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Preventing phase segregation in mixed-halide perovskites: a perspective

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Mixed-halide perovskites are ideal materials for the demanding applications of tandem solar cells and emission-tunable light-emitting diodes (LEDs) because of their high compositional flexibility and optoelectronic performance. However, one major obstacle to their use is the compositional instability some mixed-halide perovskites experience under illumination or charge-carrier injection, during which the perovskite material demixes into regions of differing halide content. Such segregation of halide ions adversely affects the electronic properties of the material and severely limits the prospects of mixed-halide perovskite technology. Accordingly, a considerable amount of research has been performed aiming to uncover the underlying mechanisms and mitigating factors of the halide segregation process. Here we present a perspective of strategies designed to reduce the effects of halide segregation in working mixed-halide perovskite devices, based on recent literature reports. We discuss a multitude of mitigating techniques, and conclude that a combination of stoichiometric engineering, crystallinity control and trap state passivation is clearly imperative for abating halide segregation. In addition, the reduction of halide vacancies and control over illumination and temperature can, to a certain extent, mitigate halide segregation. Less direct approaches, such as a change in atmospheric environment, perovskite incorporation into a nanocrystalline composition, or direct control over the crystallographic structure of the perovskite, may however prove too cumbersome to be of practical use. This perspective paves the way for the design and creation of phase-stable, mixed-halide perovskite materials for photovoltaic and LED applications.

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Broader context

Lead-halide perovskites are leading candidates for a new generation of solar cells because of their high efficiencies, low cost and facile manufacturing methods. In particular, the optoelectronic properties of mixed-halide perovskites can be tuned by altering their chemical composition, making them ideal for use in LEDs with controllable output colour, or in efficient tandem solar cells. Unfortunately, under illumination or charge-carrier injection, some compositions of mixed-halide perovskites suffer from a reversible phase instability problem known as ''halide segregation'', which limits the viability of this technology and remains a largely unexplained mechanism. Here we review the vast literature on halide segregation in mixed-halide perovskites, with our focus on how halide segregation may be impeded or prevented in such materials. We report on a myriad of techniques that improve the phase-stability of mixed-halide perovskites, some of which have yet to be fully explored, and conclude that combining the most auspicious techniques will be necessary to prevent halide segregation in working, real-world perovskite solar cells and LEDs. This work consolidates the research on halide segregation in mixed-halide perovskites, and highlights new and promising areas of study, thereby paving the way for the creation of cheap, efficient perovskite solar cells for the utilisation of green energy.

1 Introduction

Metal-halide perovskites are unique among semiconductors in their ability to accommodate large amounts of ion migration and reorganisation and yet retain the excellent electronic transport properties required of high-efficiency photovoltaic and light-emitting devices.[1–4] The combination of mechanical flexibility and optoelectronic performance makes perovskite materials extremely promising for commercial solar energy harvesting and lighting applications.[5–8] The flexibility of the perovskite ABX_3 structure allows for a degree of ionic mixing on the crystal lattice sites, which can be used to tune the various optoelectronic and structural properties of the perovskite.[9–12] Of particular importance, the bandgap of the perovskite can be easily tuned by altering the composition of the halide ions on the X-sites of the crystal structure.[13–17] High-performance, bandgap-tunable materials are ideal ingredients for producing

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light-emitting diodes (LEDs) with a particular emission wavelength, or for use in tandem solar cells where the overall efficiency of two-terminal cells is highly sensitive to the bandgaps of the two composite layers.[18,19] Accordingly, mixed-halide perovskites are already being implemented to great success as layers in perovskite–silicon[20,21] and perovskite–perovskite[22–25] tandem solar cells, and in a range of LEDs with emission across the entire visible spectrum.[17,26] The mixing of halide ions on the X-sites of the perovskite structure is key to the versatility of this material, and will likely be integral for the commercialisation of perovskite device technology.

The biggest challenge currently facing the commercialisation of perovskite-based devices is the instability of the perovskite itself,[27,28] especially when continuously exposed to oxygen,[29–31] humidity,[32–34] or light.[14] Specifically for mixed-halide perovskites, a peculiar process referred to as ''halide segregation''[14] has been found to be a major source of instability. Here, exposure to above-bandgap illumination or charge-carrier injection results in a loss of phase-stability and the separation of halide ions of different type, causing the formation of inclusions of lower and higher bandgap perovskite with a different halide composition to the remaining well-mixed perovskite phase.[14] The formation of a spatially inhomogeneous bandgap under illumination or current injection seriously limits the prospects of mixed-halide perovskites for tandem solar cell and tunable LED applications. Fortunately, several reports in the literature have elucidated methods by which halide segregation may be mitigated in mixed-halide perovskite materials, and it is the focus of this perspective to analyse and review these approaches.

While X-ray diffraction (XRD)[14,35] and absorption measurements[36–40] often suggest that only a small fraction of the perovskite actually participates in halide segregation under illumination (estimates go as low as $\sim$1%[41]), photoluminescence (PL) measurements[14] and the performance of photovoltaic devices[41–44] are disproportionately affected. Such exacerbation of deleterious effects results from the funnelling and concentration of charge carriers into the phase-segregated regions of perovskite which exhibit a lower bandgap than the rest of the material. The PL emitted from the halide-segregated material therefore typically displays a strong redshift and increased intensity, making halide segregation easily detectable through PL even for a low concentration of afflicted regions.[14] Most puzzling, however, is that the segregation of halide ions does not persist once the perovskite is shielded from the illumination, with the material eventually returning to its pre-illumination state under darkness.[14] It is now widely thought that excited charge carriers drive the segregation process, given that halide segregation has been observed in perovskite materials subjected to charge-carrier injection even in the absence of light.[26,42,43,45,46] It is further believed that entropic mixing drives the recovery to the pristine state upon the removal of the excitation source.[39,47] However, despite the large amount of research into the halide segregation phenomenon, many facets of the process are still debated in the literature and many questions remain as to the underlying fundamental mechanisms that drive the process.

In this perspective, we focus our discussion on how halide segregation may be prevented in mixed-halide perovskite photovoltaic devices and LEDs, given that material stability is a critical factor in the future commercial prospects of mixed-halide perovskite technologies. Our discussion is primarily based on the empirical evidence reported in the literature on how both internal properties of the perovskite and external conditions affect the extent to which segregation of the halide ions is induced. In addition, we consider and discuss theoretical ideas about the underlying halide segregation mechanisms in order to supplement and explain these empirical results where possible. We highlight three easily implemented methods with strong impact on the stability of the material against halide segregation, which are: changing the stoichiometry of the A-site cation in the perovskite structure, improving the perovskite

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crystallinity, and reducing the trap state density within the perovskite. To a lesser extent, a reduction in the density of halide vacancies in the perovskite structure has also been shown to mitigate halide segregation. Other methods that have proven promising, but require further research, are identified as: changing the stoichiometry of the B-site cation, altering the incident illumination, and changing the perovskite temperature. Alterations in the perovskite crystallographic structure could also theoretically help to mitigate halide segregation but are difficult to achieve practically without affecting other properties of the perovskite material. Structuring of the perovskite into relatively insulated, nanocrystalline domains does appear to mitigate halide segregation under certain conditions, but also reduces the optoelectronic performance of devices made from such perovskite materials. Unfortunately, achieving the necessary balance between suppressing ion migration and maintaining good electronic conductivity appears to be extremely difficult in such nanocrystalline materials. Utilising a Br/Cl ionic mixture on the X-sites of the perovskite structure and changing the atmospheric environment of the perovskite are concluded to be insignificant and/or impractical methods to mitigate halide segregation. Overall, the breadth of these investigations highlights the impressive quantity and potential of factors available to mitigate halide segregation and indicates the future scope of research to be done in this area. We conclude that in order for halide segregation to be completely prevented in working photovoltaic devices and LEDs, a combination of stoichiometric engineering, crystallinity control, and trap state passivation will have to be implemented, which conveniently comprise a set of factors already being investigated in the pursuit of high device efficiencies.

2 Stoichiometric engineering

We commence by exploring how stoichiometric tailoring within the ABX_3 structure affects the propensity of a metal halide perovskite towards halide segregation on the X-sites. In this context, it is important to consider that any changes to the constituents of the A-, B- and X-sites may also affect the optoelectronic properties of the resulting perovskite material, which limits the extent to which ingredients may be independently tuned to limit halide segregation. In particular, the composition of the ions on the B- and X-sites in the perovskite structure directly influence the electronic energy states in the conduction and valence bands, respectively,[10,48,49] and so altering these components tunes the bandgap energy. Changing the A-component does not directly affect the electronic energy states at the band edge, but can have an indirect influence on the bandgap energy by altering the degree of octahedral distortions or inducing other structural changes.[48]

In the following, we discuss how changes in the A-cation, metal B-cation and halide X-anion in turn affect the phase-stability of the material against halide segregation. In order for us to have a reference point, we generally attempt to compare findings for particular compositions against those for the archetypal perovskite $MAPb(Br_xI_{(1-x)})_3$ ($MA = CH_3NH_3^+$) which has been examined repeatedly in halide segregation studies and is observed to segregate for halide ratios $0.2 < x < 1$.[14,38,50–55] Because most early reports on perovskite solar cells were based on methylammonium lead halide perovskites,[56–59] bandgap tunability across the UV, visible, and near IR also initially centred around $MAPb(Br_xCl_{(1-x)})_3$[15,60,61] and $MAPb(Br_xI_{(1-x)})_3$.[13,14,62,63] Here, the latter Br/I perovskite is of particular interest, as it offers bandgaps near 1.7 eV, the target for efficient two-terminal tandem solar cells with silicon.[64,65] Below, we compare the stability of $MAPb(Br_xI_{(1-x)})_3$ against that of other metal halide perovskites with various ions or ionic mixtures incorporated onto the A-, B- and X-sites, and show how stoichiometric engineering may be utilised to mitigate halide segregation in a perovskite material.

2.1 A-site cation variation

Other than methylammonium (MA, $CH_3NH_3^+$), the A-site cations typically implemented in metal halide perovskites for photovoltaic devices and LEDs are formamidinium (FA, $CH(NH_2)_2^+$), and caesium (Cs^+). Halide segregation has been observed in metal halide perovskite materials for a wide range of different ions and ionic mixtures incorporated onto the A-sites of the perovskite structure.[9,14,16,21,52,66,67] However, different perovskite compositions require different timescales and excited charge-carrier densities for the effects of halide segregation to emerge, and thus represent materials of different phase-stability. In particular, FA/Cs and FA/MA/Cs metal halide perovskites are observed to be significantly more resistant against halide segregation than other perovskites, *e.g.* with only MA on the A-cation sites. Below we discuss the phase-stability of perovskites as the composition of the A-site cation increases in complexity from neat MA, FA or Cs through to triple- and quadruple-cation perovskites.

While $MAPb(Br_xI_{(1-x)})_3$ has been found to segregate for halide ratios $0.2 < x < 1$,[14,38,50–55] its neat FA and Cs counterparts exhibit comparable halide segregation only within the narrower approximate compositional ranges $0.55 < x < 0.9$[14,66] and $0.4 < x < 1$,[16,39,45,68] respectively, thus presenting slightly improved stability ranges. Significant halide segregation has also been reported for perovskites with a mixture of MA and Cs incorporated into the perovskite lattice, specifically for compositions $Cs_{0.6}MA_{0.4}Pb(Br_xI_{(1-x)})_3$ ($0.4 < x < 0.8$)[52] and $Cs_{0.1}MA_{0.9}Pb(Br_{0.4}I_{0.6})_3$.[42] However Bischak *et al.* reported that the effects of halide segregation diminished in their $MAPb(Br_{0.86}I_{0.14})_3$ perovskite microcrystals when a MA-to-Cs cation exchange reaction was utilised to change the stoichiometry of the microcrystals to $Cs_{0.39}MA_{0.61}Pb(Br_{0.85}I_{0.15})_3$, suggesting that some MA/Cs perovskite materials could potentially be more phase-stable than their equivalent MA-only compositions.[69]

Considerable success for mitigating halide segregation was demonstrated early on by McMeekin *et al.*, who showed that for certain mixtures of FA/Cs, the material stability against halide segregation was much enhanced compared to that of the equivalent FA-only lead halide perovskites, across the entire

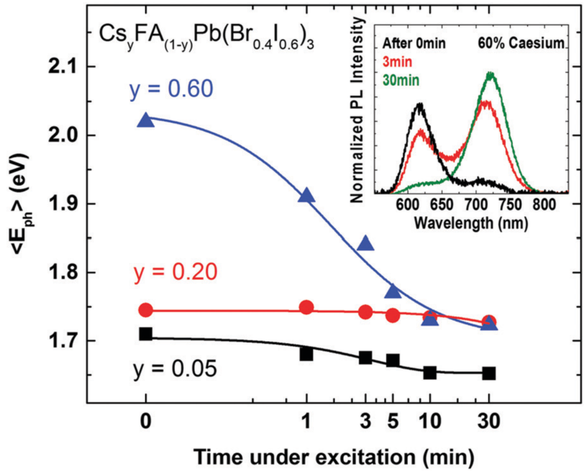

Fig. 1 Work by Rehman *et al.* highlighting how changes of the FA/Cs ratio on the A-cation sites of a lead halide perovskite affects the rate of halide segregation under illumination.[9] The main figure plots the average PL photon energy $\langle E_{ph}\rangle$ over time for $Cs_yFA_{(1-y)}Pb(Br_{0.4}I_{0.6})_3$ perovskite films with $y = 0.05$, $y = 0.2$, and $y = 0.6$ under 100 mW cm^{-2} ($\sim$1 sun), 400 nm illumination. For 20% Cs little energetic shift is observed, suggesting negligible halide segregation. The inset shows the spectral evolution of the PL emitted by the $y = 0.6$ sample. [Ref. 9] – Published by The Royal Society of Chemistry.

bromide to iodide compositional range.[70] Rehman *et al.* followed on from this work by investigating the photostability of FA/Cs perovskites as the ratio of FA to Cs is altered, and concluded that a 20% Cs fraction on the A-cation site is close to ideal for minimal halide segregation; see Fig. 1.[9] Braly *et al.* showed that while FA/Cs perovskites are much more stable against halide segregation than their MA or MA/Cs counterparts, and could withstand 1 sun intensity illumination with no detectable halide segregation, a PL redshift was still observed in the emission from their $Cs_{0.17}FA_{0.83}Pb(Br_{0.34}I_{0.66})_3$ films when exposed to high illumination intensities ($\sim$32 sun).[42] Sutter-Fella *et al.* observed halide segregation in their $Cs_{0.17}FA_{0.83}Pb(Br_xI_{(1-x)})_3$ films under 50 mW cm^{-2} ($\sim$0.5 sun) illumination for compositions $x = 0.5$ and $x = 0.6$, but not for $x < 0.5$, a smaller compositional region of instability than that of $MAPb(Br_xI_{(1-x)})_3$.[71] Similarly, Zhou *et al.* reported on $Cs_{0.17}FA_{0.83}Pb(Br_xI_{(1-x)})_3$ films that were observed to be photostable over the course of minutes under 150 mW cm^{-2} ($\sim$1.5 sun) illumination for composition $x = 0.27$, but underwent halide segregation for compositions $x = 0.4$, 0.5, and 0.6 under similar conditions.[72]

Triple-cation perovskites, with a mixture of Cs, MA, and FA incorporated onto the A-sites of the perovskite structure, have proven to be the most promising to date in terms of stability against halide segregation. While halide segregation is still observed in these triple-cation materials, the timescales and photon doses required to cause significant halide ion redistribution are often much greater than those needed to cause equivalent segregation in single- or double-cation perovskites.[67,73,74] In particular, Andaji-Garmaroudi *et al.* noted that the segregation process in their $(Cs_{0.06}MA_{0.15}FA_{0.79})Pb(Br_xI_{(1-x)})_3$ perovskite films took 30 minutes to approach equilibrium, and a photon dose three orders of magnitude higher than that required to segregate typical $MAPb(Br_xI_{(1-x)})_3$ films.[67] Duong *et al.* investigated the nature of halide segregation in quadruple-cation, $Rb_{0.05}(Cs_{0.1}MA_{0.15}FA_{0.75})_{0.95}Pb(Br_{0.33}I_{0.67})_3$ perovskite films, in which the characteristic redshift of PL was observed over the course of 12 hours under 2 sun illumination,[43] again suggesting a significant improvement in photo-stability over typical $MAPb(Br_xI_{(1-x)})_3$ films which may segregate over the course of seconds to minutes under illumination intensities of 1 sun or lower.[14]

While engineering the composition of the A-site cation in the mixed-halide perovskite crystal presents perhaps the most promising method in which to completely prevent, or at least slow the progression of, halide segregation in working perovskite solar cells and LEDs, the reason for the changes in photo-stability is still a matter of debate. One explanation proposed is that the composition of the A-site cation is strongly linked to the crystallinity and quality of the resulting perovskite film,[9,42,70,75] and therefore the choice of A-site cation has a large influence on a number of factors that could possibly be integral to halide segregation (perovskite crystallite size, trap state density, grain boundaries, halide vacancies, *etc.*, as discussed further below). For example, by investigating $MA_yFA_{(1-y)}Pb(Br_{0.4}I_{0.6})_3$ perovskite films as the ratio of MA to FA was tuned, Xie *et al.* were able to correlate the composition of the A-site cation with both the crystallinity of the resulting film and with the photostability of the perovskite against halide segregation.[75] Alternatively, Bischak *et al.* have suggested that polaronic interactions (interactions between excited charge carriers and the ionic perovskite lattice) are both the driving factor behind halide segregation, and are affected by the composition of the A-site cation in the perovskite crystal.[54,69] Regardless of the underlying cause, given the observed strong influence of the A-site cation on the photostability of the perovskite, engineering the perovskite stoichiometry is clearly an important tool for eliminating halide segregation from metal halide perovskite materials.

2.2 B-site cation variation

While lead-based perovskites are the most commonly investigated metal halide perovskites for optoelectronic applications, variants incorporating tin onto the B-sites have also been explored. Tin-based perovskites are of interest since tin has a lower toxicity than lead, and mixed tin–lead iodide perovskites offer bandgap tunability in the near-IR spectral range.[11,12,22,25,76–84] With regards to halide segregation, partially replacing lead with tin in the perovskite structure has been reported to have a beneficial effect on the stability of the material, however the amount of research on the subject is unfortunately still limited. Yang *et al.* reported that a photovoltaic device incorporating $MAPb_{0.75}Sn_{0.25}(Br_xI_{(1-x)})_3$ exhibited, in comparison with a $MAPb(Br_{0.4}I_{0.6})_3$ device, much less change in measured photocurrents, transient absorption spectra, and XRD patterns[83] over tens of minutes under 1 sun illumination. The stability of the 25% tin composition was attributed to reduced levels of halide segregation resulting from the different properties of the tin-halide as compared to the lead-halide bond. Unfortunately, because the PL quantum efficiency of the tin-based device was too low a PL spectrum could not be acquired over an illumination period of 90 minutes under 1 sun, and it was therefore impossible to confirm the extent to which halide segregation had actually taken place in the tin-containing films. In another study, Li *et al.* were able to acquire PL from their $CsPb_{0.75}Sn_{0.25}(Br_{0.67}I_{0.33})_3$ perovskite (25% tin) films and observed no redshift in the emitted PL when the sample was held under illumination (at an unspecified intensity) for 15 minutes, suggesting phase stability against halide segregation.[85] Under similar conditions, a small peak was observed to emerge below the bandgap energy in the PL spectrum emitted from the $CsPb(Br_{0.67}I_{0.33})_3$ lead-only perovskite counterpart, suggesting that the replacement of lead with 25% tin had improved the photostability of the perovskite, in agreement with the conclusions of Yang *et al.*[85]

While incipient studies suggest that tin incorporation has a beneficial effect on the stability of a perovskite material against halide segregation,[83,85] we note that other studies have reported difficulties in forming tin-based perovskite samples with good crystallinity,[86–89] at least for certain lead–tin compositions. Given that crystallinity has a large impact on the stability of a perovskite material against halide segregation (see Section 3.1 below), it is likely that the effects of tin incorporation on halide segregation are more multi-faceted than existing reports suggest. Thus we recommend that further research should be performed on the topic of halide segregation in tin-based perovskite materials before definite conclusion are drawn on the subject.

Overall, while additional studies on the effect of B-metal substitution on halide segregation would be highly useful, incipient investigations suggest that partially replacing lead with tin has a beneficial effect. The stability considerations of hybrid lead–tin perovskites are especially important for perovskite–perovskite tandem solar cell applications, where the wide tunability of lead–tin, iodide–bromide perovskite systems allows for the stacking of multiple layers with carefully tuned bandgaps to yield matched photocurrents in double- or triple-junction cells.[22,23,25,90]

2.3 X-site anion variation

As already mentioned above, the halide composition on the X-sites of metal halide perovskites has a strong impact on their propensity towards halide segregation, with compositions in the central range (*i.e.* around 50% iodide : 50% bromide) being particularly prone to segregation, and majority-iodide perovskites generally reported as more stable than majority-bromide.[14,16] Therefore, one obvious method by which halide segregation may be prevented is to push the halide ratio into a stable region of the compositional space, which unfortunately limits the range of bandgaps achievable. However, Bush *et al.* demonstrated that by carefully tuning both the ratio of Cs to FA on the A-site cation sites and the Br to I ratio on the X-site cation sites, many compositions of perovskite could be fabricated with a given target bandgap, but with differing stability properties.[49] In particular, devices with perovskite compositions of $Cs_{0.25}FA_{0.75}Pb(Br_{0.2}I_{0.8})_3$ and $Cs_{0.4}FA_{0.6}Pb(Br_{0.3}I_{0.7})_3$ were fabricated with bandgaps measured at 1.68 eV and 1.75 eV respectively, and were found to be stable against halide segregation when illuminated for 10 minutes under 10 sun illumination intensity. In contrast, perovskite films with similar bandgaps but higher bromide contents were found to be unstable under 10 minutes of 0.1 sun illumination. Such careful tuning highlights the key role that stoichiometric engineering will play in controlling the photostability of mixed-halide perovskite photovoltaic devices and LEDs.[49]

While mixed bromide–iodide perovskites offer particularly attractive bandgaps for tandem solar cell applications, combining chloride and bromide has been shown to tune the bandgap (alongside quantum confinement effects in nanocrystals) in the UV-visible region of 400–570 nm, making these materials suitable for blue-green LEDs.[15,17,26,46,91] However, some conflicting reports still exist in the literature as to the extent of halide segregation in bromide–chloride lead perovskites. Sadhanala *et al.* reported on a $MAPb(Br_{0.4}Cl_{0.6})_3$ perovskite material with stable PL emission under white light illumination of 1 sun intensity for 10 minutes, suggesting that minimal halide segregation had occurred.[15] However, multiple alternative studies have instead reported apparent halide segregation for similar bromide/chloride perovskites, such as $MAPb(Br_{0.5}Cl_{0.5})_3$,[54,92] and $CsPb(Br_xCl_{(1-x)})_3$ for the range $0.3 < x < 0.83$,[26,46,91,93–96] suggesting that the halide segregation mechanism is not limited to mixed bromide–iodide systems, but can be found in bromide–chloride systems as well.

2.4 Conclusions on stoichiometric effects

In conclusion, engineering the A-site cations in the perovskite structure seems to be a powerful method for mitigating halide segregation. Triple A-cation perovskites, with Cs, MA, and FA incorporated into the perovskite structure, are observed to be particularly stable,[67,73,74] as are quadruple A-cation perovskites which additionally include Rb ions.[21] Altering the composition of the B-site ions from Pb to a $Pb_{0.75}Sn_{0.25}$ mixture has also shown a promising increase in photostability,[83,85] however further research is required to fully explore the possibility of photostable lead–tin perovskites, and the compositional lead–tin range over which this may apply. Finally, replacing all iodide at the X-anion sites with chloride does not appear to significantly improve the stability of the perovskite against halide segregation.[15,26,46,91–96] Careful tuning of the overall stoichiometric space therefore emerges as a powerful tool towards suppression of halide segregation for a given target bandgap.

3 Crystallinity control

3.1 Increased crystallinity

There is a compelling body of literature evidence that metal halide perovskite films with better crystallinity (*i.e.* films with a larger average crystal grain size) are more stable against halide segregation.[9,42,53,72,75] Analysis of comparable perovskite films made *via* slightly different processing methods has revealed a clear impact of crystalline quality on the propensity of the material to commence halide segregation under illumination. In one such study, Hu *et al.* showed that deposition of $MAPb(Br_{0.27}I_{0.73})_3$ perovskite films on a non-wetting, poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) surface yielded larger grain size and improved photostability than those of films deposited on a poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) surface.[53] Depositing a thicker perovskite layer on PTAA, on the other hand, reduced the beneficial effect of the non-wetting surface, resulting in the growth of smaller perovskite crystal grains, which again led to faster halide segregation.[53] In another study, Braly *et al.* examined photovoltaic devices incorporating $FA_{0.83}Cs_{0.17}Pb(Br_{0.34}I_{0.66})_3$ and found that a perovskite annealing step of 165 °C for 50 minutes resulted in much improved crystallinity and photostability as compared to an annealing step of 75 °C for 10 minutes.[42] Zhou *et al.* demonstrated that the addition of small amounts of $(CsI)_{0.17}(FAI)_{0.83}[Pb(SCN)_2 + 3FAI]_{(1-1.5x)}[Pb(SCN)_2 + 3FABr]_{1.5x}$ to their $Cs_{0.17}FA_{0.83}Pb(Br_xI_{(1-x)})_3$ perovskite precursor solution prior to spincoating resulted in larger crystal grains and improved photostability of the resulting perovskite films.[72] However, Zhou *et al.* also proposed that the additive passivated trap states and altered the nature of the grain boundaries in the perovskite films, leaving unclear whether the larger perovskite crystal grains themselves resulted in the improved photostability.[72] Rehman *et al.* investigated correlations between crystallinity and photostability in $Cs_yFA_{(1-y)}Pb(Br_{0.4}I_{0.6})_3$ perovskite films as a function of caesium content, y, for the range between 0 and 0.6. This study clearly demonstrated that good material crystallinity (indicated by the width of X-ray diffraction peaks and the charge-carrier mobilities and lifetimes) led to improved photostability against halide segregation.[9] The evidence in the literature therefore either directly or indirectly points to perovskite film crystallinity being a critical factor in controlling and preventing halide segregation.

The exact reason why a larger grain size is correlated with greater photostability of mixed-halide perovskites is still a matter of debate. However, films with larger crystal grains necessarily have a lower grain boundary density, and several groups have reported low-bandgap domains forming during halide segregation to be clustered around grain boundaries, *e.g.* in $MAPb(Br_xI_{(1-x)})_3$[54,97] and $CsPb(Br_xI_{(1-x)})_3$[68] perovskite films. In particular, Tang *et al.*[97] and Li *et al.*[68] only observed halide segregation to occur at the grain boundaries of $MAPb(Br_{0.3}I_{0.7})_3$ and $CsPb(Br_{0.67}I_{0.33})_3$ films, respectively, while PL spectra taken from the grain centres were stable, suggesting that grain surfaces are integral for the halide segregation mechanism – see Fig. 2. These findings show that an improvement in the crystallinity of a perovskite film reduces the density of grain boundaries, which may in turn offer fewer nucleation points for the formation of halide-segregated regions, or reduce the efficacy of the segregation mechanism. There are several reasons why grain boundaries may induce halide segregation in mixed-halide perovskites. First, ionic motion has been reported to be particularly fast along grain boundaries in single-halide[98–101] and multi-halide[102] perovskites, which may suggest that halide segregation is particularly effective at grain boundaries because of the increased mobility of the halide ions in these regions. Second, trap state density has also been correlated with halide

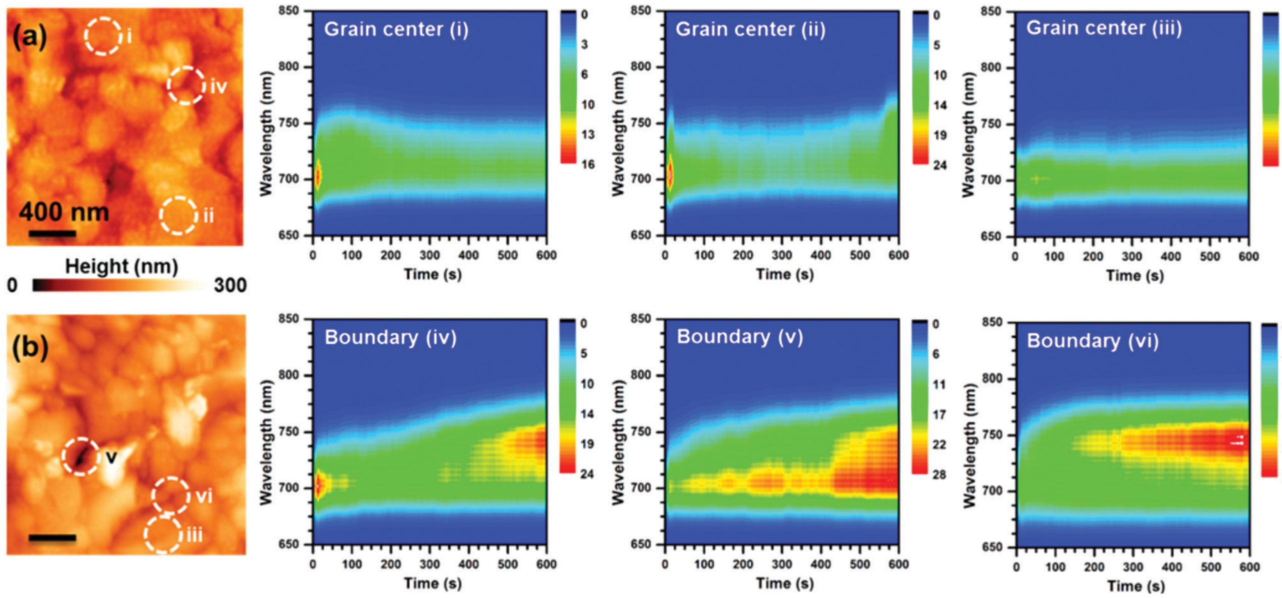

Fig. 2 Work by Tang *et al.* highlighting how stability against halide segregation differs between the grain centres and boundaries of a $MAPb(Br_{0.3}I_{0.7})_3$ perovskite thin film.[97] (a) and (b) Topography of the film, with regions of interest circled as grain centres (regions i–iii) or grain boundaries (iv–vi). Plotted is the emitted PL from each region while individually illuminated under 500 000 mW cm^{-2} (~5000 sun), 636 nm illumination for 10 minutes. Only the PL emitted from the grain boundaries shows signs that halide segregation is occurring, through the emergence of redshifted features. Reprinted with permission from [ref. 97]. Copyright 2018, American Chemical Society.

segregation,[68,97,103–105] as discussed in more detail in Section 4 below. Therefore, while the exact nature of trap states located at grain boundaries is still being debated,[106,107] grain boundaries in the perovskite film may associate with halide segregation by simply being locations that contain a high density of traps. Finally, grain boundaries may be areas that relieve lattice strain caused by the ion redistribution inherent in the halide segregation process, thereby reducing the energetic barrier to the segregation of the halide ions.[9,71] Through this mechanism, perovskite films with better crystallinity and lower grain boundary density would be less accommodating to halide segregation and would therefore be more stable.

From the above considerations, it would at first appear that single crystals of mixed-halide perovskite represent ideal environments in which to study how grain boundaries (or the lack thereof) affects halide segregation. However, it is important to note that single crystals have surfaces that have been reported to be highly defective[108] and that techniques used to study halide segregation are often highly surface-sensitive. It is therefore perhaps not surprising that literature reports on halide segregation in perovskite microplatelets and macro-sized single crystals are largely inconsistent. While it is generally agreed upon that halide segregation can occur in both $\mathrm{MAPb(Br}_x\mathrm{I}_{(1-x)})_3$[14,69,109,110] and $\mathrm{CsPb(Br}_x\mathrm{I}_{(1-x)})_3$[105] mixed-halide perovskite microplatelets (single crystals with dimensions of the order of micrometres to tens of micrometres), there is disagreement on the locations where segregation occurs. While some reports have suggested that under illumination, iodide-rich perovskite domains form almost exclusively at the microplatelet surfaces,[110] others conclude conversely that the iodide-rich domains can form anywhere within the microplatelet crystals.[69,109] For truly macro-sized single crystals, there are still only a few reports on the occurrence of halide segregation, and these are, unfortunately, also somewhat contradictory. Tang *et al.* presented PL spectra taken from millimetre-sized $\mathrm{MAPb(Br}_{0.3}\mathrm{I}_{0.7})_3$ single crystals that showed no signs of an emission shift over the course of minutes under 100 mW cm^{-2} ($\sim$1 sun) illumination,[97] suggesting the absence of halide segregation. Conversely, Byun *et al.* observed significant halide segregation in their millimetre-sized, bromide-rich, $\mathrm{MAPb(Br}_x\mathrm{I}_{(1-x)})_3$ perovskite single crystals over tens of minutes, albeit under a significant illumination intensity of 50 000 mW cm^{-2} ($\sim$500 sun).[111] In general, it is therefore difficult for solid conclusions to be drawn from the literature on the extent to which halide segregation is suppressed in perovskite single crystals, and we note that there remains significant scope for further research to be carried out on this subject.

In summary, literature reports highlight the crystallinity of the perovskite as a key parameter for the mitigation of halide segregation, with an increasing body of evidence suggesting that grain boundaries are important, or even integral, to triggering segregation.[68,73,97,110] However, major questions remain as to the mechanism linking grain boundaries to halide segregation. Possible explanations are that grain boundaries represent regions of high ionic mobility,[98–102] that the lattice strain induced by the segregation of halide ions can be relieved at grain boundaries,[9,71] and that grain boundaries represent regions of high trap density, which is itself linked to halide segregation[68,97,103–105,112] (see Section 4 below). Regardless of the underlying mechanism, the management of grain boundaries through the crystallinity of perovskite thin films represents a critical control factor over halide segregation for device manufacturers.

3.2 Nanocrystalline films

Interestingly, a number of research studies have suggested that the photostability of mixed-halide perovskite films composed of nanocrystals is much improved compared to that of standard bulk polycrystalline materials.[39,52,113,114] Such apparent suppression of halide segregation in nanocrystalline materials is surprising at first, given that the previous sections detailed how a propensity for halide segregation normally correlates with low levels of crystallinity. However, the Kuno group proposed that the reduction of halide segregation in nanocrystal films derives from the suppression of charge-carrier diffusion.[39] Restricting the spatial freedom of excited charge carriers makes it less likely for them to channel into the forming low bandgap regions of the perovskite, where they may stabilise such regions or increase their size[39] – see Fig. 3. Such a mechanism is thus specific to the nature of films made directly from solution pre-cursors which contain small perovskite nanocrystals. For this preparation method, nanocrystals are usually decorated with surface ligands that confer solubility and passivate surface states. Upon casting of a nanocrystalline film, surface ligands initially remain, unless a ligand exchange reaction is successfully carried out and/or the film is sintered leading to the fusion of nanocrystals into a nanoporous but relatively continuous perovskite solid.[115–119] Nanocrystalline perovskite films may therefore differ substantially by the extent to which insulating material between individual crystals limits both the movement of ions and excited charge carriers.[120] The restriction of ionic and charge-carrier movement in nanocrystalline films is in contrast to normal polycrystalline perovskite films in which grain boundaries typically do not obstruct carrier motion significantly. Therefore, the degree to which halide segregation in such nanocrystalline films can be suppressed may also vary widely depending on film treatments following the casting from nanocrystal solutions.[39,113]

We note in particular that nanocrystalline films fabricated with suppressed halide segregation in mind, and therefore hindered charge-carrier migration between perovskite domains, may not be ideal for optoelectronic device applications whose efficiency relies on excellent long-range charge-carrier transport across the film. Perovskite nanocrystalline films are commonly utilised for LED applications,[7,15,17,26,45,46,91,121,122] whose emission colour can be easily tuned either through the nanocrystal size, or the chemical composition of the perovskite,[7,15,17,26,45,46,91,121,122] and some nanocrystalline films have also been utilised in photovoltaic devices.[116,117] While some level of insulation between adjacent nanocrystals in thin films leads to stability improvements and better quantum confinement control over the emitted PL wavelength, sufficiently long range charge-carrier transport is still essential. Therefore, our below examination of the

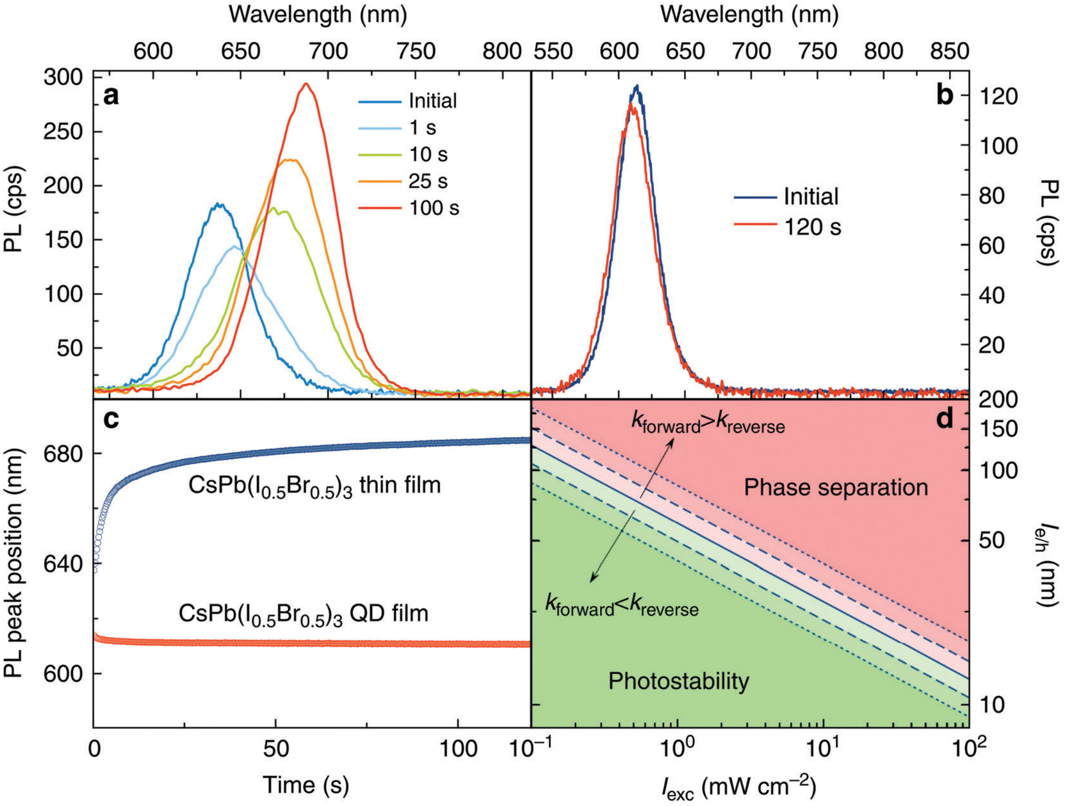

Fig. 3 Data presented by Draguta *et al.* showing the stability of films made from perovskite nanocrystal solutions *versus* that for standard polycrystalline thin perovskite films.[39] (a) and (b) Evolution of the PL emitted from both a $CsPb(Br_{0.5}I_{0.5})_3$ perovskite thin film (a) and a nanocrystal film (b) under 60 mW cm^{-2} ($\sim$0.6 sun), 405 nm illumination. (c) The tracked PL peak position from (a) and (b), highlighting that only the bulk thin film experienced a PL redshift and halide segregation. (d) Theoretically predicted phase diagram of the photostability of $MAPb(Br_xI_{(1-x)})_3$ perovskites as a function of illumination intensity (I_{exc}) and excited charge-carrier diffusion length ($l_{e/h}$). Reprinted from [ref. 39]. Copyright 2017, Nature Publishing Group.

literature concludes that while limiting the spatial freedom of excited charge carriers in mixed-halide perovskite materials does indeed inhibit halide segregation in thin nanocrystal films, this strategy cannot by design be applied to high performance perovskite optoelectronic devices.

To elucidate the reasons for the reported[39,52,113,114] suppression of halide segregation in nanocrystal films, the Kuno group suggested the concomitant reduction in charge-carrier diffusion lengths as the cause,[39,123] given that the accumulation of photoexcited charge carriers in low-gap regions have been blamed for perpetuating halide segregation.[42,43,54,69] In this study, Draguta *et al.* fabricated separate $CsPb(Br_{0.5}I_{0.5})_3$ thin bulk polycrystalline films and nanocrystal films (nanocrystal dimensions $\sim$10 nm), with the bulk polycrystalline films displaying signs of halide segregation when held under 60 mW cm^{-2} ($\sim$0.6 sun) and the nanocrystal films remaining stable unless held under extremely high excitation intensities ($\sim$500 W cm^{-2}, 5000 sun), see Fig. 3.[39] Similarly, Wang *et al.* observed stable PL from their nanocrystal guest–host composite films – comprised of $\sim$7.5 nm sized $CsPb(Br_xI_{(1-x)})_3$ perovskite nanocrystals dispersed in a $Cs_4Pb(Br_xI_{(1-x)})_6$ non-perovskite matrix – across the entire Br–I range when held under 300 mW cm^{-2} ($\sim$3 sun) for several hours.[114] Xiao *et al.* compared $Cs_{0.6}MA_{0.4}Pb(Br_xI_{(1-x)})_3$ films created with and without the incorporation of *n*-butylammonium, an organic ligand that occupied the grain surfaces of the perovskite and limited the diffusion of halide ions and charge carriers between the small (dimensions $\sim$10 nm) crystal grains inside the film.[52] Xiao *et al.* found that while bulk polycrystalline $Cs_{0.6}MA_{0.4}Pb(Br_xI_{(1-x)})_3$ films showed signs of halide segregation under 1 sun illumination over 20 minutes for $0.4 < x < 0.8$, films whose grain size was limited by BA incorporation remained stable for 8 hours under 1 sun illumination across the entire compositional range.[52]

The above work demonstrates that separating a perovskite film into nano-scale, highly insulated domains increases the stability of the material against halide segregation under illumination. However, a further survey of the literature suggests that such films are impractical to use in optoelectronic devices because they offer insufficient long-range charge-carrier transport between the domains. Efficient LEDs based on nanocrystalline mixed-halide perovskite films indeed appear not to share the phase-stability of films formed of small, completely insulated perovskite domains. Reports on $CsPb(Br_xCl_{(1-x)})_3$[26,46,93–95] and $CsPb(Br_xI_{(1-x)})_3$[26,45] nanocrystalline perovskite films optimised for LED applications have demonstrated the clear presence of halide segregation under various illumination and/or current injection conditions. In such LED nanocrystalline films a redshift of the EL or PL emission spectrum is observed to occur over the course of seconds[45] to tens of minutes[26,45,46] depending on the excitation conditions and perovskite chemical composition. Similarly, a number of reports show that sintering phase-stable mixed-halide nanocrystal perovskite films – thereby increasing the size of and interconnecting crystalline domains – reduces the phase stability and allows halide segregation to proceed.[39,113] Thus only severe electronic isolation appears sufficient to suppress halide segregation in mixed-halide nanocrystal films.

In conclusion, while insulated, nanocrystalline perovskite domains are stabilised against halide segregation by the inhibition of charge-carrier and ionic motion, such lack of long-range transport would render optoelectronic devices inefficient. Careful balancing may potentially create nanocrystalline films that somewhat mitigate halide segregation while just about retaining the long-range charge-carrier transport properties required for optoelectronic devices. However we consider this to be too challenging a method by which to produce mixed-halide perovskite materials with long-term phase stability for efficient optoelectronic devices.

4 Charge-carrier extraction and injection and trap state passivation

There is now sufficient consensus in the literature that excited charge carriers – generated either from photoabsorption or current injection – are the driving factor behind the halide segregation mechanism.[26,42,43,45,46] Halide segregation may therefore be controlled by manipulating the charge-carrier density within the perovskite, *e.g.* by altering charge-carrier extraction or injection, or the recombination dynamics. For example, Duong *et al.* showed that increasing the rate of charge-carrier extraction from photovoltaic devices based on quadruple-cation $Rb_{0.05}(Cs_{0.1}MA_{0.15}FA_{0.75})_{0.95}Pb(Br_{0.33}I_{0.67})_3$ perovskite significantly reduced the amount of halide segregation observed.[21] Perovskite solar cells may therefore be more stable under working conditions, when significant current extraction takes place, than would be expected from simple photoluminescence measurements on corresponding perovskite films in the absence of charge-extraction layers.

Several studies have linked trap-mediated recombination of excited charge carriers with halide segregation, highlighting trap passivation as a viable method to mitigate halide segregation.[73,104,105,124–126] A myriad of different passivating agents have been linked to the reduction or prevention of halide segregation, including: trioctylphosphine oxide,[104] potassium iodide,[73] potassium bromide,[126] polymethyl methacrylate (PMMA),[105] triiodide (I_3^-) molecules (minor effects),[124] and benzylamine molecules (minor effects).[125] However, we note that the incorporation of a trap passivation agent into a perovskite film often also alters other material properties, such as the nature of grain boundaries and the ion migration channels, which are themselves linked to halide segregation. Abdi-Jalebi *et al.* showed that the changes in $(Cs_{0.06}MA_{0.15}FA_{0.79})Pb(Br_xI_{(1-x)})_3$ perovskite films resulting from halide segregation over 30 minutes under 60 mW cm^{-2} (∼0.6 sun) illumination were almost entirely prevented for all halide ratios by the addition of potassium iodide to the perovskite precursor solution prior to the deposition of the films; see Fig. 4.[73] The added potassium iodide was assumed to provide an excess of iodide that passivated trap

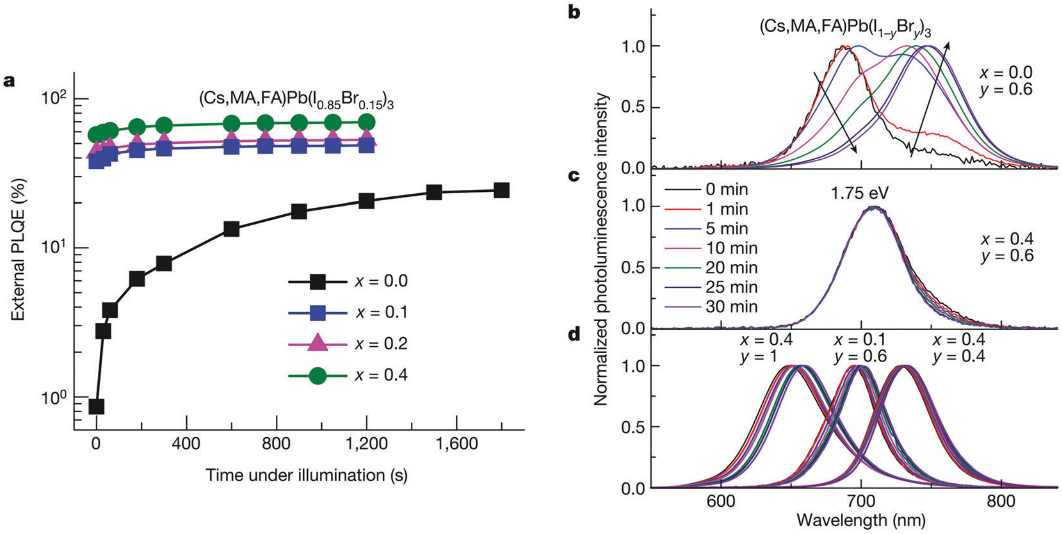

Fig. 4 Data presented by Abdi-Jalebi *et al.* highlighting the effects of a potassium iodide passivating agent on the photostability of $(Cs_{0.06}MA_{0.15}FA_{0.79})Pb(Br_yI_{(1-y)})_3$ perovskite films.[73] (a) External PL quantum efficiency over time under illumination (60 mW cm^{-2}, ∼0.6 sun, 532 nm) for 4 perovskite films with different ratios of potassium iodide to A-site cations (x) added to the perovskite precursor solutions. The external PL quantum efficiency increases in perovskite films undergoing halide segregation due to the funnelling and concentration of excited charge carriers in the forming regions of low-bandgap perovskite. (b) PL spectra observed over 30 minutes for a $(Cs_{0.06}MA_{0.15}FA_{0.79})Pb(Br_{0.6}I_{0.4})_3$ film with no passivating agent (x = 0) under the same illumination conditions as in (a). (c) and (d) PL spectra over 30 minutes for perovskite films with varying halide content (y = 0.6 (c), y = 1, 0.6, 0.4 (d)) and varying amounts of passivating agent added (x = 0.4 (c), x = 0.4, 0.1, 0.4 (d)) under the same illumination conditions as in (a). Reprinted by permission from Springer Nature: Nature [ref. 73], 2018.

states resulting from halide vacancies and reduced the halide ion mobility. The potassium ions were shown to accumulate at the grain surfaces of the perovskite, passivating more trap states and limiting halide ion movement in these regions.[73] In general, passivating agents represent a powerful method to control halide segregation in perovskite materials, capable of reducing halide segregation on more than one front, *e.g.* by passivating trap states and also potentially altering ion migration pathways and mobilities. The disadvantages of using such passivating agents mostly stem from the challenges in finding suitable agents, and incorporating the agent into the perovskite film *via* an appropriate processing method. Additionally, many additives produce side effects that can harm the perovskite material properties – such as charge-carrier transport across grain boundaries – resulting in a sweet spot in the concentration of the additive that must be found in order to optimise the overall optoelectronic performance of the perovskite.[73] The discovery and fine-tuning of effective additives for the mitigation of halide segregation is therefore a direct, but complex, target for the production of stable mixed-halide perovskite solar cells and LEDs.

Several reports have suggested that the link between trap passivation and halide segregation stems from charge carriers caught in localised trap states or at grain boundaries driving the halide segregation mechanism.[68,97,103–105,112] In particular, in a recent study we tuned the charge-carrier recombination dynamics in a $\mathrm{MAPb(Br_{0.5}I_{0.5})_3}$ perovskite film from the trap-mediated recombination regime under low illumination intensities to the radiative recombination regime under high intensities,[103] and observed the effect on halide segregation. By examining illumination periods of identical total photon dose, but stretched over different time durations, we were able to show that a higher fraction of trap-mediated recombination in the perovskite resulted in greater halide segregation.[103] Through quantitative modelling we were thus able to explain past literature findings on how different illumination conditions can affect the rate of halide segregation.[103,127] As an explanation for these effects, we have, alongside others, suggested that electric fields generated by excited charge carriers caught in localised trap states or at grain boundaries in the perovskite may be the cause of the observed ionic movement and subsequent halide segregation.[68,97,103–105,112] In this mechanism, the electric field generated between holes funnelled into nascent low-bandgap regions of the perovskite, and electrons trapped in localised defect states then provide the driving force for halide ion transport and segregation.

These considerations demonstrate the feasibility to improve the phase-stability of a mixed-halide perovskite by simply manipulating the recombination dynamics into the radiative recombination regime, thus reducing the fraction of charge carriers that are caught in trap states. For example, Yang *et al.* exposed $\mathrm{MAPb(Br_{0.57}I_{0.43})_3}$ perovskite films to pulsed laser illumination at various pulse fluences, with the repetition rate of the illumination also changed in order to keep the average illumination intensity constant across the whole experiment.[127] A lower extent of halide segregation occurred at higher pulse fluences since these created a high initial charge-carrier density, leading to a predominance of radiative bi-molecular over trap-mediated monomolecular recombination.[103] We note that pulsed charge-carrier generation in photovoltaic applications is not particularly feasible, given that illumination from the sun has a relatively continuous intensity. However, for mixed-halide perovskite LEDs, pulsed charge-carrier injection may prove a highly promising concept to lower the fraction of charge carriers undertaking trap-mediated recombination and therefore improving the phase-stability of the perovskite material. We note that such pulsed charge-carrier injection into LEDs has further beneficial side-effects, such as raising the radiative efficiency of the device and reducing heat generation that is in itself a source of instability.

In conclusion, phase segregation in mixed-halide perovskites can clearly be manipulated through a tuning of charge-carrier recombination, extraction and injection rates. Charge-carrier trapping has been linked to the halide segregation process,[68,97,103–105] possibly through the electric fields these stationary charges generate. Therefore a reduction in trap-mediated recombination through either extraction of charge carriers *via* an electrical circuit,[21] or trap passivation,[73,104,105,124–126] or by utilising pulsed charge-carrier injection[127] is effective at decreasing the extent of halide segregation.

5 Atmospheric effects

Environmental conditions such as changes in humidity or immersion of the perovskite into different gases are expected to affect the halide segregation mechanisms in mixed-halide perovskites, for a range of reasons. First, environmental conditions have previously been shown to alter the nature and distribution of trap states in metal halide perovskites.[29,103,128–135] Second, Brenes *et al.* suggested that halide vacancy sites may be filled by superoxide molecules ($\mathrm{O_2{}^-}$) formed from the reaction between oxygen and excited electrons,[128] which may interfere with the halide ion migration pathways in the perovskite structure.[123] Given our discussion in the previous section, which links trap states and ion migration to halide segregation, one would therefore expect the atmospheric environment to have an indirect impact on the extent of phase segregation.

There is indeed ample evidence in the literature for atmospheric effects on halide segregation, however most of it is inconsistent, which could derive from differences in material morphology, composition or experimental conditions between studies. Citing the trap-passivating and vacancy-filling nature of oxygen as the cause, Fan *et al.* reported greater stability against halide segregation – and even recovery from halide segregation while still under illumination – for $\mathrm{MAPb(Br_xI_{(1-x)})_3}$ films immersed in a pure oxygen atmosphere, in contrast to a nitrogen-based atmosphere.[136] Conversely, Ruf *et al.* observed significantly more halide segregation in $\mathrm{(Cs_{0.05}MA_{0.16}FA_{0.79})}$-$\mathrm{Pb(Br_{0.17}I_{0.83})_3}$ perovskite photovoltaic devices under ~1 sun illumination and an applied AC bias (sinusoidal, amplitude 0.5 V, frequency 990 Hz) when the samples were held under an

80% relative humidity, oxygen environment as compared to air or nitrogen environments with a similar relative humidity level.[74] Other studies have not necessarily agreed on the effect of oxygen on halide segregation, reporting only minor changes in the speed of halide segregation in perovskite samples held under ambient air as compared to inert nitrogen[103] or helium[67] atmospheres. Therefore, the effect of an oxygen atmosphere on halide segregation is still somewhat debatable.

For measurements of halide segregation in perovskites held under vacuum, Tang *et al.* reported near-identical changes in the Fourier-transform photocurrent spectra taken from $MAPb(Br_{0.3}I_{0.7})_3$ photovoltaic devices when held under vacuum or air.[97] However, we observed what could be identified as reduced amounts of halide segregation in $MAPb(Br_{0.5}I_{0.5})_3$ films held under vacuum instead of nitrogen or air, see Fig. 5.[103] We note that such differences may also in part be related to the presence of additional layers (such as encapsulant, or charge-extraction layers in a devices) which may act as partial barriers to gas exchange with the active perovskite layer.[103]

Finally, with regards to water vapour, Ruf *et al.* observed faster segregation rates in their $(Cs_{0.05}MA_{0.16}FA_{0.79})Pb(Br_{0.17}I_{0.83})_3$ perovskite photovoltaic devices under illumination (∼1 sun) and an AC bias (sinusoidal, amplitude 0.5 V, frequency 990 Hz) when the devices were exposed to air with 80% relative humidity as opposed to air with 23% relative humidity.[74] Howard *et al.* observed a redshift of the PL emission from $Cs_yFA_{(1-y)}Pb(Br_{0.38}I_{0.62})_3$ films when the perovskite was held under a humid air environment.[137] The redshift was observed to increase with the relative humidity level, and recovered when the relative humidity was reduced. The PL measurements were made with minimal light-soaking (0.015 s at 6000 mW cm^{-2}, ∼60 sun) on timescales significantly shorter than the several seconds to minutes typically required for halide segregation to take place, and so Howard *et al.* suggest that the PL emission redshifts were caused by humidity-induced halide segregation.[137] However further work must be done to determine if the observed PL peak shifts were indeed the result of halide ion movement, or some reversible, humidity-caused chemical or structural changes to the perovskite, as have been observed elsewhere.[138,139]

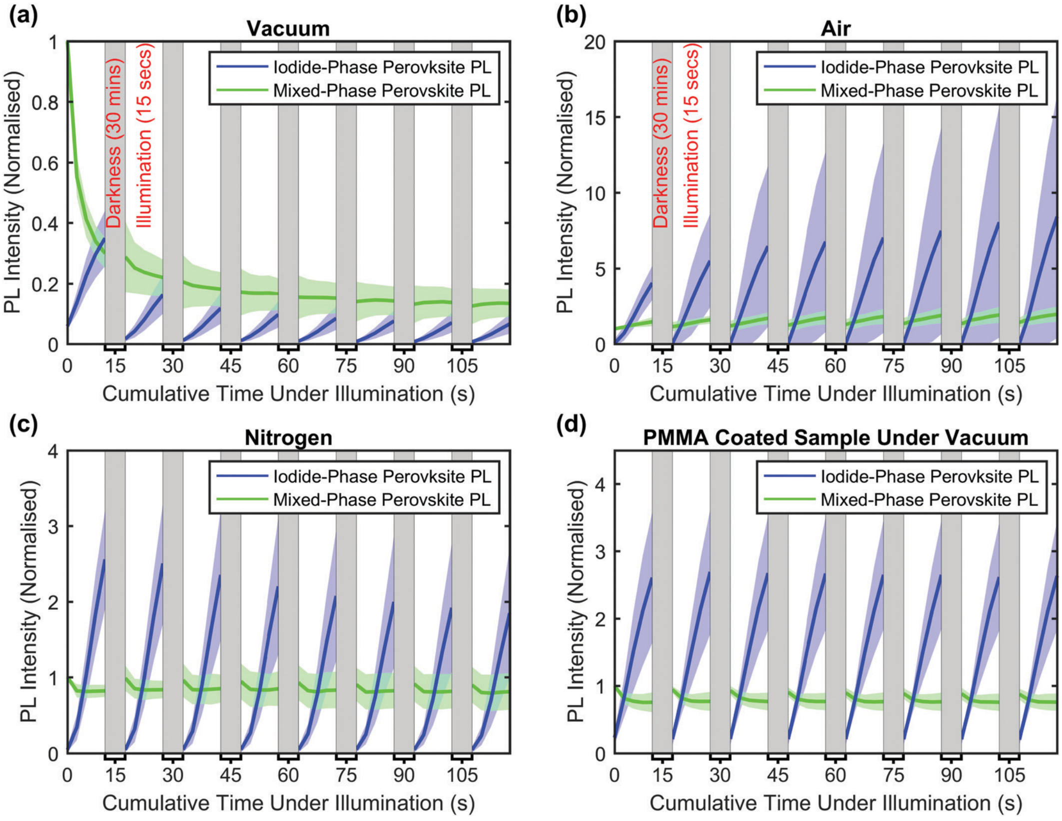

Fig. 5 Atmospheric dependence of spectral shifts resulting from light-induced halide segregation in $MAPb(Br_{0.5}I_{0.5})_3$.[103] Films were subjected to 8 periods of 15 s-long illumination at 60 mW cm^{-2} (∼0.6 sun) intensity and 400 nm wavelength under different atmospheric conditions. All consecutive illumination periods were separated by 30 minutes in darkness (indicated by the grey zones). The solid blue lines indicate the average intensity of the emitted below-bandgap PL (integrated from 720–770 nm) attributed to iodide-rich phases, and the solid green lines indicate the average intensity of the initial mixed-phase perovskite PL (integrated from 640–690 nm). The averages were taken over several experimental runs on fresh sections of perovskite. The shaded blue and green regions indicate the values within one standard deviation of their respective averages. (a) Perovskite films held under vacuum (∼0.2 mbar). (b) Films held under ambient air. (c) Films held under pressurised nitrogen (∼2 bar). (d) Films topped with a layer of PMMA and held under vacuum (∼0.2 mbar) Reprinted with permission from [ref. 103], 10.1021/acsenergylett.8b02002. Further permissions related to the material excerpted should be directed to the ACS.

In summary, the effects of the atmospheric content on halide segregation in mixed-halide perovskites are generally reported to be minor,[67,97,103] although the conclusions of some reports suggest more significant effects that warrant further research.[74,136,137] We note that the somewhat incongruous nature of the literature regarding atmospheric effects on halide segregation may stem from several different effects. One problem is that the property of the perovskite being monitored as a measure of halide segregation (usually the emitted PL from the perovskite) is often not only affected by halide segregation itself, but also independently influenced by the environmental atmosphere.[103] In addition, subtle differences in material morphology and crystallinity may result in an inconsistency of results between groups, particularly if the atmospheric effects are subtle, or dependent on the defect density originally present. Finally, the effects of atmosphere on the photoluminescent properties of perovskite can be moderated or delayed in the short term by coating the perovskite film with a thick encapsulant layer, such as polymethyl methacrylate (PMMA) (Fig. 5d),[103] or with the charge-carrier transport and contact layers of a device architecture.[112] These encapsulant layers may in turn affect comparability of measurements based on films in free space with those embedded in devices structures. In conclusion, some further work will be required before the direct influence of atmosphere on halide segregation can be fully understood. However, given that commercial perovskite photovoltaic devices and LEDs will likely be encapsulated and held in air, whether or not halide segregation can be mitigated by holding the perovskite material under an exotic atmosphere may not be of the utmost relevance for this technology.

6 Management of halide ion vacancies

Preparation of mixed-halide perovskites with a stoichiometric excess of halide ions is another well-explored method for the prevention of halide segregation.[38,73,123,124,126] Here, the aim is a reduction in the density of halide vacancies in the material in order to suppress the mobility of halide ions that the segregation process relies on. Halide ion movement in perovskite materials is thought to occur predominantly through a nearest-neighbour hopping mechanism *via* vacant corresponding lattice sites in the perovskite crystal.[36,38,123,140] Therefore, vacant halide lattice sites are integral for both halide mobility and the halide segregation mechanism, and altering the nature and density of halide ion vacancies in the perovskite is a potential method of improving perovskite photostability.

Experimentally, this approach has found good success, albeit sometimes at the expense of degrading other material properties. Both Barker *et al.*[38] and Ruth *et al.*[123] explored the link between halide ion vacancies and halide segregation and observed that a reduction in halide vacancies suppressed the extent of halide segregation. However, if the halide ion density was taken too far away from the stoichiometric ideal, the material properties of the perovskite were frequently found to suffer. Barker *et al.* prepared nominally $\mathrm{MAPb(Br_{0.6}I_{0.4})_3}$ films with a 1 : 5 ratio of lead to halide ions (thus providing a halide ion excess), which they compared with films made from a more stoichiometric 1 : 3 ratio of lead to halide ions.[38] The films created with a halide excess showed improved stability under $\sim$20 mW cm^{-2} ($\sim$0.2 sun) illumination compared to the stoichiometric films, according to measurements of PL and photothermal deflection spectra. However, the incorporation of excess halide was also found to turn the material more bromide-rich because of the preferential binding of lead to bromide (as compared to iodide),[75,141] leading to blueshifts in the PL emission peak and absorption edge.[38] Ruth *et al.* found that the speed at which halide segregation occurred in $\mathrm{MAPb(Br_{0.4}I_{0.6})_{(3-y)}}$ films increased as the halide content was reduced from excess ($y < 0$) to deficiency ($y > 0$). However, we note that the bandgap and crystallinity of their samples were also both significantly affected by the halide content, meaning that changes in crystallinity may also have influenced the halide segregation rates (see Section 3.1 above).[123] Ruth *et al.* also performed Monte-Carlo simulations of the halide segregation process in modelled $\mathrm{MAPb(Br_{0.5}I_{0.5})_{(3-y)}}$ systems with varying levels of halide ion deficiencies, y. The results of the Monte-Carlo simulations were found to match qualitatively with the experimental work, with faster modelled segregation rates correlated with higher halide ion vacancy densities.[123]

Based on these first studies set by Barker *et al.* and Ruth *et al.*, others have explored excess halide incorporation directly for perovskite photovoltaic and LED applications, with a good deal of success.[73,124,126] As mentioned above in Section 4, Abdi-Jalebi *et al.*[73] and Yang *et al.*[126] incorporated similar potassium iodide and potassium bromide passivating agents into $\mathrm{(Cs_{0.06}MA_{0.15}FA_{0.79})Pb(Br_xI_{(1-x)})_3}$ polycrystalline films and $\mathrm{CsPb(Br_xI_{(1-x)})_3}$ nanocrystalline films, respectively. Both reported that significant improvements in the stability of the perovskite material against halide segregation occurred as the excess halide ions reduced the number of halide vacancies. However, trap and surface passivation by the potassium ions accompanied these changes, which unfortunately makes it difficult to evaluate the true effect of the halide ion excess. Importantly, there appeared to be no significant detrimental effect on the perovskite material from the inclusion of excess halides in the precursor solutions. Interestingly, Balakrishna *et al.* observed only minor stability improvements against halide segregation in $\mathrm{MAPb(Br_{0.5}I_{0.5})_3}$ perovskite when an $\mathrm{I_3^-}$ additive was added to the precursor solutions,[124] indicating that while a halide excess alone will improve the stability of a perovskite material to halide segregation, it is unlikely to eliminate halide segregation completely.

In summary, a reduction in halide vacancies has been suggested theoretically[123] and shown experimentally[36,38,73,123,124,126] to affect the rate of halide segregation in mixed-halide perovskites. The main caveat to note is that other properties of the perovskite material are often also inadvertently altered by incorporation of excess halide in the precursor solutions, which can be either beneficial[73] or detrimental[38] for optoelectronic applications. Finally, we caution that the given formation energy of defect states in perovskite materials will always result in a finite population of halide vacancies at room temperature. Therefore, basic thermodynamic considerations dictate that vacancy-mediated halide ion transport can never be completely eliminated through the incorporation of excess halide ions. In addition, halide ion motion can, to a certain extent, progress even in the absence of halide vacancies. Overall, we conclude that while a reduction in halide vacancy density will lower halide segregation in mixed-halide perovskites, it is unlikely to yield completely phase-stable materials unless used in tandem with some of the other approaches discussed in this Perspective.

7 Regulating illumination

The illumination falling upon a solar cell may vary dramatically depending on the location of the solar cell on the globe, the solar cell architecture, and external factors such as implementation in a solar concentrator design[142] or tracking arrangements. Therefore, it is important to consider how properties of the illumination may affect and mitigate halide segregation in mixed-halide perovskites. We note that because LEDs are operated under charge-carrier injection, rather than under illumination, information presented in this section is not applicable for perovskite materials designed for light-emitting applications.

As one would expect, several groups have observed that an increase in illumination intensity results in faster halide segregation in mixed-halide perovskites.[14,37,39,40,51,103,104,123] Given that excited charge carriers are thought to be responsible for halide segregation,[42,43] a higher illumination intensity photogenerates more excited charge carriers within the perovskite material per second, leading to faster halide segregation. However, we note that the observed changes may not necessarily be linear in light intensity, given that the efficiency with which absorbed photons induce halide segregation may also change with illumination intensity. For example, a higher charge-carrier density may lead to enhanced radiative and reduced trap-mediated recombination, as discussed above,[103] or a certain threshold charge-carrier density may be required before halide segregation may commence.[39,40,66,123,143] Therefore, while generally a higher illumination intensity leads to a greater degree of halide segregation in a given timeframe,[14,37,39,40,51,103,104,123] the exact relationship between the two parameters is likely to be complex.

For example, several studies have reported halide segregation to be suppressed for illumination below an extremely low, material-dependant threshold intensity.[39,40,66,123,143] Slotcavage *et al.* showed that an original mixed-halide perovskite PL emission peak remained dominant for $MAPb(Br_{0.4}I_{0.6})_3$ films under 0.5 mW cm^{-2} ($\sim$0.005 sun) illumination for 3 hours, indicating suppression of halide segregation.[143] Additionally, Draguta *et al.* observed no segregation for $MAPb(Br_{0.5}I_{0.5})_3$ films when the illumination was kept below a 0.04 mW cm^{-2} ($\sim$0.0004 sun) intensity threshold.[39] Interestingly, Elmelund *et al.* found that the highest threshold illumination intensity for which halide segregation in $MAPb(Br_{0.5}I_{0.5})_3$ films remained suppressed increased linearly with increasing sample temperature (this result is discussed further in Section 8).[40] These observations may be explained by considering the counteracting effects of halide segregation under illumination and the entropic diffusion of ions against the formed concentration gradients.[39,40,97] The point of maximum halide segregation will occur when these two dynamics are balanced. As the strength of the halide segregation dynamic is reduced with decreasing illumination intensity, below a certain low threshold intensity the stabilization point between ion segregation and mixing is reached before significant segregation has occurred. For photostable perovskite solar cells, it is therefore essential that the threshold illumination intensity for which halide segregation becomes insignificant over $\sim$12 hours is identical to or greater than AM1.5 solar illumination conditions.

In addition, halide segregation may potentially be affected by the light absorption profile and the resulting profile of the photoexcited charge-carrier density through a thin film. Barker *et al.* investigated $MAPb(Br_{0.6}I_{0.4})_3$ and $MAPb(Br_{0.85}I_{0.15})_3$ films,[38] reporting three key observations that together suggest that the nature of a non-uniform charge-carrier generation profile – resulting from more charge carriers being generated at the illumination side of the film than at the back side – is a primary driver of halide segregation. First, the wavelength of the illumination was found to influence the speed at which halide segregation took place, with a wavelength of 635 nm inducing much slower segregation than 532 nm wavelength photons whose energy was further above the band edge, see Fig. 6a.[38] Since the optical density of a semiconducting material is lower near the band edge, these observations suggest that a more uniform internal light profile and photoexcited charge-carrier density profile through the films will lead to less halide segregation. Second, Barker *et al.* reported that the changes observed in the PL dynamics as halide segregation progressed were somewhat reversed if the perovskite film was illuminated from both sides (despite the fact that this doubled the overall illumination intensity), again leading to more uniform illumination throughout the film, see Fig. 6b.[38] Finally, halide segregation was found to progress more slowly in thin perovskite films (thickness 70 nm as compared to 280 nm),[38] see Fig. 6c, which again sustain flatter initial charge-carrier density profiles, although it was also noted that the crystallinity was likely to be different between the films. As a caveat, we note that charge-carrier redistribution across film profiles of typically several hundred nanometres is relatively fast, leading to flattening of the distribution on the time scale of $\sim$nanoseconds.[144,145] Therefore, in order for the charge-carrier generation profile through a perovskite film to have an influence on the resulting charge-carrier dynamics, the trapping rate in the material must be equally fast and/or the trap states in the perovskite must be unevenly distributed throughout the film. Both of these explanatory scenarios are possible, but they are unlikely to apply to all perovskite compositions that have been observed to undergo halide segregation, meaning that further experiments are needed to probe the universality of this scenario. However, if the internal light profile within the perovskite is more generally

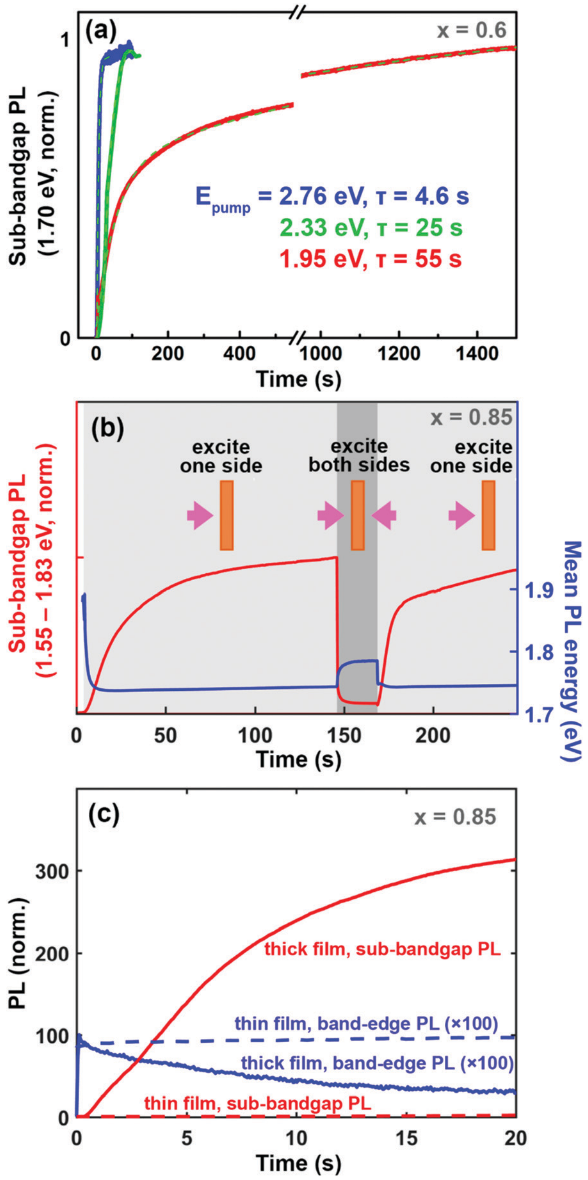

Fig. 6 Data presented by Barker *et al.* suggesting a link between the illumination profile within a perovskite thin film and the amount of halide segregation induced in the material.[38] (a) The emergence of sub-bandgap PL from a $MAPb(Br_{0.6}I_{0.4})_3$ film under illumination at different photon energies (E_{pump}) and intensities, but similar photon flux. (b) Changes in the sub-bandgap PL (associated with iodide enriched domains) and average PL energy emitted from a $MAPb(Br_{0.6}I_{0.4})_3$ film under either one- or two- (one incident on each side of the film) beam illumination of 100 mW cm^{-2} (~1 sun) intensity, 405 nm wavelength each. (c) Changes in the PL intensities emitted from thick (280 nm) and thin (70 nm) $MAPb(Br_{0.85}I_{0.15})_3$ perovskite films under the same, one-sided illumination as in (b). Reprinted with permission from [ref. 38], 10.1021/acsenergylett.7b00282. Further permissions related to the material excerpted should be directed to the ACS.

confirmed to have an important influence on phase-stability of the material, then it may be possible to manufacture photostable perovskite solar cells by utilising a back-reflecting cell design and carefully controlling the device layer thicknesses and absorption properties[146] to mitigate halide segregation.

8 Temperature control

Temperature is another potential parameter offering mitigation of mixed-halide perovskites, whose influence is important to explore because of the elevated operating temperatures of solar cells and LEDs. Fortunately, temperature can also to a certain extent be controlled *e.g.* by passive cooling, and through substrate and overall module design. Temperature is thought to have two major influences on the halide segregation mechanism. Firstly, it has been shown that the halide segregation mechanism is governed by an Arrhenius relation in the temperature range ~151 to 375 K,[14,38,40,54] see Fig. 7 for data on a portion of this range.[40] Given that halide segregation relies on ion migration, it is understandable that the temperature of the perovskite system is positively correlated with the speed of the segregation dynamics. Secondly, in the case of mixed-halide perovskites, entropy is thought to be the driving mechanism for the mixing of the halide ions. Since the entropic contribution to the free energy of a thermodynamic system is partially determined by its temperature, theoretical calculations suggest that raising the temperature of the perovskite increases the affinity of the halide ions for mixing, and therefore increases the photostability of the material.[47,54] The disparity between these two effects of temperature on halide segregation – the first suggesting that halide segregation happens faster at higher temperature, the second proposing that the perovskite material is more phase-stable at higher temperature – is an interesting dichotomy that has yet to be fully explored by the research community.

While there is plenty of experimental evidence for ion migration and segregation occurring faster at higher temperatures,[14,38,40,54] the second aspect mentioned above – *i.e.* an increased entropy at higher temperatures resulting in more stable perovskite materials – has been observed relatively rarely. Experimental work by Elmelund *et al.* showed that the threshold highest illumination intensity that could be applied to $MAPb(Br_{0.5}I_{0.5})_3$ without inducing significant halide segregation increased with temperature.[40] These observations suggest that the photostability of the perovskite may indeed increase with temperature, in qualitative agreement with theoretical studies.[47,54] Additionally, Wang *et al.* characterised the effects of temperature on the photoinduced changes in slightly unconventional samples consisting of $CsPb(Br_xI_{(1-x)})_3$ perovskite nanocrystals embedded in a $Cs_4Pb(Br_xI_{(1-x)})_6$ endotaxial matrix.[114] In PL spectra taken after several hours of high intensity, 440 000 mW cm^{-2} (~4400 sun) illumination, Wang *et al.* observed that, depending on the exact sample composition, a low-energy emission peak emerged and/or separated from the main emission peak at low temperatures, but the films remained photostable at higher temperatures. The authors attributed these observations to lower photostability at lower temperature,[114] however, we note that other studies have reported similar changes in the PL emitted from single-halide perovskites at low temperatures that are unrelated to halide segregation.[147,148] Finally, by probing the halide segregation dynamics in near-photostable $MAPb(Br_xI_{(1-x)})_3$ (bromide fraction, x, around 0.2) at a low illumination intensity

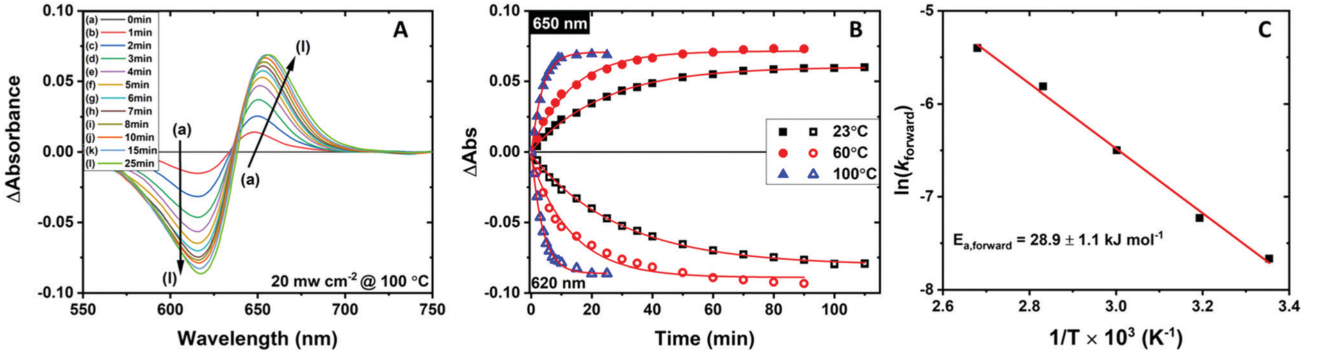

Fig. 7 Work of Elmelund *et al.* tracking the speed of halide segregation in $MAPb(Br_{0.5}I_{0.5})_3$ perovskite films at different temperatures.[40] The films were illuminated with a white light source at 20 mW cm^{-2} (~0.2 sun) intensity. (a) Changes in the absorption spectra of an illuminated sample over time as compared to the pre-illumination measurement of absorption. The temperature of the sample was 100 °C. (b) Growth of the sub-bandgap absorption (measured at 650 nm, solid symbols) and shrinkage of the above-bandgap absorption (measured at 620 nm, open symbols) over time for perovskite samples at 23, 60, and 100 °C (black squares, red circles and blue triangles respectively). (c) Plot of the natural log of the rate constant associated with halide segregation *versus* the inverse temperature of the perovskite material, with the linear trend highlighting an Arrhenius relation. The rate constant associated with halide segregation was obtained from mono-exponential fits to the data in (b). Reprinted with permission from [ref. 40]. Copyright 2019, American Chemical Society.

(1.5 mW cm^{-2}, ~0.015 sun), Nandi *et al.* observed halide segregation within a composition-dependent temperature window, and observed photostability over 4 hours at higher and lower temperatures under otherwise identical conditions.[51] The work of Nandi *et al.* highlights the interesting interaction between entropic forces and ionic motion at different temperatures, and invites further investigations into how these effects may be utilised to stabilise perovskite optoelectronic devices.

In summary, while there are some experimental studies reporting increased photostability of mixed-halide perovskites at elevated temperatures,[40,51,114] most appear to find the opposite effect.[14,38,40,54] Exploring the conditions under which either of these scenarios dominate would be greatly beneficial for furthering our understanding of how temperature may be used to mitigate halide segregation in mixed-halide perovskites. Illumination intensity may well play a crucial role in delineating different regimes here. While the culmination of faster ionic movement and increased entropic factors at higher temperatures result in perovskite materials that are harder to segregate in the low illumination intensity regime (~0.01 mW cm^{-2}, 0.0001 sun according to Elmelund *et al.*[40]), it may well lead to faster halide segregation under intense illumination regimes. Direct verification of how ion motion and entropic forces interact in hybrid metal halide perovskites at different temperatures would be a fruitful avenue for further research. Given that the temperature of LEDs and photovoltaic devices can be controlled *via* a number of different methods, such research could directly lead to practical means of reducing halide segregation in perovskite optoelectronic devices.

9 Crystal structure engineering

Incipient studies have indicated that the underlying crystal structure of the mixed-halide perovskite may play a role in the halide segregation dynamics. Such links would be fortunate, given that the perovskite structure is relatively easily tuned, for example through changes in A-cation that may influence octahedral tilting. As noted by others,[35,39,123] the highest bromide fraction x that produces photostable $MAPb(Br_xI_{(1-x)})_3$ films, $x = 0.2$, also denotes the highest fraction for which the perovskite remains tetragonal, with a transition to a cubic structure and ample halide segregation observed as x passes above the threshold of 0.2.[13,14] Ruth *et al.* performed computational Monte-Carlo simulations of halide segregation in both cubic and tetragonal perovskite materials to explore how crystal structure may affect the photostability of $MAPb(Br_{0.5}I_{0.5})_3$ perovskites.[123] In a cubic structure, the nearest-neighbour hops available for a halide ion are all symmetrically identical, whereas in a tetragonal structure there are two distinct hop pathways, with distinct energetic barriers. Ruth *et al.* found that the halide segregation rate was sensitive to the difference in the energetic barriers of the two distinct migration pathways in the tetragonal perovskite structure, and so halide segregation could occur at a different rate in tetragonal perovskite structures (where there is some difference in the energetic barriers) compared to cubic perovskite structures (where there is symmetrically no difference in the energetic barriers).[123] However, the exact difference in segregation rate between tetragonal and cubic structures – or even in which structure halide segregation would occur faster – was not determined, and Ruth *et al.* concluded that halide segregation would likely proceed in both tetragonal and cubic perovskites.[123] However, this work could possibly explain the observation that halide segregation does not occur in $MAPb(Br_xI_{(1-x)})_3$ perovskites when $x < 0.2$, when the perovskite is in a tetragonal phase.

While $MAPb(Br_xI_{(1-x)})_3$ perovskites have a clear transition from tetragonal to cubic crystal structures around $x = 0.2$,[13,14] the structure of $FAPb(Br_xI_{(1-x)})_3$ perovskites across the x compositional range is a matter of some discussions.[66,149–151] Furthermore, some reports suggest an amorphous structural region for $FAPb(Br_xI_{(1-x)})_3$ within the approximate composition range $0.3 < x < 0.5$.[66,149] The lack of a clear structural transition in FA-based, mixed-halide perovskites complicates any efforts to correlate crystal structure with stability against halide segregation stability in these materials.

A significant study researching the link between crystal structure and halide segregation was recently conducted by Beal *et al.*[152] An examination of the XRD patterns of $Cs_yFA_{(1-y)}Pb(Br_xI_{(1-x)})_3$ perovskite materials as the bromide and caesium content (x and y, respectively) was tuned allowed the mapping of a phase diagram for the perovskite material, from a cubic structure at $x \sim 50\%$ and low y, to a cubic-tetragonal mixed phase at low x and $y \sim 50\%$. These compositions were then determined to be either stable or unstable towards halide segregation through measurements of PL spectra under $\sim$110 mW cm^{-2} ($\sim$1.1 sun) for 10 minutes, and examinations of potential redshifts over time. While perovskites of cubic structure were consistently observed to exhibit halide segregation, cubic-tetragonal perovskites showed both stable and unstable behaviour, leading to the conclusion that the crystal structure is a somewhat unreliable indicator of phase-stability in mixed-halide perovskites.[152] We also note that, as mentioned in Section 2.1 above, tuning the A-site cation may also influence the photostability of perovskite films by changing the crystallinity of the perovskite, making it difficult to determine whether trends observed by Beal *et al.* resulted solely from changes in the crystal structure. Overall, we conclude that crystal structure is at best a secondary consideration for phase-stability of perovskites, and in any case, may prove too difficult to alter without changing other critical properties of the perovskite material, such as its bandgap, in particular if compositional changes beyond the A-cation are involved.

10 Summary

In this Perspective, we have critically evaluated a wide range of means by which halide segregation can be mitigated in mixed-halide perovskites. Applied in combination, such approaches may ultimately yield materials with sufficient photostability for a given application, enabling colour-tunable perovskite semiconductors for applications such as tandem solar cells and light-emitting diodes and displays. Below, we summarise our findings, grouping key strategies by their effectiveness for suppressing halide segregation, according to our literature survey.

Amongst the most promising tools by which to suppress halide segregation significantly are the judicious choice of ions populating the A-cation site, improvements in material crystallinity, and a reduction in trap density. The modification of the A-site cation in the ABX_3 structure from solely MA, FA or Cs species to a mixture of either FA/Cs or MA/FA/Cs currently presents the most substantial and easily implemented method of increasing the photostability of a lead mixed-halide perovskite with minimal effect on its bandgap.[9,42,67,70,72,73] An alternative, highly promising method for limiting halide segregation is an improvement in the crystallinity of the perovskite, *i.e.* creating films with a larger average grain size,[9,42,53,72,75] which may affect properties at the grain boundaries such as trap density, strain, or ion migration channels.[54,68,97] In addition, passivation of electronic trap states through the use of various additives has also been shown to be successful at mitigating halide segregation,[73,104,105,124,125] with potassium iodide being particularly effective.[73] This effect may derive from trapped, excited charge carriers and their associated electric fields acting as primary drivers of halide ions.[97,103–105,112] As a consequence, working mixed-halide perovskite solar cells are also more photostable under charge-extraction conditions, during which they experience a lower density of charge carriers[43] than under open-circuit voltage, or under the comparable situation of photoexcitation of plain films.

Moderate success has also been reported for the incorporation of excess halide ions into the mixed-halide perovskite, which has been shown to reduce the density of halide vacancies and suppress halide segregation to a certain extent.[38,73,123,124] However, moving the perovskite stoichiometry too far from its ideal will negatively impact on the perovskite material quality;[38,123] therefore, the incorporation of excess halide ions must be carefully tuned. In addition, basic thermodynamic arguments dictate that halide vacancies can never be completely eliminated from a perovskite structure, meaning that inclusion of excess halide ions is a technique best used in tandem with other methods aimed at preventing halide segregation.

Other factors explored to enhance the photostability of mixed-halide perovskites have been found to be less promising or impractical to implement. Utilising a bromide/chloride ionic mixture in the perovskite structure realises bandgaps suitable for blue-green LEDs, but these mixed-halide perovskite compositions appear to be similarly unstable towards halide segregation as bromide/iodide perovskite compositions.[26,46,91,92] While the adoption of nanocrystalline materials has been shown to limit the effects of halide segregation through the suppression of charge-carrier diffusion lengths,[39,113,114,123] this technique is impractical to implement in optoelectronic devices where efficient charge-carrier transport is key to high performance.[115–117] Whether or not the composition of the surrounding atmosphere alters the speed at which halide segregation takes place is still a matter of debate,[67,74,97,103,136,137] but we note that tuning such exposure is again an impractical idea, given that oxygen- or humidity-rich atmospheres will also eventually degrade the perovskite material,[28–31,33,34] and devices may ultimately operate under encapsulation. Despite a significant recent study,[152] the influence of crystal structure still needs further experimental exploration to assess its significance for the photostability of mixed-halide perovskites. Theoretical predictions have suggested that structure could impact on the ion migration pathways in the perovskite,[35,123] however tuning crystal structure without impacting on important parameters such as electronic bandgaps and material crystallinity may prove difficult.

Finally, as a perspective on the future research avenues in the field of mixed-halide perovskites, we note that some methods for mitigating halide segregation require substantial further research, but could prove potentially promising. Partially replacing lead with tin on the B-site cation has shown some promising initial results,[83,85] however, further work is required to elucidate more fully the role of tin on the mixed-halide perovskite photostability. The type of illumination upon the perovskite has been shown to affect the halide segregation dynamics,[14,37–40,51,66,103,104,123,127,143] and while the nature of solar illumination is an external parameter, the overall photovoltaic device architecture determines the light profile within the perovskite film and could therefore influence halide segregation.[38] The temperature of the mixed-halide perovskite film is another factor affecting halide segregation in mixed-halide films, although the precise trade-off between entropic mixing and ionic diffusion still requires further research. That said, temperature control could to some extent be utilised to mitigate halide segregation in a mixed-halide perovskite solar cell or LED though passive cooling systems.[14,38,40,47,51,54,114] Additional topics for further investigation centre on the role of grain boundaries and interfaces on the halide segregation mechanism. Material crystallinity can clearly affect halide segregation, however there is still no real consensus on the exact mechanism by which grain boundaries influence the halide segregation mechanism. Some studies have also started to investigate the role of surfaces in halide segregation,[104,105] however interface engineering has yet to be fully explored, and could have a large impact on halide segregation due to the strong links between interfaces and crystallinity, trap states, ion migration and charge-carrier extraction.[153,154] Such investigations are particularly important because the interfaces between the perovskite and charge-extraction layers can vary significantly depending on the device architecture used. Finally, we note that 2D perovskites have proven to be generally more stable (especially against moisture) than 3D perovskites, and ion motion has also been shown to be somewhat limited in a 2D perovskite structure.[155,156] Therefore, it would be interesting to contrast the stability of 2D layered perovskites against halide segregation with that of their 3D (bulk) counterparts, but little research has so far been done on this topic.

Overall, we are optimistic that, through a combination of the above factors, halide segregation will be mitigated in working perovskite solar cells and LEDs to the extent required for stable operation. Fortuitously, the most promising approaches for reducing halide segregation significantly (*i.e.* high crystallinity, low trap state density, efficient charge-carrier extraction) are also factors that yield high performance devices, making rapid progress highly likely. Mixed-halide perovskites therefore remain extremely promising candidates for the demanding applications of tandem solar cells and tunable light-emitting diodes.

Conflicts of interest

There are no conflicts to declare.

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