$\text{Cs}_{0.15}\text{FA}_{0.85}\text{PbI}_3$ perovskite solar cells for concentrator photovoltaic applications

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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Recently developed, highly stable perovskite materials show promise for use in concentrator photovoltaics where the illumination intensity far exceeds standard test conditions. Here, we demonstrate solar cell devices employing different perovskite absorber layers featuring balanced charge generation and extraction characteristics at high light intensities greater than 10 suns. Using a mixed cesium-formamidinium perovskite, we are able to achieve over 18% PCE at 1 sun and 16% PCE at 13 suns with negligible performance loss after several hours of high intensity light soaking.

Perovskite solar cells (PSCs) based on organic and inorganic components have exhibited an extraordinary rise in power conversion efficiency (PCE) in the past few years. With current PCEs in excess of 22%¹ and device stability regularly exceeding 1,000 hours with little degradation,^{2–4} perovskite solar cells seem a promising next-generation solar technology. Despite this promise, many challenges remain before commercialisation can become a reality: Issues such as current-voltage scan hysteresis call into question the validity of reported efficiencies⁵ and stability must be further improved.^{6–8} One significant route to improving both performance and stability, in particular, is cation substitution within the perovskite crystal structure. The perovskite methylammonium lead triiodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$ or MAPbI_3) has historically been a popular choice of absorber material owing to its ease of processing and phase stability at room temperature. However, there remain issues with this material such as a phase transition at potential operational temperatures,⁹ as well as a sensitivity to moisture.¹⁰ An alternative to MAPbI_3 perovskite is formamidinium lead triiodide^{11–13} ($\text{HC}(\text{NH}_2)_2\text{PbI}_3$ or FAPbI_3) which possesses a wider band gap and superior phase stability at elevated temperatures compared to MAPbI_3 .^{11,14,15} A crucial disadvantage of FAPbI_3 is

its phase instability at room temperature, allowing it to crystallise into either a preferable photoactive α -phase, or an undesirable photoinactive γ -phase.^{9,11} This instability has been resolved, in part, by incorporating cesium into the perovskite structure. With an ionic radius smaller than that of the MA and FA cations, the inclusion of Cs in the perovskite lattice stabilises the desirable α -phase by reducing the perovskite's Goldschmidt tolerance factor, permitting a stable α -phase to exist at temperatures in excess of 230°C.^{13,16} FA-containing perovskites are now commonly reported with Cs components ranging between 5–20% molarity with respect to the other cation used.^{13,16–19}

Beyond the optimisation of light-absorbing and charge-extracting layers within the PSC, there exists other ways of increasing device performance beyond the Shockley–Queisser limit of 30% PCE for a 1.6 eV single junction.²⁰ One option to bypass this limit is to increase irradiation intensity beyond the ASTM AM1.5G standard 100 mW cm^{−2} using an array of mirrors or lenses to focus sunlight onto a photovoltaic device. Such devices are known as concentrator photovoltaics (CPV). For materials with high charge carrier concentrations and low defect densities, PCEs can be retained at elevated light levels thanks to an increase in open circuit-voltage (V_{oc}) and a preservation of fill factor. PSCs have demonstrated exceptional performance under irradiance levels at and below the ASTM standard 100 mW cm^{−2} owing to the low trap density and high carrier diffusion lengths in many widely-used perovskites, which further increase under reduced illumination.^{1,13,21–24} However, investigation of the perovskite absorber material's performance under higher light intensities has received little attention until recently.^{25–27} As light intensity is increased, the rate of charge carrier generation within a solar cell too increases: for these carriers to be efficiently extracted under high light intensities, the absorber material and charge extraction layers must be capable of conveying photocurrents many times greater than those experienced under typical '1 sun' operating conditions. A recent article by Lin and coworkers²⁷ predicts carrier concentration within perovskite absorber films to be high

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

enough so as not to be a performance barrier in CPV applications beyond 100 suns of illumination. The relative balance of charge generation, recombination and extraction rates were found to be key parameters in determining performance at high solar concentration. Although it is noted that material stability is likely to be a key challenge for such an application of perovskite materials.

In this initial study, we investigate the suitability of MAPbI₃ and Cs_{0.15}FA_{0.85}PbI₃ perovskite light absorbers for use in concentrator photovoltaics. In this case, simple 'iodine-only' perovskite compositions are used instead of commonly reported iodine-bromine mixes to exclude the influence of halide segregation under illumination.²⁸ While such segregation is inhibited in Cs-stabilised FA blends, the same cannot be said for MA-only compositions which would otherwise be used as control devices.²⁹ We measure current-voltage curves, charge extraction behaviour, transient photovoltage (TPV) and photocurrent (TPC) measurements, as well as device stability over light intensities ranging between 2 mW cm⁻² (0.02 suns) and 1,300 mW cm⁻² (13 suns). We find that the preservation of fill factor at high light intensities permits the performance of Cs_{0.15}FA_{0.85}PbI₃ devices to be maintained over a wide range of illumination levels: 18% at 1 sun and 16% at 13 suns. This is compared to 17% at 1 sun and below 10% at 13 suns for the more commonly used MAPbI₃ perovskite. In addition, while stability trends between the two perovskites appear similar under 1 sun illumination, at higher light intensities MAPbI₃ based devices begin to rapidly degrade as a result of perovskite film photo-bleaching. By comparison, the Cs_{0.15}FA_{0.85}PbI₃ suffers no appreciable degradation in efficiency, making the material a potential choice for use in CPV applications.

Figure 1a plots the current-voltage characteristics of two planar n-i-p structured perovskite solar cells with different absorber layers measured under AM1.5G conditions. The general structure of the device is comprised as follows: Glass/ITO/SnO₂/PC₆₀BM/Perovskite/Spiro-OMeTAD/Au where the perovskite employed is either MAPbI₃ or Cs_{0.15}FA_{0.85}PbI₃. The latter perovskite was selected because of its reportedly high thermal stability¹⁶ – a quality that is likely to be required in CPV applications. A full account of the experimental procedures for

Figure 1 a) Reverse current-voltage sweeps of perovskite solar cells with different absorber layers. Subplot portrays the stabilized efficiency of the devices at VMPP (asterisks) as a function of time. b) External quantum efficiency spectra and integrated current density for perovskite solar cells.

Figure 2 a) PCE, b) J_{sc} , c) V_{oc} , d) fill factor as a function of light intensity for different perovskite absorber layers.

device fabrication may be found in the ESI. We note differences in V_{oc} between the two perovskite materials owing to a reduced band gap in the case of the Cs_{0.15}FA_{0.85}PbI₃ perovskite. This is further illustrated in Figure 1b, showing differences in the position of the absorption edge: We calculate the band gap of the MAPbI₃ and Cs_{0.15}FA_{0.85}PbI₃ perovskite to be 1.61 eV and 1.57 eV respectively. This narrowing of the band gap is also responsible for the Cs_{0.15}FA_{0.85}PbI₃ perovskite's higher short-circuit current density (J_{sc}) compared to MAPbI₃ devices. The degree of hysteresis present in these devices is low, with stabilised (Figure 1a subfigure) and J - V derived PCE values in close agreement. A plot of representative forward and reverse J - V scans is shown in Figure S1, indicating less than 3% variation in PCE between scan directions, along with a table of device parameters (Table S1) and statistical spread (Figure S2). Overall PCEs from the J - V sweeps are 17.8% and 18.0% respectively for MAPbI₃ and Cs_{0.15}FA_{0.85}PbI₃ perovskites, indicating very similar performance at 1 sun illumination. In order to study the impact of different light levels on the photovoltaic characteristics of different perovskite absorber materials, we consider the evolution of J_{sc} , fill factor and V_{oc} as a function of light intensity. Figure 2 illustrates key photovoltaic parameters for both MAPbI₃ and Cs_{0.15}FA_{0.85}PbI₃ perovskites at laser-induced light levels ranging between 2 mW cm⁻² (0.02 suns) and 1,300 mW cm⁻² (13 suns). Figure 2a shows a trend towards higher PCEs over a wider range of illumination intensities in the case of the Cs_{0.15}FA_{0.85}PbI₃ perovskite when compared to MAPbI₃. Crucially, PCEs around 18% are maintained in the Cs_{0.15}FA_{0.85}PbI₃ device between 0.5 and 3 suns illumination, whereas the MA-containing device shows a far more severe efficiency dependency on light intensity. We observe, in Figure 2b, a linear relationship between J_{sc} and illumination intensity (slope=1.00), implying weak or entirely absent bimolecular recombination in both perovskite devices at short-circuit conditions. The trend of V_{oc} as a function of light intensity (Figure 2c) provides a direct insight into the role of trap-assisted recombination within the

Figure 3 Photo-generated current density, J_{ph} vs effective voltage ($V_0 - V$), V_{eff} at 100 mW cm⁻² (a) and at 1,300 mW cm⁻² (b) obtained from J - V curves in reverse bias. (c) shows charge carrier lifetime, τ and V_{oc} as a function of charge density, n for MAPbI₃ and Cs_{0.15}FA_{0.85}PbI₃ perovskite solar cells, obtained using transient photovoltage (TPV) and transient photocurrent (TPC) measurements at open-circuit.

different perovskite films.^{30,31} Entirely trap-assisted recombination may be identified by a slope of $2kT/q$, while a slope in the order of $1kT/q$ is indicative of purely bimolecular recombination under open-circuit conditions.^{32,33} We calculate the slope for the Cs_{0.15}FA_{0.85}PbI₃ device to be $1.2 kT/q$, compared to $1.6 kT/q$ in the case of the MAPbI₃ device, indicating the presence of fewer trap states within the FA-containing perovskite and a general reduction in trap-assisted recombination compared to the more conventional MA-containing device. While differences in V_{oc} with light intensity between the two perovskite systems certainly contribute to variation in overall device performance, the most significant factor affecting PCE is fill factor. As depicted in Figure 2d, the

MAPbI₃ device shows a fill factor decrease from 0.74 at 10 mW cm⁻² (0.1 suns) to 0.41 at 1,000 mW cm⁻² (10 suns), whereas the Cs_{0.15}FA_{0.85}PbI₃ device delivers fill factor values between 0.75 and 0.60 over the same range. These behaviours are linked to the different capability of various perovskite materials to support balanced charge generation and extraction over a range of light intensities. It is also worth noting that the decrease in fill factor with light intensity may be a consequence of charge extraction limitations within the charge selective layers: SnO₂, PCBM and spiro-OMeTAD. The investigation of these layers in the context of CPV, while critical to the success of perovskite CPV, are beyond the scope of this preliminary study.

To elucidate the fill factor reduction in MAPbI₃ devices at high light intensity, we measure the photocurrent density (J_{ph}) as a function of effective voltage (V_{eff}), as shown in Figure 3a,b. J_{ph} is defined as $J_{ph} = J_l - J_d$ where J_l and J_d are the current densities in light and dark conditions respectively. V_{eff} is given by $V_{eff} = V_0 - V$ where V_0 is the compensation voltage defined as $J_{ph}(V_0) = 0$, and V is the applied voltage. Figure 3a shows device photocurrent under 1 sun conditions: In this case, the response of both MAPbI₃ and Cs_{0.15}FA_{0.85}PbI₃ devices is remarkably similar, displaying a saturation of photocurrent at 0.50 V and 0.51 V respectively (V_{sat}), indicating similar charge extraction behaviour in the two perovskite systems. At 13 suns (Figure 3b), the Cs_{0.15}FA_{0.85}PbI₃ perovskite device features a similar J_{ph} vs V_{eff} trend to the one observed at 1 sun, with a V_{sat} around 0.54 V. However, at high light levels, the MAPbI₃ device exhibits a stronger photocurrent dependence on the electric field, yielding V_{sat} around 1.22 V. This indicates a charge extraction limitation in MAPbI₃ film at high light intensity, calling into question the material's suitability for CPV applications. A quantification of the charge generation rate at maximum power point (G_{mpp}) may be found in Figure S3. At 1 sun, we calculate a G_{mpp} for MAPbI₃ and Cs_{0.15}FA_{0.85}PbI₃ of 80% and 85%

Figure 4 Stability of J - V parameters for Cs_{0.15}FA_{0.85}PbI₃ and MAPbI₃ solar cells under 1 sun equivalent conditions using a LED light source (a) and 13 sun equivalent conditions using a laser light source (b).

respectively. However, at 13 suns, G_{mpp} of MAPbI₃ devices decreases to 60% whereas the optimized cells maintain a G_{mpp} value of 84%. Using TPV and TPC techniques, we plot charge carrier lifetime, τ as well as V_{oc} against charge density, n for both perovskites in Figure 3c. In agreement with our previous observations, we find similar carrier lifetimes under 1 sun conditions for both studied perovskites. These lifetimes diverge at higher illumination intensities, with Cs_{0.15}FA_{0.85}PbI₃ maintaining notably longer lifetimes at 13 suns compared to MAPbI₃. This finding is corroborated by our previous observations both in the divergence in fill factor in Figure 2d, as well as in the lower kT/q observed in Figure 2c for Cs_{0.15}FA_{0.85}PbI₃ compared to MAPbI₃. We identify recombination orders of 2.41 and 2.02 for MAPbI₃ and Cs_{0.15}FA_{0.85}PbI₃ respectively from the slope of the charge carrier lifetime trend. A recombination order (R) of 2, as in our Cs_{0.15}FA_{0.85}PbI₃ device, is indicative of a device exhibiting almost entirely bimolecular recombination at open-circuit voltage conditions.^{34,35} The $R = 2.41$ in the MAPbI₃ cell therefore displays a higher defect density leading to increased trapping at higher light intensities.

One key challenge to overcome in order to prove the viability of perovskite solar cell technology in CPV applications is that of stability. It has been reported that MAPbI₃ is inherently unstable under certain conditions such as high humidity, temperature and ultraviolet radiation.^{7,10} In addition, there are reported structural changes for this perovskite between 54–57°C³⁶ which may accelerate degradation. However there are also reports of MAPbI₃ perovskite remaining stable at operational temperatures in excess of 80°C,^{37–39} indicating structural stability may not be the prime factor in determining device stability. Cs_xFA_{1-x}Pb(I_yBr_{1-y})₃ perovskites, on the other hand, have been reported in extremely stable devices thanks in part to the exclusion of the MA cation and the phase stabilisation by Cs.^{16,18,40–42} We present, in Figure 4, J - V stability data at both 1 sun and 13 suns of light intensity for both perovskites. Figure 4a shows 950 hours of stability data at 1 sun, demonstrating a high degree of stability for both compositions: Following an initial drop in fill factor during the first 100 hours, performance remains relatively constant for the remainder of the experiment. This stability is attributed, in part, to the favourable environmental conditions imposed on devices: Only 1 sun of illumination, combined with a nitrogen atmosphere and relatively low cell temperature (40°C). After 950 hours of light soaking under open-circuit conditions, the Cs_{0.15}FA_{0.85}PbI₃ device retains 83% of its original PCE, while the MAPbI₃ device retains 69%. When moving to higher light intensities, the trends of the two perovskite absorbers become more divergent. Figure 4b shows devices measured periodically under 13 suns of laser irradiation. This measurement may be interpreted either as accelerated lifetime testing for lower light conditions, or real-time testing at high light conditions. Similar to the testing at 1 sun, V_{oc} remains consistent for both perovskites over a period of several hours: This V_{oc} stability excludes the possibility of any significant device heating under the high illumination, as such heating would narrow the perovskite bandgap and manifest as

a reduction in V_{oc} .⁴³ Nevertheless, we observe a deterioration in the MAPbI₃ cell's J_{sc} and fill factor over a period of hours subjected to this light intensity. This decrease is attributed to photo-bleaching of the perovskite film, as investigated by Nie and coworkers.⁴⁴ In this instance, formation of light-induced, localised polarons within the band gap exist alongside photo-generated free carriers; these defects dominate the photocurrent of the device, causing a reduction in J_{sc} and fill factor under light soaking. This photobleaching is accompanied by a slight reduction in light absorption, in the case of MAPbI₃ perovskite, with no such reduction seen in the mixed cation perovskite (Figure S4). Interestingly, we observe no significant crystallographic changes during the course of this light soaking, with no evolution of any PbI₂ peaks in the XRD patterns for either MAPbI₃ or Cs_{0.15}FA_{0.85}PbI₃ perovskites (Figure S5). The Cs_{0.15}FA_{0.85}PbI₃ device shows superior photo-fastness and suffers no degradation of J_{sc} after nearly 6 hours of exposure to 1,300 mW cm⁻² light. This finding further supports the notion that the FA-containing perovskite chemistry is more resistant to defect formation, despite the fact that the device is generating and extracting charges in excess of 300 mA cm⁻² at these illumination levels.

Conclusions

In summary, we present an initial study into the suitability of MAPbI₃ and Cs_{0.15}FA_{0.85}PbI₃ perovskites for use in concentrated photovoltaic systems. Using electrical characterisation techniques, we determine Cs_{0.15}FA_{0.85}PbI₃ to be a more suitable material for exposure to high irradiation intensities: This is the result of fewer traps within the material compared to MAPbI₃, leading to nearly all recombination being bimolecular in nature, and allowing high fill factors at light levels greater than 1 sun, with 16% PCE still attainable at 13 suns with 60% fill factor. In addition, the stability of the FA-containing material shows no appreciable drop in performance despite 6 hours of illumination at 13 equivalent suns. This study represents a first step towards the realisation of perovskites in CPV. However, for this to come to pass, the development of thermally stable charge selective layers must be a priority to ensure all layers within the device are sufficiently resistant to the high temperatures incurred by concentrated sunlight.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

The authors acknowledge KAUST Solar Centre Competitive Fund (CCF) for financial support.

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