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Managing Phase Purities and Crystal Orientation for High-Performance and Photostable Cesium Lead Halide Perovskite Solar Cells

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1. Introduction

Inorganic cesium lead halide perovskites, expressed in brief as CsPbI$_3$/C$_x$Br$_{3-x}$ with $x$ ranging from 0 to 3, have been under intense investigation for photovoltaic applications.[1–3] In contrast to lead halide perovskites containing volatile organic cations, such as methyl ammonium,[4] cesium lead halides exhibit excellent thermal stability. Although pure iodide CsPbI$_3$ has the most promising bandgap of 2.5 eV, the inherent thermodynamic instability of its photocactive cubic ($\alpha$) phase at room temperature remains challenging.[5] Recent works on CsPbI$_3$ have used a promising strategy to make a relatively low bandgap (1.68 eV) inorganic perovskite with high efficiency.[2,6,7]
By integrating the organic cation dimethylammonium (DMA+) into the precursor solution of CsPbI$_3$ perovskite, crystallization of the tetragonal (β) phase of CsPbI$_3$ perovskite can be improved, and the phase better stabilized.[2,6] DMA+ in CsPbI$_3$ would beneficially increase the Goldschmidt tolerance factor, however, whether it remains in the resultant film is still debated[2,8] and is likely annealing temperature-dependent.[8] An alternative strategy to achieve stability is through halide alloying with bromide in CsPbI$_{3-x}$Br$_x$ compositions, which has the further advantage of optical bandgap tenability across a range of phase-stable perovskite compositions (in an inert atmosphere at room temperature).[9,10] Indeed, many works on CsPbI$_3$Br perovskite have shown significant progress with the photovoltaic performance.[9,11,12]

In our previous work,[13] we studied stable compositions of CsPbI$_{3-x}$Br$_x$ prepared using pulsed infrared annealing. We found that with a bromide ratio (x) of no less than 1.2, the compounds showed negligible degradation under environmental conditions (relative humidity of 30% at 25 °C) in either absorption or X-ray diffraction (XRD) measurements. As such, we investigated perovskite solar cells with x = 1.2, 1.5, and 1.8; however, these halide compositions have an optical bandgap of over 1.93 eV, which significantly limits their light-harvesting capability and results in devices with low photocurrent and power conversion efficiency (PCE). For a two-junction tandem cell, with a crystalline silicon[14] or Cu(In, Ga)Se$_2$[3] thin film that has a bandgap no wider than 1.2 eV as the bottom cell, a top cell with a bandgap in the range of 1.7–1.8 eV is required to provide an optimal short-circuit photocurrent density ($J_{sc}$) of over 18 mA cm$^{-2}$, to match that of the bottom cell. For all-perovskite tandem cells, the wide-bandgap layer could be up to 1.9 eV, because the narrow bandgap perovskite with metal alloying of lead and tin has a minimum bandgap beyond 1.2 eV.[15] Recent works on all-perovskite tandem cells used tin-lead mixed perovskite with a narrow bandgap of 1.22,[16] 1.25,[17] and 1.27 eV[18] and the wide bandgap perovskite of 1.77, 1.75, and 1.8 eV correspondingly. Meanwhile, the photocurrent required from the wide bandgap perovskite in all-perovskite tandem cells can be as low as 16 mA cm$^{-2}$, opening the possibility for CsPbI$_{3-x}$Br$_x$ with x up to a value of 1.2.

In this work, we studied the photostability [light soaking under maximum power point (MPP) tracking] of solar cells composed of CsPbI$_{3-x}$Br$_x$ with low bromide content in a nitrogen atmosphere, to exclude the influence of moisture on the crystal structure of CsPbI$_{3-x}$Br$_x$. More specifically, we reduced the bromide content in CsPbI$_{3-x}$Br$_x$ with x from 1.2 to 0.3 and studied the influence of the bromide content on the optical properties and crystallization behavior. We found that the first annealing step in a three-step annealing process played a critical role in determining the final film texture and phase behavior. In devices, this translated into significant solar cells performance variation for the compositions CsPbI$_{1.8}$Br$_{1.2}$, CsPbI$_{2.0}$Br$_{1.0}$, and CsPbI$_{2.8}$Br$_{0.8}$, depending on the temperature of the first step. Phase impurity, with photoinactive regions of a δ-phase in CsPbI$_{2.0}$Br$_{1.0}$ and CsPbI$_{2.2}$Br$_{0.8}$ films, resulted in less ideal quantum efficiency for CsPbI$_{2.0}$Br$_{1.0}$ (less than 90%) and CsPbI$_{2.8}$Br$_{0.8}$ (less than 85%) perovskite solar cells. In the case of CsPbI$_{1.8}$Br$_{1.2}$, we found a low first annealing step temperature (42 °C) resulted in non-perovskite phase impurity, whereas a high first annealing step temperature (60 °C) led to more than one crystallographic orientation of the perovskite phase. At the optimized annealing temperature of 50 °C, CsPbI$_{2.0}$Br$_{1.0}$ films showed the highest phase purity of the photoactive orthorhombic perovskite phase and only one dominant crystal orientation, with (110) oriented in the out-of-plane (OOP) direction. This scenario resulted in the highest PCE of up to 14.6% with external quantum efficiencies (EQEs) of over 90% in a broad spectral range of 450–560 nm. Moreover, these devices exhibited excellent solar cell performance and photostability over 300 h of MPP tracking, under continuous light illumination in a nitrogen atmosphere. This work provides further insights into the enhancement of operational lifetime of perovskite solar cells.

2. Results and Discussion

Scheme 1 shows the deposition protocol we used for CsPbI$_{3-x}$Br$_x$ thin films; further details of this process are described in the Experimental Section (see Supporting Information). In brief, we used an antisolvent-free crystallization approach; after spin coating, the substrates were processed with three annealing steps at three temperatures. For CsPbI$_{1.8}$Br$_{1.2}$, CsPbI$_{2.0}$Br$_{1.0}$, and CsPbI$_{2.2}$Br$_{0.8}$ perovskite films, the annealing temperatures for step II and step III were set at 100 and 160 °C, whereas we studied the influence of the temperature in step I on the final product. For CsPbI$_{2.0}$Br$_{0.6}$ and CsPbI$_{2.2}$Br$_{0.3}$ perovskite films, the annealing temperatures for step II and step III were set at 150 and 310 °C to form a black phase. It should be noted that CsPbI$_{1.8}$Br$_{1.2}$, CsPbI$_{2.0}$Br$_{1.0}$, and CsPbI$_{2.2}$Br$_{0.8}$ perovskite films all became darker after annealing in step II and step III compared with step I. In contrast, CsPbI$_{2.4}$Br$_{0.6}$ and CsPbI$_{2.6}$Br$_{0.3}$ perovskite films first formed a brown film in step I, and then transitioned first through a colorless phase in step II, and finally, a dark brown film formed in step III.

We first investigated the optical and structural properties across a broad mixed-halide compositional range. Figure 1a shows the recorded Tauc plots for the various CsPbI$_{3-x}$Br$_x$ perovskites prepared using the method given in Scheme 1. The absorption coefficient (α) of CsPbI$_{3-x}$Br$_x$ perovskite given in Figure S1a, Supporting Information, is comparable to that of organic cation-containing lead halide perovskite, such as methylammonium lead iodide (MAPbI$_3$)[20] with all films...
emission for hybrid organic cation-containing perovskites. This results (Le Bail method) for CsPbI$_2$Br$_x$$_x$ with PCEs of 14.6%, 13.9%, and 12.8%, respectively. With the decrease in bromide content and bandgap, the open-circuit voltage ($V_{oc}$) is reduced from 1261 mV (CsPbI$_{2.2}$Br$_{1.0}$) to 1207 mV (CsPbI$_{2.2}$Br$_{1.0}$) to 1166 mV (CsPbI$_{2.2}$Br$_{1.0}$). Notably, with the CsPbI$_{2.2}$Br$_{1.0}$ perovskite, we achieved among the highest reported $V_{oc}$ values and PCEs for inorganic perovskite solar cells with a wide bandgap.$^ {12,13,19,24}$ Although we might expect an increase in the photocurrent with more I-rich compositions, alternative strategies must be developed to enhance phase formation and stability, which we will continue to investigate.

Figure 2a gives the $J$–$V$ curves of the champion devices for CsPbI$_{2.2}$Br$_{1.0}$, CsPbI$_{2.2}$Br$_{1.0}$, and CsPbI$_{2.2}$Br$_{1.0}$ with PCEs of 14.6%, 13.9%, and 12.8%, respectively. With the decrease in bromide content and bandgap, the open-circuit voltage ($V_{oc}$) is reduced from 1261 mV (CsPbI$_{2.2}$Br$_{1.0}$) to 1207 mV (CsPbI$_{2.2}$Br$_{1.0}$) to 1166 mV (CsPbI$_{2.2}$Br$_{1.0}$). Notably, with the CsPbI$_{2.2}$Br$_{1.0}$ perovskite, we achieved among the highest reported $V_{oc}$ values and PCEs for inorganic perovskite solar cells with a wide bandgap.$^ {12,13,19,24}$ Although we might expect an increase in the photocurrent with more I-rich compounds, the value of $\approx$29° highlight a shift to lower angles for the (110)/(002) and (220)/(004) scattering as the bromide content decreases, indicating a larger unit cell with more I-rich perovskite compositions. Moreover, (110)/(002) and (220)/(004) peaks splitting becomes more pronounced as the bromide content is reduced from $x = 1.2$ to 0.8.

Next, we prepared solar cells across the CsPbI$_{1-x}$Br$_x$ perovskite compositional series, as described in the Experimental Section (see Supporting Information). Figure S4, Supporting Information, presents the $J$–$V$ curves for the best CsPbI$_{2.2}$Br$_{1.0}$ and CsPbI$_{2.2}$Br$_{1.0}$ solar cells with a PCE of 5.12% and 9.45%. Table S1, Supporting Information, summarizes the photovoltaic parameters. Unfortunately, these devices quickly degraded after 1 day to less than half of their initial PCEs despite storage inside a nitrogen-filled glovebox. We think the poor stability in these I-rich devices could be caused by the less phase stability of I-rich perovskites. As such, these compositions, alternative strategies must be developed to enhance phase formation and stability, which we will continue to investigate.
\( J_{sc} \) is quite similar for all compositions. This observation can be rationalized from EQE measurements given in Figure 2b. We find that for solar cells with composition CsPbI\(_{1.8}\)Br\(_{1.2}\), the EQE peaks at \( \approx 90\% \) in the wavelength range from 450 to 560 nm and remain over 80% for most of the spectrum. The high EQE indicates efficient charge collection at short-circuit conditions for CsPbI\(_{1.8}\)Br\(_{1.2}\) perovskite solar cells. In contrast, the EQE of CsPbI\(_{2.0}\)Br\(_{1.0}\) perovskite solar cell peaks below 90%, and for the CsPbI\(_{2.2}\)Br\(_{0.8}\) device, the maximum EQE is \( \approx 80\% \), indicating less effective charge extraction in these cells. The relatively low fill factor (FF) in these solar cells also points to a charge extraction problem. As revealed in XRD measurements (Figure 1c and Figure S3, Supporting Information), the presence of photoinactive \( \delta \)-phase in CsPbI\(_{2.0}\)Br\(_{1.0}\) and CsPbI\(_{2.2}\)Br\(_{0.8}\) may impede charge extraction. Alternatively, the loss of \( J_{sc} \) in these devices could simply come from there being less absorbing material in the film. The series resistance (\( R_s \)) and shunt resistance (\( R_{sh} \)), estimated from the linear intercepts of the \( J-V \) curves (Figure 2a) at \( J_{sc} \) and \( V_{oc} \) points, respectively, are summarized in Table S2, Supporting Information, together with the photovoltaic parameters of \( J-V \) curve given in Figure 2a. We find a reduced \( R_{sh} \) in the more I-rich devices, which could be explained by higher \( \delta \)-phase content and its interface with the perovskite phase contributing to more defects in the system. Interestingly, \( R_s \) was estimated to be lower in the more I-rich solar cells, revealing that the contact ohm resistance is decreased for perovskites with a smaller bandgap. Figure 2b also shows that CsPbI\(_{1.8}\)Br\(_{1.2}\), CsPbI\(_{2.0}\)Br\(_{1.0}\), and CsPbI\(_{2.2}\)Br\(_{0.8}\) perovskite solar cells have the EQE spectral onset at 655, 666, and 677 nm, which agrees well with the absorption spectra given in Figure S1b, Supporting Information. The integrated \( J_{sc} \) from EQE spectra shows a \( J_{sc} \) of 14.21, 14.62, and 14.05 mA cm\(^{-2}\) for CsPbI\(_{1.8}\)Br\(_{1.2}\), CsPbI\(_{2.0}\)Br\(_{1.0}\), and CsPbI\(_{2.2}\)Br\(_{0.8}\), respectively. The value of \( J_{sc} \) extracted from \( J-V \) measurement shows an overestimation of 7.0%, 6.7%, and 8.9% for CsPbI\(_{1.8}\)Br\(_{1.2}\), CsPbI\(_{2.0}\)Br\(_{1.0}\), and CsPbI\(_{2.2}\)Br\(_{0.8}\), respectively, compared with the EQE measurement. The absence of a shallow mask during the \( J-V \) measurement may be the reason for an overestimation of the \( J_{sc} \).[25]

We then investigated the photostability of devices with varying halide composition under operational conditions, with constant 1 sun illumination and MPP tracking. Figure 2c shows the normalized, averaged efficiency of at least six solar cells over 300 h of testing, conducted at room temperature and in a nitrogen atmosphere, adopting the ISOS-L-1I protocol.[26] The \( T_{500} \) parameter, which represents the time taken for a solar cell to degrade to 80% of its maximum efficiency (counting from \( T_{\text{max}} \) when maximum efficiency is reached), is roughly 300 h for CsPbI\(_{1.8}\)Br\(_{1.2}\) perovskite solar cells, yet only around 192 h for CsPbI\(_{2.0}\)Br\(_{1.0}\) and 134 h for CsPbI\(_{2.2}\)Br\(_{0.8}\) perovskite solar cells. This demonstrates clearly that CsPbI\(_{1.8}\)Br\(_{1.2}\) cells have superior operational lifetime to CsPbI\(_{2.0}\)Br\(_{1.0}\) and CsPbI\(_{2.2}\)Br\(_{0.8}\) cells, with better performance retention during testing.

To further understand the perovskite phase formation process, we tried modifying the step I temperature and found that it plays a critical role in determining device efficiency. Figure 2d shows the efficiencies of solar cells fabricated when varying the annealing temperature in step I (as shown in Scheme 1). It shows that for all three compositions, both the average efficiency (solid line) and champion efficiency

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**Figure 2.** a) \( J-V \) curves and b) EQE spectra of champion perovskite solar cells with compositions CsPbI\(_{1.8}\)Br\(_{1.2}\) (black line), CsPbI\(_{2.0}\)Br\(_{1.0}\) (red), and CsPbI\(_{2.2}\)Br\(_{0.8}\) (blue). c) MPP tracked performance for perovskite solar cells under constant 1 sun illumination and in a nitrogen atmosphere at room temperature, plotting normalized average efficiency of a minimum of six solar cells and the standard deviation as the error bar. d) Average (solid line) and champion (dashed line) efficiencies of perovskite solar cells for each composition dependent on the step I temperature.
(dashed line) of cells have a similar performance trend, dependent on the temperature in step I. CsPbI$_{1.8}$Br$_{1.2}$ perovskite solar cells are most efficient with the step I temperature of 50 °C. In contrast, CsPbI$_{2.0}$Br$_{1.0}$ and CsPbI$_{2.2}$Br$_{0.8}$ perovskite solar cells reach the highest efficiency at temperatures of 60 and 65 °C. This trend indicates that for this composition range, with higher bromide content, less thermal energy is required for the initial crystallization, consistent with lead bromide perovskite phases generally having lower formation enthalpies than iodide equivalent compounds.\textsuperscript{[27]} We speculate that with this antisolvent-free processing route, step I removes remnant solvent and initiates the perovskite crystallization, which may proceed via an intermediate solvent-adduct phase, with the temperature and halide content both impacting the nucleation process.\textsuperscript{[19]} As we will discuss in the following section, for the CsPbI$_{1.8}$Br$_{1.2}$ perovskite, the selection of the temperature in step I has a significant influence on the final product. Box charts of photovoltaic parameters of solar cells prepared at different temperatures in step I are summarized in Figure S5, Supporting Information. An average solar cell prepared at different temperatures in step I are functional products. Box charts of photovoltaic parameters of solar cells prepared at different temperatures in step I are summarized in Figure S5, Supporting Information. An average solar cell prepared at each temperature. Solar cells made with the optimal step I temperature.

CsPbI$_{1.8}$Br$_{1.2}$ perovskite is studied as an example to understand the influence of the step I temperature on the optical and crystal structural properties of the films. First, we investigated the surface morphology using scanning electron microscopy (SEM). Figure 3 shows the surface morphology of CsPbI$_{1.8}$Br$_{1.2}$ samples prepared at four different step I temperatures, i.e., 42, 50, 55, and 60 °C. The low magnification SEM images in the top panels show that all of the perovskite films have good coverage on top of the mesoporous titanium dioxide (TiO$_2$) layer. The high magnification SEM images along the bottom row show larger crystalline domains for CsPbI$_{1.8}$Br$_{1.2}$ perovskite as the temperature in step I is increased from 42 to 60 °C. Between 42 and 50 °C, there is a significant evolution of morphology, and for 60 °C, the structure appears to be more merged or fused together. Cross-sectional SEM images of the films are given in Figure S6, Supporting Information, showing that all films have similar thicknesses of ~500 nm. Organized, columnar grains are apparent for samples prepared at 50 °C, minimizing grain boundaries between the selective contacts. This ideal grain growth is critical in enabling the highest efficiency of CsPbI$_{1.8}$Br$_{1.2}$ cells, evident in an increase in FF from 52% to 75% when comparing 42 and 50 °C (Figure S5, Supporting Information).

Figure S7, Supporting Information, shows that the optical bandgap is negligibly influenced by the step I temperature. However, films prepared at 42 °C show a more gradual absorption onset and a slightly lower optical bandgap of 1.91 eV, compared with films made at other temperatures. As we will further discuss in the XRD and grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements, this difference may originate from the presence of photoinactive domains (δ-phase) in samples prepared at 42 °C. This trend indicates that for this composition range, with higher bromide content, less thermal energy is required for the initial crystallization, consistent with lead bromide perovskite phases generally having lower formation enthalpies than iodide equivalent compounds.\textsuperscript{[27]} We speculate that with this antisolvent-free processing route, step I removes remnant solvent and initiates the perovskite crystallization, which may proceed via an intermediate solvent-adduct phase, with the temperature and halide content both impacting the nucleation process.\textsuperscript{[19]} As we will discuss in the following section, for the CsPbI$_{1.8}$Br$_{1.2}$ perovskite, the selection of the temperature in step I has a significant influence on the final product. Box charts of photovoltaic parameters of solar cells prepared at different temperatures in step I are summarized in Figure S5, Supporting Information. An average solar cell prepared at each temperature. Solar cells made with the optimal step I temperature.  

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Figure S7, Supporting Information, shows that the optical bandgap is negligibly influenced by the step I temperature. However, films prepared at 42 °C show a more gradual absorption onset and a slightly lower optical bandgap of 1.91 eV, compared with films made at other temperatures. As we will further discuss in the XRD and grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements, this difference may originate from the presence of photoinactive domains (δ-phase) in samples prepared at 42 °C. Despite this, Figure 4a reveals that the perovskite films in the stack of FTO/c-TiO$_2$/m-TiO$_2$/CsPbI$_{1.8}$Br$_{1.2}$ have similar PL peak positions. Films prepared at 42 °C have the lowest PL intensity, followed by 55 and 50 °C, with 60 °C showing the highest PL intensity. Moreover, we calculated the internal quasi-Fermi level splitting (QFLS) from the absolute PL spectra following our previously reported approach.\textsuperscript{[28]} The obtained QFLS is shown in Figure 4b, together with the $V_{oc}$ obtained from the $J$–$V$ measurement. It shows that solar cells made at 50 °C have the highest $V_{oc}$ and the smallest potential loss (53 mV) when compared with the neat absorber on FTO/c-TiO$_2$/m-TiO$_2$. For CsPbI$_{1.8}$Br$_{1.2}$ samples prepared with 60 °C step I temperature, we also notice the potential loss of up to 144 mV. As these samples show the highest QFLS, indicating reduced non-radiative recombination at the interface with TiO$_2$, the high potential loss is very likely to originate from the interface with spiro-OMeTAD.\textsuperscript{[29]} As we will discuss in the GIWAXS data, samples prepared at 60 °C resulted in two constrained crystal orientations or textures. In other words, the second facet orientation may cause an issue for the molecular interaction between CsPbI$_{1.8}$Br$_{1.2}$ perovskite and spiro-OMeTAD.\textsuperscript{[30]}

Figure 4c shows the $J$–$V$ curves of champion perovskite solar cells prepared at each temperature. Solar cells made with the step I temperature of 50, 55, and 60 °C result in significantly enhanced FF, $V_{oc}$, and $J_{sc}$ compared with those prepared at 42 °C. The enhancement is also observed in the EQE spectra (Figure 4d). It presents that cells made at 42 °C may suffer from

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**Figure 3.** SEM highlighting the surface morphology of CsPbI$_{1.8}$Br$_{1.2}$ films as a function of the step I temperature. Layers were deposited on FTO/c-TiO$_2$/m-TiO$_2$ to mimic completed devices. Scale bars are 2 μm for the top panels and 800 nm for the bottom panels.
poor charge collection with the EQE below 80% over the whole spectral range. The much lower \( J_{sc} \) in solar cells with 42°C step I temperature may also originate from the presence of photoinactive domains (δ-phase) in the perovskite film, as will be discussed later. Solar cells prepared at 50°C exhibit a higher \( V_{oc} \) and \( J_{sc} \) than solar cells made with 55 and 60°C step I temperatures. Figure 4e shows the shelf-lifetime measurement of solar cells prepared at the discussed temperatures. In this measurement, \( J-V \) curves on at least 12 cells were measured on separate days, whereas in between, solar cells were kept in the dark under nitrogen. Figure 4e displays that solar cells made at 42°C underwent rapid performance degradation. Solar cells prepared at 55 and 60°C also showed a clear trend of degradation in the first 2 weeks, with 50°C retaining the most performance. Figure 4f displays the MPP tracked performance, with constant 1 sun illumination in a nitrogen atmosphere and at room temperature. All error bars are calculated from the standard deviation.

To investigate further, Figure 5a,b shows 2D GIWAXS patterns for samples prepared at 50 and 60°C, with the 42 and 55°C patterns given in Figure S11, Supporting Information. The azimuthally integrated 1D patterns from 2D data are given in Figure S12a, Supporting Information. In the case of the sample prepared at 42°C, additional low-intensity scattering rings at \( 2\theta \) of \( 9.9° \) and \( 13.2° \) are assigned to the δ-phase of the perovskite film; these features are highlighted in Figure S12b, Supporting Information.
Information. The enlarged $2\theta$ range in Figure S12c, Supporting Information, highlights a small peak shift of the scattering feature associated with the (004)/(220) planes, suggesting some variation in halide composition as the step I temperature is varied. This trend is most significant with the 42°C/C sample shifted to lower angles, indicating shrinking of the lattice with higher annealing temperatures, which could be explained by this step modifying the final film, such that more bromide becomes coordinated with Pb during this step.

Critically, we note that the (110)/(002) scattering ring for step I temperatures of 42–55°C is dominated by a single partial scattering ring in the OOP direction (Figure 5a,b and Figure S11, Supporting Information), with the orthogonal (002)/(110) scattering in-plane (IP). The (111) scattering ring has its maximum at 60°C, expected for $<110>$ orientation, as shown in Figure 5c,e. However, this is not the case for the 60°C sample. Figure 5d,f,g shows that the (110) ring has a second intensity maximum at 45°, confirmed by the (111) ring also have higher intensity at ≈40°, corresponding to $<100>/<020>$ orientation. The additional texture introduced in the 60°C sample is most likely caused by changes in biaxial strain during the initial crystallization process. Here, it is very interesting to see how the step I temperature could have such a significant influence on the final texture of perovskite films. As we discussed earlier in Figure 4, solar cells with step I annealing temperature of 60°C are less photostable and suffer from a higher potential loss than devices fabricated at 50°C during step I. It indicates that the additional texture with (110) scattering at 45°, in addition to the OOP direction, may lead to worsened photostability observed in the MPP tracking measurements.

3. Conclusion

In summary, we found that the step I annealing temperature was critically important for management of phase purity and crystal orientation of inorganic perovskites and, thus, significantly influences the photovoltaic performance and operational stability of inorganic perovskite solar cells. The difference in textures of the final perovskite films is most likely caused by the changes in biaxial strain during the initial crystallization. Moreover, in the studied perovskite samples, the optimized annealing temperature decreases with an increase in bromide ratio in CsPb$_{1-x}$Br$_x$. With a low step I temperature of 50°C, CsPb$_{1.8}$Br$_{1.2}$ exhibited a pure orthorhombic phase and only one crystal orientation of the (110) plane. Consequently, this allowed for the highest efficiency of up to 14.6%. Starting with an average efficiency of 12.9%, CsPb$_{1.8}$Br$_{1.2}$ perovskite solar
cells achieved the $T_{300}$ lifetimes of $\approx 300$ h, averaged of over six solar cells, following the ISOS-L-II protocol. In contrast, CsPbI$_2$Br$_{1.0}$ and CsPbI$_2$Br$_{0.8}$ solar cells, due to phase impurity in their perovskite films, presented an initial average efficiency of 11.9% and 10.8% and resulted in a $T_{300}$ of around 192 and 134 h. It should also be noted that solar cells composed of high I-rich compositions of CsPbI$_2$Br$_{0.6}$ and CsPbI$_2$Br$_{0.5}$ exhibited a poor photovoltaic performance and operational stability. Alternative strategies must continue to develop to enhance the phase purity and thermodynamic stability of more I-rich cesium lead halides.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Q.W. designed the experiment, drafted the manuscript, fabricated, and characterized the solar cells and prepared the samples for the measurements involved in this work. J.A.S. and D.S. conducted and contributed to the data analysis of the GIXWAXS measurements for this work. J.A.S. conducted refinement for the crystal structure and texture analysis of the studied inorganic perovskite thin films. C.M.W., P.C., and M.S. conducted and contributed to the data analysis of the PL measurements for this work. H.K. conducted the ageing test of solar cells in this study and thermodynamic stability of more I-rich cesium lead halides.

Keywords

cesium lead halides, crystal orientation, inorganic perovskites, ISOS-L-II protocol, phase purity, photostability

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