Check for updates

Towards enabling stable lead halide perovskite solar cells; interplay between structural, environmental, and thermal stability

Tomas Leijtens, [iD]* Kevin Bush, Rongrong Cheacharoen, Rachel Beal, Andrea Bowring and Michael D. McGehee

Metal halide perovskite solar cells are rapidly becoming increasingly competitive with conventional PV technologies. While their efficiencies have been often touted as exceptional, they have received a lot of criticism for an apparent lack of stability. This perspective describes some of the most pressing stability concerns facing perovskite solar cells, and describes some of the recent advances made in this area. We will demonstrate that the solutions to the areas of structural, thermal, and environmental stability are closely linked, and that rational design of the perovskite and careful encapsulation can result in efficient and stable perovskite solar cells. We will conclude with some very promising results, demonstrating perovskite solar cells passing an IEC damp heat stability test.

1. Introduction

Solar cells comprised of metal halide perovskite active layers are now achieving performance metrics that make them attractive for commercial applications. They employ low cost, simple precursors and deposition processes to make crystalline

Department of Materials Science, Stanford University, Lomita Mall, Stanford, CA, USA. E-mail: leijtens@stanford.edu

semiconductors with great optoelectronic properties. This class of semiconductors then promises to combine the highest performance with the lowest cost. Progress in device performance has been great due to improved processing techniques, tuned compositions, and optimized interfaces and contacts. As a result, the best metal halide perovskite solar cells have surpassed 22% in solar power conversion efficiency (PCE),[1–4] while the best monolithically integrated perovskite–silicon tandems have reached an impressive 23.6% PCE.[5] However, deployed

Dr Tomas Leijtens obtained his PhD from Oxford University in 2014 under supervision of Professor Henry J. Snaith, where his work focused on understanding charge transport mechanisms and stability of dye sensitized and metal halide perovskite solar cells. From 2013–2015 he was a Marie Curie (ITN) fellow at the Center for Nano Science and Technology in Milan, where he investigated photophysical processes and degradation in metal halide perovskite semiconductors under supervision of Dr Annamaria Petrozza. He currently holds a postdoctoral Marie Curie Fellowship as a researcher at Stanford University working with Professor Michael McGehee. His present research is focused on the development of small bandgap perovskite absorbers and their use in all-perovskite tandem solar cells.

Kevin Bush is a PhD candidate in Michael McGehee's group in the materials science department at Stanford university. His work focuses on the development of efficient and stable perovskite–silicon and all perovskite tandem solar cells. Prior to coming to Stanford, he spent time at Boeing working on flight controls.

This journal is © The Royal Society of Chemistry 2017

J. Mater. Chem. A, 2017, 5, 11483–11500 | **11483**

photovoltaics (PV) must be capable of maintaining their performance over 25 years of operation to be viable for utility and residential power generation, and concerns over metal halide perovskite solar cells' stability have raised questions over their readiness for commercialization.

Most metal halide perovskites used in solar cells take the form ABX_3, where A is a monovalent cation such as methylammonium (MA), formamidinium (FA), or cesium, B is a divalent metal cation such as lead or tin, and X is a halide anion. The highest performing perovskite solar cells are lead based materials which are composed of mixtures of MA, FA, and Cs on the A site and I and Br on the X site: $FA_{1-y-z}MA_zCs_yPb(I_{1-x}Br)_3$.[1,4,6–8] The composition determines the bandgap, crystallographic phase, crystallization kinetics, and even stability of the resultant solar cells. In addition, perovskite solar cells can be made in varying architectures using an array of selective contact layers, which can introduce or eliminate degradation routes.[9–15]

In this perspective, we will provide an overview of degradation routes inherent to the lead halide perovskite semiconductor layer and the progress that has been made in overcoming these, mainly through tuning of the perovskite structure and careful encapsulation. Recent results[5] in our laboratory demonstrate that solar cells made with lead halide perovskites can withstand industry standard environmental stability tests set out by the International Electrotechnical Commission (IEC), an exciting milestone for perovskite solar cells. This perspective aims to summarize the great progress that has been made in the area of stability, focusing on the perovskite absorber and encapsulation. We take the optimistic view that many degradation problems have been resolved and that most others will be soon.

While there are many sources of degradation, this perspective will focus on four crucial areas that have generally been considered as perovskites' weak points and have recently seen great advances:
- Structural stability
- Thermal stability
- Atmospheric stability
- Electrodes and encapsulation

Rongrong Cheacharoen received her B.S. in Materials Science and Engineering with a double major in Physics from Northwestern University in 2012. She is currently a Ph.D. candidate under the supervision of Professor Michael D. McGehee in the department of Materials Science and Engineering at Stanford University. Her research focuses on understanding degradation mechanisms and improving the stability of organic and perovskite solar cells. She is also an amateur scientific photographer.

Andrea Bowring completed her B.S. in Materials Science and Engineering in 2011 from Cornell University and is currently pursuing a Ph.D. in Materials Science and Engineering at Stanford University under the supervision of Dr Michael D. McGehee. She is working on the stability and performance of halide perovskite solar cells.
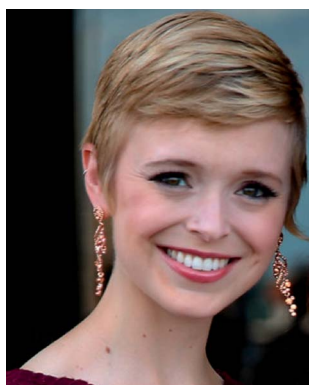
Rachel Beal is a Ph.D. candidate in Department of Materials Science and Engineering at Stanford University under the direction of Professor Michael D. McGehee. She received a B.A. in Materials Science from Northwestern University in 2014. Her research focuses on the development and characterization of novel perovskite materials for tandem solar cell applications.

Mike McGehee is a Professor in the Materials Science and Engineering Department and a Senior Fellow of the Precourt Institute for Energy. His research interests are developing new materials for smart windows and solar cells. He has taught courses on nanotechnology, nanocharacterization, organic semiconductors, polymer science and solar cells. He received his undergraduate degree in physics from Princeton University and his PhD degree in Materials Science from the University of California at Santa Barbara, where he did research on polymer lasers in the lab of Nobel Laureate Alan Heeger. He won the 2007 Materials Research Society Outstanding Young Investigator Award.

11484 | *J. Mater. Chem. A*, 2017, **5**, 11483–11500

This journal is © The Royal Society of Chemistry 2017

It becomes clear that the solutions to all four are complimentary, with appropriate choices in perovskite composition, electrode design, and encapsulation methods working together to overcome these stability issues and enable extremely stable perovskite solar cells.

2. Structural stability

3D metal halide compounds following the ABX_3 structure do not always form a perovskite phase. Indeed, being comprised of ionic salts, the precursors can arrange themselves into a variety of crystalline or amorphous non-perovskite phases that are not suited for photovoltaic operation. Even if a perovskite phase is formed during film deposition and subsequent annealing, this does not guarantee that the perovskite phase is stable at all operating temperatures nor that it is maintained over many years of operation. Here, structural stability is defined as the ability of a material to exist in a perovskite phase suitable for photovoltaic action within conditions (temperature and pressure) relevant to photovoltaic performance.

Since the lead halide octahedra form a cubic corner sharing structure in the cubic perovskite phase, a given lead halide octahedral size (determined by size and electronegativity of the B and X site ions) determines the volume that can be occupied by the A site cation.[16–20] If the A site cation is large relative to this volume, then the lead halide octahedra will need to be distorted and tilt to accommodate the large A cation.[17,21,22] Similar lead halide octahedral distortion and tilting will occur if the A site cation is extremely small.[23] Such distortions usually result in tetragonal or orthorhombic perovskite phases if they are relatively small. The optoelectronic properties of lead halide

perovskite in these phases are very similar, with only small shifts in bandgap, carrier lifetime, and mobilities;[24,25] this allows materials in any of these perovskite phases to function effectively as solar cells and removes concerns over transitions between these phases that may exist at operating temperatures.[25] If the mismatch between the lead halide octahedral size and the A site cation size is too large, then the compound will not exist in a perovskite phase.[16,26,27] The tolerance factor of a given compound gives a rough indication of its ability to form a perovskite crystal structure, and even a rough indication of whether this phase is expected to be cubic ($t = 1$) or deviate into the tetragonal or orthorhombic phases characterized by lead halide octahedral distortion and tilting ($0.7 < t < 0.9$). We should point out that since the ionic radii of the constituents cannot be taken as an absolute value irrespective of the bonding environment, this model should only serve as a rough first indication.[28,29]

The structure, tolerance factor and phase transition information of some of the most commonly employed perovskite semiconductors are depicted and listed in Fig. 1 and Table 1. The first perovskite to be used for photovoltaic applications was $MAPbI_3$, which exists in a perovskite phase with tetragonal distortion at room temperature. The symmetry is further reduced at lower temperatures, as the material enters an orthorhombic phase, while it is increased with higher temperatures as it transitions to the cubic phase. The fact that the material exists in the useful tetragonal and cubic phases at relevant temperatures (0–100 °C) means that this material, at least, is unlikely to suffer from any structural degradation throughout its lifetime.

Nevertheless, the concerns over MA's volatility and this compound's thermal instability[33,34] (see Section 3) have led
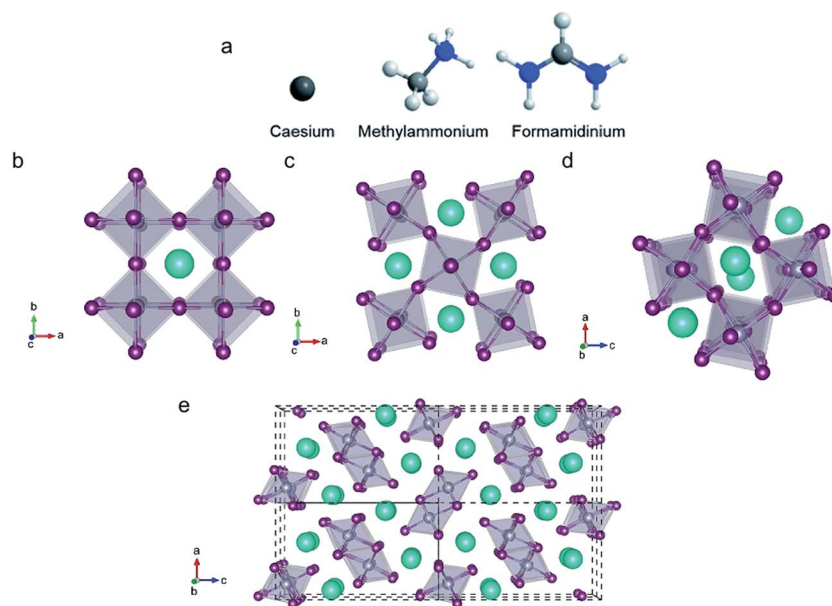
Fig. 1 Schematic depiction of the most commonly used monovalent A-site cations, Cs, methylammonium, and formamidinium in order of ionic size (a). Grey depicts carbon, blue nitrogen, and white hydrogen. 3D perovskite structures are shown in (b–d); (b) depicts the high symmetry cubic phase, (c) the tetragonal phase, and (d) the orthorhombic phase. The yellow, 1D, non perovskite phase of $CsPbI_3$ is also displayed in (e). Reprinted from ref. 23 with permission from the American Physical Society.

This journal is © The Royal Society of Chemistry 2017

J. Mater. Chem. A, 2017, 5, 11483–11500 | 11485

Table 1 3D metal halide perovskite compounds commonly used in PV

	Tolerance factor	RT phase, color	RT phase post anneal	E_g	Best PCE (%)	Relevant phase transitions
$MAPbI_3$	0.89	Tetragonal, black	Tetragonal	1.55	20.3 (ref. 30)	⇒cubic, 60 °C
$FAPbI_3$	1.02	Hexagonal, yellow	Cubic	1.49	17 (ref. 1)	⇒cubic, 150 °C
$CsPbI_3$	0.79	Orthorhombic, yellow	Orthorhombic, yellow	1.72	10.77 (ref. 31)	⇒cubic, 300 °C
$CsPb(I_{0.67}Br_{0.33})_2$	0.81	Orthorhombic, yellow	Cubic	1.9	6.5 (ref. 32)	⇒cubic, 250 °C
$FA_{0.85}Cs_{0.15}PbI_3$	0.99	Tetragonal, black	Tetragonal	1.52	17.3 (ref. 27)	
$FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$	1.01	Cubic, black	Cubic	1.62	22.1 (ref. 1 and 2)	
$FA_{0.85}Cs_{0.15}Pb(I_{0.83}Br_{0.17})_3$	1.01	Tetragonal, black	Tetragonal	1.74	20.0 (ref. 3)	

researchers to attempt replacing it with the larger FA cation, with some success. The larger size of the A cation, however, means that $FAPbI_3$ does not form a black, cubic or tetragonal perovskite phase at room temperature but exists as a yellow film consisting of a hexagonal non perovskite phase also called the δ phase.[6,27,35] Annealing at temperatures above the tetragonal phase transition (150 °C) allows a black perovskite phase to be formed, which is retained after cooling to room temperature.[35] Unfortunately, presence of the δ phase, which seems to worsen over time, limits the performance and stability of this material. Seok et al.[1,6] developed a perovskite compound employing both FA and MA on the A site, as well as both I and Br on the X site, to great effect. Combining these ions led to an effective tolerance factor close to 1, allowing a black, cubic perovskite phase to be easily formed at low temperatures and to be stable at room temperature. While these exhibit some of the highest performances of any perovskite solar cells, they do still contain the volatile MA species.

In attempts to make more thermally stable perovskites, researchers have replaced the organic A cations with the inorganic Cs, to make purely inorganic perovskites.[31,32,36–38] As shown in Table 1, the small ionic radius of Cs means that $CsPbI_3$ does not form a stable perovskite phase at room temperature, but exists in a 1D yellow orthorhombic δ phase. Eperon et al. have been able to make solar cells using acid additives to form films of small $CsPbI_3$ crystals that appear to be meta-stable, but still decompose upon exposure to any stresses such as exposure to water. Since bromide is smaller than iodide, $CsPbBr_3$ can be prepared and is structurally stable at room temperature, but has an unsuitably high bandgap over 2.3 eV.[39] Hence, one approach to stabilize Cs lead halide perovskite structures with appropriate bandgaps is to mix both iodide and bromide, reducing the size of the metal halide octahedra. We demonstrated,[32] as did Snaith et al.,[40] that bromide incorporation above 20% allowed us to make fully inorganic compounds that exist in the cubic phase at room temperature after annealing, exhibit excellent thermal stability and have bandgaps (1.7–1.9 eV) suitable for perovskite–silicon or perovskite–perovskite tandems, though initial device performances are low (~6%). Further research should determine whether these materials are fundamentally structurally stable or whether the films will regress to the δ phase over long periods of time or exposure to stresses relevant to solar cell operation. Recently, $CsPbI_3$ has been stabilized at lower temperature by utilizing the higher surface energy of nano-sized crystal grains to increase

the structural stability of the cubic phase. Swarnkar et al.[31] have fabricated 10.77% efficient, surfactant capped, phase stable $CsPbI_3$ quantum dots, highlighting the link between structural and atmospheric stability. It appears that in the $CsPbI_3$ case at least, minimizing the grain size to increase the surface energy results in improved structural stability. These results are promising, but further work should be done to improve the device efficiencies, determine longer-term stability, and the scalability of such nano-crystals.

Seok et al.[6] first demonstrated that mixing the large FA cation with the smaller MA cation could result in highly efficient, stable compounds, a step that led to the development of more perovskite compounds with mixed stoichiometries. Substituting some of the FA with the smaller Cs on the A site allowed Zhu et al.[27] to tune the tolerance factor of $FA_{1-x}Cs_xPbI_3$ perovskites to close to one and obtain structurally stable materials with high efficiencies (Fig. 2). It would appear that this material (with 0.1 < Cs < 0.3), combines structural stability with an expected improvement in thermal stability, making it extremely promising as the candidate for high performance, stable perovskite solar cells. McMeekin[41] went on to make structurally stable and very efficient $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$ compounds with tunable bandgaps suitable for multijunction applications. Some[3,42] have also substituted Rb into the $FAPbI_3$ perovskite with similar results, while Saliba et al.[3] have made compounds using various mixtures of four of the most suitable A site cations (FA, MA, Cs, Rb) with success. Incorporating smaller cations in the FA based compounds appears to be the most promising solution developed thus far, as it results in both enhanced structural stability as well as some of the highest performances of any perovskite solar cells to date.[3,8,43]

We have also observed that materials with questionable structural stability (that do not readily form black perovskite phases at low temperatures) appear to suffer from an increased propensity to degrade when exposed to stresses such as ambient humidity. The black perovskite phase in these materials is likely only slightly energetically favored over the non-perovskite phases in inert conditions, and introduction of water, for example, may result in the formation of a hydrated non-perovskite phase that is thermodynamically favored over the perovskite phase. As a result, the structural stability does not merely determine a material's likelihood to exist in a desirable black perovskite phase at operating temperatures, it appears to also play a large role in determining a compound's ability to withstand stresses relevant to photovoltaic operation such as moisture, mechanical stresses, and heat.
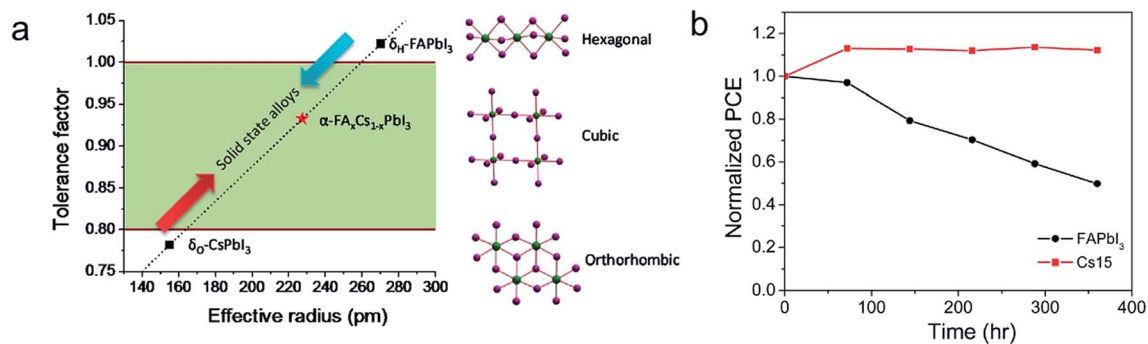
11486 | *J. Mater. Chem. A*, 2017, **5**, 11483–11500

This journal is © The Royal Society of Chemistry 2017

Fig. 2 (a) Schematic illustrating the importance of the A site cation size on tolerance factor and structural properties. Substituting small amounts of FA with Cs on the A site results in more structurally stable compounds. (b) Solar cell performance of a $FAPbI_3$ and $FA_{0.85}Cs_{0.15}I_3$ over time stored in the dark at room temperature and 15% RH. Reprinted from ref. 27 with permission from the American Chemical Society.

Another kind of structural instability arises when bromide is substituted for iodide on the X site. One of the great advantages of perovskite semiconductors is that the bandgap can be readily tuned from 1.5–2.3 eV by substitution of iodide with bromide,[35,44] but this does not always result in the desired results. For example, $FAPb(I_{1-x}Br_x)_3$ films rapidly revert to a yellow, non perovskite films in the range of $x = 0.3$ to 0.6,[41] indicating a new kind of structural instability arising from the inclusion of Br anions into the perovskite lattice. In addition, Hoke *et al.*[45] first demonstrated that the $MAPb(I_{1-x}Br_x)_3$ compounds that could be formed suffer from rapid light induced halide segregation;[46] light exposure results in the formation of iodide rich and iodide poor regions, where the iodide rich regions (with small bandgaps) act as trap sites that pin the Fermi level and limit device performances. As a result, it was not possible to make efficient, high bandgap devices that were stable upon prolonged solar irradiation when using either $MAPb(I_{1-x}Br_x)_3$ or $FAPb(I_{1-x}Br_x)_3$ compounds.

However, we demonstrated that pure inorganic perovskites using the smaller Cs cation on the A site could be formed over the full range of Br contents and that these were far less susceptible to the light induced degradation (at a given bromide content) observed for other bromide containing perovskites using MA or FA cations.[32] These compounds also benefit from the fact that using Cs as the A site cation increases bandgap for a given bromide content; less bromide is necessary to reach a desired bandgap. Unfortunately, their performances are still limited to 6.5%. As mentioned above, McMeekin also prepared very efficient and structurally stable compounds over the full range in bromide content by substituting some of the FA by Cs in $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$ perovskites.[41] These materials were also surprisingly stable to light exposure and showed greatly improved resistance to halide segregation when compared to $FAPb(I_{1-x}Br_x)_3$, though further work is required to evaluate whether they will resist halide segregation over the timescales required for real photovoltaic deployment. The observation that the $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$ compounds are both more structurally stable and less prone to light induced halide segregation than $FAPb(I_{1-x}Br_x)_3$ suggests a somewhat intuitive link between structural stability and the materials' ability to undergo large scale compositional restructuring. This section has

demonstrated that tuning the A site composition to improve structural stability also has a dramatic influence on this type of light dependent halide segregation.

The summary presented above suggests that combining FA with Cs on the A site to make $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ is a promising route forward. Compensating for the large ionic radius of FA with the smaller Cs enables the formation of a compound that exists in a favorable black perovskite phase at relevant temperatures. This compound contains no volatile species and is thus expected to be more thermally stable than the other structurally stable compound $MAPbI_3$. Combining FA with Cs appears also to have enabled the successful inclusion of bromide and reduces light induced instability, opening up the possibility of making highly efficient and stable wide bandgap (1.7–1.9 eV) solar cells for efficient multijunction cells employing silicon, CIGS, or Sn based perovskite rear cells.

3. Thermal stability

While making a structurally stable perovskite compound is the first step to achieving stable solar cells, the compounds must also be stable to external conditions such as heat. Operating temperatures of deployed solar cells can vary from −40 to >85 °C depending on location. All the compounds identified in the section above as being promising maintain perovskite phases at high temperatures. While $MAPbI_3$, for example, transitions from tetragonal to cubic at the relatively low temperature of 60 °C, both phases are capable of efficient photovoltaic action so these phase transitions are unlikely to cause any concern for device operation at elevated temperatures.[24,25] While the exact phase transition temperatures of $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ compounds remain to be elucidated, we are optimistic that the materials will exhibit similarly stable performance across the high temperature phase transition as $MAPbI_3$, while those that are cubic at room temperature are unlikely to undergo any further phase transitions at elevated temperatures.

The most important concern with regards to thermal stability is the chance of thermal decomposition. Early thermogravimetric analysis (TGA) studies on $MAPbI_3$ powders suggested that the material was extremely thermally stable (Fig. 3a–c). Dualeh *et al.*[33] showed that the first signs of mass loss were

around 250 °C due to sublimation of HI and CH_3NH_2, followed by sublimation of the lead halide octahedra at >500 °C. This was consistent with the fact that CH_3NH_3I sublimes at 250 °C. The conclusion would appear to be that $MAPbI_3$ should be intrinsically thermally stable at temperatures relevant to photovoltaic operation. However, with a sublimation temperature of 250 °C, it is possible that the organic components will very slowly sublime at temperatures relevant to device operation. Indeed, Conings et al.[34] used X-ray diffraction (XRD), absorption, X-ray photoelectron spectroscopy (XPS), photoluminescence (PL), and conductive atomic force microscopy (AFM) measurements to convincingly demonstrate $MAPbI_3$ does degrade at 85 °C even in inert conditions (N_2 filled glovebox). As expected, the decomposition is simply due to evolution of the organic components (as HI and CH_3NH_2), leaving behind PbI_2 and even some metallic $Pb_{(0)}$ clusters. Fig. 3d depicts PL spectra of perovskite films before and after heating at 85 °C in various atmospheres, also demonstrating the growth of a PL peak associated with PbI_2 in all atmospheres. This process is greatly accelerated in the presence of either oxygen or water, which interact with the organic part of the structure via complex formation and hydrogen bonding to disrupt the perovskite crystal lattice and reduce the attraction between inorganic octahedra and the organic cations (more in Section 4). Thus, while this occurs slowly in inert conditions (<10% degradation in device performance over 24 h), $MAPbI_3$ cannot be considered as a promising compound for long term operation at elevated temperatures.

However, as stated in the previous section, compounds with less volatile components can be made to overcome such thermal decomposition. The most obvious route to overcome the problems associated with evolving organic components is simply to remove those organic components. Snaith and co workers, as well as ourselves, successfully made solar cells using the purely inorganic $CsPbI_2Br$ perovskite.[32,40] This material exhibited greatly enhanced thermal stability, not decomposing even at 180 °C over 30 minutes, a temperature at which $MAPbI_3$ decomposed within 5 minutes (Fig. 4a). Purely inorganic perovskites may then offer a solution to the thermal instability of $MAPbI_3$, but still suffer from questionable structural instability and low device performances.

Replacing MA with the larger and heavier FA is another option for raising the thermal stability of perovskite solar cells. In the first demonstration of FA based perovskite solar cells, Eperon et al.[35] compared films of $MAPbI_3$ and $FAPbI_3$ heated at 150 °C in air to show that the $FAPbI_3$ did not degrade over 60 minutes while the $MAPbI_3$ film had converted almost completely to PbI_2 (Fig. 4b). McMeekin et al. showed that their $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$ compounds do not degrade over the course of six hours at 130 °C in inert conditions (Fig. 4c), while the film preparation involves annealing for three hours at 180 °C in air.[41] Docampo et al.[47] also demonstrated via TGA that the mass loss associated with sublimation of the organic component occurred 50 °C higher in $FAPbBr_3$ than in $MAPbBr_3$. In addition, it is important to consider that the mechanism of organic sublimation from a perovskite compound involves the initial evolution of HI gas, followed by the organic conjugate base (CH_3NH_2 or $NHCHNH_2$).[26,33,48] Thus, the rate of degradation is proportional to the probability of HI formation, which is directly related to the acidity of the organic cation. The more acidic the organic cation, the stronger the interaction with halides and the higher the chance that the organic cation can be deprotonated to yield HI (or HBr) and the conjugate organic base. The importance of acid–base interactions on thermal stability is especially apparent when considering recent work by Kelly et al.,[49] demonstrating that the use of basic zinc oxide
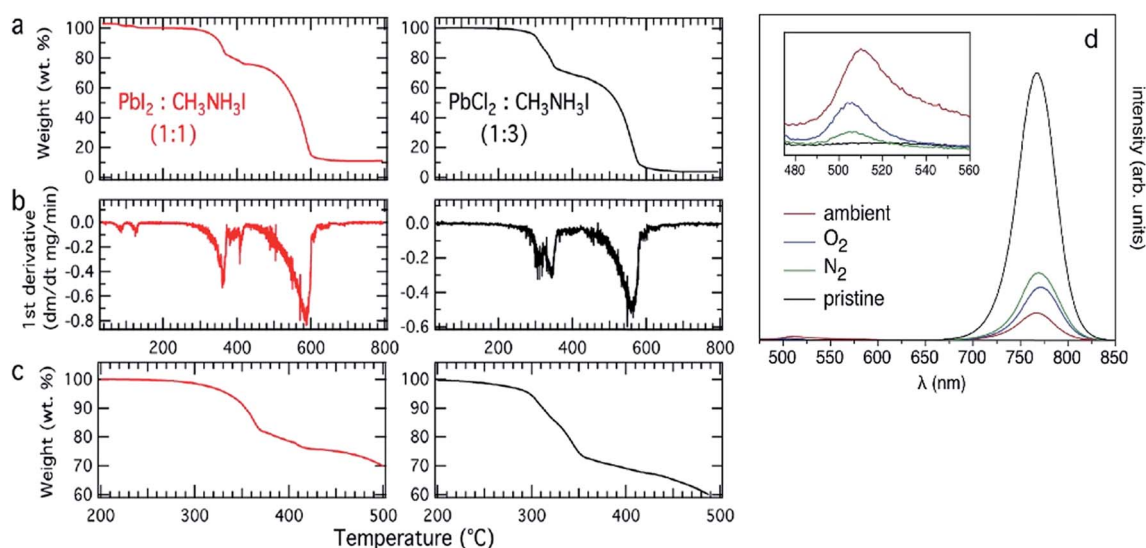

Fig. 3 (a and b) Thermogravimetric analysis (TGA) of $MAPbI_3$ samples prepared via a stoichiometric synthesis as well as by a synthesis using $PbCl_2$ as the lead precursor. (c) focuses on the region in which the organic compounds are being evolved from the samples. Reprinted from ref. 33 with permission from the American Chemical Society. Photoluminescence (PL) spectra for samples annealed at 85 °C in varying atmospheres are depicted in (d). The inset highlights the evolution of PL from PbI_2 degradation products. Reprinted from ref. 34 with permission from Wiley.
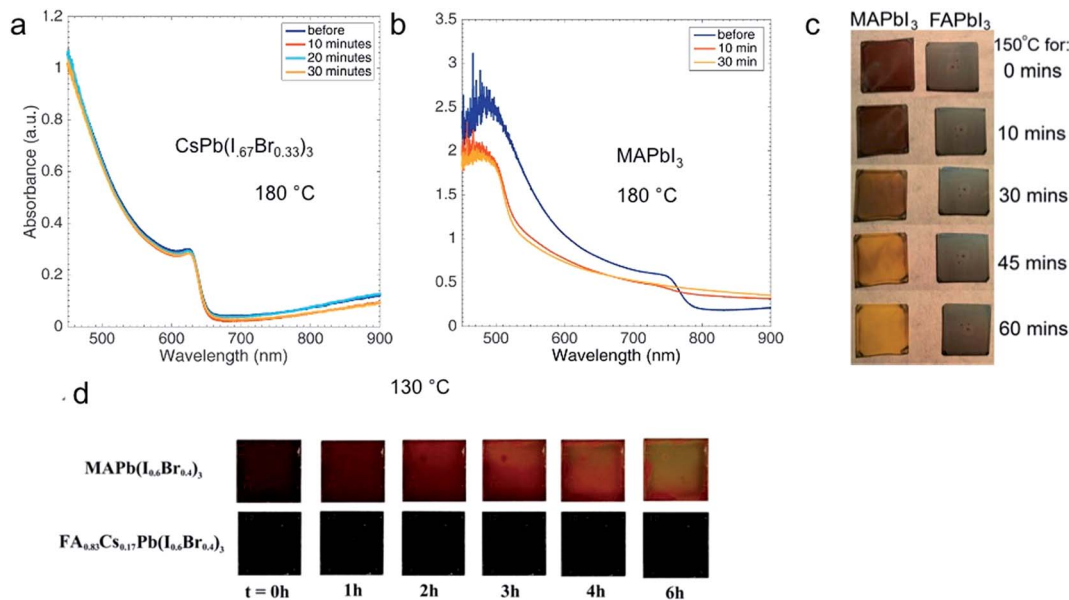
11488 | *J. Mater. Chem. A*, 2017, **5**, 11483–11500

This journal is © The Royal Society of Chemistry 2017

Fig. 4 Comparison of MAPbI$_3$ and CsPb(I$_{0.67}$Br$_{0.33}$)$_3$ thermal stability at 180 °C in a N$_2$ atmosphere (a and b). Reprinted from ref. 32 with permission from the American Chemical Society. Comparison of MAPbI$_3$ and FAPbI$_3$ thermal stability at 150 °C in air (c). Reprinted from ref. 35 with permission from the Royal Society of Chemistry. Comparison of MAPb(I$_{0.6}$Br$_{0.4}$)$_3$ and FA$_{0.83}$Cs$_{0.17}$Pb(I$_{0.6}$Br$_{0.4}$)$_3$ thermal stability at 130 °C in a N$_2$ atmosphere (d). Reprinted from ref. 41 with permission from the American Association for the Advancement of Science.

(ZnO) electron selective layers leads to rapid thermal degradation of MAPbI$_3$ because the acidic MA cation can be deprotonated by ZnO. Since MA is more acidic than the larger FA, in which the positive charge can be delocalized over two amine groups (amidines are generally more basic than amines and their conjugate acids thus less acidic than the amides), it is only natural that the rate of thermal decomposition is slowed in FA-based perovskites for this reason as well as the simple fact that it is heavier. This same logic should apply to the interaction with water, which is dictated by acid–base interactions, and where FA perovskites should hence exhibit improved stability (to be discussed further in the Atmospheric stability section).

Thus, the volatility of the organic cations presents a concern for the thermal stability of perovskite solar cells. However, replacing the volatile MA cation with FA or Cs results in substantially improved thermal stability while maintaining high device performances. Here, we point out that some of the highest performance perovskite solar cells have been made with mixed A site cations including small amounts of MA.[3,43,50] Some of these have even looked to be surprisingly stable even under illumination at 85 °C. Perhaps small amounts of MA and can be tolerated since a small fraction of it evolving over time results in a very small fraction of the overall A sites. Nevertheless, the thermal stability of such compounds remains unclear and should be thoroughly evaluated and compared to completely MA-free compounds. Again, it appears that the perovskites using both FA and Cs on the A site should allow for the best possible combination of structural and thermal stability in highly efficient solar cells. Indeed, the last section will present some very recently published findings demonstrating that solar cells made from these compounds can pass industry standard IEC thermal stability tests.

4. Atmospheric stability

Oxygen induced degradation

Of the external factors that influence semiconductor performance, oxygen and moisture may be some of the most harmful. All PV technologies deployed to date suffer from degradation in the presence of these two pervasive stressors, which can oxidize and solubilize many of the functional components in solar cells. Every deployed solar cell will benefit from thorough encapsulation, usually in the form of laminated plastic/glass or glass/glass packaging. Nevertheless, enhancing the intrinsic stability of unencapsulated solar cells is a first step towards relaxing the requirements for encapsulation of perovskite solar cells and ensuring that encapsulation used on commercial crystalline Si and thin film PV will be sufficient for perovskite solar cells. An advantage of perovskite solar cells is that they could be made into flexible PV modules. Here, thorough encapsulation is more difficult, and the best atmospheric barrier layers can be prohibitively expensive. Again, the more stable the unencapsulated solar cell, the less stringent the encapsulation requirements will be, perhaps enabling flexible perovskite modules.

Many "shelf-life" studies demonstrate that perovskite solar cells can be stored in ambient conditions in the dark for months without changes to their performance, suggesting that the materials are not susceptible to oxidation in the ground state.[51,52] Reports by Haque and coworkers[53–55] as well as by Pearson et al.[56] demonstrate that MAPbI$_3$ can be readily photo-oxidized, however. Pearson et al. demonstrate that when aged under AM 1.5G irradiation in 10% dry O$_2$ at open circuit, MAPbI$_3$ solar cells will degrade to 20% of their initial performance within several hours. Haque proposes a mechanism for

This journal is © The Royal Society of Chemistry 2017

J. Mater. Chem. A, 2017, **5**, 11483–11500 | **11489**

photo-oxidation and subsequent decomposition:[54] first, super-oxide (O_2^-) anions are formed as molecular oxygen accepts photo-excited electrons from the perovskite conduction band. These superoxide anions can then deprotonate the methyl-ammonium cation to result in decomposition to lead iodide and methylamine gas, similar to the thermal degradation products.

The mechanism proposed by Haque *et al.* suggests that the acidity of the organic cation again plays a large part in the decomposition pathway. As a result, substituting MA with FA and/or Cs should result in improved resistance to oxidation and subsequent decomposition. Only recently, Snaith and coworkers[57] compared the stability (at open circuit) of $FA_{0.83}$-$Cs_{0.17}Pb(I_{0.6}Br_{0.4})_3$ to $MAPbI_3$ solar cells under full AM 1.5G illumination in air, without encapsulation. As expected, the $MAPbI_3$ solar cells decomposed rapidly with T_{80} (time for the device performance to reach 80% of the initial performance) lifetimes of 20 h, while those made with $FA_{0.83}Cs_{0.17}Pb(I_{0.6}-Br_{0.4})_3$ had much superior T_{80} lifetimes of over 650 h and still operated at 10% PCE. Such good results for unencapsulated devices are very reassuring and give us confidence that photo-oxidation will not be a problem for these compounds when they are properly encapsulated.

We should also emphasize that while light can degrade perovskite compounds in the presence of oxygen, the materials appear to be stable to full solar irradiation in inert environments (with the exception of the halide segregation discussed in Section 1). This was first demonstrated in 2012, when Lee[58] monitored the absorption of encapsulated $MAPbI_3$ films under illumination over 1000 h and observed no changes. These results are supported by the numerous reports of photocurrent stability over many hundreds of hours for encapsulated devices.[11,15,51,59–61]

Moisture induced degradation

Whereas oxygen only decomposes the perovskite under light exposure, exposure to moisture causes rapid decomposition of the perovskite even in the dark. This was one of the first degradation pathways to be investigated and great deal of work has gone into elucidating the degradation mechanism of $MAPbI_3$ in moisture, as well as the synergistic effects of moisture, heat, and electrical biasing.[10,15,62–65] We will not describe all of the work here, but refer the reader to several thorough review articles.[15,66–68] In essence, water can penetrate the perovskite lattice to form hydrated perovskite phases in which the organic species can be readily mobilized and evolved, eventually leaving just lead iodide. Crystal structures derived for the hydrated phases demonstrate that while some hydrogen bonding could occur with the lead halide octahedra, the strongest interactions are by far through hydrogen bonding with the organic methyl-ammonium cation, forming cation–water–cation chains.[69,70] Of course, since MA is acidic, it can donate a proton to water, breaking bonds between the A site and the lead halide octahedra to allow the volatile CH_3NH_2 to be evolved and decompose the perovskite structure.
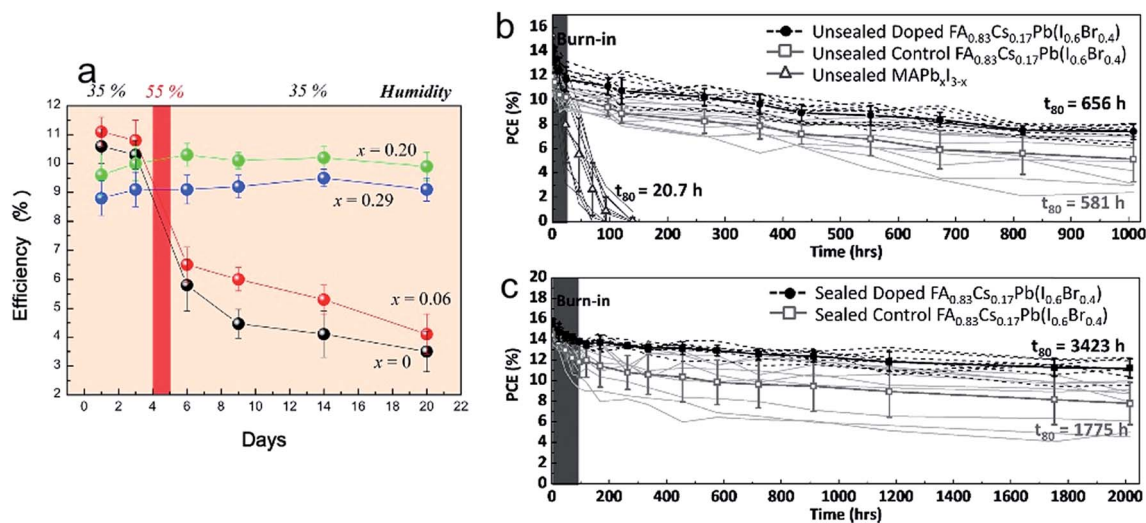
In $MAPbI_3$, this occurs over tens of hours under ambient conditions at 80 °C.[10] Seok *et al.*[44] first showed that this could be

slowed by incorporating Br onto the X site, demonstrating that compositional tuning can affect the susceptibility to moisture-induced decomposition (Fig. 5a). They postulated that introducing Br shrinks the lattice parameter and strengthens the hydrogen bonding between the MA cation and the lead halide octahedra, reducing the ability for water to intercalate and form a hydrated phase. Similarly, Jiang *et al.*[71] has shown that substitution of a thiocyanate anion for some of the I on the X site of $MAPb(I_{1-x}SCN_x)_3$ results in the formation of a perovskite compound with similar optoelectronic properties to $MAPbI_3$ but enhanced moisture stability. Several studies have incorporated SCN into $MAPb(I_{1-x}SCN_x)_3$, and although though the exact content of SCN is unclear due to the deposition routes used, all have demonstrated that the perovskite maintains its characteristic absorption over many hours at elevated temperature and humidity, with devices demonstrating enhanced moisture stability over $MAPbI_3$.[71,72] It was even possible to make efficient perovskite solar cells in conditions of 70% RH when $Pb(SCN)_2$ was used as the lead precursor for the in a two step deposition process.[72] These results are promising, though the light stability of these materials has not yet been tested.

Tuning the A site cation also influences moisture stability. $FAPbI_3$, however, does not exhibit superior moisture stability than $MAPbI_3$. In fact, moisture destabilizes the black polymorph and accelerates its return to the yellow hexagonal phase. A similar effect is observed for pure $CsPbI_3$ and even $CsPbI_2Br$ perovskites; which rapidly return to the yellow orthorhombic phase when exposed to air. It is apparent that while the pure FA and Cs perovskites benefit from enhanced thermal stability, their poor structural stability is reflected in their poor moisture stability. Hence there appears to be a link between structural stability and moisture stability. Accordingly, mixing FA and Cs on the A site significantly enhances the moisture stability. While $FAPbI_3$ degrades to half its initial device performance after storage in air with 15% RH over the course of just 15 days in the dark, $FA_{0.85}Cs_{0.15}PbI_3$ actually improves in performance by close to 20% (ref. 27) (Fig. 2b). Similarly, Park demonstrated that $FA_{0.9}Cs_{0.1}PbI_3$ films maintain their absorption for approximately four times as long (4 h) as $FAPbI_3$ under 85% RH at room temperature.[74] Going further, Snaith demonstrated (as discussed above) that $FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})_3$ can be stable for over 650 h under full solar illumination under ambient conditions (Fig. 5b and c), while $MAPbI_3$ based solar cells degraded in less than 100 h.[57] This can be rationalized when we consider that the mechanism of water intercalation and formation of the hydrated phases relies on strong hydrogen bonding between water and the organic cation. Hence, the more delocalized the positive charge of the organic cation and the less acidic it is, the weaker the interaction will be with water. As a result, FA based compounds should exhibit superior moisture stability, but as stated above, these require the addition of the smaller Cs cation. Again, the mixed cation perovskite seems to combine the best of all of the properties: structural, thermal, and atmospheric stability.

Making 2D Ruddlesden Popper perovskite structures offers another route towards designing stable perovskite structures.[75,76] Here, large organic cations form 2D sheets that

11490 | *J. Mater. Chem. A*, 2017, **5**, 11483–11500

This journal is © The Royal Society of Chemistry 2017

Fig. 5 (a) Performance over time of MAPb$(I_{1-x}Br_x)_3$ on exposure to humidity in the dark. The red section corresponds to a day spent in 55% RH at room temperature. FA$_{0.83}$Cs$_{0.17}$Pb(I$_{0.6}$Br$_{0.4}$)$_3$ compared to that of MaPbI$_3$ in solar cells with and without doping of the C$_{60}$ fullerene electron selective contact (b). Reprinted from ref. 73 with permission from the American Chemical Society. The unsealed solar cells were held at open circuit under full spectrum AM 1.5G irradiation. The same experiment was performed for devices encapsulated using two-part epoxy and glass slides (c). T_{80} refers to the time taken for the device performance to reach 80% of the initial value, ignoring the initial "burn in" decay. Reprinted from ref. 57 with permission from Wiley.

separate blocks of 3D perovskite. Controlling the number of perovskite unit cells between each organic sheet controls the electronic properties of the material through dielectric confinement, and also protects the perovskite units from exposure to ambient conditions. A balance can thus be found between obtaining suitable photovoltaic properties (small bandgap, high carrier lifetimes and mobility) and protecting the material with the 2D sheets of large hydrophobic organic cations. While such structures were first proposed by Smith et al.[75] (Fig. 6A and B), Mohite et al.[76] demonstrated high performances over 11% and very promising stability. Unencapsulated devices maintained 60% of their initial performance after 1000 hours of AM 1.5G irradiation in air, while

encapsulated devices did not demonstrate any signs of degradation after 1000 h of illumination or 1000 h of exposure to 65% RH at RT (Fig. 6C and D). MAPbI$_3$ reference solar cells, of course, degraded rapidly. Further work needs to be done to raise the efficiency of such materials to closer to their 3D counterparts, which would make these some of the most exciting perovskite absorbers so far developed.

Atmospheric degradation can also be slowed by using moisture barriers as the selective contacts. There are many reports introducing new hydrophobic and moisture resistant contact layers that appear to drastically slow moisture induced degradation. Some of the most promising results have been achieved by employing thick moisture blocking carbon hole
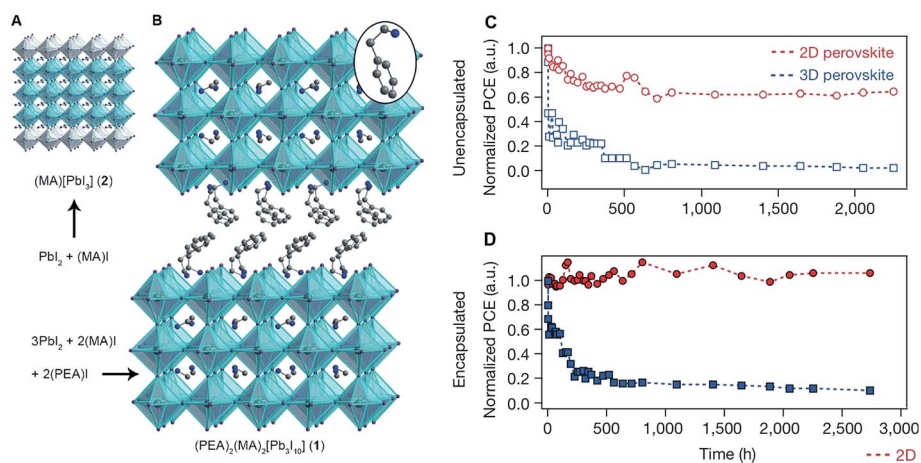
Fig. 6 (A and B) Structure of 2D Ruddlesden Popper perovskites PEA)$_2$MA$_2$Pb$_3$I$_{10}$ developed by Smith et al. Reprinted from ref. 75 with permission from Wiley. (C) Stability of (BA)$_2$(MA)$_3$Pb$_4$I$_{13}$ Ruddlesden Popper 2D perovskite solar cells compared to those of MAPbI$_3$ perovskite solar cells, at open circuit under ambient conditions and AM 1.5G illumination. (D) Encapsulated stability of the same. Reprinted from ref. 76 with permission from Nature Publishing group.

This journal is © The Royal Society of Chemistry 2017

J. Mater. Chem. A, 2017, 5, 11483–11500 | 11491

transport layers and by using inert moisture resistant polymers such as polymethylmethacrylate (PMMA) in a composite structure with carbon nanotubes.[9,10,13,30,60,77] These have enabled hundreds of hours of device operation under ambient conditions and even enabled unencapsulated devices to be annealed at 80 °C for 100 h with negligible drops in performance.[60,78] A recent study demonstrated that devices can be simply encapsulated by a hydrophobic polymer,[79] with solar cells showing only minor degradation after three months of aging on a rooftop in Italy during the summer. The reader is referred to a thorough summary of the various contact layers and their influence on moisture stability, written by Habisreutinger and colleagues.[66]

The results described in this section demonstrate that the organic cation plays a large role in determining the stability of the perovskite even under oxygen and air exposure. It then appears that the A site cation is essential in influencing structural, thermal, and even atmospheric stability. Both the thermal and atmospheric stability appear to be heavily influenced by the acidity of the cation, leading to FA based perovskites being more thermally and atmospherically stable. This conclusion suggests that further improvements could be made with even less acidic cations, and preferably even nonprotic cations.

5. Electrodes and encapsulation

While very promising results can be obtained by careful design of the perovskite absorber, it is clear that encapsulation will be of paramount importance to prevent photo-oxidation and decomposition in perovskite solar cells over tens of years. The organic light emitting diode (OLED) and organic photovoltaic (OPV) communities have faced this same challenge,[80–82] since they use highly oxygen sensitive polymers and small molecules that require effective encapsulation. Work on encapsulation starts with a careful selection of oxygen and moisture resistant selective contacts, followed by industry standard module encapsulation. This generally takes the form of plastic/glass, glass/glass or glass/metal foil packaging held together with adhesives such as ethylene vinyl acetate (EVA) or Surlyn for rigid modules, or composite SiN/polymer layers for flexible modules.

Electrodes

After the selective contact layers, the electrodes provide the first layer of encapsulation. This takes the form of metal in the vast majority of perovskite solar cells, with silver, aluminum, and gold being metals of choice. Metals are dense and impermeable to oxygen and water. When deposited in a conformal layer, they offer perovskite solar cells excellent protection from both oxygen and moisture. Unfortunately, metals readily form metal halides.[11,83–85] Silver and aluminum are especially prone to the formation of their halides, while gold is less reactive. Thus, any contact between the metal electrode and the perovskite will result in the formation of a black metal halide, especially at elevated temperatures and applied electric fields; the metal halide is resistive and does not function as an electrode while its

formation must introduce an iodide deficiency within the perovskite. This problem is exacerbated by the ability of both metal atoms and iodide to diffuse through the perovskite as well as the selective contact layers. It was observed in some of the first reports on perovskite stability,[11] and was more thoroughly investigated later,[83–85] where it was demonstrated that the commonly used HTM Spiro-OMeTAD becomes permeable to metal diffusion at elevated temperatures (Fig. 7a–c). Here, we must highlight the very impressive device stability results obtained by several groups, achieving only small performance losses under operation over at least 500 hours when using metal electrodes in ambient conditions:[43,50,57] replacing the metal electrodes in their device architecture would likely result in very stable solar cells.

Several strategies have been employed to overcome this effect. Domanski et al.[83] employed a Cr/Au contact to slow the reaction, but since even chromium can form a halide, it seems unlikely that this could be a viable solution over the course of tens of years. Similarly, Huang et al.[84] used Cu electrodes with improved stability, though again here we must be concerned that its small size and ability to form copper iodide mean it may not be able to provide the 25 year lifetimes required. Carbon electrodes have also been used, yielding vastly improved stability but not at the highest performances.[9,60] In their recent report on high performance rubidium containing perovskite compounds, Saliba et al.[3] replaced the commonly used Spiro-OMeTAD HTM with a thin layer of polytriarylamine (PTAA) polymer. They propose that the gold is not able to diffuse through this polymer layer, and demonstrate very impressive stability: their solar cells only lose approximately 10% of the initial efficiency during maximum power point tracking over
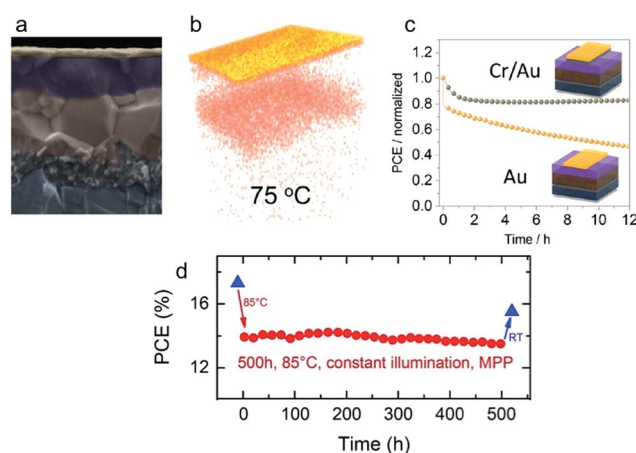

Fig. 7 Depiction of metal diffusion process given by (a) a cross-sectional scanning electron microscope image of a perovskite device (capped with Spiro-OMeTAD and gold) and (b) reconstruction of the gold concentration profile through the solar cell layers as verified by ToF-SIMS. The associated drop in device performance can be mitigated by using a chromium/gold bilayer electrode to slow metal diffusion at elevated temperatures (c). Reprinted with from ref. 83 with permission from the American Chemical Society Further improvements are made by replacing the Spiro-OMeTAD HTM with PMMA, a polymeric HTM (d). Reprinted from ref. 3 with permission from the American Association for the Advancement of Science.

11492 | J. Mater. Chem. A, 2017, 5, 11483–11500

This journal is © The Royal Society of Chemistry 2017

500 h of illumination at 85 °C in a nitrogen environment (Fig. 7d). These results are very promising, but gold is expensive as an electrode in commercially viable solar cells. The next step would be to determine whether the polymer HTM can also prevent the diffusion and reaction of the less stable and more mobile silver and aluminum electrodes.

In our own work,[14] we have opted to completely remove the metal electrode and replace it with Indium Tin Oxide (ITO), used in most commercially available displays and many PV modules. ITO is not reactive, dense enough to prevent moisture, oxygen, and metal (from eventual grid lines) diffusion, and is deposited *via* a relatively cheap sputtering process. Because it is transparent it also enables perovskite–silicon tandems. Of course, it is also the transparent electrode used on the many of substrates on which perovskite solar cells are built. The high kinetic energy of the plasma in the sputtering process can damage the soft organic layers used as selective contacts in perovskite solar cells, so a dense "buffer" layer must be used. Others have used MoO_x as the buffer layer on top of their HTM with some success.[86] Using the inverted architecture with the top of the solar cell stack being the electron-extracting side, we required electron transporting buffer layers, and first used a thin solution processed layer of aluminum doped zinc oxide (AZO) nanoparticles. This enabled ITO to be sputtered with no damage to the perovskite, resulting in solar cells with improved stability.

These solar cells, using ITO as the bottom and top contact, were effectively metal free and effectively encapsulated from both from the external as well as internal stresses. As expected, they exhibited excellent stability, and otherwise unencapsulated $MAPbI_3$ based solar cells showed no signs of degradation over the course of 250 h of illumination at their maximum power point in air. These $MAPbI_3$ based solar cells even showed surprisingly good thermal stability; they maintained 80% of their initial efficiency even after maximum power point tracking under full illumination for 100 h at 100 °C (Fig. 8). This is

remarkable since $MAPbI_3$ is notoriously thermally unstable, as described in Section 2. Since ITO is impermeable to diffusion of most gases, we propose that as HI and CH_3NH_2 evolve with heating, a vapor pressure is built up within the active layers of the solar cells. As a result, the MAI sublimation process is in equilibrium with re-inclusion into the perovskite structure, and the perovskite degrades much more slowly than if it were not covered by the impermeable ITO. Hence, the ITO layer not only prevents oxygen and moisture from entering the perovskite, it also prevents thermal decomposition of the material. Such results are not possible with most metal electrodes due to their reactivity, especially at elevated temperatures.

Of course, a thin (500 nm) ITO layer does not constitute a completely effective level of encapsulation; rigid PV modules will benefit from glass and polymer encapsulation. The ITO electrode does, however, facilitate industry standard encapsulation processes. To laminate a solar cell between two glass sheets using EVA or Surlyn binders requires heating to 140 °C for approximately 30 minutes, so using a nonreactive electrode that can contain evolving organic species is essential.

Towards passing IEC standard tests

Because solar cells deployed for utility and residential scale power generation are expected to perform at high efficiencies for over 25 years, it is important to develop accelerated stability tests. Simply testing a solar cell in outdoor conditions for several months as is often done in the perovskite research community, while promising, gives very little indication of how the solar cells will perform over 25 years. For this reason, the IEC has developed a series of accelerated tests to probe the various failure modes observed for deployed PV panels. The tests include ultraviolet light exposure, moisture and temperature stressing, and temperature cycling to list just a few. It is critical for the perovskite research community to start performing more accelerated stress tests to determine the maturity of the technology.
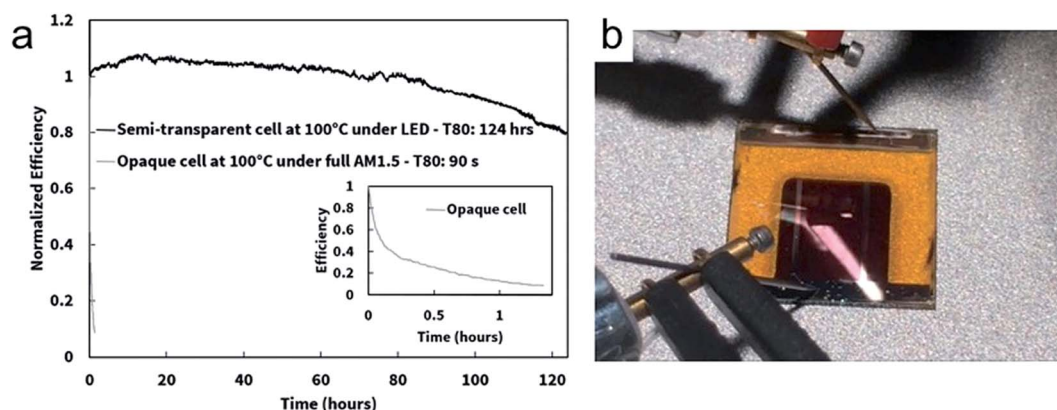

Fig. 8 Stability of $MAPbI_3$ devices where the top metal electrode is replaced by a sputtered ITO layer, enabled by a thin, solution processed AZO nanoparticle buffer layer. The normalized performance for an otherwise unencapsulated solar cell operated at its maximum power point at 100 °C in air and under 1 sun equivalent irradiation from a sulfur plasma lamp is plotted in (a), while (b) is a photograph of the sample during the test. The yellow area is perovskite that has degraded to PbI_2, while the brown area is protected by the sputtered ITO layer and maintains its perovskite structure and associated solar cell performance. T_{80} denotes the time taken for the device performance to be reduced to 80% of its initial value. Reprinted from ref. 14 with permission from Wiley.

With this in mind, we have recently succeeded in making efficient and very stable, fully packaged devices by considering both the effect of the perovskite composition on stability and the importance of appropriate electrodes and encapsulation.[5] From Sections 2–4, we can conclude that MA should be avoided in the interest of stability: though it is structurally stable, it can sublime from the perovskite structure at elevated temperatures and makes the material sensitive to atmospheric stresses. As a result, we turned to $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ compounds, which are structurally and atmospherically stable, and most importantly, are very thermally stable. The latter is important to prevent thermal decomposition over tens of years even in encapsulated modules, but also to enable encapsulation at 140 °C. We chose to use a 1.63 eV $FA_{0.83}Cs_{0.17}Pb(I_{0.83}Br_{0.17})_3$ compound. Rather than the AZO nanoparticles first used, we used an ALD SnO_2/ZTO (tin oxide/zinc doped tin oxide) layer as the sputter buffer layer. This layer is conformal even over rough perovskite surfaces, ensuring complete protection from the ITO sputter process regardless of perovskite morphology. In addition, AZO is basic (as discussed in Section 3)[49] and can degrade the perovskite;[49] SnO_2 is more stable.[4] The cell architecture is shown in Fig. 9a. When deposited on top of a heterojunction (HIT) silicon solar cell to make a monolithic tandem solar cell,

this architecture can deliver an NREL certified and record setting 23.6% PCE (Fig. 9b). Crucially, the otherwise unencapsulated single junction solar cells exhibited excellent light stability, and only started to drop below its initial performance after 1000 hours of maximum power point tracking under full illumination in air (Fig. 9c).

The ITO covered device with enhanced thermal stability can then be packaged between two glass sheets using EVA as the polymer binder, and butyl rubber as edge sealant. Once encapsulated in this way, our perovskite solar cells exhibited unprecedented stability. One of the most difficult IEC tests to pass is the damp heat test, which entails 1000 h at 85 °C and 85% RH. Our encapsulated solar cells did not degrade in performance but even improved when placed in a damp heat chamber at 85 °C and 85% RH for 1000 h (Fig. 9d). The implications are very encouraging for perovskite solar cells; careful selection of the perovskite composition allows conventional encapsulation to adequately protect the perovskite material from atmospheric and thermal degradation. It is possible that even less atmospherically stable compounds would have been stable to moisture and oxygen when packaged in this way, but there is no doubt that the thermal stability of $FA_{1-y}Cs_y$-$Pb(I_{1-x}Br_x)_3$ was key both for enabling the encapsulation and

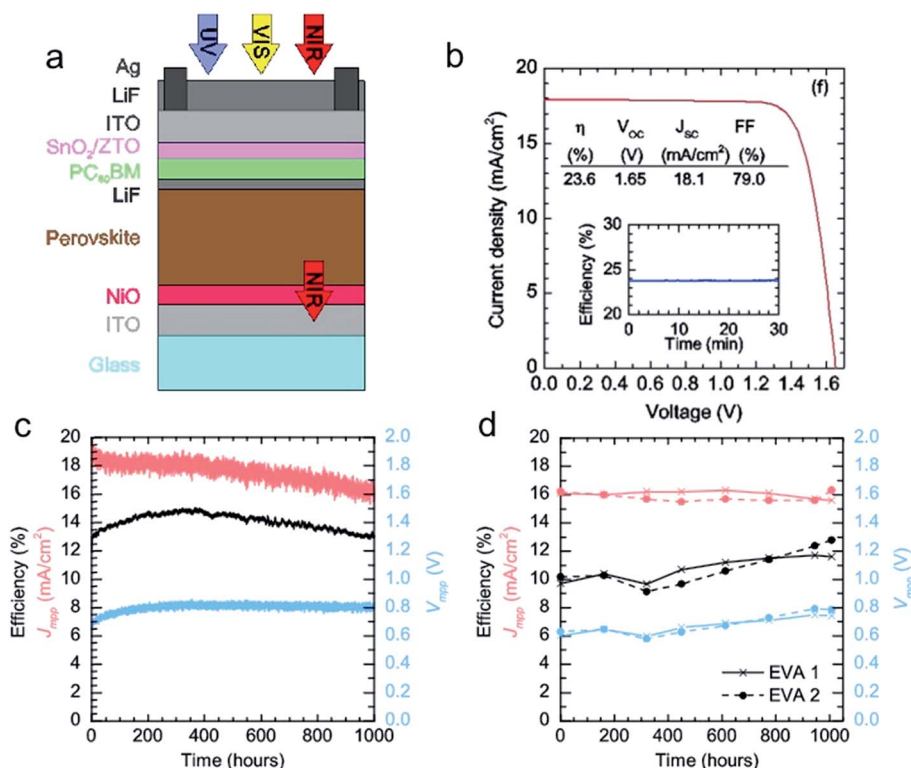

Fig. 9 Stability results for perovskite solar cells using $FA_{0.83}Cs_{0.17}Pb(I_{0.83}Br_{0.17})_3$, conformal SnO_2/ZTO sputter buffer layers, and sputtered ITO electrodes. The device structure is shown in (a), while the current–voltage (J–V) curve of a monolithic perovskite/Si tandem made using the device stack in (a) as the top cell on top of a heterojunction c-Si cell is plotted in (b). Performance over time is plotted in (c) for a non-encapsulated single junction cell in the configuration depicted (a). The device was held at its maximum power point in ambient conditions, under 1 sun equivalent irradiation from a sulfur plasma lamp. Single junction solar cells as in (a) were laminated between two glass sheets using EVA as a binder, while edges of the resulting package were sealed with butyl rubber to prevent lateral moisture ingress. These were exposed to an 85 °C/85% RH test as specified by the IEC protocol 61215 for "Crystalline Silicon Terrestrial Photovoltaic (PV) Modules", and the device performance results are plotted in (d) over time. Reprinted from ref. 5 with permission from Nature Publishing group.

for allowing the solar cells to survive long exposures to elevated temperatures.

Further tests must be performed to determine whether such packaged solar cells can pass the remaining IEC tests such as UV light exposure, temperature cycling, light soaking, electrical stressing, and mechanical load. Still, passing the damp heat test is a major milestone for perovskite solar cells, which have often been criticized as being too thermally and atmospherically unstable to be commercially viable. The great performance during our 85 °C/85% RH test demonstrate that these problems, at least, can be resolved by appropriate selection of both the perovskite composition and encapsulation strategy.

6.   Future outlook and conclusion

In this review, we have discussed several of the key concerns for perovskite stability and highlighted rational paths to overcoming them through careful selection of the perovskite composition and thorough encapsulation. Considering the promising developments showcased here, perovskite PV may soon exhibit the stability required for commercial applications. Still, there are a few outstanding concerns. The first is the ionic mobility in perovskite solar cells. Ions can move readily throughout the materials, and while hysteresis-free solar cell can now be made, the implications to long-term stability are unclear.[50,64,87–89] Indeed, two research groups have recently demonstrated that their solar cells suffer from a small and reversible loss in performance over the course of several hours that they assign to ion migration. Since the effect is reversible, the hope is that is will not lead to long-term degradation.[43,50] On the other hand, other research groups (including ourselves) have now demonstrated 100s of hours stable operation at the maximum power point with no drop in performance whatsoever. It is unclear where the difference stems from; it could be to do with the choice in selective contacts or the absorber layer itself.[5,8,3] In addition, it is possible that the ion motion that occurred from operation during the day could be reversed at night so long as it did not induce any irreversible reactions or changes to the solar cell. Nevertheless, even silicon solar cells have suffered from a potential induced degradation that results from an offset between the potential of the solar cells at the end of a string of modules and the ground.[90] This can be remedied by effective encapsulation, as well as module and inverter schemes, but it remains uncertain whether the high ionic mobility of perovskites will introduce new or more severe potential induced degradation.

In addition, the ionic motion in metal halide perovskite solar cells can result in light-induced phase segregation, preventing mixed halide perovskites from operating stably under prolonged light exposure.[45] Since perovskites offer an extremely exciting pathway to making tandems with CIGS, Si, and low gap perovskite rear cells, making photo-stable mixed halide perovskites is of paramount importance. Some groups have presented strategies to improve the resistance of the materials to light induced phase segregation by tuning both the composition[32,40,41] and morphology[91] of the films. Nevertheless, it is difficult to simulate the effects of 25 years of light exposure, and

the type of tests typically performed are only over the course of minutes to hours. As a result, this must remain a subject of intensive study and development to ensure the development of fully stable wide bandgap perovskite solar cells for tandem applications.

Two exciting new routes have been recently proposed: cesium lead halide quantum dots and 2D Ruddlesden Popper perovskites. These both possess higher bandgaps than their 3D counterparts, and can obtain bandgaps suitable for tandem applications without incorporating significant amounts of bromide. In addition, preliminary tests suggest that the 2D materials are some of the most stable perovskite absorbers yet developed, while the quantum dots exhibited surprisingly long lifetimes for Cs-based perovskites. Both approaches deliver somewhat lower performances than their 3D counterparts at the moment, but certainly provide exciting pathways to improved moisture stability and decreased risk for light induced halide segregation.

Very few research groups have performed mechanical stress tests on perovskite solar cells, but Rolston et al.[92] have found that the adhesion between various layers in the devices stacks and even between perovskite grains to be surprisingly weak. The same group also demonstrated that the fullerenes layers often used as electron selective contacts in perovskite solar cells suffer from extremely poor adhesive qualities and this layer is often the weakest link in a perovskite solar cell.[93] Such poor mechanical properties in the selective layers could be overcome by crosslinking the active materials, but the fact remains that the perovskite itself displays low fracture energies due to week adhesion. While we observed no delamination during our thermal stressing of the encapsulated devices, it is possible that the weak adhesion in perovskite solar cells could pose problems for eventual flexible solar cell applications. Further work is required to evaluate the severity of the problem as well as its eventual solutions. Still, we are tentatively confident that at least in rigid, glass/glass encapsulated devices the stresses on the active layer will be minute and the modules mechanically robust.

On a more speculative note, we can also consider a property that has often been lauded as making perovskite materials special: their defect tolerance.[94–97] This concept has usually been discussed in terms of its effect on device efficiency, but we consider that it might also be extremely important when considering perovskite solar cell stability. The extensive work done by the community demonstrates that perovskite absorbers can degrade when exposed to sufficient stresses, and likely more easily than most other semiconductors used in PV. However, the main degradation product is always just a lead halide, usually PbI_2.[15,54,62,65] PbI_2 is a wide gap semiconductor and thus its presence will not introduce any nonradiative recombination losses. A great deal of recent work has even suggested its presence to be beneficial, as it can passivate the surface of perovskite grains.[8,98] The main degradation product of lead halide perovskite absorbers is thus inert or even benign, a rare quality in a PV material. Of course, as PbI_2 is formed during degradation, the remaining perovskite material is expected to contain some other defects. Most of these, as

discussed by Yan et al.,[94] will have energy levels that fall outside of the bandgap and thus not introduce new recombination pathways. Indeed, MAI deficient materials have been often shown to make efficient solar cells.[7,99] It is then possible that the class of lead halide perovskites benefits from defect tolerance even during degradation; this would make it unique among all PV technologies and promises great long-term performance for perovskite modules.

Conclusion

This work has discussed strategies to overcome the issues of structural, thermal, and atmospheric degradation *via* a combined approach of compositional engineering and thorough encapsulation. Removing methylammonium from the perovskite composition seems to be critical to slow most degradation pathways, as its volatility and acidity make it prone to various degradation pathways. The larger, less volatile, and less acidic formamidinium cation is too large to make structurally stable perovskites on its own, but can be combined with small amounts of cesium to make robust materials with excellent photovoltaic properties. Once the metal electrode is replaced by a stable non metallic electrode such as ITO, the $FA_{1-y}Cs_yPb(I_{1-x}Br_x)_3$ solar cells can be extremely stable. Without further care being given to moisture resistant selective layers, it is possible to package this material with conventional encapsulation and even pass IEC damp heat tests. This speaks strongly to the ability of perovskite solar cells' ability to be atmospherically stable and makes us optimistic that perovskite solar cells can reach the level of stability required for commercial applications.

References

1 W. S. Yang, J. H. Noh, N. J. Jeon, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, High-Performance Photovoltaic Perovskite Layers Fabricated through Intramolecular Exchange, *Science*, 2015, **348**(6240), 1234–1237.

2 NREL, *Best Research-Cell Efficiencies*, 2017.

3 M. Saliba, T. Matsui, K. Domanski, J.-Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J.-P. Correa-Baena, W. R. Tress, A. Abate and A. Hagfeldt, Incorporation of Rubidium Cations into Perovskite Solar Cells Improves Photovoltaic Performance, *Science*, 2016, **354**(6309), 206–209.

4 E. H. Anaraki, A. Kermanpur, L. Steier, K. Domanski, T. Matsui, W. Tress, M. Saliba, A. Abate, M. Gratzel, A. Hagfeldt and J.-P. Correa-Baena, Highly Efficient and Stable Planar Perovskite Solar Cells by Solution-Processed Tin Oxide, *Energy Environ. Sci.*, 2016, **9**(10), 3128–3134.

5 K. A. Bush, A. Palmstrong, S. Bent, Z. Holman and M. McGehee, 23.6%-Efficient Monolithic Perovskite/Silicon Tandem Solar Cells with Improved Stability, *Nat. Energy*, 2017, **2**, 17009.

6 N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, Compositional Engineering of Perovskite Materials for High-Performance Solar Cells, *Nature*, 2015, **517**(7535), 476–480.

7 D. Bi, W. Tress, M. I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J.-P. Correa Baena, J.-D. Decoppet, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel and A. Hagfeldt, Efficient Luminescent Solar Cells Based on Tailored Mixed-Cation Perovskites, *Sci. Adv.*, 2016, **2**(1), e1501170.

8 M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate and A. Hagfeldt, Cesium-Containing Triple Cation Perovskite Solar Cells: Improved Stability, Reproducibility and High Efficiency, *Energy Environ. Sci.*, 2016, **9**(6), 1989–1997.

9 A. Mei, X. Li, L. Liu, Z. Ku, T. Liu, Y. Rong, M. Xu, M. Hu, J. Chen, Y. Yang, M. Grätzel and H. Han, A Hole-Conductor-free, Fully Printable Mesoscopic Perovskite Solar Cell with High Stability, *Science*, 2014, **345**, 295–298.

10 S. N. Habisreutinger, T. Leijtens, G. E. Eperon, S. D. Stranks, R. J. Nicholas and H. J. Snaith, Carbon Nanotube/polymer Composite as a Highly Stable Charge Collection Layer in Perovskite Solar Cells, *Nano Lett.*, 2014, **14**(10), 5561–5568.

11 T. Leijtens, G. E. Eperon, S. Pathak, A. Abate, M. M. Lee and H. J. Snaith, Overcoming Ultraviolet Light Instability of Sensitized TiO_2 with Meso-Superstructured Organometal Tri-Halide Perovskite Solar Cells, *Nat. Commun.*, 2013, **4**, 2885.

12 S. A. Bretschneider, J. Weickert, J. A. Dorman and L. Schmidt-Mende, Research Update: Physical and Electrical Characteristics of Lead Halide Perovskites for Solar Cell Applications, *APL Mater.*, 2014, 40701.

13 J. Liu, W. Yongzhen, C. Qin, X. Yang, T. Yasuda, A. Islam, K. Zhang, W. Peng, L. Han, W. Chen and Y. Wu, A Dopant-Free Hole-Transporting Material for Efficient and Stable Perovskite Solar Cells, *Energy Environ. Sci.*, 2014, **7**, 2963–2967.

14 K. A. Bush, C. D. Bailie, Y. Chen, A. R. Bowring, W. Wang, W. Ma, T. Leijtens, F. Moghadam and M. D. McGehee, Thermal and Environmental Stability of Semi-Transparent Perovskite Solar Cells for Tandems Enabled by a Solution-Processed Nanoparticle Buffer Layer and Sputtered ITO Electrode, *Adv. Mater.*, 2016, **28**(20), 3937–3943.

15 T. Leijtens, G. E. Eperon, N. K. Noel, S. N. Habisreutinger, A. Petrozza and H. J. Snaith, Stability of Metal Halide Perovskite Solar Cells, *Adv. Energy Mater.*, 2015, **5**(20), DOI: 10.1002/aenm.201500963.

16 D. B. Mitzi, Synthesis, Structure, and Properties of Organic–Inorganic Perovskites and Related Materials, in *Progress in Inorganic Chemistry*, ed. K. D. Karlin, John Wiley & Sons, Inc., 2007, pp. 1–121.

17 J. L. Knutson, J. D. Martin and D. B. Mitzi, Tuning the Band Gap in Hybrid Tin Iodide Perovskite Semiconductors Using Structural Templating, *Inorg. Chem.*, 2005, **44**(13), 4699–4705.

18 D. B. Mitzi and K. Liang, Synthesis, Resistivity, and Thermal Properties of the Cubic Perovskite $NH_2CHNH_2SnI_3$ and Related Systems, *J. Solid State Chem.*, 1997, **381** (134), 376–381.

19 C. C. Stoumpos, C. D. Malliakas and M. G. Kanatzidis, Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties, *Inorg. Chem.*, 2013, **52**(15), 9019–9038.

20 D. B. Mitzi, Hybrid Organic–Inorganic Electronics, *Funct. Hybrid Mater.*, 2005, 347–386.

21 I. Borriello, G. Cantele and D. Ninno, Ab Initio Investigation of Hybrid Organic–Inorganic Perovskites Based on Tin Halides, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**(23), 235214.

22 A. M. Glazer, The Classification of Tilted Octahedra in Perovskites, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1972, **28**(11), 3384–3392.

23 E. L. Da Silva, J. M. Skelton, S. C. Parker and A. Walsh, Phase Stability and Transformations in the Halide Perovskite $CsSnI_3$, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2015, **91**(14), 144107.

24 R. L. Milot, G. E. Eperon, H. J. Snaith, M. B. Johnston and L. M. Herz, Temperature-Dependent Charge-Carrier Dynamics in $CH_3NH_3PbI_3$ Perovskite Thin Films, *Adv. Funct. Mater.*, 2015, **25**(39), 6218–6227.

25 C. Quarti, E. Mosconi, J. M. Ball, V. D'Innocenzo, C. Tao, S. Pathak, H. J. Snaith, A. Petrozza and F. De Angelis, Structural and Optical Properties of Methylammonium Lead Iodide across the Tetragonal to Cubic Phase Transition: Implications for Perovskite Solar Cells, *Energy Environ. Sci.*, 2016, **9**(1), 155–163.

26 J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. Van Schilfgaarde and A. Walsh, Atomistic Origins of High-Performance in Hybrid Halide Perovskite Solar Cells, *Nano Lett.*, 2014, **14**, 2584–2590.

27 Z. Li, M. Yang, J.-S. Park, S.-H. Wei, J. J. Berry and K. Zhu, Stabilizing Perovskite Structures by Tuning Tolerance Factor: Formation of Formamidinium and Cesium Lead Iodide Solid-State Alloys, *Chem. Mater.*, 2016, **28**(1), 284–292.

28 G. Kieslich, S. Sun and T. Cheetham, An Extended Tolerance Factor Approach for Organic–Inorganic Perovskites, *Chem. Sci.*, 2015, **6**, 3430.

29 W. Travis, E. N. K. Glover, H. Bronstein, D. O. Scanlon and R. G. Palgrave, On the Application of the Tolerance Factor to Inorganic and Hybrid Halide Perovskites: A Revised System, *Chem. Sci.*, 2016, **7**(7), 4548–4556.

30 Q. Wang, Q. Dong, T. Li, A. Gruverman and J. Huang, Thin Insulating Tunneling Contacts for Efficient and Water-Resistant Perovskite Solar Cells, *Adv. Mater.*, 2016, **28**(31), 6734–6739.

31 A. Swarnkar, A. R. Marshall, E. M. Sanehira, B. D. Chernomordik, D. T. Moore, J. A. Christians, T. Chakrabarti and J. M. Luther, Quantum Dot-induced Phase Stabilization of α-$CsPbI_3$ Perovskite for High-Efficiency Photovoltaics, *Science*, 2016, **354**(6308), 92–95.

32 R. E. Beal, D. J. Slotcavage, T. Leijtens, A. R. Bowring, R. A. Belisle, W. H. Nguyen, G. F. Burkhard, E. T. Hoke and M. D. McGehee, Cesium Lead Halide Perovskites with Improved Stability for Tandem Solar Cells, *J. Phys. Chem. Lett.*, 2016, **7**(5), 746–751.

33 A. Dualeh, P. Gao, S. I. Seok, M. K. Nazeeruddin, M. Gratzel and M. Grätzel, Thermal Behavior of Methylammonium Lead-Trihalide Perovskite Photovoltaic Light Harvesters, *Chem. Mater.*, 2014, **26**(21), 6160–6164.

34 B. Conings, J. Drijkoningen, N. Gauquelin, A. Babayigit, J. D'Haen, L. D'Olieslaeger, A. Ethirajan, J. Verbeeck, J. Manca, E. Mosconi, F. D. Angelis and H.-G. Boyen, Intrinsic Thermal Instability of Methylammonium Lead Trihalide Perovskite, *Adv. Energy Mater.*, 2015, **5**(15), 1500477.

35 G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz and H. J. Snaith, Formamidinium Lead Trihalide: A Broadly Tunable Perovskite for Efficient Planar Heterojunction Solar Cells, *Energy Environ. Sci.*, 2014, **7**, 982–988.

36 G. E. Eperon, G. M. Paterno, R. J. Sutton, A. Zampetti, A. A. Haghighirad, F. Cacialli and H. J. Snaith, Inorganic Caesium Lead Iodide Perovskite Solar Cells, *J. Mater. Chem. A*, 2015, **3**(39), 19688–19695.

37 Q. Ma, S. Huang, X. Wen, M. A. Green and A. W. Y. Ho-Baillie, Hole Transport Layer Free Inorganic $CsPbIBr_2$ Perovskite Solar Cell by Dual Source Thermal Evaporation, *Adv. Energy Mater.*, 2016, **6**(7), 1502202.

38 L. A. Frolova, D. V. Anokhin, A. A. Piryazev, S. Y. Luchkin, N. N. Dremova, K. J. Stevenson and P. A. Troshin, Highly Efficient All-Inorganic Planar Heterojunction Perovskite Solar Cells Produced by Thermal Coevaporation of CsI and PbI_2, *J. Phys. Chem. Lett.*, 2017, **8**(1), 67–72.

39 M. Kulbak, D. Cahen and G. Hodes, How Important Is the Organic Part of the Lead Halide Perovskite Photovoltaic Cells? Efficient $CsPbBr_3$ Cells, *J. Phys. Chem. Lett.*, 2015, **6**(13), 2452–2456.

40 R. J. Sutton, G. E. Eperon, L. Miranda, E. S. Parrott, B. A. Kamino, J. B. Patel, M. T. Hörantner, M. B. Johnston, A. A. Haghighirad, D. T. Moore and H. J. Snaith, Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells, *Adv. Energy Mater.*, 2016, **6**(8), 1502458.

41 D. P. McMeekin, G. Sadoughi, W. Rehman, G. E. Eperon, M. Saliba, M. T. Hörantner, A. Haghighirad, N. Sakai, L. Korte and B. Rech, A Mixed-Cation Lead Mixed-Halide Perovskite Absorber for Tandem Solar Cells, *Science*, 2016, **351**(6269), 151–155.

42 T. Duong, H. K. Mulmudi, H. Shen, Y. Wu, C. Barugkin, Y. O. Mayon, H. T. Nguyen, D. Macdonald, J. Peng and M. Lockrey, Structural Engineering Using Rubidium Iodide as a Dopant under Excess Lead Iodide Conditions for High Efficiency and Stable Perovskites, *Nano Energy*, 2016, **30**, 330–340.

43 H. Tan, A. Jain, O. Voznyy, X. Lan, F. P. García de Arquer, J. Z. Fan, R. Quintero-Bermudez, M. Yuan, B. Zhang, Y. Zhao, F. Fan, P. Li, L. N. Quan, Y. Zhao, Z.-H. Lu, Z. Yang, S. Hoogland and E. H. Sargent, Efficient and Stable Solution-Processed Planar Perovskite Solar Cells *via* Contact Passivation, *Science*, 2017, **355**(6326), 722–726.

44 J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal and S. I. Seok, Chemical Management for Colorful, Efficient, and Stable

Inorganic–Organic Hybrid Nanostructured Solar Cells, *Nano Lett.*, 2013, **13**(4), 1764–1769.

45 E. T. Hoke, D. J. Slotcavage, E. R. Dohner, A. R. Bowring, H. I. Karunadasa and M. D. McGehee, Reversible Photo-Induced Trap Formation in Mixed-Halide Hybrid Perovskites for Photovoltaics, *Chem. Sci.*, 2015, **6**(1), 613–617.

46 D. J. Slotcavage, H. I. Karunadasa and M. D. McGehee, Light-Induced Phase Segregation in Halide-Perovskite Absorbers, *ACS Energy Lett.*, 2016, **1**(6), 1199–1205.

47 F. C. Hanusch, E. Wiesenmayer, E. Mankel, A. Binek, P. Angloher, C. Fraunhofer, N. Giesbrecht, J. M. Feckl, W. Jaegermann, D. Johrendt, T. Bein and P. Docampo, Efficient Planar Heterojunction Perovskite Solar Cells Based on Formamidinium Lead Bromide, *J. Phys. Chem. Lett.*, 2014, **5**(16), 2791–2795.

48 I. Deretzis, A. Alberti, G. Pellegrino, E. Smecca, F. Giannazzo, N. Sakai, T. Miyasaka and A. L. Magna, Atomistic Origins of $CH_3NH_3PbI_3$ Degradation to PbI_2 in Vacuum, *Appl. Phys. Lett.*, 2015, 131904.

49 J. Yang, B. D. Siempelkamp, E. Mosconi, F. De Angelis and T. L. Kelly, Origin of the Thermal Instability in $CH_3NH_3PbI_3$ Thin Films Deposited on ZnO, *Chem. Mater.*, 2015, **27**(12), 4229–4236.

50 K. Domanski, B. Roose, T. Matsui, M. Saliba, S.-H. Turren-Cruz, J.-P. Correa-Baena, C. R. Carmona, G. Richardson, J. M. Foster, F. De Angelis, J. M. Ball, A. Petrozza, N. Mine, M. K. Nazeeruddin, W. Tress, M. Gratzel, U. Steiner, A. Hagfeldt and A. Abate, Migration of Cations Induces Reversible Performance Losses over Day/night Cycling in Perovskite Solar Cells, *Energy Environ. Sci.*, 2017, **10**(2), 604–613.

51 J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Grätzel, Sequential Deposition as a Route to High-Performance Perovskite-Sensitized Solar Cells, *Nature*, 2013, **499**, 316–319.

52 J. You, L. Meng, T.-B. Song, T.-F. Guo, Y. M. Yang, W.-H. Chang, Z. Hong, H. Chen, H. Zhou, Q. Chen, Y. Liu, N. De Marco and Y. Yang, Improved Air Stability of Perovskite Solar Cells *via* Solution-Processed Metal Oxide Transport Layers, *Nat. Nanotechnol.*, 2016, **11**(1), 75–81.

53 A. D. Sheikh, A. Bera, M. A. Haque, R. B. Rakhi, S. D. Gobbo, H. N. Alshareef and T. Wu, Atmospheric Effects on the Photovoltaic Performance of Hybrid Perovskite Solar Cells, *Sol. Energy Mater. Sol. Cells*, 2015, **137**, 6–14.

54 N. Aristidou, I. Sanchez-Molina, T. Chotchuangchutchaval, M. Brown, L. Martinez, T. Rath and S. A. Haque, The Role of Oxygen in the Degradation of Methylammonium Lead Trihalide Perovskite Photoactive Layers, *Angew. Chem., Int. Ed.*, 2015, **54**(28), 8208–8212.

55 F. T. F. O'Mahony, Y. H. Lee, C. Jellett, S. Dmitrov, D. T. J. Bryant, J. R. Durrant, B. C. O'Regan, M. Graetzel, M. K. Nazeeruddin and S. A. Haque, Improved Environmental Stability of Organic Lead Trihalide Perovskite-Based Photoactive-Layers in the Presence of Mesoporous TiO₂, *J. Mater. Chem. A*, 2015, **3**(14), 7219–7223.

56 A. J. Pearson, G. E. Eperon, P. E. Hopkinson, S. N. Habisreutinger, J. T. W. Wang, H. J. Snaith and N. C. Greenham, Oxygen Degradation in Mesoporous $Al_2O_3/CH_3NH_3PbI_{3-x}Cl_x$ Perovskite Solar Cells: Kinetics and Mechanisms, *Adv. Energy Mater.*, 2016, **6**(13), 1600014.

57 Z. Wang, D. P. McMeekin, N. Sakai, S. van Reenen, K. Wojciechowski, J. B. Patel, M. B. Johnston and H. J. Snaith, Efficient and Air-Stable Mixed-Cation Lead Mixed-Halide Perovskite Solar Cells with N-Doped Organic Electron Extraction Layers, *Adv. Mater.*, 2017, **29**(5), 1604186.

58 M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites, *Science*, 2012, **338**(6107), 643–647.

59 K. Wojciechowski, T. Leijtens, S. Spirova, C. Schlueter, M. Hoerantner, J. T.-W. Wang, C.-Z. Li, A. K.-Y. Jen, T.-L. Lee and H. J. Snaith, C_{60} as an Efficient and Stable N-Type Compact Layer in Perovskite Solar Cells, *J. Phys. Chem. Lett.*, 2015, **6**(12), 2399–2405.

60 X. Li, M. Tschumi, H. Han, S. S. Babkair, R. A. Alzubaydi, A. A. Ansari, S. S. Habib, M. K. Nazeeruddin, S. M. Zakeeruddin and M. Grätzel, Outdoor Performance and Stability under Elevated Temperatures and Long-Term Light Soaking of Triple-Layer Mesoporous Perovskite Photovoltaics, *Energy Technol.*, 2015, **3**(6), 551–555.

61 F. Matteocci, S. Razza, F. Di Giacomo, S. Casaluci, G. Mincuzzi, T. M. Brown, A. D'Epifanio, S. Licoccia and A. Di Carlo, Solid-State Solar Modules Based on Mesoscopic Organometal Halide Perovskite: A Route towards the up-Scaling Process, *Phys. Chem. Chem. Phys.*, 2014, **16**(9), 3918–3923.

62 A. Leguy, Y. Hu, M. Campoy-Quiles, M. I. Alonso, O. J. Weber, P. Azarhoosh, M. van Schilfgaarde, M. T. Weller, T. Bein, J. Nelson, P. Docampo and P. R. F. Barnes, The Reversible Hydration of $CH_3NH_3PbI_3$ in Films, Single Crystals and Solar Cells, *Chem. Mater.*, 2015, **27**(9), 3397–3407.

63 J. A. Christians, P. A. Miranda Herrera and P. V. Kamat, Transformation of the Excited State and Photovoltaic Efficiency of $CH_3NH_3PbI_3$ Perovskite upon Controlled Exposure to Humidified Air, *J. Am. Chem. Soc.*, 2015, **137**(4), 1530–1538.

64 T. Leijtens, G. Grancini, G. E. Eperon, J. M. Ball, M. d Bastianni, K. Wojciechowski, N. Martino, H. J. Snaith and A. Petrozza, Mapping Electric Field-Induced Switchable Polarization and Structural Degradation in Hybrid Lead Halide Perovskite Thin Films, *Adv. Energy Mater.*, 2015, **5**(20), DOI: 10.1002/aenm.201500962.

65 J. Yang, B. D. Siempelkamp, D. Liu and T. L. Kelly, Investigation of $CH_3NH_3PbI_3$ Degradation Rates and Mechanisms in Controlled Humidity Environments Using *in situ* Techniques, *ACS Nano*, 2015, **9**(2), 1955–1963.

66 S. N. Habisreutinger, D. P. McMeekin, H. J. Snaith and R. J. Nicholas, Research Update: Strategies for Improving the Stability of Perovskite Solar Cells, *APL Mater.*, 2016, **4**(9), 91503.

11498 | *J. Mater. Chem. A*, 2017, **5**, 11483–11500

This journal is © The Royal Society of Chemistry 2017

67 G. Niu, X. Guo and L. Wang, Review of Recent Progress in Chemical Stability of Perovskite Solar Cells, *J. Mater. Chem. A*, 2015, **3**(17), 8970–8980.

68 T. A. Berhe, W.-N. Su, C.-H. Chen, C.-J. Pan, J.-H. Cheng, H.-M. Chen, M.-C. Tsai, L.-Y. Chen, A. A. Dubale and B.-J. Hwang, Organometal Halide Perovskite Solar Cells: Degradation and Stability, *Energy Environ. Sci.*, 2016, **9**(2), 323–356.

69 B. R. Vincent, K. N. Robertson, T. S. Cameron and O. Knop, Alkylammonium Lead Halides. Part 1. Isolated PbI_6^{4-} Ions in $(CH_3NH_3)_4PbI_6 \cdot 2H_2O$, *Can. J. Chem.*, 1987, **65**(5), 1042–1046.

70 O. Knop and R. E. Wasylishen, Alkylammonium Lead Halides. Part 2. $CH_3NH_3PbX_3$ (X = Cl, Br, I) Perovskites: Cuboctahedral Halide Cages with Isotropic Cation Reorientation, *Can. J. Chem.*, 1990, **68**, 412–422.

71 Q. Jiang, D. Rebollar, J. Gong, E. L. Piacentino, C. Zheng and T. Xu, Pseudohalide-Induced Moisture Tolerance in Perovskite $CH_3NH_3Pb(SCN)_2I$ Thin Films, *Angew. Chem.*, 2015, **127**(26), 7727–7730.

72 Q. Tai, P. You, H. Sang, Z. Liu, C. Hu, H. L. W. Chan and F. Yan, Efficient and Stable Perovskite Solar Cells Prepared in Ambient Air Irrespective of the Humidity, *Nat. Commun.*, 2016, **7**, 11105.

73 J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal and S. I. Seok, Chemical Management for Colorful, Efficient, and Stable Inorganic–Organic Hybrid Nanostructured Solar Cells, *Nano Lett.*, 2013, **2**, 28–31.

74 J.-W. Lee, D.-H. Kim, H.-S. Kim, S.-W. Seo, S. M. Cho and N.-G. Park, Formamidinium and Cesium Hybridization for Photo- and Moisture-Stable Perovskite Solar Cell., *Adv. Energy Mater.*, 2015, **5**(20), 1501310.

75 I. C. Smith, E. T. Hoke, D. Solis-Ibarra, M. D. McGehee and H. I. Karunadasa, A Layered Hybrid Perovskite Solar-Cell Absorber with Enhanced Moisture Stability, *Angew. Chem., Int. Ed.*, 2014, **53**(42), 11232–11235.

76 H. Tsai, W. Nie, J. Blancon, C. C. Stoumpos, R. Asadpour, B. Harutyunyan, A. Neukirch, R. Verduzco, J. J. Crochet, S. Tretiak, L. Pedesseau, J. Even, M. A. Alam, G. Gupta, J. Lou, P. M. Ajayan, M. J. Bedzyk, M. G. Kanatzidis and A. D. Mohite, High-Efficiency Two-Dimensional Ruddlesden–Popper Perovskite Solar Cells, *Nature*, 2016, **536**(7616), 312–316.

77 T. Leijtens, T. Giovenzana, S. N. Habisreutinger, J. S. Tinkham, N. K. Noel, B. A. Kamino, G. Sadoughi, A. Sellinger and H. J. Snaith, Hydrophobic Organic Hole Transporters for Improved Moisture Resistance in Metal Halide Perovskite Solar Cells, *ACS Appl. Mater. Interfaces*, 2016, **8**(9), 5981–5989.

78 S. N. Habisreutinger, T. Leijtens, G. E. Eperon, S. D. Stranks, R. J. Nicholas and H. J. Snaith, Enhanced Hole Extraction in Perovskite Solar Cells Through Carbon Nanotubes, *J. Phys. Chem. Lett.*, 2014, **5**(23), 4207–4212.

79 F. Bella, G. Griffini, J.-P. Correa-Baena, G. Saracco, M. Grätzel, A. Hagfeldt, S. Turri and C. Gerbaldi, Improving Efficiency and Stability of Perovskite Solar Cells with Photocurable Fluoropolymers, *Science*, 2016, aah4046.

80 M. Jørgensen, K. Norrman and F. C. Krebs, Stability/degradation of Polymer Solar Cells, *Sol. Energy Mater. Sol. Cells*, 2008, 686–714.

81 M. Jørgensen, K. Norrman, S. a. Gevorgyan, T. Tromholt, B. Andreasen and F. C. Krebs, Stability of Polymer Solar Cells, *Adv. Mater.*, 2012, **24**(5), 580–612.

82 C. H. Peters, I. T. Sachs-Quintana, W. R. Mateker, T. Heumueller, J. Rivnay, R. Noriega, Z. M. Beiley, E. T. Hoke, A. Salleo and M. D. McGehee, The Mechanism of Burn-in Loss in a High Efficiency Polymer Solar Cell., *Adv. Mater.*, 2012, **24**, 663–668.

83 K. Domanski, J.-P. Correa-Baena, N. Mine, M. K. Nazeeruddin, A. Abate, M. Saliba, W. Tress, A. Hagfeldt and M. Grätzel, Not All That Glitters Is Gold: Metal-Migration-Induced Degradation in Perovskite Solar Cells, *ACS Nano*, 2016, **10**(6), 6306–6314.

84 Y. Deng, Q. Dong, C. Bi, Y. Yuan and J. Huang, Air-Stable, Efficient Mixed-Cation Perovskite Solar Cells with Cu Electrode by Scalable Fabrication of Active Layer, *Adv. Energy Mater.*, 2016, **6**(11), 1600372.

85 Y. Kato, L. K. Ono, M. V. Lee, S. Wang, S. R. Raga and Y. Qi, Silver Iodide Formation in Methyl Ammonium Lead Iodide Perovskite Solar Cells with Silver Top Electrodes, *Adv. Mater. Interfaces*, 2015, **2**(13), 1500195.

86 J. Werner, C.-H. Weng, A. Walter, L. Fesquet, J. P. Seif, S. De Wolf, B. Niesen and C. Ballif, Efficient Monolithic Perovskite/Silicon Tandem Solar Cell with Cell Area >1 cm^2, *J. Phys. Chem. Lett.*, 2016, **7**(1), 161–166.

87 Y. Yuan, J. Chae, Y. Shao, Q. Wang, Z. Xiao, A. Centrone and J. Huang, Photovoltaic Switching Mechanism in Lateral Structure Hybrid Perovskite Solar Cells, *Adv. Energy Mater.*, 2015, **5**(15), 1500615.

88 H. J. Snaith, A. Abate, J. M. Ball, G. E. Eperon, T. Leijtens, N. K. Noel, S. D. Stranks, J. T.-W. Wang, K. Wojciechowski and W. Zhang, Anomalous Hysteresis in Perovskite Solar Cells, *J. Phys. Chem. Lett.*, 2014, 1511–1515.

89 J. M. Azpiroz, E. Mosconi, J. Bisquert and F. De Angelis, Defect Migration in Methylammonium Lead Iodide and Its Role in Perovskite Solar Cell Operation, *Energy Environ. Sci.*, 2015, **8**, 2118–2127.

90 W. Luo, Y. S. Khoo, P. Hacke, V. Naumann, D. Lausch, S. P. Harvey, J. P. Singh, J. Chai, Y. Wang, A. G. Aberle and S. Ramakrishna, Potential-Induced Degradation in Photovoltaic Modules: A Critical Review, *Energy Environ. Sci.*, 2017, **10**, 43–68.

91 M. Hu, C. Bi, Y. Yuan, Y. Bai and J. Huang, Stabilized Wide Bandgap $MAPbBr_xI_{3-x}$ Perovskite by Enhanced Grain Size and Improved Crystallinity, *Adv. Sci.*, 2016, **3**(6), 1500301.

92 N. Rolston, B. L. Watson, C. D. Bailie, M. D. McGehee, J. P. Bastos, R. Gehlhaar, J.-E. Kim, D. Vak, A. T. Mallajosyula, G. Gupta, A. D. Mohite and R. H. Dauskardt, Mechanical Integrity of Solution-Processed Perovskite Solar Cells, *Extreme Mechanics Letters*, 2016, **9**(3), 353–358.

This journal is © The Royal Society of Chemistry 2017

J. Mater. Chem. A, 2017, **5**, 11483–11500 | **11499**

93 B. L. Watson, N. Rolston, K. A. Bush, T. Leijtens, M. D. McGehee and R. H. Dauskardt, Cross-Linkable, Solvent-Resistant Fullerene Contacts for Robust and Efficient Perovskite Solar Cells with Increased JSC and VOC, *ACS Appl. Mater. Interfaces*, 2016, **8**(39), 25896–25904.

94 W.-J. Yin, T. Shi and Y. Yan, Unusual Defect Physics in $CH_3NH_3PbI_3$ Perovskite Solar Cell Absorber, *Appl. Phys. Lett.*, 2014, **104**(6), 063903.

95 W.-J. Yin, T. Shi and Y. Yan, Superior Photovoltaic Properties of Lead Halide Perovskites: Insights from First-Principles Theory, *J. Phys. Chem. C*, 2015, **119**(10), 5253–5264.

96 J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. van Schilfgaarde, A. Walsh, *et al.*, Atomistic Origins of High-Performance in Hybrid Halide Perovskite Solar Cells, *Nano Lett.*, 2014, **14**(5), 2584–2590.

97 A. Buin, P. Pietsch, O. Voznyy, R. Comin, A. H. Ip, E. H. Sargent and B. Xu, Materials Processing Routes to Trap-Free Halide Perovskites, *Nano Lett.*, 2014, **14**(11), 6281–6286.

98 Q. Chen, H. Zhou, T.-B. Song, S. Luo, Z. Hong, H.-S. S. Duan, L. Dou, Y. Liu and Y. Yang, Controllable Self-Induced Passivation of Hybrid Lead Iodide Perovskites toward High Performance Solar Cells, *Nano Lett.*, 2014, **14**(7), 4158–4163.

99 T. J. Jacobsson, J.-P. Correa-Baena, E. Halvani Anaraki, B. Philippe, S. D. Stranks, M. E. F. Bouduban, W. Tress, K. Schenk, J. Teuscher, J.-E. Moser, H. Rensmo and A. Hagfeldt, Unreacted PbI_2 as a Double-Edged Sword for Enhancing the Performance of Perovskite Solar Cells, *J. Am. Chem. Soc.*, 2016, **138**(32), 10331–10343.