

Kinetics and Mechanism of Light-Induced Phase Separation in a Mixed-Halide Perovskite

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Summary

Halide ion phase separation is a barrier to the application of mixed-halide perovskites, whereby the presence of large populations of photo-generated or injected carriers causes undesirable changes in the local band gap. We investigate the mechanism of phase separation in $\text{CsPbI}_x\text{Br}_{3-x}$ perovskite single crystals driven by light. The phase separation process and its dynamics are visualized at the nanometer scale at cryogenic temperatures using *in-situ* scanning transmission electron microscopy - cathodoluminescence. Combined with phase field modeling that accounts for the coupling between electronic and chemical driving forces, our observations point to a spinodal decomposition mechanism in which both the amplitude of composition fluctuation and the characteristic length scale grow non-linearly with time. Our findings provide microscopic insights that can assist in further engineering mixed-halide perovskites either for stability or for intentional programming of the local halide ion composition, opening pathways to a wide range of applications.

Introduction

Halide perovskites are a very promising class of materials for optoelectronic devices such as solar cells^{1,2} and light emitting diodes (LEDs)^{3,4}. Capable of being prepared using inexpensive and scalable synthesis methods, they are earth-abundant semiconductors that exhibit desirable optical properties including near unity quantum yield⁵. The compositions of both the cation and anion (halide) sublattices of perovskite crystals can be manipulated over a wide range^{6,7} to engineer their light absorption and emission. Halide ion phase separation is a widely recognized problem for the application of mixed-halide perovskites in solar cells and LEDs, whereby the presence of large populations of photo-generated or injected carriers cause undesirable and time-dependent red shifting of the absorption edge and emission wavelengths.

Previous reports^{6,7} have established that illuminating mixed iodide-bromide perovskites with light having energy exceeding the nominal band gap energy causes phase separation into iodide- and bromide-rich domains, and this process can be reversed over time in the dark. Structural changes consistent with phase separation of mixed-halide perovskite alloys have been observed by X-ray diffraction (XRD)⁷⁻⁹. It was hypothesized that the phase separation mechanism involves a self-reinforcing demixing of Br- and I- ions driven by reducing the potential energies of photogenerated carriers that trap in regions of smaller band gap^{6-8,10-19}. Subwavelength imaging has been performed to visualize the process in single crystalline^{20,21} and poly-crystalline^{14,22,23} organic perovskites; however, inconsistencies exist in the reported spectral and microstructural evolution. Furthermore, it is possible that chemical decomposition of these rather unstable materials is complicating observation of the carrier-driven phase separation. Prior reports^{24,25} have described improvements of stability with respect to halide ion demixing focusing on the roles of composition, surface passivation and crystallite size. However, several aspects of the phase separation phenomenon are poorly understood, such as the mechanism (spinodal decomposition versus nucleation and growth²⁶), the length scale and temporal evolution of composition fluctuations, and the bounds on the local composition achieved in the phase separated state.

We probe correlations among the structural and optical properties during the time-evolution of phase separation in a single crystalline mixed halide perovskite alloy, and the influence of illumination conditions and temperature using TEM cathodoluminescence with high spatial resolution. This technique offers the ability to develop microscopic insights by focusing on phase separation in single crystalline islands of halide perovskite films at 173 K, a temperature at which material degradation and effects of high electron beam dosage can be minimized compared to room temperatures. The use of single crystalline material also excludes complicating factors such as grain boundaries that may affect carrier concentrations and, thus, influence phase separation driven by local heterogeneity of the electronic structure. Varying the light flux and temperature and combining these experiments with phase field modeling provides new mechanistic insights into mixed-halide perovskite phase separation. Cathodoluminescence (CL) performed in a scanning transmission electron microscope (STEM) is used to visualize the phase separation process as it evolves in time, and with spatial resolution at the nanometer scale. Compared to prior reported XRD⁷ and CL¹⁴ studies, these experiments quantify the length scale of phase separation with a spatial resolution of a few nm and are performed at sufficiently low temperatures to resolve kinetic aspects because of the relatively slow ion diffusion in the dark at such temperatures.

Reports in the literature show the abrupt formation of a red-shifted emission peak far from the initial photoluminescence^{20,27} or cathodoluminescence¹⁴ peak of the sample. These findings are consistent with a nucleation-and-growth mechanism for phase separation, which may be related to the iodide composition, the presence of local defects (grain boundaries, triple junctions, etc.) or partial decomposition of the perovskites at ambient conditions providing nucleation sites that initiate the phase separation in the studied samples. In contrast, in single crystalline material at cryogenic conditions, we observe a spatial and temporal evolution of composition fluctuations having a characteristic wavelength, pointing to a spinodal-

decomposition mechanism in which the characteristic length scale of the composition fluctuation eventually coarsens²⁸ non-linearly as a function of time. These observations provide fundamental insights into the phase separation process in the absence of poorly-characterized structural defect populations that may alter the morphology and rate of phase separation.

Prior phase field models have adopted a basic Cahn-Hilliard formulation to capture general spinodal decomposition phenomena¹¹. However, halide perovskite phase segregation involves collective effects including ion de-mixing, interface effects, local electronic structure changes and polaron effects which cannot be described in the prior model¹¹. Phase field modeling reported herein not only supports interpretation of the experimental observations, but also provides insight into the driving forces for phase separation that cause the observed evolution of the local composition.

Results

Spatio-temporal characterization with cryo-STEM-CL

We perform CL characterization using STEM with a 0.5 nm probe size at 173 K (Figure 1). The $\text{CsPbBr}_{2.1}\text{I}_{0.9}$ sample remains kinetically trapped in a phase separated state in the absence of continued illumination during imaging because, at this temperature, the rate of re-homogenization of the composition in the dark is significantly slower than the rate of phase separation in the light. In addition, according to modeling (Figure S8), phase separation in the dark is not thermodynamically possible at this temperature. CL imaging in the STEM permits visualization with nanometer resolution of the spatial distribution of the band gap. Figure 1d shows a STEM image of a $\text{CsPbBr}_{2.1}\text{I}_{0.9}$ thin film (~200 nm thick) grown on a 10 nm thick Si_3N_4 membrane, where the area of study is indicated by the white dashed box. Before phase separation (0 min), we observe a CL spectrum with an emission peak centered at 2.09 eV (595 nm) shown in Figure 1a, obtained by integrating over the entire area. The CL map at 595 nm (integrated over a bandwidth of 5 nm) in Figure 1b indicates an initially homogeneous mixed-halide composition. To induce phase separation, the electron beam is blanked and the sample is illuminated with a 450 nm diode laser at 6.37 mW/mm² at 173 K. Then the laser is turned off and the CL map is collected. After 5 min of illumination, the center of the CL spectrum redshifts to 1.94 eV (640 nm), indicating phase separation. The CL map at 640 nm reveals the formation of inhomogeneous iodide-rich clusters. The bromide-rich region has weak CL emission and therefore no bromide-rich peak is visible. We then illuminated the material in increments of 5 min duration under the same conditions. After 25 min, the phase separation produces a saturated redshifted emission at 1.74 eV (716 nm), indicating the composition of the iodide-rich regions in the film is no longer changing with illumination time. This also verifies that halide ion phase separation kinetics are enhanced by excess carriers even at 173 K, while the reverse kinetics are slow relative to the measurement time when there is no illumination.

Reported measurements of halide ion diffusion during illumination of the related ammonium lead iodide (MAPbI_3) compound²⁹ suggest that photocarrier generation greatly enhances the halide vacancy concentration in the perovskites, thus promoting an unusually large anion diffusivity even at low temperatures. Unlike previously reported⁽¹³⁾ CL maps of locally red-shifted emission obtained from fine-grained polycrystalline perovskite films that suggest the

phenomenon is strongly spatially correlated with grain boundaries, the iodide-rich clusters observed from these $\text{CsPbI}_x\text{Br}_{3-x}$ single crystal islands do not appear to be correlated with any obvious microstructural defects. For all measurements, a second CL scan was taken to verify that no re-homogenization occurs in the dark in the timeframe of the measurement, and also to verify that the electron beam did not cause local chemical changes (Figure S11-19).

The spatio-temporal dependence of emission energy is extracted from the CL maps by plotting the center of emission energy at each scan position, as shown in Figure 1c (0 min, 5 min, 25 min) and Figure S23. While the initial band gap distribution is homogeneous, iodide-rich clusters indicated by the band gap energy contours, increase as a function of illumination time. The distribution of nearest neighbor distances of iodide rich clusters is fitted to a log normal distribution function $f_X(x) = \frac{1}{x\sigma\sqrt{2\pi}} \exp \frac{(\ln x - \mu)^2}{2\sigma^2}$. The nearest-neighbor distance after 5 min illumination is ~ 200 nm and coarsens non-uniformly with time (also verified in Figure 4) to ~ 500 nm, as shown in Figure 1 e,f. No sudden onset of a domains with I-rich composition, characteristic of nucleation, was observed.

Spinodal decomposition

CL-STEM imaging was performed at 173 K with lower light intensity (2.45 mW/mm^2), under which conditions the kinetics of phase separation are relatively slow. This enables imaging of the earlier-stage evolution of the phase separation morphology, shown in Figure 2a. The gradual redshift of the emission peak wavelength of the integrated CL spectra indicates a change of the de-mixed composition distribution as phase separation proceeds, shown in Figure 2d. The intensity of the spectra also increases gradually as a function of time shown in Figure 2c, which is a combined effect of increased amplitude of the composition fluctuations and the increased emission from smaller band gap areas having locally higher iodide composition. Quantitative analysis for a wavelength (626 nm) that is within the peak of the iodide-rich emission focuses on the average nearest neighbor distances of the iodide rich clusters in CL emission maps. This gives the characteristic length scale of the phase separated microstructure, are shown in Figure 2b, which remains constant (~ 250 nm) between 5 min to 20 min. Later, the iodide rich domains coarsen.

Spinodal decomposition is most clearly indicated by the growth in amplitude of the composition fluctuation (5-20 min) – increasing iodide concentration in the emitting regions – without any change in the length scale of phase separation. Spinodal decomposition is also indicated by the gradual increase in emission wavelength integrated across the entire sample (Figure 1 c-d and Figure 2d) rather than a sudden appearance of a second iodide emission peak. Although the granular cluster morphology³⁰ of the microstructure is not typical of chemically-driven spinodal decomposition (which often exhibits tortuous, “maze”-like shapes), the characteristic wavelength (in the initial stages)²⁶, and the local composition fluctuations with growing amplitude both point to a spinodal decomposition process.

In-situ structural and photoluminescence characterization

To confirm that the structural changes observed in STEM-CL result from light-induced phase separation (instead of other processes that may have been caused by the electron beam), *in-situ* TEM selected area electron diffraction (SAD) was performed. A single crystal was examined along the [100] zone axis (Figure 3a). After using a 450 nm laser to illuminate the sample, we observe elongation of the diffraction spots (Figure 3c) in the radial direction relative to the situation without illumination (Figure 3b), consistent with the coexistence of iodide- and bromide-rich compositions in the sample. *In-situ* XRD characterization and *in-situ* ellipsometry confirm light-induced phase separation (Figure S23 and Figure S26).

Time resolved photoluminescence as function of illumination intensity and temperature were collected and fitted to a simple exponential time dependence (in agreement with experimental data), which was expected for spinodal decomposition. The rate-constant of phase separation increases with increasing illumination intensity (Figure 3d) and decreases with increasing temperature (Figure 3e). For the reverse phase separation process in the dark, the rate constant increases with increasing temperature, shown in Figure 3f. The data suggest that illumination provides a driving force for the observed change, which is consistent with the expectation that the phase separation is caused by photo-generated charge carriers⁷. The local variations in the band gap^{8,11,20,31} induced by the composition fluctuations cause further segregation of the charge carriers, producing a self-reinforcing interaction, which will be further examined by phase field modeling herein. With a larger photon flux, there are more photo-generated carriers, accelerating the phase separation process and thus increasing the rate constant, as shown in Figure 3d. The rehomogenization process depends on diffusion of anions to homogenize the composition. Increasing temperature is expected to increase the influence of entropy in the mixing free energy of the halide alloy, reducing the driving force for phase separation. This may contribute to the temperature dependence of the forward rate constant shown in Figure 3e. Additionally, increasing temperature increases the contribution of nonradiative carrier recombination, which may further slow the phase separation process by reducing the carrier concentration that drives the instability.

For the reverse phase separation process, a simple Arrhenius temperature dependence with an activation energy of $20.5 \pm 0.25 \text{ Jmol}^{-1}$ is observed (Figure 3f). This is in contrast to a literature report³², where both the forward and the reverse phase separation rate constant was observed to increase as temperature increases, in absorption measurements of $\text{MAPbBr}_{1.5}\text{I}_{1.5}$ at particular wavelengths under illumination, with a larger activation energy for the recovery process than for the forward process.

Phase field modeling

A quasi-2D phase field model (PFM) was developed to investigate the controlling mechanism of light-induced phase separation in halide perovskites, with the focus on microstructure evolution. While there have been prior works using phase field modeling to analyze phase separation of mixed halide perovskites¹¹, the phase field model developed herein is novel because it systematically considers mixing free energy, the coupling between compositional distributions and carrier density distributions, electronic contributions to the free energy, and phenomenological terms to account for polaron and temperature effects. The model enables predictions of the

inter-related carrier density and composition evolution under a given condition (including initial compositional distribution, temperature, illumination intensity, and etc), for investigating phase separation mechanisms.

The fundamental degrees of freedom of the PFM contain the iodide composition field $c(\mathbf{x})$, as well as the carrier concentration fields of electrons $n(\mathbf{x})$ and holes $p(\mathbf{x})$. For a given instantaneous $c(\mathbf{x})$, it is assumed that $n(\mathbf{x})$ and $p(\mathbf{x})$ always reach a steady state, as the kinetics governing the electronic degrees of freedom are expected to be much faster than those governing the chemical degrees of freedom (that require ionic diffusion). The electronic steady state is characterized by the quasi-Fermi levels E_{Fn} and E_{Fp} for the electrons and holes, respectively. Their values are auto-adjusted to satisfy the constraint of total charge neutrality, with additional consideration of the balance between carrier annihilation and generation rates (see Methods). Once the steady state solutions for $n(\mathbf{x})$ and $p(\mathbf{x})$ are obtained, they are used in G_{ele} due to the composition dependent bending of the band structure, as well as the coupling term G_{sep} to effectively account for the polaron effect²⁴ (see Methods and SI). These two terms provide the light-induced driving force for phase separation, through the evolution of $c(\mathbf{x})$ governed by a Cahn-Hilliard type (diffusive) equation.

Two independent simulations were performed at carrier generation rates of $G_1 = 1.2 \times 10^{21} \text{ cm}^{-3}/\text{s}$ and $G_2 = 2.0 \times 10^{21} \text{ cm}^{-3}/\text{s}$ respectively, exhibiting different behaviors of I-rich region growth (Figure 4a). At a lower rate G_1 , an incubation stage was clearly observed, followed by a quick ramp-up period before the final slowing-down of the growth speed, whose trend was comparable to the experimental data. When the generation rate was increased to G_2 , the initial incubation period was greatly shortened, while the curve quickly plateaued, indicating a self-limited behavior. These simulations result in patterns (represented by the distribution of $n(\mathbf{x}) \cdot p(\mathbf{x})$) consisting of well-dispersed granular clusters, also in good agreement with the patterns obtained in cathodoluminescence characterization. Because, in the PFM, the phase evolution occurs through a Cahn-Hilliard type equation, a standard model for spinodal decomposition, the consistency between the simulated and experimental results lends support to the notion that the phase separation in these halide perovskite films proceeds by a spinodal decomposition mechanism.

The appearance of granular microstructures³⁰ may seem atypical because spinodal decomposition is often associated with formation of tortuous “maze”-like microstructures. The observed microstructure may arise because the illumination in these experiments creates a free-energy landscape only weakly dependent on the I-composition within the spinodal decomposition regime. This argument is supported by the variation of the free energy density as a function of I-composition (x_I) (Figure 4c). In this figure, the total free energy G_{tot} , free energy contribution of polaron formation²⁴ G_{sep} , and free energy contribution of mixing G_{mix} are illustrated (see SI for more details). Considering that the spinodal region is in the range of $0.28 < x_I < 0.72$, for an average I-composition of approximately 0.3 the system is initially near the edge/boundary of the spinodal domain (including the electronic and light-induced effects) in the phase diagram. The average I-composition will affect the morphology evolution, which is depicted by simulations shown in Figure S4. For very I-poor (<0.28) compositions, nucleation-

and-growth-like behavior has been reported^{14,20}; nucleation-and-growth-like behavior is also expected for very I-rich (>0.72) compositions.

Additional analyses were conducted of the simulation at generation rate G_1 , to further clarify the similarity between the simulation results and the experimental observations. In Figure 4b, the evolution of a granular morphology of iodide rich regions was observed, comparable with the TEM-CL maps shown in Figure 2a. As expected, the spatial distribution of $n(\mathbf{x}) \cdot p(\mathbf{x})$ follows the same pattern (Figure S6) as the composition field $c(\mathbf{x})$.

The kinetics of this unconventional spinodal decomposition process (for initial average composition at 0.3) were further examined in Figure 4d, where the simulated phase separation was divided into three stages. In Stage 1 when the magnitude of the x_I variations is small, the average nearest neighbor distance (d_{nn}) between the I-rich clusters roughly remains a constant at around 300 nm, consistent with the results extracted from a linear stability analysis (Fig. S9). Then in Stage 2, undulations with certain wavelengths exhibit a significantly higher growth rate, resulting in a spectrum of granular I-rich clusters that effectively suppress slowly-growing patterns at other wavelengths. Thus, as shown in Figure 4d, the d_{nn} manifested a clear tendency to grow. All these simulation results are in very good agreement with the experimental data shown on the same plot (filled circles). The phase field model predicts a Stage 3, in which further separation of the phases generate more clusters that cause a reduction of the d_{nn} ; this stage has not been directly observed in the time period of our experiments. Furthermore, the phase field simulations predict that when the time is sufficiently long, the iodide composition inside each granular cluster already passes the upper-boundary of the spinodal range of $x_I=0.72$, reaching a characteristic value of $x_I=0.85$ that represents the upper composition of the miscibility gap (Figure 4c). Under this condition, the chemical compositions are already at the free energy minima everywhere in the material (except at interfaces between phase-separated domains), where the driving force for further phase separation vanishes, and the d_{nn} of the clusters is expected to show a self-limiting behavior (Figure 4a and Figure S7). Eventually, we expect Ostwald-ripening to occur, where the larger I-rich clusters gradually coarsen, with smaller clusters shrinking and disappearing over time, leading to a gradual increase of d_{nn} (not shown).

Discussion

Altering the composition of semiconductor crystals at controlled length scales is a proven approach to engineer the local properties and occupancy of electronic states with great precision. The converse process, in which local changes in electronic carrier density drive compositional restructuring of the semiconductor lattice, is far rarer. The experimental and modeling results reported herein indicate that light induced carrier generation produces halide ion demixing via a diffusion process akin to spinodal decomposition. For the cesium lead bromide iodide halide perovskite alloys studied, a gradual and fully reversible red-shifting of light emission is observed after illumination. Cryo-TEM-CL mapping with high spatial resolution of alloy single crystallites shows the formation and morphological evolution of iodide-rich clusters with illumination time, and quantifies the evolution of the characteristic length scale of phase separation with illumination time. The experimental results indicate a characteristic period of growth in the composition modulation amplitude with little change in the length

scale, consistent with spinodal decomposition, followed by coarsening of the phase separated microstructure. In agreement with these observations, phase field modeling that accounts for the coupling between chemical and electronic processes predicts the halide composition amplitude and length scale variation consistent with a spinodal decomposition mechanism.

Mixed halide perovskites have a carrier-driven emission amplitude and emission wavelength whose speed of active tuning depends on the rate of carrier generation influenced by the illumination intensity and temperature. For application in solar cells, a quantitative understanding of carrier-driven phase separation in mixed-halide perovskite alloys may inform design principles for optimizing device stability. On the other hand, intentional programming of the local halide ion composition controlled by the studied kinetics of carrier induced phase separation may open up a range of new applications for these alloys⁶. Promising new applications point out the need for additional research on halide ion demixing mechanisms and kinetics. In particular, experiments and models that can link the spinodal decomposition behavior reported herein for single crystal perovskite islands to the phase separation process in more heterogeneous, solution-derived films should be a fruitful direction for future study.

Supplemental Experimental Procedures

Resource availability

Lead Contact

Further information and requests for resources should be directed to the lead contact, Paul C. McIntyre (pcm1@stanford.edu).

Materials Availability

The study did not generate new unique reagents.

Data and Code Availability

All experimental and theoretical data are available upon reasonable request from the lead contact.

Synthesis

Halide perovskite thin film was synthesized via physical vapor deposition in a tube furnace at 620 °C with N₂ as the carrier gas. The deposition source was placed 15 cm away from the growth substrate. For the TEM characterization, a 10 nm thick Si₃N₄ membrane was used as the growth substrate. For the kinetics characterization, XRD, and ellipsometry characterization, SrTiO₃ (100) was used as the growth substrate³³.

In-situ cryo-CL TEM

STEM CL was performed on a spherical aberration image-corrected FEI Titan Environmental Scanning/Transmission Electron Microscope at 300 kV accelerating voltage; with a probe size of 0.5 nm. The holder is a TEM cathodoluminescence-cryogenic holder (Gatan, Inc.). The 450 nm laser is a CW diode laser (Thorlabs). CL was collected by a top and the bottom optical fiber from the CL holder into a spectrometer. To phase separate the materials, the 450nm laser power was set to 10 mW (measured before entering the CL holder) and was guided into the CL holder from the top port (2% one-way efficiency of coupling light into the holder), which creates approximately a 200 μm diameter spot. To collect CL maps for the phase separation process, the CL holder was cooled with liquid nitrogen to -100 °C. The phase separation during the CL

experiments was performed at -100 °C. Dwell time of the electron beam on each pixel was varied between 0.05 s to 10^{-6} s, based on the emission intensity. The CL spectrum was then normalized based on the dwell time. For the recovery process, the holder was heated to 50 °C and 60 °C.

Photoluminescence

Photoluminescence spectra were measured using a Horiba FluoroLog-3 Fluorimeter equipped with a 450W HgXe arc lamp source, a Horiba PPD-900 photon counting detector, and an iHR320 imaging spectrometer. 1200 nm/groove 300 nm and 500 nm blazed excitation and emission gratings were used, respectively. Emission spectra were collected using 2s integration time and 405 nm illumination wavelength. Time dependent PL switch-on behavior was measured by observing the PL intensity at 2s intervals at the new, photo-induced peak wavelength (627 nm) with the illumination turned on; the switch-off behavior was measured the same way with chopped illumination keeping the light off except for short periods of time (duration $\sim$ 5s, frequency $\sim$ 8 mHz) to measure the decay of intensity in the photo-induced peak.

Focusing on the iodide-rich emission wavelength at 627 nm (center wavelength of iodide rich PL emission in Figure S24a), we obtain PL emission intensity as a function of illumination time. The normalized PL intensity is fitted to $1-e^{-kt}$ for the forward phase separation process and $1+e^{-kt}$ for the reverse phase separation process assuming a kinetic process with a single (temperature-dependent) time constant k . This functional dependence was previously reported in phase separation of organic mixed halide perovskite thin films⁸. This simple exponential time dependence of the peak iodide concentration was expected for spinodal decomposition. The fitted function is in agreement with the experimentally observed data (Figure S24 c-f).

Supplemental Note 1

Phase-field Modeling

The phase-field simulations are performed on a 2D square domain with 3000 nm side length and 300×300 square mesh elements. The system is subjected to periodic boundary conditions. During the simulations, the phase field evolves to reduce the total free energy of the system. The total free energy G_{tot} of the halide perovskite system can be expressed as a functional of the solute fraction field $c(x)$ ($c(x) \in [0,1]$, $c(x) = 0$ when $x_I = 0$ and $c(x) = 1$ when $x_I = 1$),

$$G[c(x)] = G_{\text{mix}}[c(x)] + G_{\text{grad}}[c(x)] + G_{\text{ele}}[c(x)] + G_{\text{sep}}[c(x)] \quad (1)$$

where G_{mix} , G_{sep} and G_{ele} are the mixing, gradient and electronic contributions respectively, with a generation rate dependent G_{sep} term for providing extra driving force of phase separation.

The solute fraction field $c(x)$ evolves toward the direction of minimizing the total free energy, whose thermodynamic driving force is determined by the variational derivative of the free energy G with respect to $c(x)$,

$$\frac{\delta G}{\delta c(x)} = \frac{\delta G_{\text{mix}}}{\delta c(x)} + \frac{\delta G_{\text{grad}}}{\delta c(x)} + \frac{\delta G_{\text{ele}}}{\delta c(x)} + \frac{\delta G_{\text{sep}}}{\delta c(x)} \quad (2)$$

In this model, the $c(\mathbf{x})$ dependent local energies of the valence and conduction bands lead to a natural coupling between the chemical and electronic degrees of freedom. To lower the total

free energy, electrons and holes preferentially accumulate in regions of greater $c(\mathbf{x})$ where the band gap is smaller. Conversely, the accumulation of carriers in these regions favors a further increase of iodide concentration in this region by diffusion. However, our simulations at 173K show that the scale of this coupling effect is about three orders of magnitude smaller (see Table S1 and Figure S5) than needed to overcome the mixing and interfacial free energies (as described in Equation S19 and S20). This implies that other factors need to be introduced, to induce phase separation as observed in the experiments. For this purpose, the term G_{sep} is incorporated into the free energy functional, following the approach used in²⁴ (Figure S1). When the perovskite enters the illumination-induced non-equilibrium state, G_{sep} takes effects to modify the effective enthalpy of mixing by an amount dependent on $n(\mathbf{x}) \cdot p(\mathbf{x})$. While in²⁴ this energy has been explained by the strain energy associated with polarons^{21,34}, we note that the exact physical origin of the effect has yet to be well understood, and several other possibilities exist. For instance, facile and relatively long-lived trapping of holes at shallow states near the valence band edge associated with interstitial halide defects^{35,36} can produce a large effective density ($\sim 10^{17} \text{ cm}^{-3}$) of electronic carriers, that will contribute to the photo-induced instability in addition to carriers in the bands, although such a contribution is not explicitly included in the model developed herein, it would be implicitly included in G_{sep} should such shallow states exist. Overall, the G_{sep} term is considered to collect such additional physical processes (beyond band energy coupling) that promote phase separation. The resulting phase diagram in comparison with that under the dark condition is given in Figure S8. The above model was implemented in Python. More details of the model as well as necessary input parameters for reproducing the simulations were provided in the SI.

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Author Contributions

S.P. and P.C.M. conceived the experiment; S.P., A.C.M., W.T. and K.S. performed materials synthesis; S.P., A.C.M. and B.S. performed in-situ PL characterizations; S.P., M.B., A.F.M. and K.S. performed in-situ TEM and CL characterizations; Y.W., Y.Y. and W.C. performed phase field modeling; all authors contributed to writing the manuscript.

Declaration of Interests

The authors declare no competing interests.

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Figure 1 Spatio-temporal dependence of phase separation at 173K (a) CL spectrum at 0, 5 and 25 minutes of illumination (b) CL map at 0, 5 and 25 min of illumination (c) spatio dependence of emission energy at 0, 5 and 25 min of illumination (d) STEM image of a single crystalline halide perovskite thin film with 30% iodide concentration, where the investigated area is indicated by the white dashed box (e) first nearest neighbor distances of the iodide rich emission at 640 nm at 5 min of illumination (f) first nearest neighbor distances of the iodide rich emission at 716 nm at 25 min of illumination.

Figure 2 (a) CL emission maps at 626 nm at 0 min, 5 min, 10 min, 15 min, 20 min, 30 min, 40 min, 50 min and 60 min (b) time dependent nearest neighbor distance at 626 nm shown by the purple dots, where the dashed line is a cube spline fit of the data points (c) integrated CL peak intensity as a function of time of phase separation shown by the blue dots (d) integrated CL peak emission energy as a function of time of phase separation shown by the yellow dots.

Figure 3 Phase separation in a mixed-halide perovskite alloy: (a) TEM image of a halide perovskite crystal showing bend contours, which likely occur during post-deposition cooling due to thermal expansion mismatch of the film/substrate. The circle marks the selected area for diffraction, which is on the $\langle 100 \rangle$ zone axis. (b) Diffraction before phase separation and (c) diffraction after phase separation. Radial streaking of the diffraction spots is observed. Diffraction points are indexed based on the cubic phase^{37,38}. The extra reflections in both patterns show that the films have the orthorhombic crystal structure^{39,40}, (d) log of rate constant k of phase separation versus light intensity at room temperature determined by fitting $5-5e^{-t/2283}$ (black), $3-3e^{-t/5000}$ (red), $0.2-0.2e^{-t/9937}$ (blue) to PL emission at 627 nm (e) log of rate constant of phase separation versus temperature by fitting $8-8e^{-t/2387}$ (black), $4-4e^{-t/4000}$ (red), $8-8e^{-t/15299}$ (blue) to PL emission at 627 nm from room temperature to 318 K (f) log of reverse rate constant of phase separation versus temperature by fitting $-1.3+27e^{-t/904}$ (black), $-0.5+9e^{-t/846}$ (red), $0.3+7e^{-t/536}$ (blue) to PL emission at 627 nm from room temperature to 318 K.

Figure 4 Phase field simulations of a mixed-halide perovskite alloy system: (a) Spatial distributions of the carrier concentrations ($n \cdot p$) at the end of the simulation at carrier generate rates of $1.2 \times 10^{21} \text{ cm}^{-3}/\text{s}$ (blue) and $2.0 \times 10^{21} \text{ cm}^{-3}/\text{s}$ (red), in comparison with the experimental data at 173 K; The total area of the I-rich regions plotted as a function of time at carrier generate rates of $1.2 \times 10^{21} \text{ cm}^{-3}/\text{s}$ (blue line) and $2.0 \times 10^{21} \text{ cm}^{-3}/\text{s}$ (red line) respectively, with the corresponding in comparison with the experimental data (black dots). (b) The evolution of iodide compositional distribution during the simulation. (c) The total free energy density with its detailed decomposition plotted as functions of iodide concentration, where G_{sep} , G_{mix} , G_{tot} are free energy contribution of separation, mixing, and total free energy respectively, aside by a zoom-in view of the variations of the Gibbs free energy and its 2nd derivative, and the distribution of the iodide concentration from a phase-separated simulation configuration. Two separate minima at $x_{\text{I}}=0.15$ and $x_{\text{I}}=0.85$ for the conditions simulated are identified on the G_{tot} curve with a small barrier of $\sim 0.007 \text{ eV/nm}^3$ in between. (d) The average nearest-neighbor distance between I-rich clusters plotted as function of time, in comparison with the experimental data.