efficiency and Stability, *Accounts of Chemical Research* **2016**, 49, 286-293.
15. Samu, G. F.; Janáky, C.; Kamat, P. V. A Victim of Halide Ion Segregation. How Light Soaking Affects Solar Cell Performance of Mixed Halide Lead Perovskites, *ACS Energy Letters* **2017**, 2, 1860-1861.
16. Peng, W.; Aranda, C.; Bakr, O. M.; Garcia-Belmonte, G.; Bisquert, J.; Guerrero, A. Quantification of Ionic Diffusion in Lead Halide Perovskite Single Crystals, *ACS Energy Letters* **2018**, 3, 1477-1481.
17. Gualdrón-Reyes, A. F.; Yoon, S. J.; Barea, E. M.; Agouram, S.; Muñoz-Sanjosed, V.; Meléndez, Á. M.; Niño-Gómez, M. E.; Mora-Seró, I. Controlling the Phase Segregation in Mixed Halide Perovskites through Nanocrystal Size, *ACS Energy Letters* **2019**, 4, 54-62.
18. Vashishtha, P.; Halpert, J. E. Field-Driven Ion Migration and Color Instability in Red-Emitting Mixed Halide Perovskite Nanocrystal Light-Emitting Diodes, *Chemistry of Materials* **2017**, 29, 5965-5973.
19. Gualdrón-Reyes, A. F.; Yoon, S. J.; Mora-Seró, I. Recent insights for achieving mixed halide perovskites without halide segregation, *Current Opinion in Electrochemistry* **2018**, 11, 84-90.
20. Shao, Y., et al. Grain boundary dominated ion migration in polycrystalline organic-inorganic halide perovskite films, *Energy & Environmental Science* **2016**, 9, 1752-1759.

21. Yang, B., et al. Enhancing Ion Migration in Grain Boundaries of Hybrid Organic–Inorganic Perovskites by Chlorine, *Advanced Functional Materials* **2017**, 27, 1700749.
22. Miyata, K.; Atallah, T. L.; Zhu, X.-Y. Lead halide perovskites: Crystal-liquid duality, phonon glass electron crystals, and large polaron formation, *Science Advances* **2017**, 3, e1701469.
23. Akkerman, Q. A.; D’Innocenzo, V.; Accornero, S.; Scarpellini, A.; Petrozza, A.; Prato, M.; Manna, L. Tuning the Optical Properties of Cesium Lead Halide Perovskite Nanocrystals by Anion Exchange Reactions, *Journal of the American Chemical Society* **2015**, 137, 10276-10281.
24. Ravi, V. K.; Scheidt, R. A.; Nag, A.; Kuno, M.; Kamat, P. V. To Exchange or Not to Exchange. Suppressing Anion Exchange in Cesium Lead Halide Perovskites with PbSO₄–Oleate Capping, *ACS Energy Letters* **2018**, 3, 1049-1055.
25. Elmelund, T.; Scheidt, R. A.; Seger, B.; Kamat, P. V. Bidirectional Halide Ion Exchange in Paired Lead Halide Perovskite Films with Thermal Activation, *ACS Energy Letters* **2019**, 4, 1961-1969.
26. Draguta, S.; Sharia, O.; Yoon, S. J.; Brennan, M. C.; Morozov, Y. V.; Manser, J. M.; Kamat, P. V.; Schneider, W. F.; Kuno, M. Rationalizing the Light-Induced Phase Separation of Mixed Halide Organic-Inorganic Perovskites, *Nature Communications* **2018**, 8, Article No. 200 (DOI: 10.1038/s41467-017-00284-2).
27. Knight, A. J.; Wright, A. D.; Patel, J. B.; McMeekin, D. P.; Snaith, H. J.; Johnston, M. B.; Herz, L. M. Electronic Traps and Phase Segregation in Lead Mixed-Halide Perovskite, *ACS Energy Letters* **2019**, 4, 75-84.
28. Futscher, M. H.; Lee, J. M.; McGovern, L.; Muscarella, L. A.; Wang, T. Y.; Haider, M. I.; Fakharuddin, A.; Schmidt-Mende, L.; Ehrler, B. Quantification of Ion Migration in CH₃NH₃PbI₃ Perovskite Solar Cells by Transient Capacitance Measurements, *Materials Horizons* **2019**, 6, 1497-1503.
29. Chatterjee, R.; Pavlovets, I. M.; Aleshire, K.; Hartland, G. V.; Kuno, M. Subdiffraction Infrared Imaging of Mixed Cation Perovskites: Probing Local Cation Heterogeneities, *ACS Energy Letters* **2018**, 3, 469-475.
30. Tang, X.; van den Berg, M.; Gu, E.; Horneber, A.; Matt, G. J.; Osvet, A.; Meixner, A. J.; Zhang, D.; Brabec, C. J. Local Observation of Phase Segregation in Mixed-Halide Perovskite, *Nano Letters* **2018**, 18, 2172-2178.
31. Brivio, F.; Caetano, C.; Walsh, A. Thermodynamic Origin of Photoinstability in the CH₃NH₃Pb(I_{1-x}Br_x)₃ Hybrid Halide Perovskite Alloy, *The Journal of Physical Chemistry Letters* **2016**, 7, 1083-1087.
32. Bischak, C. G.; Hetherington, C. L.; Wu, H.; Aloni, S.; Ogletree, D. F.; Limmer, D. T.; Ginsberg, N. S. Origin of Reversible Photoinduced Phase Separation in Hybrid Perovskites, *Nano Letters* **2017**, 17, 1028-1033.
33. Hoke, E. T.; Slotcavage, D. J.; Dohner, E. R.; Bowring, A. R.; Karunadasa, H. I.; McGehee, M. D. Reversible Photoinduced Trap Formation in Mixed-Halide Hybrid Perovskites for Photovoltaics, *Chemical Science* **2015**, 6, 613-617.
34. Yoon, S. J.; Kuno, M.; Kamat, P. V. Shift Happens. How Halide Ion Defects Influence Photoinduced Segregation in Mixed Halide Perovskites, *ACS Energy Letters* **2017**, 2, 1507–1514.
35. Brennan, M. C.; Draguta, S.; Kamat, P. V.; Kuno, M. Light-Induced Anion Phase Segregation in Mixed Halide Perovskites, *ACS Energy Letters* **2018**, 3, 204-213.
36. Unger, E. L.; Kegelman, L.; Suchan, K.; Sörell, D.; Korte, L.; Albrecht, S. Roadmap and roadblocks for the band gap tunability of metal halide perovskites, *Journal of Materials Chemistry A* **2017**, 5, 11401-11409.
37. Balakrishna, R. G.; Kobosko, S. M.; Kamat, P. V. Mixed Halide Perovskite Solar Cells. Consequence of Iodide Treatment on Phase Segregation Recovery, *ACS Energy Letters* **2018**, 3, 2267-2272.

38. Yoon, S. J.; Draguta, S.; Manser, J. S.; Sharia, O.; Schneider, W. F.; Kuno, M.; Kamat, P. V. Tracking Iodide and Bromide Ion Segregation in Mixed Halide Lead Perovskites during Photoirradiation, *ACS Energy Letters* **2016**, 1, 290-296.
39. Bischak, C. G.; Wong, A. B.; Lin, E.; Limmer, D. T.; Yang, P.; Ginsberg, N. S. Tunable Polaron Distortions Control the Extent of Halide Demixing in Lead Halide Perovskites, *The Journal of Physical Chemistry Letters* **2018**, 9, 3998-4005.
40. Azpiroz, J. M.; Mosconi, E.; Bisquert, J.; De Angelis, F. Defect migration in methylammonium lead iodide and its role in perovskite solar cell operation, *Energy & Environmental Science* **2015**, 8, 2118-2127.
41. Barker, A. J., et al. Defect-Assisted Photoinduced Halide Segregation in Mixed-Halide Perovskite Thin Films, *ACS Energy Letters* **2017**, 2, 1416–1424.
42. Slotcavage, D. J.; Karunadasa, H. I.; McGehee, M. D. Light-Induced Phase Segregation in Halide-Perovskite Absorbers, *ACS Energy Letters* **2016**, 1, 1199-1205.
43. Ruth, A.; Brennan, M. C.; Draguta, S.; Morozov, Y. V.; Zhukovskyi, M.; Janko, B.; Zapol, P.; Kuno, M. Vacancy-Mediated Anion Photo-segregation Kinetics in Mixed Halide Hybrid Perovskites: Coupled Kinetic Monte Carlo and Optical Measurements, *ACS Energy Letters* **2018**, 3, 2321-2328.
44. Motti, S. G.; Meggiolaro, D.; Martani, S.; Sorrentino, R.; Barker, A. J.; De Angelis, F.; Petrozza, A. Defect Activity in Metal–Halide Perovskites, *Advanced Materials* **2019**, Art. no.1901183.
45. Motti, S. G., et al. Controlling Competing Photochemical Reactions Stabilizes Perovskite Solar Cells, *Nature Photonics* **2019**, 13, doi: 10.1038/s41566-019-0435-1.
46. Yang, W. S., et al. Iodide Management in Formamidinium-Lead-Halide–Based Perovskite Layers for Efficient Solar Cells, *Science* **2017**, 356, 1376-1379.
47. Li, C.; Guerrero, A.; Huettnner, S.; Bisquert, J. Unravelling the role of vacancies in lead halide perovskite through electrical switching of photoluminescence, *Nature Communications* **2018**, 9, 5113.
48. Walsh, A.; Stranks, S. D. Taking Control of Ion Transport in Halide Perovskite Solar Cells, *ACS Energy Letters* **2018**, 3, 1983-1990.
49. Wieghold, S., et al. Halide heterogeneity affects local charge carrier dynamics in mixed-ion lead perovskite thin films, *Chemistry of Materials* **2019**, 31, 3712-3721.
50. Samu, G. F.; Balog, Á.; De Angelis, F.; Meggiolaro, D.; Kamat, P. V.; Janáky, C. Electrochemical Hole Injection Selectively Expels Iodide from Mixed Halide Perovskite Films, *Journal of the American Chemical Society* **2019**, 141, 10812-10820.
51. Eames, C.; Frost, J. M.; Barnes, P. R. F.; O'Regan, B. C.; Walsh, A.; Islam, M. S. Ionic Transport in Hybrid Lead Iodide Perovskite Solar Cells, *Nat Commun* **2015**, 6, Article No. 8497