

Phase Stability and Diffusion in Lateral Heterostructures of Methyl Ammonium Lead Halide Perovskites

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ABSTRACT. Mixed-halide hybrid organic inorganic perovskites have band gaps that span the visible spectrum making them candidates for optoelectronic devices. Diffusion of the halide atoms in methyl ammonium lead iodide (MAPbI_3) and its alloys with bromine has been observed in both dark and under illumination. While halide transport upon application of electric fields has received much attention, less is known regarding bromide and iodide interdiffusion down concentration gradients. This work provides an upper bound on the bromide-iodide interdiffusion coefficient D_i in thin films of $(\text{MAPbBr}_x\text{I}_{1-x})_3$ using a diffusion couple of a lateral heterostructure. The upper bound of D_i was extracted from changes in the interface profiles of the heterostructures upon exposure to heat. The stability of thoroughly-heated interfacial profiles suggests that the miscibility gap extends to higher temperatures and to a higher fractional composition of bromine than predicted by theory. The results of this work provide guidance for compositions of thermally stable heterostructures of hybrid halide perovskites.

Key words: halide perovskite, mixed halide, diffusion, phase diagram, heterostructure, halide substitution, diffusion couple.

INTRODUCTION

Hybrid halide perovskites have recently emerged as candidates for optoelectronic applications because they exhibit solar cell efficiencies similar to those of crystalline silicon,^{1,2} are solution processable, and are made from inexpensive, earth-abundant materials.³⁻⁶ Hybrid halide perovskites have an ABX_3 structure, where A is a cation (e.g. Cs^+ , $CH_3NH_3^+$, $CH_5N_2^+$), B is a metal (e.g. Pb, Sn, Bi) and X is a halide. Mixed A-site cations and halides can be used to tune the optical gap and structure near room temperature; the resulting alloys have the highest power conversion efficiency in solar cells.^{1,7-14} Films of nanocrystals of alloys are efficient light emitters, with quantum yields up to 90 %, ¹⁵ and have been explored for LED applications.¹⁶ Despite the successes of alloys, halides can diffuse in hybrid perovskites, ¹⁷ which negatively impacts the performance of devices. Hysteresis in the current-voltage characteristics of solar cells is attributed to halide migration.^{18,19} Mixed bromide-iodide perovskites can phase separate into I-rich and Br-rich domains upon light exposure,²⁰⁻³¹ leading to instabilities in the performance of Br-rich perovskite solar cells.³²⁻³⁷ A thorough understanding of halide movement in mixed-halide perovskites is therefore desirable for future design of efficient devices.

While much progress has been made towards understanding the mechanisms and kinetics of light-induced phase separation,²⁰⁻³¹ the diffusion of halides in $MAPb(Br_xI_{1-x})_3$ without illumination is not as well understood. Many studies have focused on ion/vacancy movement in response to an electric field,^{18,38-48} rather than on ion/vacancy movement down a concentration gradient.^{29,49} Recent work has elucidated interdiffusion behavior of bromide and chloride in $CsPb(Br_xCl_{1-x})_3$ nanowires;^{49,50} however, interdiffusion in Br-I systems has been less explored. Halide interdiffusion constants were previously extracted from $CsPbBr_3$ - $MAPbI_3$ ⁴⁹ and $PbBr_2$ - $MAPbI_3$ ²⁹ heterostructures, where distances travelled by the halides in a given time enabled calculation of

the diffusion constant.^{29,49} However, halide interdiffusion in CsPbBr₃-MAPbI₃ and PbBr₂-MAPbI₃ may differ from that in pure MAPbX₃ because of differences between the phase diagrams of the systems. Studies of Br-I interdiffusion in the MAPb(Br_xI_{1-x})₃ system are further complicated by the prediction of a miscibility gap,⁵¹⁻⁵² where compositions within the gap phase-separate into I-rich and Br-rich regions, impeding halide interdiffusion down concentration gradients.

Here, we examine interdiffusion of halides in diffusion couples with varying composition of MAPb(Br_xI_{1-x})₃ at temperatures relevant to electronic devices. Using a halide substitution procedure, we fabricated lateral heterostructures of hybrid halide perovskite thin films and examined changes in the interfacial profiles upon exposure to heat and light. The stability of interfacial profiles confirmed that the interdiffusion coefficients D_i at temperatures relevant to device operation are low, and suggests that the MAPb(Br_xI_{1-x})₃ miscibility gap extends to higher temperatures and more Br-rich compositions than expected based on computational models. These results suggest compositions where it is possible to form heat-stable heterostructures of MAPb(Br_xI_{1-x})₃.

RESULTS AND DISCUSSION

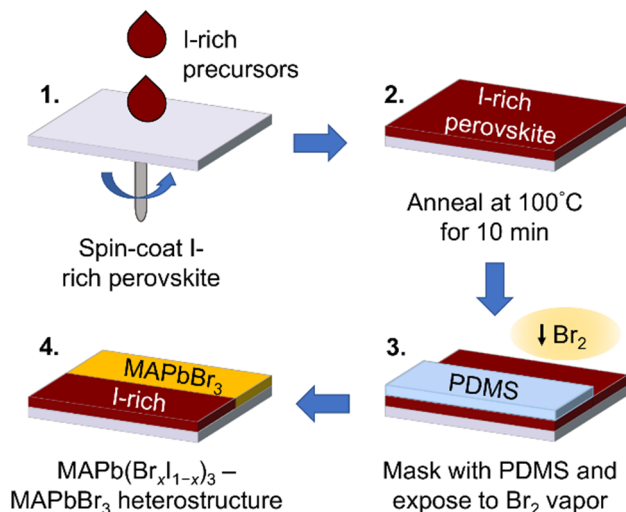


Figure 1. Fabrication procedure for perovskite-perovskite heterostructures.

To fabricate a diffusion couple comprising a lateral heterostructure of two compositions of $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$, we used a two-step process. First, we spin-coated an I-rich perovskite thin film and then we used a halide exchange reaction to form the heterostructure.⁵³ We sought a methodology that would reflect the crystallinity and microstructure of thin films typically used in devices. Other heterostructures or halide gradients have been formed by processes including solution exchange,⁵⁴ placement of microplates on top of nanowires,⁴⁹ activation of phase separation/domain merging in single crystal nanowires using light,²⁵ electron-beam lithographic patterning of nanowires,⁵⁵ and contacting nanowires with single crystals.⁵⁶ While lithographic patterning enables fabrication of very sharp patterns, developers and electron beams may cause sample damage and/or introduce vacancies in the hybrid halide perovskites.⁵⁷ Modification of the halide composition using precursors in solvent may also impact the crystallinity of the substituted layer due to recrystallization. We therefore selected substitution by reaction with a vapor of Br_2 to ensure that the I-rich and Br-rich perovskites had similar morphology and grain size,⁵³ which is

desirable for interdiffusion studies. As with many substitution procedures, the number of vacancies in the Br₂-exposed side may change relative to that on the masked side, which could change the rates of interdiffusion in these two areas relative to other methods.

The procedure to form lateral heterostructures is shown in **Figure 1**. Iodine-rich perovskites were spin-coated onto quartz substrates. We chose an I-rich perovskite spin-coating procedure that yields 17% solar cell efficiency for MAPbI₃, before any halide substitution (**Figure S1**). A ≈ 450 μm -thick PDMS conformal mask was then laid on top of the thin film of MAPb(Br_{*x*}I_{1-*x*})₃, thus covering half of the 1.5 cm \times 1.5 cm \times 300 nm thin film. The masked film was exposed to bromine vapor (≈ 0.48 atm) in a nitrogen environment. The PDMS acted as a barrier to the bromine vapor and the exposed areas were allowed to react fully with the vapor, yielding MAPbBr₃. Consistent with previous reports,⁵³ the reaction was complete within one minute, indicating rapid reaction of Br₂ with MAPbI₃. The PDMS was then peeled off, leaving behind a lateral heterostructure of MAPb(Br_{*x*}I_{1-*x*})₃|MAPbBr₃. We focused on heterostructures with three compositions: MAPbI₃|MAPbBr₃, MAPb(Br_{0.12}I_{0.88})₃|MAPbBr₃, and MAPb(Br_{0.70}I_{0.30})₃|MAPbBr₃. These are hereafter referred to as $x_{\text{Br}} = 0|1$, $x_{\text{Br}} = 0.12|1$, and $x_{\text{Br}} = 0.70|1$ heterostructures respectively. We chose to examine the response of iodine-containing phases $x_{\text{Br}} = 0.12$ and $x_{\text{Br}} = 0.70$, in addition to that of $x_{\text{Br}} = 0$, because these are at the approximate locations of the binodal lines at room-temperature predicted by calculations using density functional theory.⁵¹

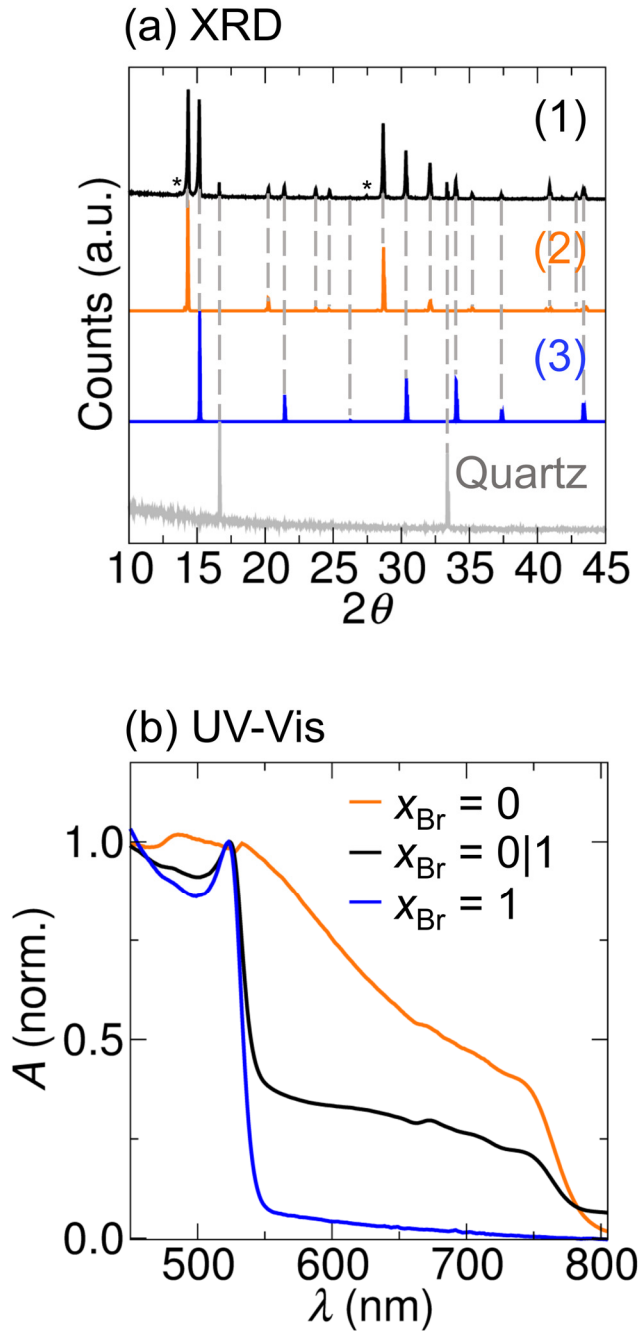


Figure 2. (a) XRD patterns of the MAPbI₃-MAPbBr₃ heterostructure ($x_{\text{Br}} = 0|1$ - black trace (1)), of simulated MAPbI₃ (orange trace (2)), of simulated MAPbBr₃ (blue trace (3)), and the quartz substrate (gray trace). Simulations were performed using the *I4/mcm* structure of MAPbI₃⁵⁸ and using the *Pm-3m* structure of MAPbBr₃.²⁶ The dotted gray lines are guides for the eye, and the black * indicate additional peaks arising from Tungsten (1.4764 Å) and CuKβ (1.3926 Å) contamination in the X-Ray source. (b) UV-Vis spectra of the MAPbI₃-MAPbBr₃ heterostructure, of spin-cast MAPbI₃ and of spin-cast MAPbBr₃.

The conformal mask and substitution by Br₂ vapor led to complete exchange of the halide along with an interfacial region (70 - 100 microns wide) of mixed composition; examination of changes along this interfacial region in response to heat was used to analyze phase behavior in MAPb(Br_xI_{1-x})₃, as will be discussed later. Formation of the desired heterostructures was confirmed via X-Ray Diffraction (XRD), UV-Vis spectroscopy (**Figure 2**), Scanning Electron Microscopy (SEM – **Figure 3**) combined with Energy-Dispersive X-ray analysis (EDX – **Figures S2, S3 and S4**) and confocal microscopy (**Figures 3 and S5**). XRD of the entire film of an $x_{\text{Br}} = 0|1$ heterostructure displayed peaks corresponding to both MAPbI₃ and MAPbBr₃, indicating full replacement of the iodine with bromine (**Figure 2a**). Similarly, the UV-Vis spectrum of an $x_{\text{Br}} = 0|1$ heterostructure displayed increased absorption at the onsets of the MAPbI₃ and MAPbBr₃ bandgaps (**Figure 2b**). XRD and UV-Vis characterization for the $x_{\text{Br}} = 0.12|1$ and $x_{\text{Br}} = 0.70|1$ heterostructures also confirmed formation of the desired phases (**Figure S6**). Plan view SEM of $x_{\text{Br}} = 0|1$ revealed the local structure of the interfacial region (**Figure 3a**). The films comprised \approx 300 nm grains contained in large, continuous domains, which is favorable for examining halide diffusion across large areas. The change in contrast in domains along the interface indicated that halide substitution occurred in the middle of the domains (**Figure 3a**). Top-view and cross-sectional EDX (**Figures 4, S2, S3, and S4**) confirmed the locations of Br and I, and thus of $x_{\text{Br}} = 0$ and $x_{\text{Br}} = 1$. No iodine was observed above noise level in the $x_{\text{Br}} = 1$ region, again suggesting complete removal of iodine from this area. Intermediate x_{Br} compositions along the interface were assigned based on halide content relative to the EDX- and optically-determined $x_{\text{Br}} = 0$ and $x_{\text{Br}} = 1$ compositions for $x_{\text{Br}} = 0|1$. Similar analysis was performed to determine macroscopic interfacial composition in the $x_{\text{Br}} = 0.12|1$ and $x_{\text{Br}} = 0.70|1$ heterostructures. EDX baseline compositions were obtained far from the interface (data not shown) to confirm lack of bromine in $x_{\text{Br}} = 0$ and lack of

iodine in $x_{\text{Br}} = 1$ (Figures 4, 6 and S3). The interface width was determined to be $\approx 100 \mu\text{m}$ (Figures 4 and S3) via both EDX, optical microscopy, and confocal laser scanning microscopy (Figures 3b-d and S5). We attribute the width of the interfacial region to our fabrication procedure in which Br_2 vapor permeates PDMS at the edge of the mask (Figure S7); and note that in a system with a miscibility gap, which is predicted for the $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ system,⁵¹ a sharp interface would be expected with an impermeable mask.

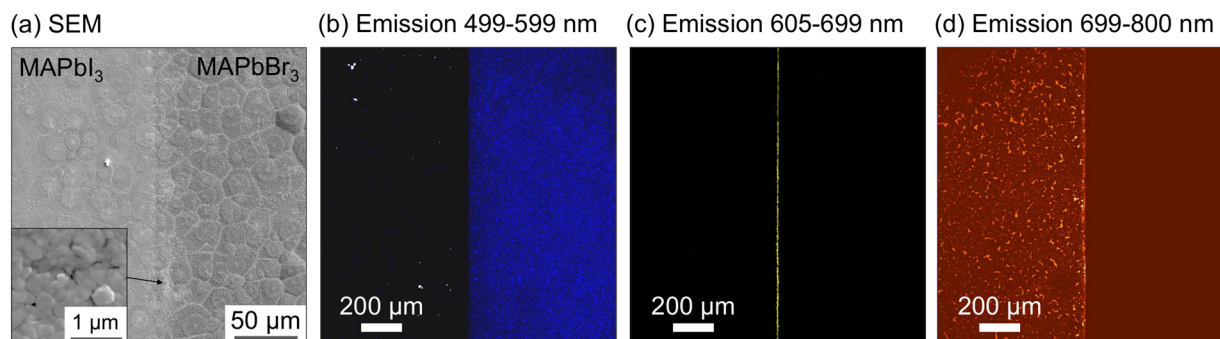


Figure 3. Plan view SEM of an MAPbI_3 - MAPbBr_3 heterostructure before heating (a). The inset in is a high-magnification view of the area indicated by the arrow. Confocal scanning luminescence emission map at three windows of emission, 499 - 599 nm (b), 605 - 699 nm (c), and 699 - 800 nm(d), each labelled with false color, of an MAPbI_3 - MAPbBr_3 heterostructure before heating, with excitation wavelength 458 nm.

We examined the phase stability of the heterostructures upon heating without light exposure, at temperatures relevant for thin film devices (see **Methods section in the SI**). Operating temperatures are typically under 70°C for solar cells⁵⁹ and lamination or curing temperatures for solar cell encapsulants can exceed 100°C .^{60,61} The miscibility gap for $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ calculated by DFT extends to 70°C ,⁵¹ leading to the expectation that halides will not diffuse down concentration gradients below this temperature. We therefore selected 100°C because it is within the window of temperatures encountered under practical conditions for devices and can test the

expected miscibility of the halide ions, at a temperature that will not be too damaging to the perovskite layer.⁶² Prior to heating, we spin-coated a thin layer of polystyrene on top of the heterostructure, both to prevent desorption of methylammonium, enabling lengthy and high-temperature experiments, and to minimize diffusion along the perovskite surface. The heterostructures were heated for extended times (up to 360 min.) on a hot plate with a heat diffuser in a nitrogen-filled glove box. Lack of degradation and changes in grain structure after heating were confirmed via XRD and top-view SEM (**Figures S8 and S9**). The heat diffuser was encased in aluminum foil to ensure that the samples were kept in the dark, as light may affect halide transport. After heating, the compositional profiles at the heterostructure interface were analyzed via optical microscopy in transmission mode and via EDX (**Figure 4**). At each time point, the samples were quickly removed from the hot plate/heat diffuser in the glove box for optical microscopy analysis and were placed again on the heat diffuser afterwards. The total time off of the hot plate, at each time point, was kept under 10 min. This method ensured rapid quenching of any halide migration, which would be visible via change in local bandgap. Using optical microscopy to obtain interface profiles enabled repeated analysis of the same location on each heterostructure at each time point, enabling very rapid analysis of the interface profiles at specific times. Optical microscopy also circumvented potential electron beam-induced sample damage (and corresponding changes in vacancy concentration) that may have occurred during EDX analysis. Interface profiles were subsequently analyzed after heating via EDX to confirm the composition.

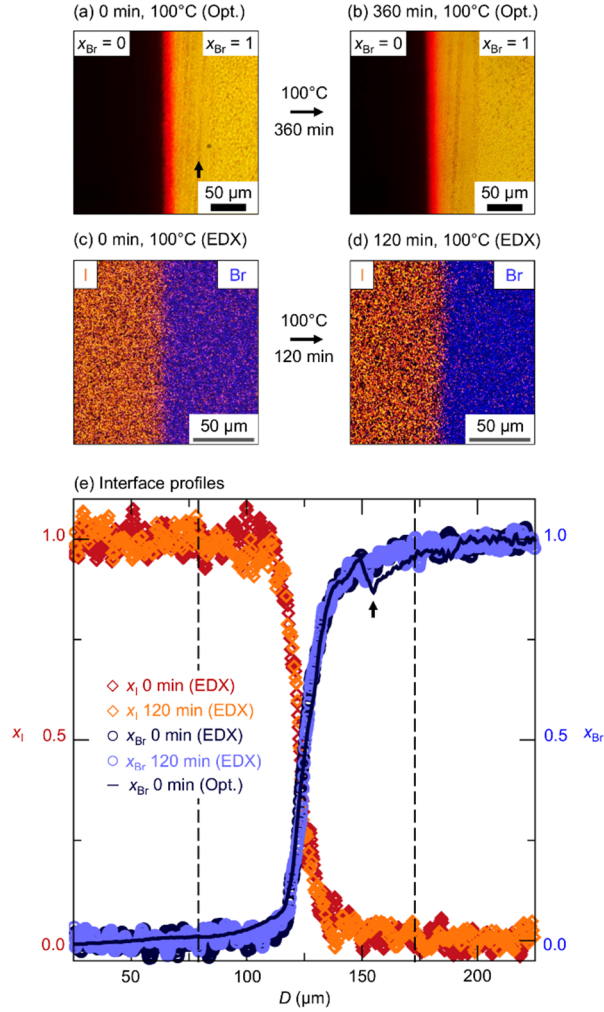


Figure 4. Optical microscopy images (transmission mode) of the same $x_{\text{Br}} = 0|1$ heterostructure before (a) and after (b) heating at 100°C for 360 min, obtained via illumination with white light. EDX maps of I and Br in separate $x_{\text{Br}} = 0|1$ heterostructures before (c) and after (d) heating at 100°C for 120 min. (e) Interface profiles (halide fraction vs. distance D) of the heterostructures in (a)-(d), showing overlap of the optical microscopy and EDX-determined x_{Br} traces. x_{I} represents the halide fraction of I obtained from the EDX images (c) and (d) (orange circles). x_{Br} represents the halide fraction of Br obtained from the EDX images (c) and (d) (blue circles) and from the optical microscopy image (a) (blue line). The dashed lines indicate the interface width. The black arrow in (a) and (e) denotes residual PDMS on the heterostructure surface (**Figure S7**), resulting in a dip in optical intensity near $\approx 150 \mu\text{m}$.

We verified that optical microscopy provided comparable interfacial profiles to EDX, enabling a measurement of the interface profiles in a quasi-real-time and non-destructive manner (**Figure**

4). The interface profiles of $x_{\text{Br}} = 0|1$ obtained before and after heating, using both optical microscopy and EDX, are shown in **Figure 4**. Because the bandgap of MAPbBr₃ is ≈ 540 nm and that of MAPbI₃ is ≈ 775 nm (**Figure 2b**), when the heterostructures were illuminated with white light, the MAPbI₃, the MAPbBr₃ and the intermediate mixed-halide regions exhibited very different transmission behavior (**Figure 4a/b**) and thus very different contrast. The dark color in **Figure 4a/b** is MAPbI₃, the yellow is MAPbBr₃, and the pink is the intermediate region. The images were converted to grayscale by taking the average values of the red, green and blue pixels, giving each pixel equal weight. We then integrated the images to obtain interface profiles, with the darker and lighter areas corresponding to MAPbI₃ and MAPbBr₃ respectively (**Figure 4e** and **Supporting Information**). Interface profiles obtained from EDX overlapped well with those obtained via optical microscopy (**Figure 4e**), confirming the validity of the optical method. The optical microscopy and EDX interfacial profiles differ at a position of ≈ 150 μm along the interface (black arrows in **Figure 4a/e**), which we attribute to residual PDMS on the sample (**Figure S7**). We assume the EDX trace is more accurate in this region. We subsequently applied the optical method to $x_{\text{Br}} = 0.70|1$ and $x_{\text{Br}} = 0.12|1$ heterostructures (**Figures 7** and **S10**), again confirming compositions using EDX.

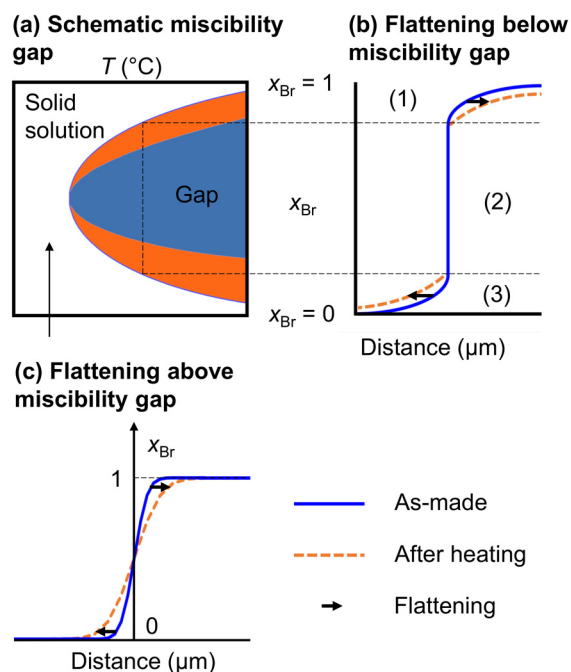


Figure 5. (a) Predicted miscibility gap for the $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ system following a regular solution model (from DFT⁵¹), with expected interface profile behavior (b) when heated to below the gap for a two-phase binary system and (c) when heated to above the gap, for a single-phase binary system.⁶³ Sections (1) and (3) refer to the Br-rich and I-rich halide miscible regions outside the miscibility gap, and section (2) refers to the halide-immiscible region within the gap. The blue and orange regions designate predicted binodal and spinodal areas of the miscibility gap.

The expected changes in the interface profiles upon exposure to heat strongly depend on whether or not the heterostructure is heated to below or above the miscibility gap.^{63,64} **Figure 5** depicts a schematic miscibility gap for the $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ system, with approximate interfacial profile shapes before and after heating shown if the heterostructure is kept at temperatures within the miscibility gap (**Figure 5b**) or is heated to above the miscibility gap (**Figure 5c**). For simplicity, the tetragonal-cubic phase transition in the I-rich region is not shown. Within the schematic gap (**Figure 5a** - shaded area), halides are expected to phase separate into I-rich and Br-rich phases. The shape of the interface profile is thus not expected to change for composition regions of the

interfacial profile that are contained within the miscibility gap (**Figure 5b** – section (2)). However, outside of the miscibility gap, halides can still intermix, which should change the shape of the profile away from the interface (**Figure 5b** – sections (1) and (3)). Due to mass balance as halides move from one side to the other, the interface should shift also slightly in location (**Figure 5b**).^{63,64} In contrast, should the heterostructures be heated to above the miscibility gap (**Figure 5c**), halides should be free to intermix across the entire interfacial profile. Br and I should thus diffuse down their respective concentration gradients, resulting in apparent flattening of the entire interfacial profile, as shown in **Figure 5c**. This flattening would be most apparent near the edges of the interface (Br-rich and I-rich regions), and least apparent near the mid-point, where the composition stays constant.

Before discussing the response of the interfacial profiles to heat, we first analyzed the behavior of the interfacial profiles upon formation. Although XRD and other characterizations indicated clear presence $x_{\text{Br}} = 0$ and $x_{\text{Br}} = 1$ in the heterostructure (**Figures 2 and 4**), no XRD peaks corresponding to intermediate compositions were identified (**Figure 2 and S6**), as the interfacial region is a small percentage of the overall area in the incident beam. Given the presence of the gap,^{25,51} one might expect the interface to be composed of crystallites with stoichiometries corresponding to the I-rich and Br-rich binodal lines. When averaged, mixtures of different amounts of these crystallites would then yield the apparently-smooth composition profiles of **Figures 4 and 6**. In agreement with this, a MAPbI₃ film exposed to Br₂ vapor for only 5 seconds (as opposed to 60s required for full bromination) exhibited highly uneven bromination, in the sense that exposure to Br₂ vapor induced formation of pockets of Br-rich regions, rather than the even, gradual composition change that would be expected if the compositions were miscible (**Figure S11**). However, emission corresponding to intermediate mixed-halide compositions (605 - 699

nm, or $0.3 < x_{\text{Br}} < 0.7$; see discussion of **Figure S5**) was observed in the interfacial region via scanning confocal microscopy (**Figures 2b** and **S5**), where sample exposure times are on the order of microseconds, indicating some retention of the $0.3 < x_{\text{Br}} < 0.7$ compositions. Prolonged exposure to above-bandgap light (405 nm, or 3.06 eV) induced a red-shifting photoluminescence emission at 730 nm (1.7 eV) that also became more intense over time, which is characteristic of light-induced phase separation into I-rich and Br-rich regions²⁰ (**Figure S12**), and suggests that some intermediate compositions were present initially. Given all these observations, it is likely that upon formation, the interface was composed of some metastable intermediate compositions, as well as of some phase separated nanoscale I-rich and Br-rich regions (**Figures 2b** and **S5**).

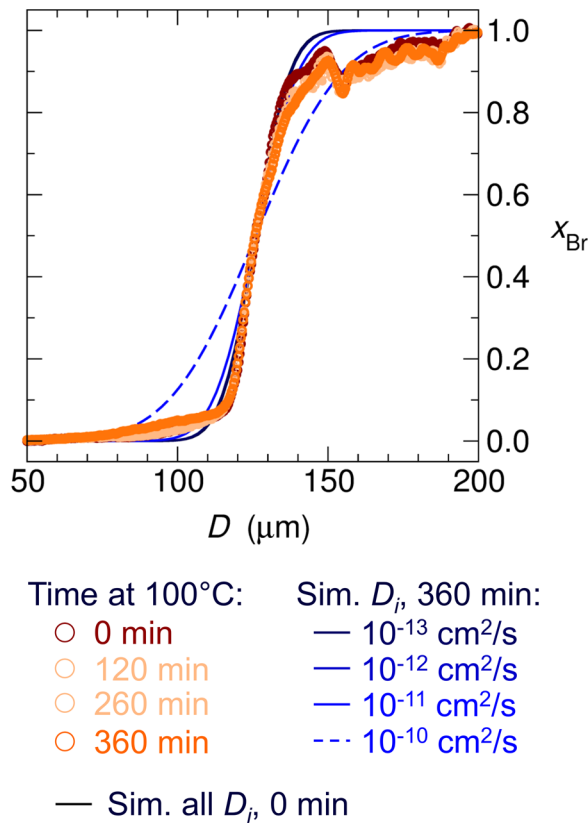


Figure 6. Compositional profiles of an $x_{\text{Br}}=0|1$ heterostructure obtained using optical microscopy after 0 min, 120 min, 260 min and 360 min of heating at 100°C. Profiles from Fick’s second law with different interdiffusion coefficients D_i were calculated as described in **Section S9**.

We then examined the effects of heating on the interfacial profiles. All heterostructures studied exhibited little interfacial profile flattening upon heat exposure (**Figures 6, 7, S10 and S15**). Slight changes in composition near $x_{\text{Br}} = 0.8$ and $x_{\text{Br}} = 0.1$ were observed in $x_{\text{Br}} = 0|1$ after heating at 100°C for 360 min (**Figure 6**); however, overall, the interfacial profiles changed very little. The profiles do not follow Fickian behavior described by **Figure 5c**, i.e. what would be expected from a solid solution (see **Figure S13**). Calculations of how the diffusion profile should change according to Fick's law (see **Section S9** of the **Supporting Information**) with interdiffusion coefficients D_i of different magnitudes were overlaid with the interfacial profiles for comparison (**Figure 6**). Although there is some uncertainty of the profile derived from microscopy at higher values of x_{Br} , D_i cannot be larger than $\sim 10^{-11}$ cm^2/s at 100°C based on examination of the profile on both sides of the interface. The profiles of the $x_{\text{Br}} = 0.12|1$ and $x_{\text{Br}} = 0.70|1$ heterostructures were also unchanged upon heating at 100°C for 260 min by microscopy and EDX (**Figures 7 and S10, S14**). We thus take $D_i \leq 10^{-11}$ cm^2/s as an upper bound of the interdiffusion coefficient for $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ at 100°C . Such a value is consistent with D_i obtained at lower temperatures and in different systems, namely 3×10^{-12} cm^2/s at 50°C using PbBr_2 as a Br-source for a PbBr_2 - MAPbI_3 heterostructure²⁹ and $\sim 1 \times 10^{-12}$ cm^2/s at room temperature for a CsPbBr_3 - MAPbI_3 heterostructure.⁴⁹ However, the poor fit to this model suggests an alternative explanation.

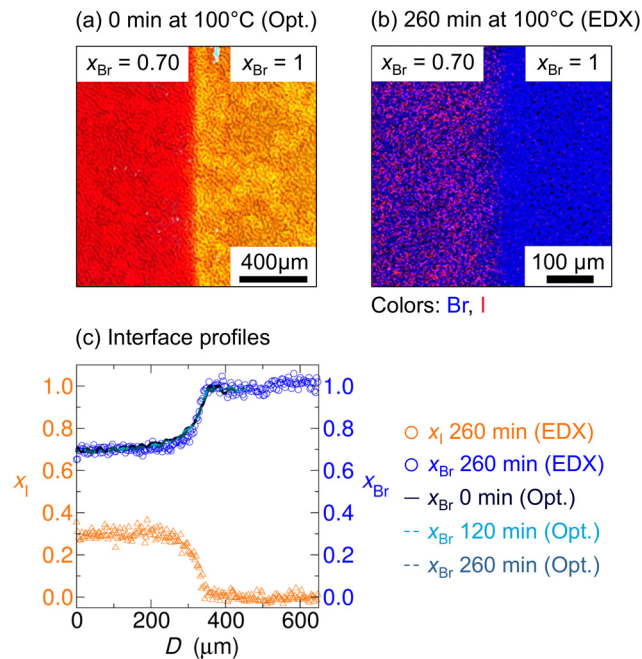
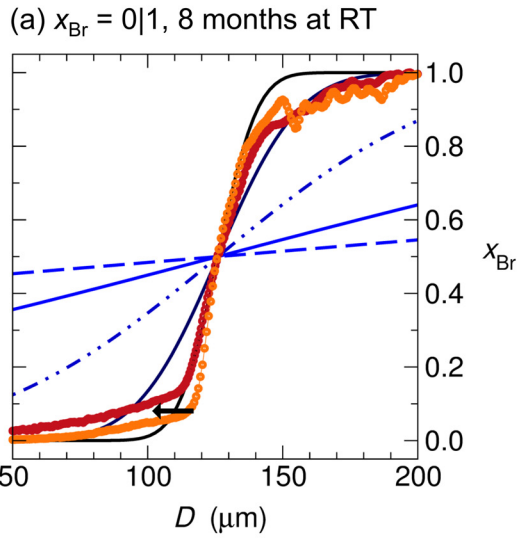


Figure 7. (a) Optical microscopy image of an $x_{Br} = 0.70|1$ heterostructure before heating. (b) EDX mapping of I and Br in the same $x_{Br} = 0.70|1$ heterostructure (in the same location) after heating at 100°C for 260 min. (c) Interface profiles (halide fraction vs. distance D) of the same $x_{Br} = 0.70|1$ heterostructure upon heating to 100°C for varying amounts of time. x_I represents the halide fraction of I obtained from the EDX image (b) (orange circles). x_{Br} represents the halide fraction of Br obtained from the EDX image (b) (blue circles) as well as from the optical microscopy image (a) (black line). Additional interface profiles obtained via optical microscopy are included (dashed blue lines).

The lack of flattening of the interfacial region may indicate slow interdiffusion, but if the miscibility gap extends to higher temperatures than predicted then we would expect different behavior than that of **Figure 5c**. The changes in the interface profile at 100°C were slight and only at the edges of the interface profiles (**Figure 6**), much like the interfacial profiles depicted in **Figure 5b**. No large changes were observed in $x_{Br} = 0.12|1$ and in $x_{Br} = 0.70|1$ heterostructures upon heating at 100°C for 260 min (**Figures 7** and **S10**). The interfacial profiles were all set to overlap at $x_{Br} = 0.5$ during analysis and we do not have a marker to track changes in the interfacial profile shifted in location as in **Figure 5b**. We also examined a $x_{Br} = 0|1$ formed using another

route to for the initial MAPbI₃ layer and found similar behavior (**Figure S15**). Overall, these results suggest a miscibility gap extending to above 100°C and well into the Br-rich region.



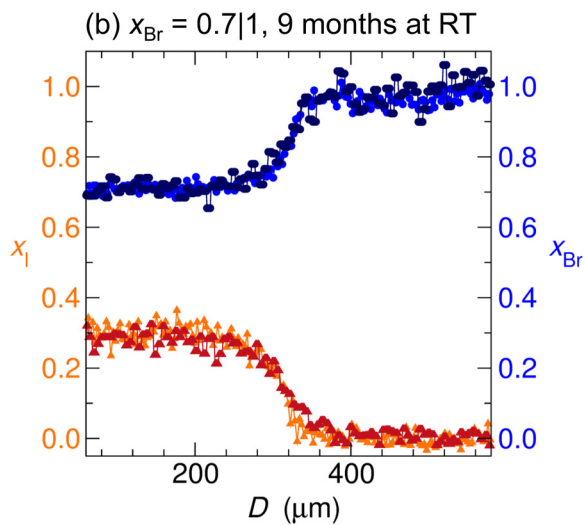
Time at RT: Sim. D_i , 8 months:

○ 0 months — 10^{-13} cm²/s

○ 8 months - - 10^{-12} cm²/s

— Sim. 0 min — 10^{-11} cm²/s

← Flattening - - 10^{-10} cm²/s



Time at RT:

→ x_i 0 months

→ x_i 9 months

• x_{Br} 0 months

• x_{Br} 9 months

Figure 8. Effects of 8-9 months of storage at room temperature on the interfacial profiles of (a) $x_{Br} = 0|1$ and (b) $x_{Br} = 0.70|1$, with overlapping simulations of Fick's law with different D_i and interfacial profile flattening (black arrow).

To rule out the possibility of slow interdiffusion at room temperature, we then examined the response of interfacial profiles to long-term storage (8-9 months), to determine the composition bounds of the miscibility gap at room temperature. All encapsulated heterostructures ($x_{\text{Br}}=0|1$, $x_{\text{Br}}=0.12|1$ and $x_{\text{Br}}=0.70|1$) were stored at room temperature in ambient for 8 to 9 months, after which the interfacial profiles were again obtained via a combination of optical microscopy and EDX (**Figures 8, S10 and S16**). We show the profiles expected for simple diffusion in the absence of a miscibility gap for a range of interdiffusion constants. Even for values as low as $\sim 10^{-13}$ cm²/s at this timescale we would expect a substantial change in the profile on both sides of the midpoint which is not observed. A noticeable change towards higher concentration of iodide was observed in the composition region from $0 < x_{\text{Br}} < 0.2$ in $x_{\text{Br}}=0|1$ stored for 8 months, consistent with the presence of a solid solution region from $0 < x_{\text{Br}} < 0.2$ (**Figure 8a**).^{20,51,65} Based on the distance that the composition shifted (≈ 20 μm), D_i in this region would be $\approx 10^{-13}$ cm²/s, which is lower than the D_i estimated in the I-rich region of a CsPbBr₃-MAPbI₃ heterostructure at room temperature.⁴⁹ In contrast, little change was observed in the composition region $0.2 < x_{\text{Br}} < 1.0$ in $x_{\text{Br}}=0|1$ (**Figure 8a**), consistent with the presence of a miscibility gap for $0.2 < x_{\text{Br}} < 1.0$. The behavior of the profile, particularly the region near $x_{\text{Br}} \approx 0.2$, is consistent with the presence of a miscibility gap (**Figure 5b**), in general agreement with the predicted phase diagram by DFT. To further probe the extent of the gap into the Br-rich region, we compared the interfacial profiles of $x_{\text{Br}}=0.70|1$ before and after 9 months of storage, via EDX. No flattening was observed, suggesting that the miscibility gap extends to very near $x_{\text{Br}} = 1$ at room temperature (**Figure 9**), which is much further into the Br-rich region than predicted by theory.⁵¹ Extension of the gap to $x_{\text{Br}} \approx 1$ may explain why mixed Br-I hybrid of very high Br-content (e.g. $x_{\text{Br}} = 0.9$) have been observed to undergo light-induced phase separation.²⁰ Because we cannot access longer times for interdiffusion at elevated

temperatures, we cannot completely rule out that diffusion is simply slow which limits our ability to set the temperature for the miscibility gap. Such very slow interdiffusion would be consistent with the slower re-mixing of halides in the dark, after light-induced phase separation, the latter of which is typically a rapid process.^{20,21} **Figure 9** shows three possibilities constrained by the magnitude of the interdiffusion constant.

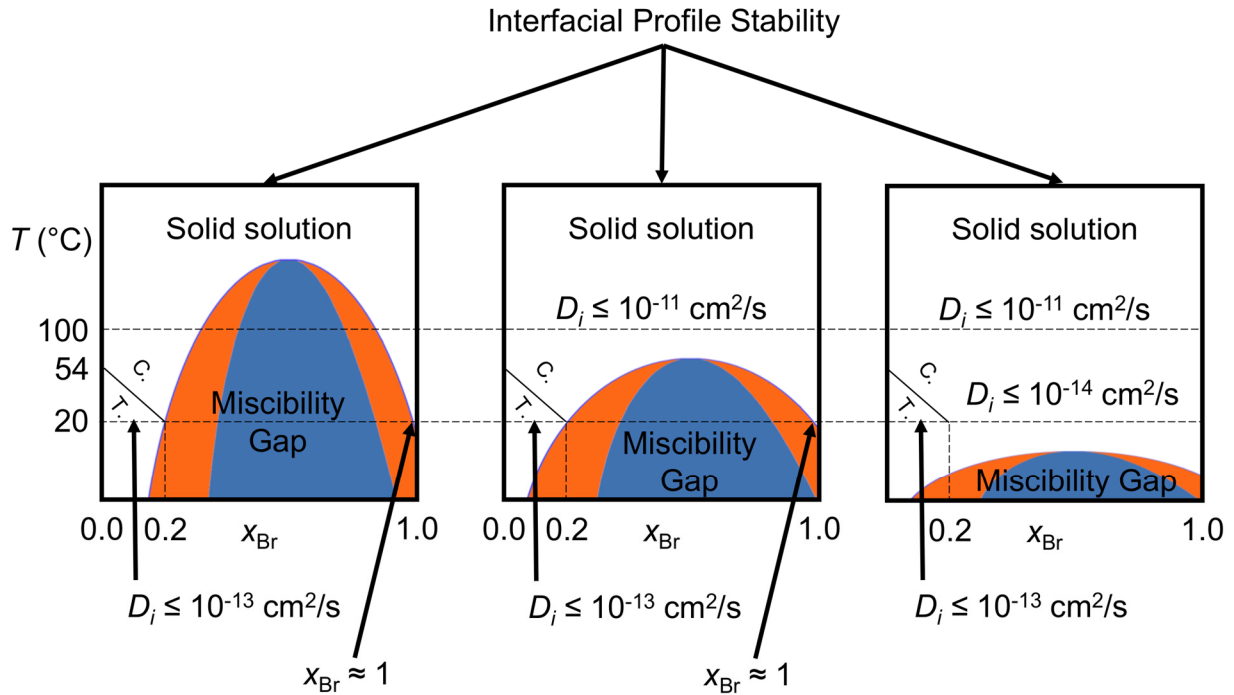


Figure 9. Summary of results, with three possible explanations for the obtained data, and with the Br-rich binodal line at room temperature near $x_{\text{Br}} = 1$. Schematic phase diagrams for the $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ system, modified from reference,⁵¹ should the miscibility gap either extend to above 100°C or extend to below 100°C , with the obtained upper bounds for D_i at room temperature and 100°C . C. and T. refer to cubic ($Pm-3m$)²⁶ and tetragonal ($I4/mcm$)⁵⁸ phases respectively, with phase transition temperatures for the $x_{\text{Br}} = 0.0$ and $x_{\text{Br}} = 0.2$ compositions reported from references.^{33,66} The blue and orange regions designate binodal and spinodal areas of the miscibility gap, respectively.

Finally, we examined the response of an $x_{\text{Br}} = 0|1$ heterostructure to light (**Figure 10**). Light-induced spinodal decomposition has been observed in single-crystal nanowires of $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$, where halides diffused up the concentration gradient.²⁵ We would thus not expect interface profile flattening when exposing an $x_{\text{Br}} = 0|1$ heterostructure to light, but rather the formation of I-rich and Br-rich regions along the interface. Consistent with these expectations, prolonged exposure of the interface region to above-bandgap light (3.06 eV) at ≈ 0.14 Suns ($\approx 14 \text{ mW/cm}^2$) induced the growing and red-shifting photoluminescence emission at 1.7 eV characteristic of light-induced phase separation into I-rich and Br-rich regions (**Figure S12**).²⁰ Previous works also reported that the I-rich domains formed during spinodal decomposition are sub-100 nm^{20,23} in polycrystalline $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$, which is below the resolution of our experiment. We tested the response of the interfacial profiles of an $x_{\text{Br}} = 0|1$ heterostructure to light by exposing the whole heterostructure to 1 Sun (AM 1.5G, 100 mW/cm²) of light for 360 min (**Figure 10**) at room temperature. In agreement with expectations, the interfacial profile of $x_{\text{Br}} = 0|1$ did not change after light exposure, providing additional confirmation that light does not activate long-range halide transport in mixed-halide perovskite thin films.

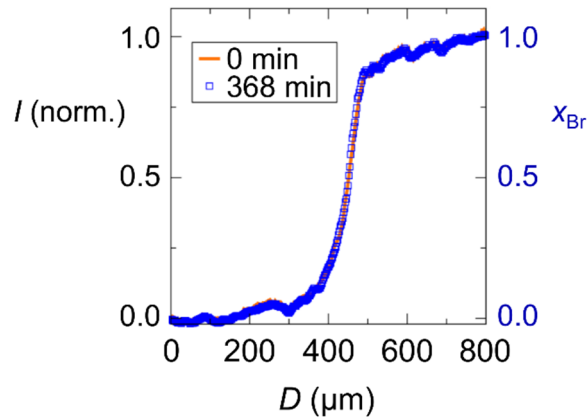


Figure 10. Integrated interfacial profiles of an $x_{\text{Br}} = 0|1$ heterostructure before and after exposure to 1 Sun for 368 min, with corresponding x_{Br} axis shown on the right.

CONCLUSIONS

In conclusion, we have examined interdiffusion in planar heterostructures of MAPb(Br_xI_{1-x})₃ films. These structures did not undergo simple interdiffusion that would be expected for a miscible system, but were more consistent with the presence of a miscibility gap at 100 °C. We also determined the upper bound of the bromide-iodide interdiffusion coefficient ($D_i \leq 10^{-11}$ cm²/s) in spin-coated MAPb(Br_xI_{1-x})₃ films at 100°C. Long term study of the interface indicates that the binodal line at room temperature extends to higher fractional composition of bromine than predicted by theory, but is in reasonable agreement at high iodide composition. Improvement of our understanding of the phase diagram of MAPb(Br_xI_{1-x})₃ will help to explain the origin of light-induced phase separation observed in very Br-rich mixed halide perovskites.

ASSOCIATED CONTENT

Supporting Information. Experimental section including heterostructure fabrication, as well as various characterizations including SEM, EDX, confocal microscopy, XRD, UV-Vis, and interface profile response to light exposure, interface profile fitting and *J-V* curve certifying that the MAPbI₃ used yields solar cells of high efficiency. (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The research reported was funded by the Department of Energy Basic Energy Science Award No. DE-SC-0012541. R.M.K. gratefully acknowledges the National Defense Science and Engineering Graduate fellowship for financial support. R.A.D. and J.A.S. acknowledge support for measurements of optical properties from Quantum Materials for Energy Efficient Neuromorphic Computing, an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under Award No.# DE-SC0019273. The authors made use of the shared facilities of the UCSB MRSEC (NSF DMR 1720256), a member of the Materials Research Facilities Network (www.mrfn.org), and of the NRI-MCDB Microscopy Facility (the Resonant Scanning Confocal supported by the NSF MRI grant DBI-1625770). R.M.K. gratefully acknowledges Professor Anton Van der Ven, Erin Perry, Naveen Venkatesan, and Collin Holgate for helpful discussions.

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