Mixed or Segregated: Toward Efficient and Stable Mixed Halide Perovskite-Based Devices

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ABSTRACT: Convenient modulation of bandgap for the mixed halide perovskites (MHPs) (e.g., CsPbBr\textsubscript{x}I\textsubscript{1−x}) through varying the halide composition (i.e., the ratio of bromide to iodide) allows for optimizing the light-harvesting properties in perovskite solar cells (PSCs) and emission color in perovskite light-emitting diodes (PeLEDs). Such MHPs, yet, severely suffered from the instability under light irradiation and electrical bias as a result of an intrinsic soft, ionic lattice and a high halide ion mobility. Understanding the halide ion migration (mediated through halide vacancies) and suppressing the halide ion segregation, thus, remain a significant challenge both in the field of PSCs and PeLEDs since it is directly linked to the long-term stability and performances of the corresponding devices. In this Mini-Review, we discuss the intrinsic instability of the MHPs arising from the ionic nature of perovskites. The liquid crystalline properties with the low formation energy of halide ion defects facilitate the defect-mediated halide ion migration. Several different mechanistic models are provided to explain the fundamental origin of the photo- or electric field-driven halide ion segregation based upon thermodynamics and kinetics. These reflect that lattice strains (internal or polaron-induced) and bandgap energy differences between parent mixed halide and iodide-rich domain serve as the thermodynamic driving forces for halide segregation. On the basis of the deeper understanding of the underpinning segregation mechanism mediated through hole trapping and accumulation at the iodide-rich sites, we further discuss the strategies to mitigate the detrimental halide segregation through composition-, defect-, dimension-, and interface-engineering. Finally, we provide a fundamental insight into designing perovskite-based photovoltaic and optoelectronic devices for the long-term operational stability.

1. INTRODUCTION

Metal halide perovskites known as the chemical structure with ABX\textsubscript{3} (wherein A = methylammonium (MA), formamidinium (FA), and cesium (Cs); B = Pb, Sn; and X = Cl, Br, and I) have been developed with significant success in the field of perovskite solar cells (PSCs) and light-emitting diodes (PeLEDs) as a result of their favorable optoelectronic properties.\textsuperscript{1a−c} These include the defect-tolerance, high absorption cross-section, long carrier lifetime and diffusion length, and nearly unitary luminescent quantum yield (~100%). These optoelectronic properties such as bandgap, exciton binding energy, and carrier lifetime can be easily tailored through varying the characteristics of dimensionality, composition, and crystal phase and structure in the mixed halide perovskites (MHPs).

These unprecedented properties inherently arise from the ionic natures of the metal halide perovskites which have both positive and negative impacts throughout synthesis and device operation. For instance, highly ionic bonding in the MHPs allows for room-temperature synthesis through the ligand-assisted reprecipitation method (LARP) because of the low formation energy of ionic crystals. This also facilitates a facile tuning of the halide composition through the postsynthetic anion exchange reactions in the solution or even in solid-state film.\textsuperscript{2a,b} Accordingly, the desirable bandgap depending on the type of perovskite-based device applications (PSCs or PeLEDs) can be effectively tunable across the entire visible spectrum (from 400 to 800 nm) as a function of different halide composition (Cl, Br, and I).

On the other hand, the highly ionic characteristics of halide perovskites have negative effects during the operation of perovskite devices. The high mobility of halide ions gives rise to the detrimental effects on performance and stability of the devices. These include the current−voltage hysteresis, drift and...
accumulation of ions at the electrode surface, and resulting degradation and failure of the corresponding devices.\(^{1b}\) In particular, the MHPs with a favorable tunability of bandgap by changing halides (e.g., bromide-iodide (Br\(^{-}\)--I\(^{-}\))) exhibit the halide ion segregation under external stimulus such as photoirradiation and electric field, which bring about the formation of two different halide-rich phases (i.e., Br-rich and I-rich). Steady-state irradiation with the above bandgap excitation enables overcoming the activation barrier of halide ion mixing to induce the segregation and local electric field generated by electron–hole pairs can also be used as drive force for halide segregation. Importantly, the iodide-rich domains with a lower bandgap further serve as a charge carrier sink that in turn results in degradation in the power conversion efficiency of PSCs due to the undesirable charge recombination at the I-rich sites.\(^{3a-c}\)

Understanding the halide ion migration in MHPs, resulting from soft, ionic lattice of the perovskites, is thus imperative for designing more stable and efficient perovskite devices. Several mechanistic models to explain the intriguing halide ion migration have been suggested for gaining a better understanding of the reversible photoinduced phase segregation (forward) and dark recovery (reverse).\(^{3b,4a-d}\) However, there is an ongoing debate regarding the fundamental mechanism of the halide ion segregation, and a universal mechanism combining theory and experiment is essentially required to

Figure 1. (A) Halide ion defects (vacancies and interstitials) in metal halide perovskites. (B) Electronic band structures for conventional II–VI and III–V semiconductors (defect-intolerant) and metal halide perovskites (defect-tolerant). (C) Highly dynamic disorder found in metal halide perovskite nanocrystals, resulting in the formation of multiple crystalline domains. (D) Bandgap tunability of metal halide perovskites by anion substitution. (E) Halide ion exchange in the solid-state films pairing MAPbBr\(_3\) and MAPbI\(_3\) films. (F) Corresponding absorption change recorded over time (up to 21 h) shown in panel (E). (G) Schematic illustration of photosegregation and dark recovery seen in mixed halide (Br--I) perovskites. (H,I) Corresponding absorption changes for mixed MaPbBr\(_{1.5}\)I\(_{1.5}\) films during steady-state light irradiation (intensity of 40 mW/cm\(^2\)) (H) and in dark for 14 h (I). Panels (B–D) are adapted with permission from ref 1a. Copyright 2017 Science American Association for the Advancement of Science (AAAS). Panels (E–F) are adapted with permission from ref 2b. Copyright 2019 American Chemical Society. Panel (G) is adapted with permission from ref 4a. Copyright 2017 American Chemical Society. Panels (H–I) are adapted with permission from ref 3c. Copyright 2020 American Chemical Society.
fully elucidate the origin of halide ion segregation. In practice, preventing the halide ion segregation (based on an understanding of the halide ion migration) is very critical in improving the efficiency and long-term stability of perovskite-based devices under operational conditions.1c,5a−d

In this Mini-Review, we discuss recent efforts to uncover the underlying mechanism of the halide ion segregation in the MHPs. First, the ionic natures of the MHPs and resulting low formation of energy for halide defects such as halide vacancies and interstitials are mainly responsible for the halide ion migration. And then, we present the theoretical and experimental models to explain the intriguing halide segregation with detailed thermodynamic and kinetic aspects of halide segregations. Finally, we provide strategies for the suppression of such undesirable halide segregation. The halide ion segregation in the MHPs and related devices can be mitigated through engineering over defects, surfaces, and grain boundaries that are criminal for segregation. A deep understanding of the mechanistic origins of segregation as seen in the MHPs can provide a fundamental insight for designing and realizing stable and high-performance perovskite devices throughout the ambient operational conditions.

2. SOFT, IONIC LATTICE OF HALIDE PEROVSKITES
Metal halide perovskites hold unprecedented optoelectronic properties including high charge carrier mobility, long carrier lifetime, and long diffusion length as compared with conventional semiconductors (II−VI and III−V) as a result of soft, ionic lattice of the crystals (also defined as liquid-crystal duality). Such liquid-crystalline properties of perovskites allow for defect-tolerant characteristics. Figure 1A illustrates that the halide defects (halide vacancy and interstitial denoted as Vx and Xx, respectively) with relatively low formation energies, oftentimes serving as trap states of charge carriers, exhibit shallow characteristic states in the electronic structure.1a This suggests that these defects do not significantly impact the optoelectronic properties of MHPs (since it is formed inside of...
band instead of midgap states) as demonstrated in Figure 1B. The soft and labile lattices in the MHPs often lead to dynamic lattice distortion and disorder as well as formation of polaron (lattice distortion coupled with charge carrier) that can effectively shield the Coulombic potential, thus increasing charge carrier lifetimes and diffusion length (Figure 1C).  

2.1. Halide Ion Exchanges. Control over the bandgap of MHPs is considerably important in the field of PSCs and PeLEDs that is directly related to the light-harvesting properties in the photovoltaics and emissive properties in the LEDs. The low formation energy of MHPs suggests that the chemical compositions (cation or anion) can be easily modulated throughout both synthesis and postsynthetic treatments. Such efforts have been made to control the bandgap of MHPs through compositional engineering with a tunable bandgap from 1.5 to 3.0 eV as a function of the halide composition (from Cl to Br and to I). Such halide ion exchange occurs in solution and solid-state phases (Figure 1D,E). For instance, simple mixing of two different lead halide perovskite nanocrystals (e.g., CsPbBr3 and CsPbI3) leads to the formation of homogeneously mixed composition of CsPb-(Br1−xIx)x(x=0−1). In the same manner, when pairing two different halide perovskite films (such as MAPbBr3 and MAPbI3), these two films exhibit homogenization through thermally assisted halide anion exchange to form MAPbBr1.5I1.5. Tracking of the excitonic band-edge absorption and emission features of these mixed halides during halide ion exchange allows for understanding the exchange kinetics and activation barrier (Figure 1F).  

2.2. Photoinduced Halide Ion Segregation. Subjecting these MHPs (e.g., MAPbBr1−xIx) to the steady-state irradiation (e.g., intensity of 5–100 mW/cm2 for 30 min) with above-bandgap excitation, the MHPs undergo halide ion segregation to yield bromide-rich (Br-rich) and iodide-rich (I-rich) domains, respectively, as shown in Figure 1G (eq 1). As confirmed through the in situ time-resolved absorption or emission measurements, the growth of two segregated phases (Br- and I-rich domains) along with the reduction of mixed halide phases are clearly seen (Figure 1H). Interestingly, upon halting the light-irradiation, the reverse process of dark remixing can readily occur due to entropic stabilization. Taking into account the change in free energy (as shown in the following eq 3) during the process of halide ion remixing, configurational entropy of mixing dominates over the penalty of enthalpy of mixing (as a result of lattice strain). This further suggests that the segregated phases preferentially turn back to the initial mixed halide composition in dark through thermally assisted halide ion movement as shown in Figure 1I (eq 2).  

Photosegregation.  

\[ 2\text{MAPb(Br}_{0.5}\text{I}_{0.5}) \rightarrow \text{MAPbBr} + \text{MAPbI} \]  

Dark Remixing.  

\[ \text{MAPbBr} + \text{MAPbI} \rightarrow 2\text{MAPb(Br}_{0.5}\text{I}_{0.5)} \]  

During the reversible halide ion segregation and dark remixing, the relative concentration of halide ion defects plays a critical role in determining the halide ion mobility. Retaining the original mixed halide phase stability and suppressing the halide ion migration remain key issues in the perovskite community. The fundamental mechanisms of halide ion segregation have been extensively studied in terms of their thermodynamics and kinetics of halide ion migration. The carrier generation following above-bandgap excitation or direct charge injections are mainly responsible for triggering halide ion migration within the perovskite lattices. As demonstrated in Figure 2G, the gradient energy landscape in the segregated phases favors the accumulation of both charge carriers (i.e., electrons and holes) at the lower bandgap I-rich sites through the interfacial charge transfers (owing to favorable band alignment), which in turn leads to the undesired radiative recombination at I-rich phases. Simultaneously, such carrier accumulation hampers the charge carrier separation and extraction to the electrode, thereby decreasing the power conversion efficiency in PSC, and also change the color purity of the MHPs in PeLEDs.  

3. MECHANISM OF HALIDE SEGREGATION  

Several research groups have explored and proposed mechanistic models thus far to elucidate the underpinning mechanism behind the thermodynamics of halide ion migrations and following segregations, including (1) miscibility gap (internal lattice strain model), (2) polaron-assisted lattice strain, and (3) photocarrier energy model (based on the band gap difference). In the former two strain models, the halide ion segregation occurs in order to release the lattice strains that are the origin of photoinstability. Thus, the driving forces of these strain-based models are associated with increased lattice strains (resulted from either intrinsic lattice mismatch between bromide and iodide or external lattice strain due to structural deformation induced by polaron). In these models, structural lattice deformation and relaxation to relieve free energy thus lead to the halide ion segregation. However, these strain models are limited in their ability to explain the critical role of photoexcited charge carriers and defects in the phase segregation. Therefore, the photocarrier energy model rather takes into account the role of the photogenerated charge carriers as driving forces to induce photosegregation. A band gap difference between parent (mixed) and segregated phases leads to charge accumulation at the lower bandgap (I-rich sites) that can trigger halide ion segregation. More importantly, the formation of halide vacancies within the lattice is directly linked to the halide ion migration through defect-mediated halide ion movement and resulting segregation. These entire processes including the lattice distortion, formation of halide defect (interstitial and vacancies), halide ion migration, and resulting segregation need to be taken into account in a synchronized manner.  

3.1. Miscibility Gap (Internal Lattice Strain). A thermodynamic rationale model behind halide phase segregation was first suggested by Walsh et al. using density functional theory (DFT) for the calculation of Helmholtz free energy variation for the mixed MAPb(Br1−xIx) with x = 0–1 (wherein x represents the bromide concentration in the MHPs) at different temperatures from 200 to 500 K (panel of Figure 2B). The free energy of the mixing (\( \Delta F_{\text{mix}} \)) to form the MHPs can be understood by deconvoluting two different energy terms of internal energy (\( \Delta U_{\text{mix}} \)) and configurational entropy (\( T\Delta S_{\text{mix}} \)) as described in the following eq 3.  

\[ \Delta F_{\text{mix}}(x) = \Delta U_{\text{mix}}(x) - T\Delta S_{\text{mix}}(x) \]  

When forming the mixed halide, the enthalpic cost of internal energy (arising from lattice strain as a result of the mismatch of different halide ion size in the corner-sharing mixed \( [\text{PbX}_{3}]^{1−} \)-octahedral (i.e., 2.20 Å for I− vs 1.96 Å for Br−) as shown in the panel of Figure 2A) is compensated by the configurational entropic stabilization. Accordingly, this model predicts that the
mixed halide \( \text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3 \) between 0.3 < \( x \) < 0.6 that is miscible above room temperature (>300 K) due to increased entropic stabilization at elevated temperature. However, it will undergo a spinodal decomposition (segregated into two different halides) below room temperature (300 K) with a miscibility gap (panel of Figure 2C). Consequently, the corresponding increased internal lattice strains at room temperature are relieved through halide segregation. A light irradiation can expedite this segregation process owing to overcoming the segregation kinetic energy barriers. However, there is a mismatch of miscibility gap between theoretical calculation and experimental observation since the MAPb-(Br_{1-x}I_x)₃ with \( x = 0-1 \) is still stable at the room temperature of 300 K.

3.2. Polaron-Mediated Lattice Strain. The second model proposed for explaining the halide migration is associated with polaron-induced lattice strain. Ginsberg et al. have proposed that a single photoexcited charge carrier coupled with the perovskite lattices is responsible for forming the localized strain that can induce halide ion segregation (Figure 2D,E). In this model, the local lattice strain and deformation induced by interaction of localized charge carrier with surrounding lattice through electron–phonon coupling play a significant role in driving local halide ion segregation. Thermodynamic calculation under the condition of light illumination and dark shows that the formation of polaron given optical illumination does significantly increase the total free energy (\( \Delta F_{\text{light}} \)) as compared with the counterpart of ground state (\( \Delta F_{\text{dark}} \)) owing to an increased term of external lattice strain energy (\( \Delta g \)), which thus needs to be released through the halide ion segregation to form Br- and I-rich domains, respectively (eq 4).

\[
\Delta F_{\text{light}}(x) = \Delta F_{\text{dark}}(x) + \Delta g(x)
\]

However, thermodynamic explanation based upon the increased local lattice strain energy as a result of the polaron does not account for the important role of concentration of charge carrier, minimum threshold excitation intensity, and halide ion defects and concentrations.

3.3. Photocarrier Energy Model (Band Gap Difference). In the photocarrier energy model, the photoexcited charge carrier can bring about the rearrangement of ions within the lattice. The relevant kinetic process for the halide ion segregation involves the generation of charge carriers, their diffusion, and accumulation and carrier recombination at the I-rich domain. Herein, the carrier concentration-dependent bandgap difference (\( \xi \Delta E_g \)) between the parent (mixed) and segregated phases as shown in Figure 2F,G can indeed serve as a main driving force of halide ion segregation that increased the total free energy (\( \Delta F_{\text{light}} \)) of the mixed halide in the excited states as described in the following eq 5. In the similar way to the strain models (and eq 4), the increased free
energy term due to bandgap energy offset ($\xi \Delta E_g$) needs to be minimized through halide segregation.

$$\Delta F_{\text{light}}^*(x) = \Delta F_{\text{dark}}(x) + \xi \Delta E_g(x)$$

(5)

In particular, the valence band edge difference (while considering the isoenergetics of the conduction band edge dictated by the energy of the Pb 6p orbitals) is mainly responsible for the bandgap difference, indicative of the decisive role of holes. A funneling and accumulation of the photoexcited hole at the I-rich phase (the smallest bandgap) driven by the energy gradient in the segregated phase can drive the demixing of halides (Figure 2G). Kuno et al. have also found the existence of incident light intensity threshold (\sim 40 $\mu$W/cm$^2$ for MAPbBr$_{1.5}$I$_{1.5}$ films) and the important role of the concentration of the photocarriers in the halide ion segregation that can induce the segregation, further confirming that a minimal photon energy is required for photosegregation in order to overcome the activation barrier of segregation. Recently, a unified thermodynamic theory for light-induced halide segregation seen in the full set of MA-, FA-, Cs-, MA/Cs-, and FA/Cs-based mixed halide perovskites has been suggested; according to this theory, the free energy of mixed halides is reduced through a photocarrier funneling to I-rich phases when being subjected to photoirradiation.

3.4. Kinetics of Halide Vacancy-Mediated Segregation. Taking into account of important role of photocarriers and their concentration, the halide ion migration occurs through halide defects (Schottky defects or vacancies) in the mixed halides, which finally leads to the formation of two different thermodynamic minima of Br-rich and I-rich phases under the photoirradiation. Importantly, the kinetics of ionic diffusion is dictated by the thermodynamic parameter of vacancy formation energy of each ion corresponding to A-, B-, and X-sites (Figure 3A). In this context, the activation energy for the halide ion migration (for Br and I) is much lower (0.17–0.43 eV) than those of A- (0.46–1.20 eV for Cs, MA, and FA) and B-site cations (0.80–2.31 eV for Pb), reflecting that halide ions exhibit the largest contribution to ionic conductivities according to the reverse order of the activation energies. This also suggests that the number of vacancies for halides ions are relatively higher than others because of the low formation energy, inevitably showing the fastest ion migration kinetics under light or dark (Figure 3B). The halide ion segregation kinetics can be conveniently tracked using time-resolved absorption spectroscopies. Taking a difference absorption spectrum by subtracting the 0 min spectrum from spectra obtained later, the absorption changes during photosegregation can be better displayed (Figure 3C). Tracking either the growth of induced absorption at Br- and I-rich domains or reduction of the bleach at the parent mixed halides, the rate constant of segregations ($k$) can be acquired (Figure 3D). When the photosegregation of the mixed halide perovskites are monitored at the different temperatures, one can see the temperature-dependent behavior of the segregation rate constants ($k$) and corresponding segregation kinetics. The segregation rate constant versus $\ln(k)$ the inverse temperature (1/T) validates the Arrhenius relationship with an activation energy of 28.9 ± 1.1 kJ mol$^{-1}$ for the photosegregation of MAPb(Br$_{1.5}$I$_{1.5}$), as illustrated in Figure 3E.  

3.5. Mechanistic Understanding of Photosegregation. Kamat and colleagues have recently established the
Figure 5. (A) Suppression of photoinduced phase segregation in triple-halide perovskites. (B) STEM-EDX maps of bromine (Br Kα) distributions before and after 3 h of operation at 2 V for a pristine device and a potassium-passivated device. Inset represents schematic diagrams of the PL measurement for the pristine and operated device without potassium passivation. (C) Schematic of iodine ion migration throughout the entire 3D perovskite device and suppressed migration in the 2.5D perovskite device (left) and evolution of efficiency of 3D and 2.5D devices at MPP (right). (D) Schematic diagram of the possible iodine migration mechanism under the in-equilibrium condition in the FAMA-based perovskite solar cell stack with and without the room temperature atomic layer-deposited Al2O3 layer. (E) Normalized PL emission spectra of perovskite films with different grain size under light irradiation (10 mW/cm²) and J–V curves of solar cells containing perovskite layer with different grain size under continuous light soaking for 0, 300, and 600 s. (F) Schematic illustration of the proposed mechanism for halide redistribution during vapor-assisted crystallization (VAC) process. Panel (A) is adapted with permission from ref 12c. Copyright 2020 Science American Association for the Advancement of Science (AAAS). Panel (B) is adapted with permission from ref 17a. Copyright 2020 John Wiley & Sons. Panel (C) is adapted with permission from ref 21. Copyright 2019 American Chemical Society. Panel (D) is adapted with permission from ref 12a. Copyright 2020 Elsevier Cell Press. Panel (E) is adapted with permission from ref 22b. Copyright 2021 American Chemical Society. Panel (F) is adapted with permission from ref 22c. Copyright 2021 Springer Nature.
significant role of holes in promoting an instability of iodide in the mixed halide phases, inducing the halide ion segregation simultaneously (Figure 4A).9a,b Only in the presence of the electron-transporting TiO$_2$ layer in air (through which electrons are transported and scavenged by ambient oxygen), will the trapping and accumulation of holes within the mixed halide phase bring about the halide ion segregation (Figure 4B).9a The photooxidation of I$^-$ to I$^*$ (instability of iodide) that favorably migrates into interstitial defects by forming halide vacancies simultaneously is responsible for halide ion migration as confirmed from the ultrafast pump–probe transient spectroscopic measurements under light irradiation (Figure 4C).9a

The halide ion migrations are also confirmed by DC galvanostatic polarization measurements reported from the Maier group (Figure 4D).10a,b To deconvolute the contribution from ionic and electronic conductivities, the polarization measurements were recorded using the ion-blocking electrodes under dark and light irradiation. Under the condition of light, the remarkable increase in conductivity more than 2 or 3 orders of magnitude compared with that of the dark is due to increased ionic movement (Figure 4E).10b By comparing the conductivity measured between dark and light, the ionic (or electronic) conductivity term can be calculated, respectively, on the basis of each fraction from the total conductivity (sum of electronic and ionic conductivity). The increased ionic conductivity under light irradiation can be thus rationalized by increased halide ion movement as a result of the formation of iodide vacancy when the iodide occupies the interstitial iodide sites upon light-soaking that is an initial step for halide movement in mixed Br–I perovskites (Figure 4F).10b Similarly, Hertz and colleagues also have revealed the electron trapping and hole localization in the mixed halide phases are responsible for the segregation.5a,11f Taken together, the localization of holes in the mixed halide lattice indeed initiates the oxidation of I$^-$ to transform into neutral I$^*$ species (smaller than I$^-$) that are readily captured into iodide interstitial sites that can further promote the formation of iodide vacancies. Hole accumulation at the I-rich domain driven by favorable energy gradient in the segregated phases leads to halide ion segregation as explained in the photocarrier model. Again, lattice strain (following distortion), iodide oxidation by holes and its migration to interstitials, halide vacancy formation, halide ion (or halide vacancy) migration, and ultimate segregation need to be considered in a holistic manner instead to fully decipher the complicated photo- or electric-driven halide ion segregation.

4. STRATEGIES FOR MITIGATING HALIDE SEGREGATION IN DEVICE

As a result of the halide segregation, MHPs are separated into two phases, I-rich and Br-rich, absorbing or emitting unintended wavelengths. The consequence of halide ion segregation in PSCs and PeLEDs results in the degradation of performances of devices. The I-rich domain acts as a recombination center in solar cells and results in a red shift of emission color in LEDs. Moreover, the halide ion that migrated from MHPs can react with the charge transport layer to deteriorate its charge extraction and transport properties, and metal electrodes such as Ag irreversibly degrade when they meet halide species. It causes not only hysteresis but also severe reduction (up to 80% after 10 h of maximum power point tracking) of performance in MHP-based devices9a which limits the practical applications of MHPs as a top absorber in the tandem solar cells and as an emitting layer in the LEDs. Recently, for realizing efficient and stable MHP-based devices, many researchers have tried to suppress the halide segregation via composition, defect, grain boundary, dimension, and interface engineering. In addition, the halide segregation could be controlled by various operating conditions.

4.1. Compositional Engineering. Recent studies verify that compositional engineering (over A-, B-, and X-sites) of MHPs effectively inhibits the halide segregation by stabilizing the lattice structure and increasing composition complexity. In particular, the devices containing multication and triple-halide perovskites show the excellent performance and stability.9a,12a–c In the mixed A-site cations, the flow and accumulation of charge carriers at I-rich domain is not very facilitated as compared with single A-site perovskites due to local inhomogeneity across the perovskite composition, which indicates a larger hurdle against halide segregation according to the photocarrier energy model. Also, replacing MA$^+$ into less polar Cs$^+$ reduces the electron–phonon coupling and the reduction of polaron-mediated lattice strain alleviates the phase separation.9b,13 X-site substitution with small halide ions renders additional robustness against the formation of halide vacancies as well as lowers the valence band potential, which suggests the increased onset anodic (oxidation) potential to induce halide segregation.9b,14a–d Cl–Br segregation with higher activation energy (∼38 kJ/mol) as compared with that of Br–I (∼28 kJ/mol) also demonstrates that rigidity of polarizability of lead halide frameworks determines the halide segregation dynamics.9c,14d

Dang et al. demonstrated the improved power conversion efficiency (PCE) of MHP-based solar cells by simultaneous addition of Cs$^+$ and Rb$^+$ into (FA$_{0.83}$MA$_{0.17}$)Pb(I$_{0.83}$Br$_{0.17}$)$_3$ perovskite film.12b An optimal combination of Cs$^+$ and Rb$^+$ (i.e., 7% Cs$^+$ and 3% Rb$^+$) promotes formation of desired α phase and enables uniform halide distribution across the film. It impedes inherent phase segregation of pristine perovskite films into MA-I-rich solvated phase and the FA-Br-rich hexagonal phase. Xu et al. proposed a triple-halide perovskite where MAPbCl$_3$ is alloyed into the lattice of FA$_{0.50}$Cs$_{0.50}$PbI$_{2.50}$Br$_{0.50}$ as a top cell absorber for perovskite/silicon tandem solar cells. In the triple-halide perovskite with much higher Cl doping (>15%), the photocarrier lifetime and mobility doubled and light-induced phase segregation was suppressed even under 100-sun illumination (Figure 5A). Semitransparent top cells including triple-halide perovskite exhibited superior device stability, maintaining 96% of initial efficiency after 1000 h of maximum power tracking at 60 °C.

In addition to Cl, F-containing halide perovskites also stabilize the perovskite structure.15b Electronegative fluoride ion can indeed form strong hydrogen bonds with N–H of organic cation and ionic bonds with lead within the perovskite lattices, so that organic cations and halide anions are immobilized through these bondings which accordingly suppressed the formation of organic cation and halide anion vacancies.15b As demonstrated, Li et al. achieved a PCE of 21.46% in triple-cation PSCs with superior operational stability (retaining 90% of its initial PCE after 1000 h operation at the maximum power point) by incorporating NaF into the perovskite.15b

4.2. Defect and Grain Boundary Engineering. Defects (halide vacancies) are the main origin for halide ion migration, as described in Section 3. Ion migration is
Accelerated at the grain boundaries rather than inside of the grains owing to the higher ion diffusion and accumulation at the grain boundaries. Therefore, defect and grain boundary passivation is essential for reducing ion migration and ultimately preventing halide segregation in MHPs.\textsuperscript{10,15,16}

Defects and grain boundaries can be passivated by an ionic additive such as ionic liquid and alkali metal cations. Decorating the surfaces of perovskite films with potassium halides immobilizes the excess halide species. In nanoscale cross-sectional chemical mapping, Stranks and co-workers found that the irreversible accumulation of bromide at the hole transporting layer (HTL)/perovskite interface, acting as an injection barrier for charge carriers and causing the non-radiative recombination, disappeared after the potassium treatment (Figure 5B).\textsuperscript{17a–c} As a result, the potassium-passivated PeLEDs showed improved external quantum efficiency (EQE) from 0.5% to 4.5%, and the half-life at the peak EQE markedly increased from less than 1 h to \textasciitilde 15 h under continuous operation. Potassium doping into perovskite films also minimized the hysteresis and enhanced PCE of MHP-based solar cells.\textsuperscript{17b,c}

Ligand treatment is another way to heal defects and grain boundaries. Zhou et al. introduced benzylicamine (BA) into the FA\textsubscript{0.15}Cs\textsubscript{0.85}Pb(I\textsubscript{0.73}Br\textsubscript{0.27})\textsubscript{3} perovskite films through a post-deposition treatment.\textsuperscript{18} BA molecules form a 2D/3D stacked structure—a thin 2D BA\textsubscript{2}PbI\textsubscript{4} layer on top of 3D perovskite layer—as well as remove defect sites in the films that could initiate phase segregation, achieving a stable and efficient wide bandgap PSCs with a PCE of 17.1%. Similarly, tetrabutylammonium bromide as a bulky organic ligand was incorporated into the perovskite films via post-treatment of the surface. Also, an efficient and color-stable PeLED with a maximum EQE of 20.3% at 620 nm was realized using MAPb(Br\textsubscript{1–x}I\textsubscript{x})\textsubscript{3} perovskite nanocrystals treated with multidentate ligands such as ethylenediaminetetraacetic acid (EDTA) and reduced L-glutathione.\textsuperscript{18b} DFT calculation accounts for that interaction between multidentate ligand and the nanocrystal surface, restrains iodine Frenkel defects, and suppresses halide segregation. Multifunctional compounds such as phenformin hydrochloride containing both electron-rich and electron-poor moieties are considered as promising materials for simultaneous passivation of anion and cation vacancies.\textsuperscript{19}

### 4.3. Dimensional Engineering

Incorporating bulky organic spacer in MHPs lowers the dimensionality of perovskite films which impacts on the durability and efficiency of MHP-based devices. Reduced three-dimensionally connected inorganic slab and increased insulating organic cation suppresses ion mobility through the halide vacancies.\textsuperscript{20a–c} Indeed, the activation energy for halide migration as a function of layer number (n) of two-dimensional (2D) perovskites has been established; the lower of n the higher activation barrier. Huang et al. reported that the rate of ion migration in quasi-two-dimensional (2.5D) PSCs that employ the allylammonium (ALA) ligand in Cs\textsubscript{0.05}FA\textsubscript{0.8}MA\textsubscript{0.15}PbI\textsubscript{2.86}Br\textsubscript{0.04}Cl\textsubscript{0.08} perovskite films is significantly reduced as compared with 3D PSCs.\textsuperscript{21} They first revealed that for typical 3D PSCs, iodide ions migrate from the perovskite layer to the HTL/Au interface by penetrating through the HTL layer and form an iodine–gold complex at the HTL/Au interface under standard operating conditions. It was confirmed that 2.5D perovskite retards iodide ion migration effectively by analyzing Au3I\textsuperscript{+} signal in TOF-SIMS spectra. Consequently, the 2.5D PSCs retained an initial PCE of 19.9% without any notable decrease in PCE after 80 h of operation, while the 3D counterparts showed a more than 50% degradation from an initial PCE of 20% within 24 h of operation (Figure 5C).\textsuperscript{21} As the number (n) of 2D perovskite layers decreases (the portion of organic spacers increases), low-dimensional (2D) perovskites derived from organic spacer ligands have enhanced stability but poor charge transport ability. In order to fulfill both high performance and stability in PSCs, it is necessary to find a proper number (n) of 2D perovskites by varying the ratio of organic spacer layer to inorganic slab. More recently, the space cations such as phenethylammonium (PEA) vs butylammonium (BA) that intercalated into the Ruddlesden–Popper phase perovskites play a determining role in controlling the phase segregation as well.\textsuperscript{22}
ance and stability in MHP-based devices. To prevent the halide ion from moving across the charge transport layer (CTL), organic and inorganic interfacial layers have been incorporated at the interface of the perovskite/CTL or CTL/electrode. For example, an ultrathin Al2O3 layer on the perovskite layer deposited by room temperature atomic layer deposition (ALD) improves the stability of the PSCs by blocking the iodide migration into the hole transporting spiro-MeOTAD layer (Figure 5D).12a

4.5. Other Approaches. Apart from compositional engineering, defect engineering, dimensional engineering, and interfacial engineering, numerous attempts have been made to reduce halide segregation in MHP-based devices.22a-c CsPb(Br0.5I0.5)3 nanocrystalline films prepared under different annealing conditions exhibited the phase segregation under continuous laser irradiation (10 mW/cm²) when the average grain size of the film is greater than 46 nm.22a This threshold grain size is in good agreement with the calculated diffusion length (45.8 nm) from the emission lifetime and segregation rate. In addition, the solar cell containing the CsPbBr5.13I4.87 perovskite light absorber with grain sizes below 43 nm showed stable performance under continuous light soaking (Figure 5E).22b Karlsson et al. developed the vapor-assembled crystallization (VAC) technique to make MHP films with a high compositional homogeneity (Figure 5F), which leads to highly efficient and spectrally stable blue and deep-blue LEDs with a maximum EQE of 11.0% and 5.5% with emission peaks at 477 and 467 nm, respectively.22a This results imply that compositional heterogeneity as well as ion migration plays a key role in triggering halide phase segregation.

4.6. Halide Segregation under Various Atmospheric Conditions. Temperature is one of the potential parameters for mitigating halide segregation during the MHP-based device operation. Photoinduced halide segregation in MAPb(Br0.24I0.76)3 was observed over a narrow temperature range of 200 to 300 K under a light intensity of 1.5 mW/cm² (Figure 6A).23 In the point of kinetics of halide migration, the temperature rise accelerates ion movement according to the Arrhenius equation, promoting halide separation.3c On the other hand, Elmelund et al. reported that the excitation intensity threshold with which halide segregation occurs in MAPb(Br0.34I0.66)3 has a positive linear relationship with temperature, reflecting that increased entropic stabilization of the mixed halides at the elevated temperature.3c On the basis of the theoretical calculation of the Helmholtz free energy of MHP as a function of the temperature, Brivio et al. suggested that phase stability of MHP increases at the high temperature (Figure 2A).23 A multitude of conflicting experimental data continue to be provided in terms of the effect of temperature on the halide segregation. The role of temperature on the halide separation still remains controversial.

Compressive strain (or pressure) can control the halide segregation. When an external pressure of 0.3 GPa was applied to the MAPb(Br1−xIx)3 layers where x is 0.25, 0.5, and 0.75, respectively, halide segregation was found to slow down by 2 orders of magnitude (Figure 6B).24a,c This could be explained by the compression-induced increase in the activation energy for the halide movement and by thermodynamic stabilization of MHP due to the change in Gibbs free energy in particular with the corresponding enthalpy involving the favorable -PAV term at the elevated pressure (as a result of unit cell volume contraction).24a,c,d Chemical compression through partial or complete replacement of MA⁺ with smaller cations such as Cs⁺ can also reduce the unit cell volume and ultimately mitigate the resulting halide segregation.24a,b

5. CONCLUSION AND FUTURE OUTLOOK

In summary, the MHPs with tunability of bandgap (as a function of varying the halide compositions) represent the most promising next-generation materials as light-absorbing layer in the PSCs and as emissive layer in the PeLEDs. As the power conversion efficiency in PSCs (~25% in 2021) and external quantum yield in PeLEDs (~21% for green in 2021) reach a plateau, recent research interests and efforts are more focused on maintaining the long-term stability of the corresponding devices. Accordingly, retaining the phase stability in the MHPs still remains a key issue in the perovskite community, which is yet to be resolved for better understanding of the intriguing phenomena as well as maintaining the long-term device stability and performances. Several different models have been proposed to explain the thermodynamic and kinetic aspects of the halide ion segregation in the MHPs and their fundamental origin under excitation of light and electric field. However, it is still essentially required to consider the multiple steps of halide ion segregation involving the lattice distortion to relieve local strain, formation of halide defect (halide ion vacancies), halide ion (or halide vacancy) migration, and resulting segregation in a synchronized manner. As suggested from many research groups, charge carrier generation, diffusion, and accumulation in particular with the hole at the MHP lattices can indeed trigger the halide ion segregation since the large iodide (I⁻) ions are oxidized to neutral iodine (I²⁻) species which are subsequently captured and migrated into the interstitial sites by forming halide ion vacancies. The halide defect-mediated ion migration and resulting segregation further suggest that passivating the surface defect sites and preventing hole accumulation at the MHP lattices represent the promising strategies for suppression of the segregation. Diverse studies demonstrate that composition-, defect-, dimension-, and interface-engineering are effective in reducing halide segregation and ultimately enhancing performance and stability at the device level. For the future research avenue of the mixed halide perovskites, the specific role and correlation of the above parameters to the segregation dynamics (in terms of thermodynamic and kinetic considerations) have to be fully investigated. Operating conditions such as temperature and atmospheric pressure also must be taken into account to mitigate halide segregation when implemented in the devices. The entropic (by increasing temperature) and enthalpic (by increasing pressure) control over the mixed halides provides an additional method to achieve the thermodynamically stable mixed halide perovskites.

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