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Understanding the enhanced stability of bromide substitution in lead iodide perovskites

Alex Aziz[†], Nicholas Aristidou[†], Xiangnan Bu[†], Robert J. E. Westbrook[†], Saif A. Haque^{*†} and M. Saiful Islam^{*†}

[†] Department of Chemistry, University of Bath, Bath, BA2 7AY, UK

^{*} Department of Chemistry, Imperial College London, London SW7 2AZ, UK

ABSTRACT: Lead halide perovskites have rapidly emerged as candidate materials for high-performing solar cells, but show serious issues related to long-term stability. Methylammonium (MA) lead perovskites with mixed iodide-bromide compositions, MAPb(I_{1-x}Br_x)₃, are reported to exhibit improved stability, but the origin of such behaviour is not fully understood. Here, we report new insights into the degradation properties of MAPb(I_{1-x}Br_x)₃ using ab initio simulations and a range of spectroscopic techniques. Absorbance spectroscopy shows that as the Br content increases the material stability towards oxygen and light increases. Isothermal gravimetric analysis and time-resolved single photon counting show that the amount of oxygen incorporation into perovskite films decreases significantly with increasing Br content. Ab initio simulations indicate that the degradation reaction involving superoxide species is energetically exothermic for pure MAPbI₃, but becomes less favourable with increasing Br content with an endothermic energy for pure MAPbBr₃. The simulations indicate shorter N-H...Br hydrogen bonds between the MA⁺ cation and Br ions, which would promote greater structural stability upon bromide substitution. Thin-film passivation with iodide salts is shown to enhance the stabilities of mixed-halide perovskite films and solar cell devices. The greater fundamental understanding of mixed iodide-bromide systems gained from this study is important for the future design of stable perovskite solar cells.

▪ Introduction

Hybrid lead halide perovskites have been generating enormous interest over the past few years for use in low cost and solution- processable solar cells as well the recent avenue of perovskite-silicon tandem cells.¹⁻¹⁸ Of particular interest has been methylammonium lead iodide (MAPbI₃), which has demonstrated promising results in terms of photovoltaic performance in a wide range of device architectures.¹⁻⁴ However, an important issue regarding its commercial application is their long-term material stability under ambient operating conditions.

There are a number of factors that affect the degradation of perovskite solar cells, namely, moisture, temperature and UV illumination.¹⁹⁻³¹ In previous studies,³²⁻³⁴ we have demonstrated that when MAPbI₃ is exposed to oxygen and light, a photodegradation process occurs via the formation of a superoxide species. From these initial findings, a technique to passivate vacancy defects was reported, involving post treatment with an iodide salt, resulting in enhanced film and device stability.³²

Recent studies have observed that anion substitution (bromide for iodide) to create mixed-halide perovskite films generates longer operational lifetimes and high power conversion efficiencies.³⁵⁻⁴² In particular, MAPb(I_{1-x}Br_x)₃ has been reported to show enhanced stability to-

wards ambient conditions and increased moisture tolerance when the bromide content is increased,^{35,43-50} although for intermediate compositions ($x = 0.5$), there are reports of halide segregation.⁵¹⁻⁵⁷ However, the origin of this stability behaviour is not fully understood and therefore remains unclear.

Herein, we investigate the mixed-halide system MAPb(I_{1-x}Br_x)₃ with the overall aim of understanding the key factors behind the enhanced stability in such materials, using a range of computational and experimental techniques, such as UV/VIS, fluorescence, time-resolved photoluminescence (TRPL), Transient absorption spectroscopy (TAS) and density functional theory (DFT) simulations. These techniques were selected as they have previously been shown to help identify the rate of degradation and the yield of superoxide along with the impact on charge separation going beyond our previous work.^{32-34,58} We show that as the bromide content is increased the yield of superoxide decreases and consequently the material stability towards oxygen and light also increases. In addition, we investigate the energetics of degradation reactions and the role that iodide salt treatment can play in obtaining more stable mixed-halide perovskite films and solar cell devices.

▪ Results and discussion

Bromide substitution and superoxide yields. We first assess the stability of MAPb(I_{1-x}Br_x)₃ perovskite films

deposited on glass substrates towards dry air (oxygen) and light, by employing UV/VIS spectroscopy to monitor the degradation. The method used is in accordance with our previous work, where a selected wavelength is used to

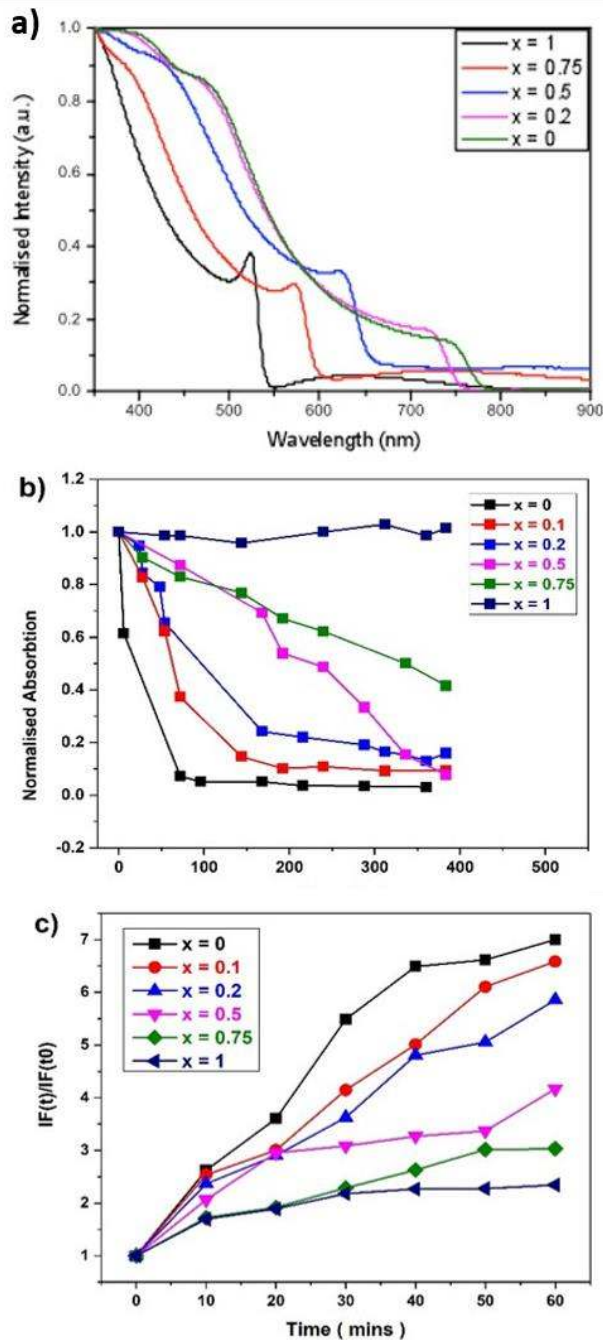


Figure 1. Raw absorbance spectra for pristine films before degradation; b) Normalised absorbance decays as a function of aging under oxygen and light conditions for MAPb(I_{1-x}Br_x)₃ where $x = 0, 0.1, 0.2, 0.5, 0.75$ and 1 . Films become more stable as the bromine content increases; c) Superoxide yield generation (raw data, as collected) for the same film compositions. Superoxide yields decrease as the bromide content increases. Note, that the data shown in Figure 1c) is presented in the form: superoxide yield (normalized for photons absorbed) versus time in our previous work by Pont *et al.*³⁵

monitor the transformation from the starting material to the degradation products.^{32,33} This is possible as the degradation mechanism results in a colour change from the dark perovskite phase to a yellow lead iodide phase. Samples with a range of values from $x = 0.0-1.0$, were selected to explore the impact of bromide substitution on stability towards the degradation conditions. The absorption spectra of the mixed halide perovskite samples studied are shown in Figure 1a.

We now consider the effect of light and oxygen on the stability of MAPb(I_{1-x}Br_x)₃ perovskite films. The UV-vis absorption spectroscopy measurements presented in Figure 1b highlight that in all cases where iodide is present degradation occurs. Importantly, the time taken for the perovskite sample to degrade increases with increasing bromide content. To emphasize this, the pristine MAPbI₃ film ($x = 0$) completely degrades within 100 hours, whilst at $x = 0.75$, degradation takes over 400 hours. Furthermore, when no iodide is present, minimal observable degradation is seen over the experimental time frame. These observations suggest that film stability can be enhanced by bromide substitution and this has important implications for enhanced stability of solar cell devices.

The mechanisms behind the enhanced stability of MAPbBr₃ to light and oxygen may be attributed to a number of factors: the generation of superoxide species, the thermodynamics of the degradation process, and the differences in oxygen incorporation into the film. First, to probe the effect of superoxide generation as a function of bromide content we measure the yield of photoinduced superoxide. Figure 1c, shows the superoxide yields measured for the same film compositions explored in Figure 1a. The data collected shows that increasing the bromide content reduces superoxide yields.

Next, we seek to understand how the role of oxygen diffusion into films may be impacted by bromide substitution and if this can also account for the enhanced stability reported in Figure 1. To investigate this, we used a combination of isothermal gravimetric analysis (IGA)³² and photoluminescence spectroscopy. In the IGA experiment, samples were prepared and sealed in an inert atmosphere, and then the weight increase was measured as a function of time under oxygen flux into the chamber. The data presented in Figure 2a and Table S1 of the supporting information shows an inverse correlation between bromide content and oxygen incorporation into the film. It appears that exchanging iodide for bromide leads to less oxygen stored within films, which can, in part account for the reduced superoxide yields observed for higher substitution levels.

To further probe this effect we used photoluminescence (PL) spectroscopy, which gives us a depth-selective probe of O₂ ingress. By exciting the perovskite at a wavelength of 404nm, at which the penetration depth of light is estimated to be 10nm, we are able to obtain specific PL information from the desired face of the perovskite film.⁵⁹ Moreover, the interaction between O₂ and MAPbX₃ is known to increase the PL signal on account of a passivation effect.^{60,61} Therefore, by probing the PL signal from the substrate of the sample (furthest from the air interface) as a function of time in

O₂ we can ascertain how easily O₂ propagates through the films. In light of this, Figure 2b shows that oxygen is incorporated into MAPbI₃ films, as evidenced by the rapid increase in PL. It is also evident that when a higher content of Br is present in the films, this effect is subdued. In fact, no increase in PL is observed in the case of MAPbBr₃. It is important to note that when the MAPbBr₃ was probed at the surface (Figure S1) there was a significant increase in PL. This data implies that oxygen is present at the surface of the MAPbBr₃ film but is blocked from entering the interior of the sample.

Degradation reaction energetics and structural effects. To complement the experimental work, *ab initio* simulation techniques were used to investigate the effects of bromide substitution on the degradation process, building on our previous successful computational studies.^{32,62-64} We first explored the degradation pathway leading to water and lead halide formation in the presence of oxygen:

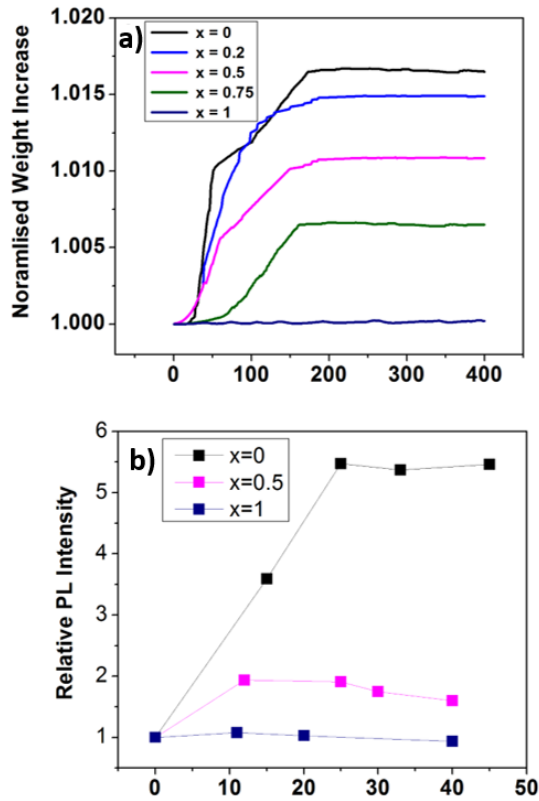
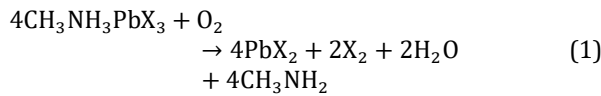


Figure 2. a) Oxygen ingress in CH₃NH₃Pb(I_{1-x}Br_x)₃ films. a) Isothermal Gravimetric Analysis (IGA) traces of CH₃NH₃Pb(I_{1-x}Br_x)₃ films after exposure to dry air flux. b) Normalized photoluminescence intensity obtained from samples pumped with a 404nm laser incident on the substrate face of the perovskite. The increase of this intensity is shown over time after exposure to ambient air in the dark.

where an O₂ molecule is introduced onto the same I vacancy site in all compositions apart from the pure Br composition, in which the site is a Br vacancy.

Figure 3 shows the reaction energies as a function of Br content in MAPb(I_{1-x}Br_x)₃ with full data given in Table S2. For MAPbI₃ the energy of reaction (1) is calculated to be 1.56 eV per oxygen molecule, indicating that the degradation process in the absence of light is unfavourable, which is consistent with observation and previous work.³² In addition, the energy for this degradation reaction (1) for MAPbBr₃ is even more unfavourable, with a calculated value of 4.98 eV, which points to the enhanced stability of this perovskite. In our analysis, we use the configuration with the highest probability of occurrence at 300 K in the mixed systems, with the number of equivalent and inequivalent configurations given in Table S3. We are now able to calculate the average lattice parameters as a function of composition (Figure S2), as well as the energy of mixing (Figure S3). Our results suggest complete mixing of Br and I, which are sta-

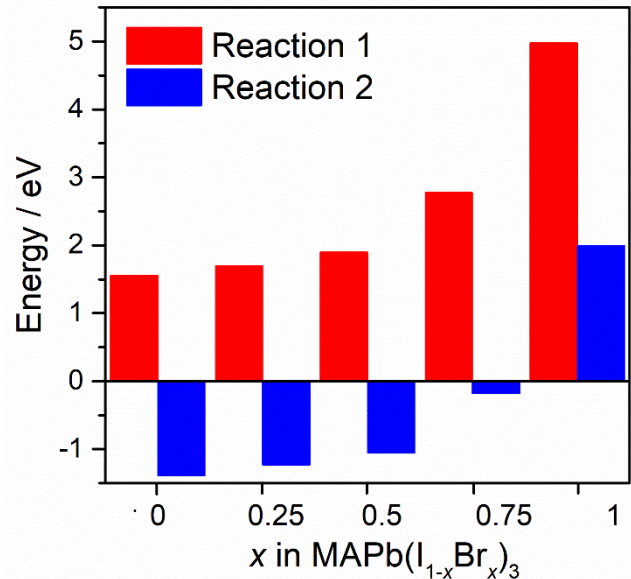
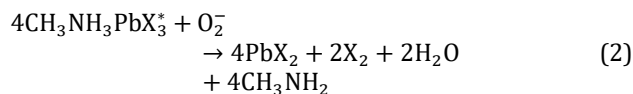


Figure 3. Calculated energies for the degradation reactions (equations 1 and 2) as a function of Br content for MAPb(I_{1-x}Br_x)₃. bilised by entropic effects. We note there has been debate concerning mixed-halide phase segregation especially in the MAPb(I_{0.5}Br_{0.5})₃ composition.⁵¹

As suggested in recent work,³⁰ we also investigated the degradation pathway where O₂ acts as a catalyst, degrading methylammonium ions into methylamine and hydrogen. We find this reaction to be ~5 eV higher in energy than degradation through water formation, indicating that the process is much less favourable, and suggests that O₂ does not act as a catalyst.

For degradation to occur the film must be exposed to O₂ and light. Under illumination O₂ acts as an electron scavenger absorbing photoexcited electrons. The next step would be for superoxide to react with the positively charged photo-oxidized perovskite, indicated by * in the following equation:



Degradation of MAPbI_3 is now found to be favourable, with a reaction energy of -1.39 eV per superoxide ion. In contrast, for MAPbBr_3 the degradation reaction is found to be unfavourable with an endothermic reaction energy of 2.00 eV (Figure 3). This is consistent with our experimental results that show O_2 / light degradation of MAPbI_3 and enhanced stability of MAPbBr_3 (Figure 1c). For comparison we also show the calculated reaction energies for the mixed-anion phases $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$, indicating that the degradation reaction in the presence of superoxide becomes less favourable with increasing Br content. This directly supports our experimental results of enhanced film stability with increasing bromide content. In the mixed systems we find the lowest degradation pathway leads to the formation of PbBr_2 and I_2 . We note that previous calculations⁴⁰ on the phase diagram for $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ reveal a thermodynamic metastability for intermediate I/Br compositions.

Other factors that could also contribute to the stability of MAPbBr_3 are a change in the hydrogen-bonding between the methylammonium cation and the anion lattice, or a decrease in optical absorbance of the perovskite. Comparing the end members MAPbI_3 and MAPbBr_3 , in which there is complete substitution of iodide with the smaller bromide ion, the calculated cell-volume is reduced by 15.8% , which is in agreement with experimentally reported values of up to 17% (Figure S2).^{65,66} XRD diffraction gives Pb-I and Pb-Br bond lengths of 3.16 and 2.97 Å respectively.^{67,68} These values are in line with our calculated bond lengths of 3.21 and 3.00 Å, suggesting stronger Pb-Br bonds that need to be broken in the degradation process. Our DFT simulations indicate that this contraction also leads to shorter H-bond distances between the NH_3 groups and Br ions, as shown in Figure 4. Consistent with our simulation results, XRD and Raman studies⁴¹ find the shortest H-Br bond distance of 2.36 Å in the tetragonal phase (between about 140 and 230 K) and 2.46 Å in the cubic phase, above 230 K (Table S4). Such structural effects would result in stronger H-bonding in MAPbBr_3 and hence impart greater structural stability. We also find that the H-X distance between the CH_3 group and the Br are greater than 3 Å showing they do not form H-bonds, which is in agreement with Yin *et al.* who report that CH_3 -Br hydrogen bonds only form in the orthorhombic phase of MAPbBr_3 .⁴¹

The contraction of the perovskite lattice also suggests an additional factor in the enhanced stability of Br-containing samples through the restriction of O_2 diffusion through the film.

This is further supported by scanning electron microscope images reported by Atourki *et al.* who show that in contrast to MAPbI_3 thin films which form fibre-like crystals with voids between them, MAPbBr_3 form larger aggregate crystals, which would further limit diffusion.⁶⁵ Indeed, the combination of the findings in this section and Figure 2 suggests that O_2 is less able to penetrate the interior of Br-rich films

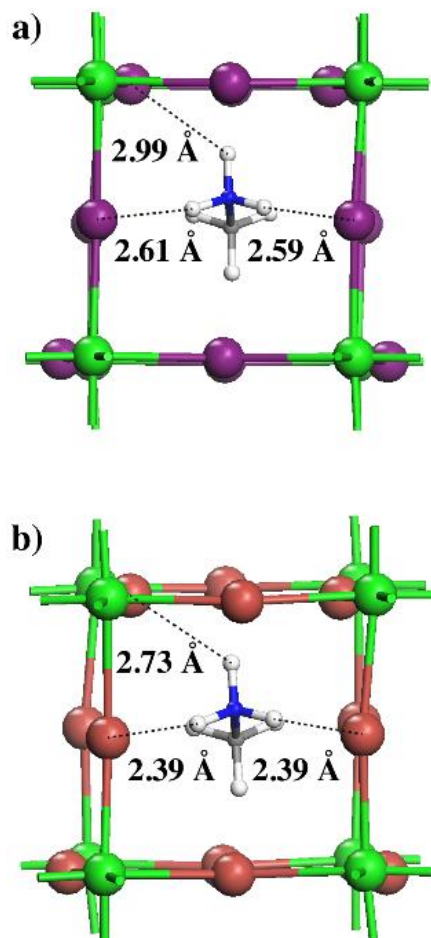


Figure 4. Calculated local structures highlighting the hydrogen-bonding between HN and X in a) tetragonal MAPbI_3 and b) tetragonal MAPbBr_3 . The H_C-X distances are calculated to be greater than 3 Å so do not form. Key: Pb (green), I (purple), Br (orange), N (blue), C (grey), H (white).

on account of the smaller unit cell providing a physical barrier to O_2 diffusion. Interestingly, such structural contraction in MAPbBr_3 would also inhibit MA^+ migration in comparison to MAPbI_3 , which warrants further investigation.

Film passivation via salt treatments. The enhanced stability of mixed-halide perovskites makes them more desirable for solar cell applications. However, as the bromide content increases the optical properties become less favourable for efficient photovoltaic devices. For example, the absorbance data (Figure 1a) shows that upon increasing the bromide content, the band edge shifts and there is less absorption at higher wavelengths, which translates to less efficient solar cell devices. Consequently, we now consider if we can further enhance the stability of the mixed-halide perovskites by surface passivation via iodide salt treatments.³⁵ Of particular interest are the lower bromide content films as they allow the stability to be optimized whilst maximizing the spectral characteristics for light harvesting.

In these experiments, we employed methylammonium iodide (MAI) as a coating agent with concentrations of 0.01M, 0.005M and 0.001M and then applied them to films

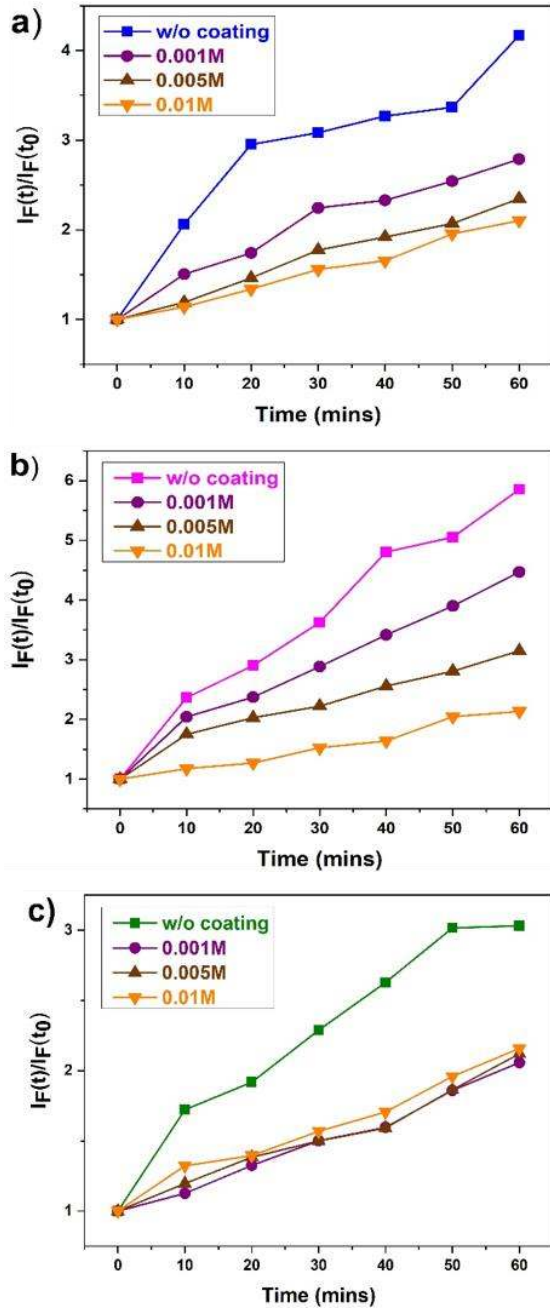


Figure 5. Application of MAI salt coatings (0.01M, 0.005M and 0.001M) to the mixed halide perovskite system $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ with compositions of a) $x = 0.2$, b) $x = 0.5$ and c) $x = 0.75$ and the impact on the normalised absorbance decay with exposure to the degradation conditions. As bromide content increases the salt concentration required to increase stability decreases.

with bromide content of $x = 0.2$, $x = 0.5$ and $x = 0.75$. UV/VIS was used to track the degradation towards oxygen and light at a selected wavelength (700 nm for $x = 0.2$, 600 nm for $x = 0.5$ and 550 nm for $x = 0.75$) and the data normalized with

respect to the fresh sample of each film and coating combination. The results obtained from this study are presented in Figure 5, which shows a plot of the absorption as a func-

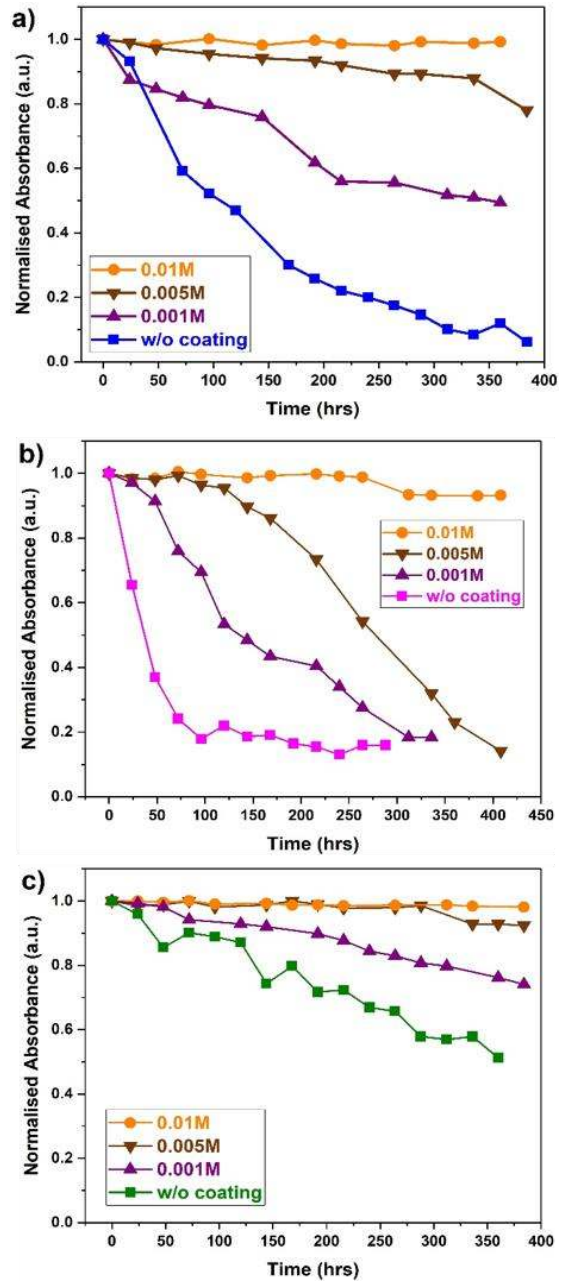


Figure 6. Superoxide generation yields for film compositions of a) $x = 0.2$, b) $x = 0.5$ and c) $x = 0.75$ in $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ as a function of MAI salt coating (0.01M, 0.005M and 0.001M). Increasing bromide content reduces the salt concentration required to reduce the yields of superoxide).

tion of ageing time for different salt concentrations. Raw absorption data (optical density versus wavelength profiles) are provided in Figure S4. It is clear from the data in Figure 5 that the stability of all samples can be improved by the application of the MAI coating, and the stability enhancement is directly related to the amount of coating used. For

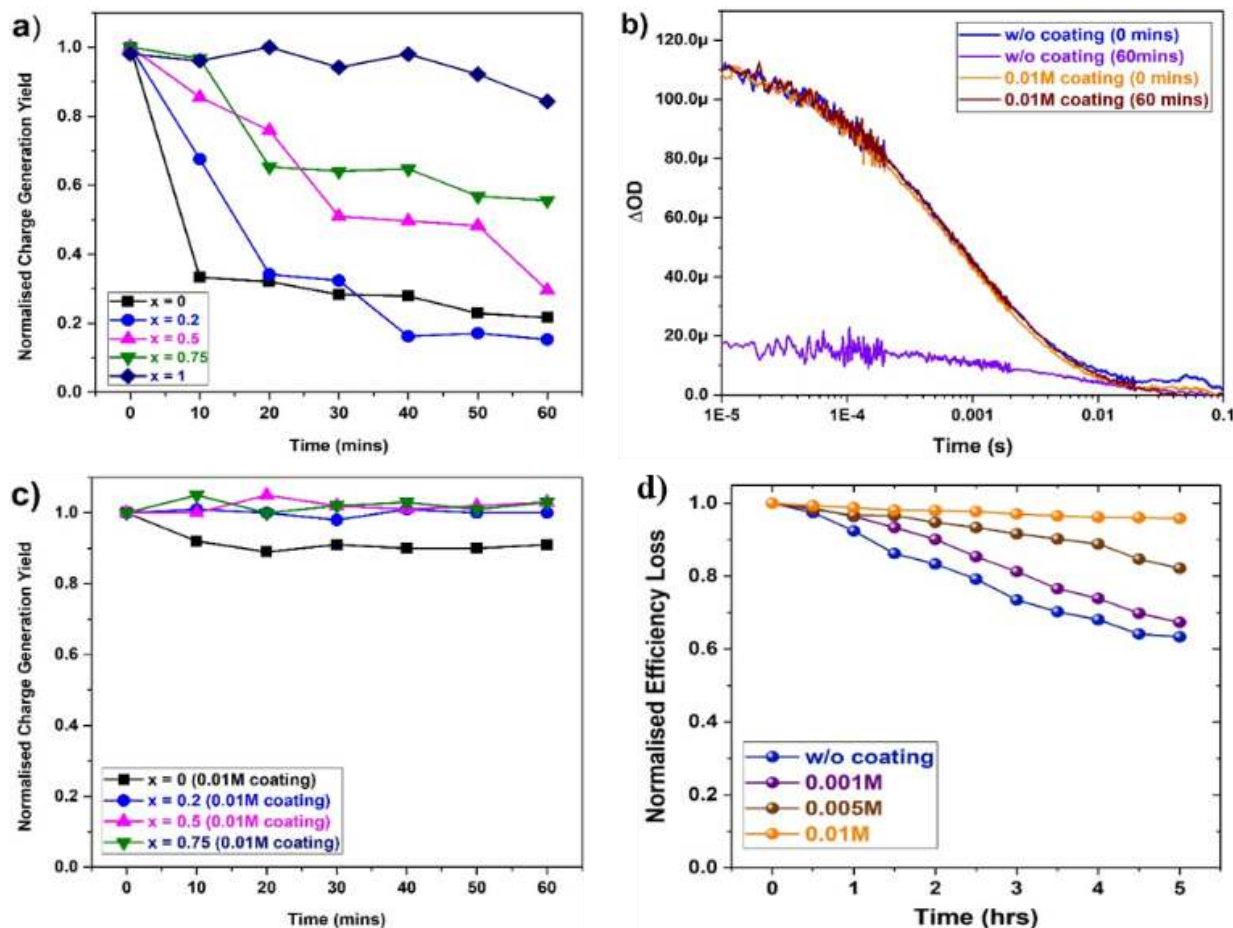


Figure 7. a) Normalised decay of charge separation losses, obtained from transient absorption spectroscopy for films with compositions $x = 0, 0.1, 0.2, 0.5, 0.75$ and 1 . Charge losses are more rapid and significant for compositions with less bromide. b) Transient absorption spectra traces for a $x = 0.2$ film composition, with and without a $0.01M$ salt coating fresh (0 min) and after 60 mins of exposure to oxygen and illumination. c) Normalised decay of charge separation losses, obtained from transient absorption spectroscopy for films with compositions $x = 0, 0.1, 0.2, 0.5, 0.75$ and 1 with a $0.01M$ MAI salt coating. d) Normalised device efficiency (Normalised PCE) loss for a device employing $x = 0.2$ perovskite composition film.

example, the tolerance of the perovskite film to oxygen and light progressively increases as the concentration of the MAI salt solution is increased. For the highest concentration applied ($0.01M$) all films exhibit enhanced lifetime, where little to no observable degradation occurs over the time frame examined. This implies that using this salt concentration enables passivation of iodide vacancies in the film.

To investigate whether the increased stability of the films as a result of the salt treatments is due to the passivation of vacancy defects and reduced superoxide generation, the superoxide yield was determined for the samples presented in Figure 6. The results of this study shows that for all Br-containing compositions, increasing the salt treatment concentration leads to reduced superoxide yields. Taken together, the data presented in Figures 5 and 6 shows that the perovskites with a higher bromide fraction can be stabilized with a lower concentration of MAI salt treatment. Additionally, as a control, we examined the impact of using methylammonium bromide (MABr) as a stabi-

lizing treatment, which showed no improvement in increasing film stability or in reducing the yield of superoxide.¹⁴ Both $MAPbI_3$ and $MAPbBr_3$ were coated with a $0.01M$ concentration of MABr and the results of these experiments are shown in Figure S5.

To gain further insight into the role of bromide substitution and the impact of film passivation with the MAI salt, time-resolved photoluminescence (TRPL) was employed. Iodide vacancies provide a source for non-radiative recombination, and so when the perovskite film is passivated, the photoluminescence lifetime is expected to increase. Figure S6, shows the TRPL data obtained for a range of 4 samples with a composition of $x = 0, 0.1, 0.2, 0.5$, and with and without a MAI coating of $0.01M$. As can be seen, passivation of the films with the iodide salt leads to an increase in PL lifetime.

Implications for device performance. We now consider the effect of bromide substitution on the yield of photoinduced charge separation to the perovskite hole

transport material heterojunctions upon exposure to oxygen and light. The rate of charge separation losses have been shown to be directly related to the decay of device performance in operating perovskite solar cells.³⁴ The yield of hole transfer from the perovskite to the hole-transporting phase, Spiro-OMeTAD, is measured using transient absorption spectroscopy as described in the experimental section. Films with compositions of $x = 0, 0.2, 0.5, 0.75$ and 1 , are examined in an architecture of glass/mp-Al₂O₃/ MAPb(I_{1-x}Br_x)₃ /Spiro-OMeTAD and probed at 1600 nm (tracking concentration of Spiro-OMeTAD hole polarons) following excitation at 458 nm. The change in optical density (ΔOD) value at 1 μ s was obtained and then normalised against the starting value, where the sample has not been exposed to the degradation conditions. The films were exposed to dry air flux and ambient illumination. Measurements were recorded at regular time intervals over the course of an hour and under an inert nitrogen atmosphere.

Figure 7a presents the relationship between ΔOD and time after being exposed to light and oxygen. It is clear that charge separation in the Br-rich films is well maintained even after exposure to light and oxygen. In fact, close correlation is found between the stability of the film, and its Br content. For example, for the fully substituted composition (100% Br) the impact on charge separation yield and therefore degradation is minimal, whilst in the I-rich perovskites, charge losses are significant within the time frame explored. The time taken for the decay to drop to 50% of its original value is found to be 10, 15, 40 and 60+ minutes for the films $x = 0, 0.2, 0.5$ and 0.75 , respectively. This further demonstrates that Br substitution enhances stability to oxygen and light, allowing films to retain optimum optoelectronic properties for longer periods of time.

We next turn our attention to the effect of iodide salt treatment on the yield of charge separation. To this end, we probed the mixed-halide perovskite films with transient absorption spectroscopy after treating them with 0.01M MAI salt solution. Figure 7b, shows the ΔOD as a function of time for the 50% Br composition, with and without a salt coating before and after 60 minutes of exposure to dry air flux and illumination. We note that the decay traces presented in Figure 7b are indicative of recombination of electrons (or holes) in the perovskite with holes (or electrons) in the transport layers. Moreover, the data in Figure 7b shows that the uncoated film undergoes degradation, where the initial amplitude of the signal (ΔOD) decreases significantly after an hour of exposure to light and oxygen. In contrast, no such drop in initial amplitude of the signal is seen in the film passivated with the MAI salt solution. Figure 7c presents the relationship between ΔOD (at 1 μ s) and aging time for perovskite films of $x = 0, 0.2, 0.5$ and 0.75 , with and without a 0.01M salt coating. Note, that all raw TAS traces are provided in Figure S7. It is clear from the data presented in Figure 7c that film passivation via MAI salt solutions generates more stable films that retain their initial charge generation capabilities.

Finally, we consider the effect of film passivation via MAI salts on the stability of mixed-halide perovskite solar

cell devices. Devices comprised of the 20% bromide composition perovskite were fabricated and treated with MAI salt solutions of 0, 0.001M, 0.005M and 0.01M to generate four devices. The power conversion efficiency (PCE) of these devices was monitored as a function of exposure to oxygen and light and the normalized PCE as a function of time is plotted in Figure 7d. We note that the current – voltage curves collected under AM1.5 simulated light and are presented in Figure S8 and Table S5. The data presented in Figure 7d confirms that mixed-halide devices can be stabilized by the application of the salt coating. In addition, increasing the concentration of the salt coating progressively increases the stability of the solar cells.

▪ Conclusions

Our combined experimental-computational study using *ab initio* simulation and spectroscopy techniques improves our fundamental understanding of the degradation behaviour of mixed iodide-bromide perovskite solar cells and indicates design rules for enhancing their long-term stability. Our systematic investigation reveals the following key results:

a) Absorbance spectroscopy shows that as the Br content in the MAPb(I_{1-x}Br_x)₃ system is increased the material stability towards oxygen and light also increases, which correlates with the decreasing yield of superoxide species. Isothermal gravimetric analysis and time-resolved single photon counting show that as the Br content is increased the amount of oxygen incorporation into perovskite films decreases significantly. This partly accounts for the reduced superoxide yields observed for higher Br substitution levels.

b) *Ab initio* simulations on MAPb(I_{1-x}Br_x)₃ show that the degradation reaction involving superoxide species leading to water, lead halide and methylamine formation is energetically favourable and exothermic for pure MAPbI₃, but becomes less favourable with increasing Br content. Indeed, for pure MAPbBr₃ the degradation reaction is unfavourable and endothermic. This may be related to structural factors: the shorter and stronger N-H...Br hydrogen bonds found between the CH₃NH₃⁺ cation and Br ions would promote greater structural stability on bromide substitution.

c) Iodide salt treatment was employed to promote greater stability of perovskites. We find that thin-film passivation with MAI salts leads to enhanced stabilities of mixed-halide perovskite films and solar cell devices.

▪ Methods

Materials. All the chemicals were used as received, including 99% of PbI₂ (Sigma-Aldrich), HI (57% in water, Sigma-Aldrich), PbBr₂ (Sigma-Aldrich), MAI (Dyesol), MABr (Dyesol), Titanium diisopropoxide bis(acetylacetonate) 97%wt in isopropanol (IPA) (Aldrich), spiro-OMeTAD (Lumtec), Bis(tri fluoromethane)-sulfonimide lithium salt (Li-TFSI, Aldrich), 4-tert-butylpyridine (TBP), acetone, ethanol, isopropanol, ethanolamine, 2-methoxyethanol, chlorobenzene, γ -butyrolactone (GBL), TiO₂ paste (Dyesol DSL 30 NR-D 30nm), Terpeneol, hydroethidine, toluene, Dimethyl sulfoxide (DMSO), acetonitrile.

MAPbI₃ and MAPbBr₃ solutions and film fabrication.

0.25 g of MAI and 0.78 g PbI₂ were mixed in a 1:1 mole ratio in 1.4 ml of anhydrous GBL and 0.6 ml of DMSO for 1 hour at 60 °C. After that, they were left to precipitate overnight. The solution was filtered out with a 0.2 µm membrane in a small plastic tube. This solution was then pipetted into 2 consecutive spin steps under a nitrogen atmosphere in a glovebox. The first spin cycle was performed at 2,000 rpm, 2,000 rpm/s for 30 seconds followed by 4,000 rpm, 4,000 rpm/s for 30 seconds. During the second step, the substrate was treated with dry toluene (approximately 500ml) drop-casting. The film was heated at 100 °C for 10 minutes. The colour of the films changed from yellow to black immediately after being placed on the hot plate. It is noted that it is entirely possible that while transporting and measuring, moisture started to corrode MAPbI₃ even though both samples are mostly degraded under a dry air environment. To minimise the amount of moisture getting into the films, the aged films were kept in a closed container with an excess of Si-drying agents underneath, before any characterization techniques were performed. MAPbBr₃ solutions and films were created using the exact same method as described above, except using the bromide derivatives, MABr and PbBr₂.

MAPb(I_{1-x}Br_x)₃ film fabrication. Stock solutions of MAPbI₃ and CH₃NH₃PbBr₃ were prepared by dissolving stoichiometric ratios of PbX₂ and MAX₃ (X = I, Br) in a DMSO and GBL solution (7:3) at 1.25 M conc. and stirred for 60 minutes at 50° C and room temperature, respectively. To obtain a range of composition in MAPb(I_{1-x}Br_x)₃ stock solutions were combined in the desired volumetric ratios. Thin film samples were prepared on glass using an anti-solvent technique adapted from a previously reported method. Glass was washed in soap, acetone, and 2-propanol followed by a 10 min oxygen plasma treatment. The perovskite precursor solution was coated using a spin coating procedure using two speeds where toluene was dripped onto the surface during the second step and then dried at 100°C post deposition.

Spiro-OMeTAD. The HTM solution was prepared by dissolving 72 mg of spiro-OMeTAD in anhydrous 1 ml chlorobenzene solution. In case for device fabrication purposes, 32 µl of Li-TFSI precursor solution (175 mg of Li-TFSI powder in 1 ml of acetonitrile) and 10 µl of 4-tert-butylpyridine (TBP) is mixed with the Spiro-OMeTAD. The solution was then filtered with a 0.2 µm membrane in a small plastic tube. It was then spun at 4,000 rpm, 4,000 rpm/s for 40 seconds. For the TAS or UV-vis measurements, the films were measured immediately after the fabrication process.

Film coatings. Iodide salt solutions were prepared by dissolving the iodide salt (MAI or MABr) in a 1:4 solvent mixture of IPA to chlorobenzene. One hundred microlitres of this solution was then dripped onto pre-deposited perovskite films with a 20 s loading time before spinning at 4,000 rpm. and annealing at 100 °C for 5 min.

Ageing conditions. Films were sealed in a controlled environment, where dry air was gassed through for the duration of the degradation and illumination was provided by

a tungsten lamp equipped with a UV-blocking filter as previously reported.

Characterizations. UV-Vis measurements were carried out using a UV-Vis spectrometer (PerkinElmer) in the wavelength range from 400 to 900 nm with a scan speed of 480 nm per minute with 1 nm data intervals and cycle times of 1 second. Its slit width was 1.0 nm. TAS measurements were performed with a 567 nm dye and a GL-301 dye laser (Photon Technology International, TSI) through an oscilloscope (TG330 Function generator with 3 MHz-Generator, 120 MHz counter/sweep). The frequency of the laser pulse was 4 Hz. The pulse was generated with a light source (Bentham IL 1 illuminator) and a voltage of approximately 12.3 V (Bentham 605). The signal size was filtered with a long pass filter monochromator (Thorlabs) and an optical shielding filter. Each reading was measured at 10 ms time scales for 64 averages for 10 times with a pulse power of 25 µJ/cm². The aged sample was illuminated against a tungsten halogen lamp (Thorlabs) with an approximate power of 20 mW/cm² with a 400 nm long pass optical filter throughout the experiments. Each sample was also purged with dry compressed air (< 2 ppm moisture) during the ageing conditions.

Superoxide probe testing was achieved by dissolving 10 ml of stock solution (31.7 µM) of the hydroethidine (HE) probe in 10 ml dry toluene. Sonication was used to facilitate miscibility. Perovskite films were submerged into this solution. Photoluminescence spectra were recorded with excitation wavelength of 520 nm and slit width of 10 nm on a Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer. The film was illuminated with visible light through a 400 nm long pass optical filter throughout the experiment. A tungsten halogen lamp provided illumination. The light intensity was approximately 1.5 mW/cm².

TAS measurements were performed with a 567 nm dye and a GL-301 dye laser through an oscilloscope (TG330 Function generator with 3 MHz-Generator, 120 MHz counter/sweep). The frequency of the laser pulse was 4 Hz and it was generated with a Bentham IL 1 illuminator and a voltage of approximately 12.3 V. The signal size was filtered with a long pass filter monochromator and an optical shielding filter. Each measurement was measured at 10 ms time scales for 64 averages for 10 times with a pulse power of 25 µJ cm⁻². Photoluminescence measurements were performed by placing perovskite samples on a Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer with same settings as the superoxide probe measurements.

Ab initio simulations. In order to accurately describe the disorder in the MAPb(I_{1-x}Br_x)₃ a symmetry-adapted ensemble of configurations was used as implemented in the Site Occupancy Disorder (SOD) program.⁶⁹ Geometric optimisations of the generated structures were performed using density functional theory (DFT) with the Vienna *Ab initio* Simulation Package (VASP).^{70,71} Electronic exchange and correlation were modelled with the Perdew-Burke-Ernzerhof (PBE) functional,⁷² with van der Waals (vdW) corrections *via* the Tkatchenko-Sheffler electrodynamic screening method.⁷³ A high kinetic energy cutoff of 520 eV was used. Geometry optimisations were performed on the

48-atom tetragonal unit cell, and a Γ -centred grid of $4 \times 4 \times 3$ k -points was employed for Brillouin-zone integrations. The ionic positions were relaxed until the forces were less than 0.01 eV/\AA on each atom. The configuration with the highest probability at 300 K was then investigated further using a $2 \times 2 \times 1$ supercell (giving a tetragonal cell of 192 atoms) in the numeric atom-centred basis set all-electron code FHI-AIMS.^{74,75} Tight basis sets were used with tier 2 basis functions for all species using the PBE exchange-correlation functional and Tkatchenko-Sheffler electrodynamic screening scheme consistent with the geometry optimisations performed in VASP. Relativistic effects were considered using an atomic zeroth-order regular approximation (ZORA).⁷⁴ A Γ -centred grid of $2 \times 2 \times 3$ k -points was used for sampling, which was tested for convergence. O_2 absorption was modelled at equatorial sites over apical sites as these were shown to be more favourable by 0.2 eV. To determine the spin state of the oxygen atoms we constrained the difference in the number of up- and down-spin electrons; corresponding to 0 for non-magnetic, 1 for the low spin state, and $2 \mu_B$ for the high spin state. Initial oxygen incorporation onto a vacancy site leads a low spin state ($1 \mu_B$), with photoexcitation shown to lead to a non-magnetic groundstate. Structures were relaxed with a convergence criterion of $10^{-4} \text{ eV \AA}^{-1}$ for forces, $10^{-5} \text{ eV \AA}^{-1}$ for electron density and 10^{-7} eV for the total energy. The virtual-crystal approximation⁷⁶ (VCA) was employed to model photoexcitation in the charged systems, this ensures the Fermi level does not change in the doped system.⁷⁷ Using this method, we model the positively charged iodide vacancies by distributing the charge uniformly over the Pb atoms. The nuclear number of all the Pb atoms are reduced in the supercell by $\Delta Z_{\text{Pb}} = -q/N_{\text{Pb}}$, where q is the charge of the iodide vacancy (+1) and N_{Pb} is the number of Pb atoms in the supercell. This leads to the introduction of vacant states at the valence band maximum (VBM).

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website <http://pubs.acs.org>.

AUTHOR CONTRIBUTIONS

Corresponding Authors

M. Saiful Islam: m.s.islam@bath.ac.uk @SaifulChemistry
Saif A. Haque: s.a.haque@imperial.ac.uk

All authors have given approval to the final version of the manuscript. The authors declare no competing financial interest. †A. Aziz and N. Aristidou contributed equally to this work.

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