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Effect of Light-Induced Halide Segregation on the Performance of Mixed-Halide Perovskite Solar Cells

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ABSTRACT: Light-induced halide segregation hampers obtaining stable wide-bandgap solar cells based on mixed iodide–bromide perovskites. So far, the effect of prolonged illumination on the performance of mixed-halide perovskite solar cells has not been studied in detail. It is often assumed that halide segregation leads to a loss of open-circuit voltage. By simultaneously recording changes in photoluminescence and solar cell performance under prolonged illumination, we demonstrate that cells instead deteriorate by a loss of short-circuit current density and that the open-circuit voltage is less affected. The concurrent red shift, increased lifetime, and higher quantum yield of photoluminescence point to the formation of relatively emissive iodide-rich domains under illumination. Kinetic Monte Carlo simulations provide an atomistic insight into their formation via exchange of bromide and iodide, mediated by halide vacancies. Localization of photogenerated charge carriers in low-energy iodide-rich domains and subsequent recombination cause reduced photocurrent and red-shifted photoluminescence. The loss in photovoltaic performance is diminished by partially replacing organic cations by cesium ions. Ultrasensitive photocurrent spectroscopy shows that cesium ions result in a lower density of sub-band-gap defects and suppress defect growth under illumination. These defects are expected to play a role in the development and recovery of light-induced compositional changes.

KEYWORDS: perovskite, halide segregation, solar cells, photoluminescence, kinetic Monte Carlo simulations, stability

1. INTRODUCTION

Metal halide perovskites containing bromide and iodide are uniquely suited as a top-cell absorber in multijunction solar cells because of their widely tunable optical band gap (∼1.5–2.3 eV).1–6 However, light-induced segregation of iodide and bromide ions in mixed-halide perovskites impedes their stability.7,8 This effect was first identified from a red shift of the photoluminescence (PL) spectrum when mixed iodide–bromide perovskites containing over ∼20% bromide ions were illuminated,9 and results from the formation of narrow-bandgap iodide-rich domains. X-ray diffraction (XRD) showed simultaneously broadening of Bragg peaks and the development of additional peaks at lower diffraction angles, confirming the formation of iodide-rich perovskite domains. Likewise, a red shift of the absorption onset and an increase in Urbach energy ($E_u$) denote the formation of iodide-rich domains under light-induced stress.10,11 Moreover, there is experimental evidence of vertical halide stratification through the thickness of perovskite films as the process of demixing unfolds, due to the migration of ionic species and defects along the light intensity gradient.11–13

The thermodynamically driven segregation into iodide- and bromide-rich phases under illumination is a consequence of reduced free energy when photogenerated charge carriers localize in low-energy iodide-rich clusters,14 likely facilitated by exchange of iodide and bromide ions via defects, e.g., in the form of halide vacancies. In fact, experimental work demonstrated the interaction of charge carriers with mobile ions and point defects, causing demixed-halide regions to localize at grain boundaries.10,11,15,16 The PL spectrum and XRD pattern of the perovskite slowly and partly recover upon storage in dark because entropy-driven remixing of halide ions restores the statistically mixed composition.13,17 Several strategies have been reported to suppress halide segregation and improve solar cell stability.18–25 Among them, the partial substitution of organic cations by cesium ions has been reported to improve the stability of a wide variety of perovskite systems.5,22,26,27 The beneficial effect is often attributed to a phase stabilization due to reduced lattice strain upon incorporating cesium, leading to a higher formation energy of point defects and thus a lower-defect concentration.28,29

The temporal evolution of photovoltaic performance as a function of halide segregation in mixed-halide perovskite has not been studied in detail. Most reports on the photostability of mixed-halide perovskites argued that iodide-rich domains...
would cause the open-circuit voltage ($V_{oc}$) of solar cells to deteriorate because these narrow-band-gap domains limit the quasi-Fermi level splitting, while few studies point at the effect on the short-circuit current density ($J_{sc}$). Mostly short stress experiments ($\lesssim 10$ min) have been used to study halide demixing and to develop mitigation strategies using thin films as the model system. However, phase segregation is a slow process that occurs over several hours and involves a complex interaction among photogenerated charge carriers, ionic species, and crystallographic defects.

Here, we investigate light-induced halide segregation in formamidinium (FA+)–methylammonium (MA+) lead mixed-halide perovskites FA$_{0.66}$MA$_{0.34}$Pb(I$_{1-x}$Br$_x$)$_3$ ($x = 0$ and 0.33) under continuous illumination and correlate changes in photoluminescence to photovoltaic performance. We begin by characterizing the photoluminescence behavior of thin perovskite films to identify several concurrently occurring light-induced processes that affect the luminescence spectra and quantum yield. We then complement experimental observations with kinetic Monte Carlo (KMC) simulations that show the light-induced development of low-energy sites and subsequent carrier localization to be the origin of the observed spectroscopic changes. Finally, by simultaneous characterization of the optical and electrical behavior of irradiated solar cells, we find that, contrary to the general notion, the performance loss of mixed-halide devices does not deteriorate primarily through a loss of open-circuit voltage, but rather due to a dramatic loss of $J_{sc}$. The degradation can be delayed, but not prevented, by partially replacing FA$^+$ and MA$^+$ with Cs$^+$. Ultrasmall sub-band-gap photocurrent spectroscopy reveals that Cs$^+$ reduces the presence of defects in these materials and their formation under illumination.

2. RESULTS AND DISCUSSION

2.1. Photoinduced Changes in Wide-Band-Gap Perovskite Thin Films. FA$_{0.66}$MA$_{0.34}$Pb(1$_{1-x}$Br$_x$)$_3$ ($x = 0$, 0.33) lead halide perovskite films were prepared using a modified two-step spin-coating technique. A lead iodide film was first spin-coated onto the substrate and the wet matrix was infiltrated with organic (FA and MA) halides (iodides and bromides) spin-coated on top. Following thermal annealing in an inert ($N_2$) atmosphere, a dark perovskite film was formed. By tuning the organic halide precursor composition in the second step of the deposition, the band gap ($E_g$) of absorber films can be altered from 1.53 eV ($x = 0$) to 1.75 eV ($x = 0.33$), as inferred from absorption and PL spectra (Figure 1a,b). XRD confirms the compositional change as (110) and (220) Bragg peaks shift from $2\theta = \sim 13.9$ and $\sim 28.1^\circ$ to wider diffraction angles ($\sim 14.2$ and $\sim 28.6^\circ$) when bromide replaces iodide (Figure 1c–e). XRD shows no noticeable peak broadening, which suggests the absence of segregation into iodide- or bromide-rich phases in pristine films. Scanning electron microscopy (SEM) of films deposited on polybis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA)-coated indium tin oxide (ITO)-covered glass substrates shows that both compositions form uniform, pinhole-free films and that the incorporation of bromide results in a marginal increase of grain size (Figure 1f).

Perovskite films on PTAA/ITO-coated substrates were illuminated using a S30 nm light-emitting diode (LED). Figures 2 and S1 (Supporting Information) show the PL spectra recorded over $\sim 25$ h of continuous illumination at $\sim 1$ sun equiv intensity (see the Experimental Section in the Supporting Information for details) for $x = 0$ and 0.33 FA$_{0.66}$MA$_{0.34}$Pb(1$_{1-x}$Br$_x$)$_3$ perovskites. The first observable change is a decrease in the PL intensity, indicating increased nonradiative recombination. This is observed for both the 0- and 33%-bromide-containing compositions within the first 100 s, implying that it occurs independently of halide segregation. A similar reduction in photoluminescence intensity under continuous illumination in inert conditions (absence of oxygen) at room temperature has previously been reported. The phenomenon has been explained by Motti et al. in terms of defect-mediated formation of I$_2$, migrating to...
the surface or to grain boundaries. The iodine imbalance between surface and bulk then triggers a series of compensating reactions that regenerate the starting equilibrium distribution of defects to compensate for their transformation to surface-bound I$_2$.

After about 100 s of illumination, the behavior of the 0- and 33%-bromide-containing films start to deviate. While the PL intensity of the 0%-bromide perovskite stabilizes at a reduced intensity (Figure 2), the high-energy emission at $\sim$1.74 eV continues to decrease for the 33%-bromide perovskite to below detection limits at $\sim$200 s. However, after about 200 s, a new PL peak appears at $\sim$1.6 eV in the spectrum of the 33%-bromide film. The intensity of this new emission, characteristic of the build-up of iodide-rich recombination sites, increases with prolonged illumination and eventually dominates the spectrum. The more intense red-shifted emission is accompanied by a 5-fold increase in PL lifetime after 5 h of illumination (Figure S2, Supporting Information). The red-shifted emission, increased PL intensity, and lifetime suggest that photoexcitations accumulate at low-energy iodide-rich regions and decay radiatively with a higher probability than in the pristine bulk film.

Ultraviolet–visible–near infrared (UV–vis–NIR) absorption spectra (Figure S3, Supporting Information) show a red shift and a less steep absorption onset in the 33%-bromide perovskite films after 28 h of continuous illumination. On the other hand, the absorption spectrum of the iodinated 0%-bromide film remains identical to that of the pristine film. The spectral changes observed in the 33%-bromide film thus demonstrate increased energetic disorder at the band edge, consistent with the formation of iodide-rich regions.

Additionally, XRD patterns also show significant peak broadening in the wide-band-gap (33%-Br) perovskite film, providing evidence for the generation of multiphase domains due to iodide segregation (Figure S4, Supporting Information).

The shift in the PL spectrum of FA$_{0.66}$MA$_{0.34}$Pb$_{(1-x)$Br$_x$)$_3$ films also occurs on glass substrates (Figure S5, Supporting Information). On glass, halide segregation is qualitatively similar but occurs somewhat earlier than on PTAA/ITO (Figure 2). This may be related to the shorter excitation wavelength used (405 nm compared to 530 nm), which increases the excitation density at the illumination side, or to the charge extracting nature of the PTAA/ITO interface. To obtain an estimate for the activation energy ($E_A$) for halide segregation, we measured the temperature dependence of the changes in the PL spectra under continuous illumination (Figure S5, Supporting Information). From the Arrhenius equation, the activation energy for halide segregation was estimated to be $\sim$0.23 eV, suggesting that it proceeds through the migration of halide vacancies for which similar activation energies have been theoretically predicted and experimentally estimated.

### 2.2. Kinetic Monte Carlo Simulations

To further rationalize the experimental findings, KMC simulations were used to study the dynamics and purity of domains during halide segregation (Figure 3). The essence of these simulations is that the system can reduce the free energy by collecting photocarriers into the small-band-gap iodide-rich regions, which leads to a driving force for halide demixing. Since I/Br mixed-halide perovskites have similarly located conduction band minima, it is the energy difference of valence band maxima for different halide compositions that provides the driving force for phase separation.

The details of KMC simulations are described in the Supporting Information. In the simulations, a periodic cubic supercell of 1728 formula units and a halide vacancy concentration ($z$) of 0.005 were used to model the evolution of the positions of halide ions in the perovskite film. Such vacancy defects are experimentally and theoretically confirmed as very shallow defects that are closely under or above the conduction band minimum, without significantly affecting the positions of valence band maximum.

Figure 3a shows that in pristine films, nanoscale iodide-rich seeds are present due to the stochastic distribution of iodide and bromide ions in pristine films. Within the supercell, we identified a domain with a radius of 2 nm containing a subsstatistical concentration (29%) of bromide ions. Under illumination, an inward diffusion of iodide ions and an outward diffusion of bromide ions leads to a thermodynamically driven growth of this iodide-rich domain, where the free energy of photocarriers is further reduced (Figure 3a−c). As a result, phase purity decreases with radial distance from this seed cluster (Figure 3d−f). The bromide concentration in the iodide-rich domain decreases to $\sim$20% after 100 000 KMC simulation steps. During the simulations, the center of the iodide-rich domain shifts slightly. After 150 000 simulation steps, a pure-iodide phase has not formed (Figure 3f) and the bromide concentration in iodide-rich domains is $\sim$13%, corresponding to a band gap of 1.6 eV (see the Supporting Information for the compositional band gap formula). This corroborates well with spectroscopic observations that the low-energy emission is blue-shifted relative to the emission energy of a pure-iodide perovskite (Figure 2a).

With increased vacancy concentration ($z = 0.01$), the process of halide segregation is accelerated, leading to a faster influx of iodide ions to replace outgoing bromide ions in narrow-band-gap domains and a higher iodide content after the same number of simulation steps (Figure S5, Supporting Information). This implies that improving the film quality by reducing the defect density can slow down halide segregation. Additionally, recent work suggests that controlling the photocarrier density of the continuous phase under a threshold value can avoid phase segregation. Therefore, controlling the carrier density through efficient extraction by selective transport layers can reduce the driving force for the segregation of halides, thereby delaying the process.

At the higher vacancy density, the halide segregation described by the KMC model converges to a nucleation of an almost pure-iodide phase with a terminal stoichiometry of x...
= 0.02. The PL experiment (Figure 2), however, does not suggest that a stoichiometry close to x = 0 is reached after prolonged illumination because the PL maximum remains blue-shifted compared to that of the pure-iodide perovskite. Several ingredients not considered in the KMC model may account for this difference. One is the empirical assumption of the critical size (10% of the total volume of the system) of the iodide-rich domain in the simulations (see the details of the KMC simulations in the Supporting Information). Second, the interfacial free energy present at the interface between the nucleated and the mixed parent phase is not considered in the model. To form a nucleus of critical size, the phase separation requires a crossing of the free energy barrier, where the interfacial and bulk free energies balance each other. Finally, we note that in a recent study a terminal value of x = 0.1 was predicted after 9400 KMC simulation steps for a MAPb-(I0.67Br0.33)3(x−0.1) perovskite with a similar vacancy density (z = 0.01).16 This suggests that a compositional dependence of the critical size of an iodide-rich domain may exist in mixed-halide perovskites.

2.3. Photoinduced Changes in Mixed-Halide Perovskite Solar Cells. To study the effect of light-induced halide segregation and the stabilization afforded by cesium substitution on solar cell performance, we investigated perovskite solar cells in the p-i-n (inverted) device architecture using PTAA and phenyl-C61-butyric acid methyl ester (PCBM) as hole- and electron-transport layers, respectively. The current–voltage (J–V) characteristics, external quantum efficiency (EQE), and initial stability are shown in Figure S7 and Table S1 (Supporting Information). We recorded the PL spectra with time under continuous illumination while simultaneously tracking solar cell performance through current–voltage sweeps (Figures 4 and S8, Supporting Information). The cells were under inert (N2) conditions throughout the measurement and at the open circuit, except during the voltage sweeps to record the J–V response.33 This allows changes in solar cell performance parameters to be correlated with changes in the PL spectra.

During the first ~1000 s of illumination, the PL intensity of FA0.66MA0.34Pb(I0.67Br0.33)3 solar cells at ~1.74 eV decreases slightly (Figure 4e), but there is no other change in the spectrum, and photovoltaic parameters (Voc, Joc, and power-conversion efficiency (η)) show minimal loss (Figure 4). Until this point in time, the photophysical and photovoltaic response is dominated by the mixed-halide phase. Thereafter, at ~104 s, the PL intensity reduces steeply, accompanied by a severe decrease in Joc and η. At that time, the J–V characteristics show increased hysteresis as inferred from differences between reverse and forward voltage scans (Figure S9, Supporting Information). This indicates a compositional change that promotes PL quenching from the mixed-halide phase and reduces charge-carrier collection. After ~12 h, a peak at ~1.6 eV dominates the PL spectrum (Figure 4a), implying the development of iodide-rich sites where charge carriers recombine radiatively, and Joc drops more steeply. We note that in solar cells the occurrence of this red-shifted peak is delayed compared to that reported in Figure 2 for films on PTAA/ITO. To explain this difference, we suggest that the photogenerated carrier density in perovskite films is lower in the solar cell due to the presence of PCBM. It has been shown that the quasi-Fermi level splitting in perovskites is smaller with PCBM than with PTAA.24,25 This implies that open-circuit photoexcitations are quenched by PCBM more than by PTAA. As a result, the density of photogenerated charge carriers is lower in the solar cell. This rationalizes the slower light-induced phase separation in the complete devices compared to thin films on PTAA.
The spectral centroid of the PL slowly shifts to higher energy in the final 10 h of illumination (Figure 4c). Such a small blue shift of the PL following an initial red shift has also been observed when illuminating MAPbI₃Br₃. After ∼28 h of illumination, $J_{sc}$ has dropped by more than 80% (Figure 4g), whereas the loss in $V_{oc}$ is only 10% (Figure 4f). Clearly, under continuous illumination, $J_{sc}$ is more affected than $V_{oc}$. Photoinduced halide segregation can contribute to this loss in $J_{sc}$ when charge carriers localize at iodide-rich domains, which provide relatively emissive regions for charge-carrier recombination with higher luminescence quantum efficiency. We note, however, that the KMC simulations (Figure 3) predict that the regions are not entirely defect free. The role of halide segregation is corroborated by the fact that $J_{sc}$ decreases more steeply when the red-shifted PL emerges at ∼12 h and increases in intensity.

Prolonged illumination (∼28 h) also results in a significant reduction in EQE along with a noticeable development of EQE contribution from the iodide-rich domains at wavelengths longer than the original band-edge (Figure S10, Supporting Information). This implies that at least some of these photogenerated domains contribute to the photocurrent. Storage in the dark leads to a partial recovery in the EQE along with a suppression of the EQE contribution from low-energy iodide-rich regions.

To understand the role of Cs-substitution in affecting light-induced halide segregation, we studied Cs₀.₁₀(FAO.₆₆MA₀.₃₄)₁₋ₙPb(I₀.₆₇Br₀.₃₃)₃-based solar cells. Figure 4 reveals a significantly slower degradation of PL and photovoltaic performance under continuous illumination than the Cs-free perovskite. It takes more than 9 h of illumination for PL intensity to be reduced to about 40%, compared to within 2 h for the Cs-free solar cell (Figure 4d) and a red-shifted PL peak does not appear within the duration of the measurement (Figure 4b) with only a minor shift in the spectral centroid after several hours (Figure 4c). Hence, while there is no direct spectral evidence of halide segregation, there is a reduction of PL intensity. Similar to the Cs-free variant, the performance degradation of the Cs₀.₁₀(FAO.₆₆MA₀.₃₄)₀.₉₀Pb(I₀.₆₇Br₀.₃₃)₃ cell is dominated by a reduced photocurrent. After 28 h, ∼25% of the initial $J_{sc}$ is lost (Figure 4g), whereas the loss in $V_{oc}$ is only ∼3% (Figure 4f). Comparison of the loss in $J_{sc}$ after 28 h for the Cs-free (∼83%) and Cs-containing (∼25%) perovskite suggests that halide segregation significantly contributes to the loss in photovoltaic performance for the Cs-free perovskite, but that other performance loss mechanisms are also present.

Similar trends for different compositions are observed when irradiating Cs₀.₁₀(FAO.₆₆MA₀.₃₄)₁₋ₙPb(I₀.₆₇Br₀.₃₃)₃ perovskites for $(x, y) = (0, 0), (0.33, 0)$, and $(0.33, 0.10)$ with blue (405 nm) light. Blue light causes the PL red shift and the resulting performance loss to occur faster (Figure S11, Supporting Information). The solar cells of the bromide-free $(x, y) = (0, 0)$ and the Cs-containing perovskites $(x, y) = (0.33, 0.10)$ show a loss of PL intensity and photovoltaic performance loss under these conditions, again indicating the existence of other degradation channels, possibly related to ion or defect movement and the defect-mediated formation of I$_3$, as identified by Motti et al. In the pure-iodide perovskite, degradation occurs faster but levels off at the same level as in the Cs-containing mixed-halide perovskite. The slower kinetics when using Cs is consistent with the associated higher formation energy for defects and lower-defect concentration. The faster degradation with blue (405 nm) light compared to green (530 nm) light is likely related to its lower penetration depth, causing a higher excitation density that accelerates degradation. As an additional factor, PTAA degrades when irradiated under inert conditions with blue (405 nm) as opposed to green (530 nm) light (Figure S12, Supporting Information). The results show that the performance loss is significantly accelerated and enhanced in solar cells where halide segregation occurs (FA₀.₆₆MA₀.₃₄Pb(I₀.₆₇Br₀.₃₃)₃) as compared to cells where halide segregation cannot occur (FA₀.₆₆MA₀.₃₄PbI₃) or was not evidenced (Cs₀.₁₀(FAO.₆₆MA₀.₃₄)₀.₉₀Pb(I₀.₆₇Br₀.₃₃)₃).

Both the FA₀.₆₆MA₀.₃₄Pb(I₀.₆₇Br₀.₃₃)₃ and the Cs₀.₁₀(FAO.₆₆MA₀.₃₄)₀.₉₀Pb(I₀.₆₇Br₀.₃₃)₃ solar cells recover most of their original performance and PL spectral position after storing in dark for several days. This indicates that the changes in $J_{sc}$ are reversible and occur largely due to light-induced halide segregation, recovering once illumination is removed.
2.4. Sub-Band-Gap Photocurrent Spectroscopy. We used sensitive photocurrent spectroscopy to understand how Cs-substitution affects solar cell stability. Figure 5 shows the sub-band-gap EQE spectra of Cs0.10(FA0.66MA0.34)0.90Pb(I0.67Br0.33)3 perovskite p-i-n solar cells. Dark solid lines represent the normalized EQE of a pristine solar cell, while the light dashed line represents the EQE of a solar cell, after continuous illumination using a 532 nm laser at 1 sun equiv intensity for 2 h. (a) (x, y) = (0, 0), (b) (x, y) = (0.33, 0). Noise level is 5 × 10−4.

The high sensitivity of the sub-band-gap EQE measurement enables observation of small changes at the band edge and the monitoring of sub-band-gap defects induced by illumination. After illuminating the solar cells for 2 h at 532 nm at 1 sun equiv intensity, the response from sub-band-gap defects in the 0%-bromide composition remains nearly identical to that from a pristine solar cell while the band edge shows no significant change (Figure 5a). A slight decrease in the above-band-gap EQE is observed in the solar cell, signifying that prolonged illumination leads to charge collection losses. In contrast, in the 33%-bromide, Cs-free perovskite solar cell, three concurrent changes can be observed after illumination (Figure 5b). First, the EQE contribution from defect states between 0.9 and 1.4 eV increases about 6-fold. Second, a decrease in the above-band-gap EQE occurs, as observed in the 0%-bromide composition. Third, a low-energy shoulder develops at the band edge around 1.6 eV, characteristic of the formation of iodide-rich perovskite domains that have a red-shifted absorption edge.

Absorption of iodide-rich perovskite domains that have a red-shifted absorption edge is no longer apparent and the defect EQE response decreases (Figure 5c). Compared to FA0.66MA0.34Pb(I0.67Br0.33)3 cells, the defect at ∼0.9 eV is virtually absent and that at ∼1.4 eV is less intense in Cs-substituted films. After illumination, there is an increased EQE contribution from the defect states at ∼1.4 eV, but at lower photon energies, the response remains unchanged. Furthermore, no low-energy shoulder forms at the band edge after illumination, suggesting the absence of iodide-rich phase formation. Notably, the above-band-gap EQE also remains stable during this stress. The correlated minimization of photocurrent contributing defects and absence of light-induced halide segregation points at possible mechanisms through which Cs-substitution can successfully be used for device stabilization. We speculate that the reduced sub-band-gap signals in the EQE spectra of Cs-substituted films may reflect a reduced vacancy density, which according to the KMC simulations would be consistent with a slowing down of halide segregation.

2.5. Synopsis. Based on the combined optical and electrical behavior, we propose the following mechanism for halide segregation in wide-band-gap mixed-halide perovskites. Under illumination, photoexcitations in FA0.66MA0.34Pb(I0.67Br0.33)3 can decrease their free energy when iodide locally replaces bromide because of the smaller optical band gap of iodide-rich regions. The halide exchange process is facilitated by defect states, such as vacancies in pristine films, and leads to the growth of iodide-rich regions due to ion migration under illumination. The small, relatively emissive iodide-rich regions thus formed cause a red shift of the PL spectrum accompanied by an increased radiative recombination, since carriers accumulate in these small-band-gap domains from other parts of the film on account of long carrier diffusion lengths and lifetimes. Their isolated nature causes them to act as trap sites that prevent charge transport to the electrodes, thus causing a severe loss in Voc in solar cells. The formation and accumulation of such low-energy sites near the band edge amounts to an increased energetic disorder, possibly underlying the mild decrease in the open-circuit voltage. Hence, the power-conversion efficiency suffers from halide segregation primarily by the obstruction of charge-carrier collection.

3. CONCLUSIONS
We have studied iodide–bromide segregation in wide-band-gap perovskite semiconductor using PL spectroscopy, atomistic simulations, device characterization, and photocurrent spectroscopy under prolonged (~28 h) illumination conditions. Prolonged illumination of FA0.66MA0.34Pb(I0.67Br0.33)3 films results in a significantly red-shifted and intensified PL signal that results from the formation of isolated low-band-gap iodide-rich regions, collecting photogenerated electrons and holes from the perovskite films that subsequently recombine radiatively. These light-induced iodide-rich regions obstruct charge-carrier collection and lead to a critical loss in Voc. Despite the formation of domains with a narrower band gap than the bulk, the Voc is found to be considerably stable and therefore less critical to solar cell stability. PL spectra, photovoltaic performance, and sub-band-gap defects are largely restored upon storage for extended durations in dark conditions via entropically driven remixing. Finally, we attribute the efficacy of Cs-incorporation in improving the
stability to suppressed defect formation in pristine solar cells and their slower growth under illumination. Such stabilization is imperative for the future use of mixed-halide wide-band-gap perovskites as subcells in perovskite-based multijunction photovoltaics.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.1c00707.

Experimental section; a description of the kinetic Monte Carlo simulations; time evolution of the PL spectra of FA0.66MA0.34Pb(I1−xBrx)3 films (Figure S1); steady-state and transient PL of FA0.66MA0.34Pb(I0.66Br0.33)3 films (Figure S2); UV–vis–NIR absorption spectra of FA0.66MA0.34Pb(I1−xBrx)3 films (Figure S3); XRD patterns (Figure S4); temperature-dependent time evolution of PL spectra of FA0.66MA0.34Pb(I0.66Br0.33)3 films (Figure S5); kinetic Monte Carlo modeling of light-induced halide phase segregation (Figure S6); photovoltaic performance of Cs6(FA0.66MA0.34)1−xPb(I1−xBrx)3 solar cells (Figure S7); photovoltaic parameters (Table S1); PL spectra of Cs6(FA0.66MA0.34)1−xPb(I1−xBrx)3 solar cells (Figure S8); time evolution of J–V measurements of ~1 sun equiv intensity (Figure S9); EQE of FA0.66MA0.34Pb(I0.67Br0.33)3 solar cells (Figure S10); time evolution of the PL spectra of Cs6(FA0.66MA0.34)1−xPb(I1−xBrx)3 solar cells (Figure S11); absorption spectra of PTAA (Figure S12); J–V measurements of Cs6(FA0.66MA0.34)1−xPb(I1−xBrx)3 solar cells (Figure S13); normalized J–V parameters (Figure S14); and sub-band-gap EQE measurement (Figure S15) (PDF)

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