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Composition-Tuned Wide Bandgap Perovskites: From Grain Engineering to Stability and Performance Improvement

Yang Zhou, Yong-Heng Jia, Hong-Hua Fang, Maria Antonietta Loi, Fang-Yan Xie, Li Gong, Min-Chao Qin, Xin-Hui Lu, Ching-Ping Wong,* and Ni Zhao*

Wide bandgap (WB) organic–inorganic hybrid perovskites (OIHPs) with a bandgap ranging between 1.7 and 2.0 eV have shown great potential to improve the efficiency of single-junction silicon or thin-film solar cells by forming a tandem structure with one of these cells or with a narrow bandgap perovskite cell. However, WB-OIHPs suffer from a large open-circuit voltage (V_{oc}) deficit in photovoltaic devices, which is associated with the phase segregation of the materials under light illumination. In this work the photoinstability is demonstrated and V_{oc} loss can be addressed by combining grain crystallization and grain boundary passivation, achieved simultaneously through tuning of perovskite precursor composition. Using $FA_{0.17}Cs_{0.83}PbI_{3-x}Br_x$ ($x = 0.8, 1.2, 1.5$, and 1.8), with a varied bandgap from 1.72 to 1.93 eV, as the model system it is illustrated how precursor additive $Pb(SCN)_2$ should be matched with a proper ratio of FAX (I and Br) to realize large grains with defect-healed grain boundaries. The optimized WB-OIHPs show good photostability at both room-temperature and elevated temperature. Moreover, the corresponding solar cells exhibit excellent photovoltaic performances with the champion V_{oc} /stabilized power output efficiency reaching 1.244 V/18.60%, 1.284 V/16.51%, 1.296 V/15.01%, and 1.312 V/14.35% for WB-OIHPs with $x = 0.8, 1.2, 1.5$, and 1.8 , respectively.

boosted from 3.8% in 2009 to a certified 22.7% in 2017.^[6,7] Another attractive feature of the OIHPs is their tunable bandgap from 1.17 to 2.3 eV,^[8–11] which has aroused intensive interests of forming tandem cells with another OIHP,^[12–14] silicon^[14–16] or copper indium gallium (di)selenide.^[17,18] According to the modeling result,^[14] double-junction and triple-junction tandem structures using an OIHP-based top cell can achieve solar cell PCEs to over 30% and 35%, respectively. Based on the requirement of current matching between the top and the bottom cells in a tandem structure, the top absorber should have a bandgap ranging between 1.7 and 2.0 eV, to achieve a maximum PCE.^[14] Such bandgap can be easily achieved by tuning the I/Br ratio in OIHPs; for example, bandgap can be tuned from 1.56 to 2.30 eV by varying x from 0 to 3 in $MAPbI_{3-x}Br_x$.^[9] However, photoinduced phase segregation, which involves formation of a lower bandgap phase in the original wide bandgap

OIHP (WB-OIHP) (e.g., $MAPbI_{3-x}Br_x$ with $E_g > 1.70$ eV),^[19,20] degrades the open-circuit voltage (V_{oc}) of the cell and also compromises the operation stability.

Several approaches have been explored to address the photoinduced phase segregation issue. Snaith et al. replaced MA with a mixture of FA and Cs at the A site of a 1.74 eV bandgap mixed-halide perovskite to suppress the light-induced phase segregation, and achieved a PCE of 17.1% and a V_{oc} of 1.2 V.^[11] It was later proposed that the improved photostability by Cs

1. Introduction

Organic–inorganic hybrid perovskites (OIHPs) with a chemical structure of ABX_3 (where A is typically methylammonium (MA), formamidinium (FA) or Cs, B is Pb or Sn, and X is I, Br, or Cl) have rapidly emerged as a competitive photovoltaic (PV) material, as they can provide high power conversion efficiency (PCE) through low-cost, top-down solution processes.^[1–5] The PCE of OIHP solar cells has been remarkably

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inclusion may originate from lattice contraction, increased entropic contribution^[21] and reduced electron–phonon coupling.^[22] Huang and co-workers utilized a hydrophobic surface to enlarge the grain size of MAPbI_{2.2}Br_{0.8} ($E_g = 1.75$ eV) in a so-called “inverted” solar cell structure and achieved a PCE of 14.9% and a V_{oc} of 1.21 V.^[23] The increased grain size increases the photostability of the films, but the requirement of a hydrophobic substrate surface imposes constraints on the device configuration and fabrication processes. Alternatively, it has been reported that including a small amount of Pb(SCN)₂ additive in the precursor of MAPbI₃ and FA_{0.8}Cs_{0.2}Pb(I_{0.7}Br_{0.3})₃ can also improve the grain size and crystallinity^[24,25] of the perovskite film. This method, however, introduces an undesirable byproduct, PbI₂, in the perovskite thin films, which has been shown to be detrimental to the photostability of the films.^[26,27] On the other hand, studies on MAPb(I_{0.4}Br_{0.6})₃^[20] and (Cs, FA, MA)Pb(I_{1- γ} Br _{γ})₃ ($\gamma = 0.4, 0.8$, and 1)^[28] show that when excess MAX (X = I and Br) or KI is introduced in the perovskite films, the film stability appears to be improved. Very recently, we found the photoinduced phase segregation can be accelerated at elevated cell temperatures that may exist during operation.^[29] By applying benzylamine modification at the film surface, we improved the thermal-photostability of a Cs_{0.15}FA_{0.85}PbI_{2.2}Br_{0.8} film (bandgap: 1.72 eV) and at the same time achieved a stable solar cell output efficiency of 17.1% and a V_{oc} of 1.24 V.^[29] It is worth noting that the aforementioned studies focused mostly on perovskite systems with a bandgap around 1.72–1.74 eV, which is estimated to be the optimal matching bandgap with silicon solar cells. For triple junction structures or for optimized perovskite-perovskite tandem cells, the perovskite bandgap of 1.75–2.0 eV is needed. Unfortunately, the wider bandgap perovskite systems are even more photo-unstable thermodynamically^[30] and cannot yield increased V_{oc} with increased bandgap. To address this limitation, the synergistic effects of the aforementioned approaches should be considered holistically, based on which, a simple fabrication process could be developed to merge the different effects and result in improved stability and solar cell performance.

In this work, we utilized a prototype WB-OIHP system, FA_{0.17}Cs_{0.83}PbI_{3- x} Br _{x} ($x = 0.8, 1.2, 1.5$, and 1.8), with a bandgap ranging from 1.72 to 1.93 eV, to explore the material strategies to improve the photostability. Spin-coating of the stoichiometrically mixed precursor solution on a hydrophilic SnO₂ surface resulted in OIHP thin film with low crystallinity and small grain size. We then modified the grain crystallization and surface chemistry by selectively adding Pb(SCN)₂, excess FAX, or a combination of both. Our results suggest the synergistic effects of the additive composition in enhancing film crystallinity and grain size, reducing impurity and grain boundary passivation. Accordingly, the carrier lifetime in the composition-optimized perovskite films shows a significant improvement, and the photoinduced phase segregation is greatly suppressed. In addition, the thermal-photostability is also improved in the films. Remarkably, the highly crystallized and well passivated WB-OIHP based solar cells show greatly reduced hysteresis and excellent photovoltaic performance. The (average, maximum) values of V_{oc} of the solar cells show monotonic increase with increasing bandgap, from (1.223 $\pm$ 0.014, 1.244) V for 1.72 eV ($x = 0.8$) to (1.254 $\pm$ 0.019, 1.284) V, (1.272 $\pm$ 0.019, 1.296) V and

(1.286 $\pm$ 0.017, 1.312) V for 1.79 eV ($x = 1.2$), 1.86 eV ($x = 1.5$), and 1.93 eV ($x = 1.8$). The champion solar cells show a stable output efficiency of 18.60%, 16.51%, 15.01%, and 14.35% for $x = 0.8, 1.2, 1.5$, and 1.8 OIHPs, respectively.

2. Results and Discussion

The Cs_{0.17}FA_{0.83}PbI_{3- x} Br _{x} ($x = 0.8, 1.2, 1.5$, and 1.8) thin films were fabricated through a one-step spin-coating process using chlorobenzene as an antisolvent and a precursor solution mixture prepared from (CsI)_{0.17}(FAI)_{0.83}(PbI₂)_{1-0.5 x} (PbBr₂)_{0.5 x} (solution A) with addition of γ vol% of (CsI)_{0.17}(FAI)_{0.83}[Pb(SCN)₂ + 3FAI]_{1-0.5 x} [Pb(SCN)₂ + 3FABr]_{0.5 x} (solution B) ($x = 0.8, 1.2, 1.5$, and 1.8; $\gamma = 0, 2.5, 5$, and 7.5). By including solution B, about 0%, 2.9%, 5.6%, and 8.3% molar ratio of excess FAX (X = I and Br) is introduced into the precursor for $\gamma = 0, 2.5, 5$, and 7.5, respectively. For simplification, the OIHP thin films prepared with the mixture of solution A and B are denoted as x - γ B, with different x and γ values. The detailed fabrication procedure can be found in the Experimental Section.

We first study the effect of solution B with the $x = 0.8$ OIHP thin film and with 5 vol% of additive solution. The proposed modification mechanism is schematically illustrated in Figure 1a. Directly depositing solution A (Route 1) results in an OIHP film (0.8-0B) with small grains and low crystallinity (Figure S1a–c, Supporting Information; Figure 1a, Route 1). Adding 5 vol% pure Pb(SCN)₂ solution in solution A (Route 2) leads to increased grain size and crystallinity but at the same time produces PbX₂ (X = I and Br) impurity that segregates randomly around the grain boundaries (Figure S1b,c, Supporting Information; Figure 1a, Route 2). This impurity may result from Pb(SCN)₂ reacting with FAX (X = I and Br) with a ratio of 1:2, analogous to a previously reported process involving similar reactants^[24]

We found the OIHP thin film prepared from Route 2 exhibit poor thermal-photostability, likely due to the PbX₂ impurity phase.^[26,27] The reaction in Equation (1) could in principle be compensated by adding extra FAX (X = I and Br) into the precursor to further react with the excess PbX₂. Accordingly, a modified route is experimented, where the Pb(SCN)₂ solution was replaced with (CsI)_{0.17}(FAI)_{0.83}[Pb(SCN)₂ + 2FAI]_{0.6}[Pb(SCN)₂ + 2FABr]_{0.4} (solution C), still with a volume ratio of 5 vol% (Route 3 in Figure 1a). The 2:1 ratio of FAX: Pb(SCN)₂ is designed to consume Pb(SCN)₂-induced PbX₂ by FAX. As verified by the X-ray diffraction (XRD) and scanning electron microscopy (SEM) results, Route 3 almost entirely eliminates PbX₂ in the OIHP thin film (denoted as 0.8-5C) while still maintaining large grain size and high crystallinity. Consequently, the thermal-photostability of the film is highly improved (Figure S2c, Supporting Information). Since previous studies also showed that excess MAX (X = I and Br) [20], or KI [28] could improve OIHP stability via defect passivation, we further increased the FAX ratio in solution B, i.e., changing the FAX: Pb(SCN)₂ ratio to 3:1 (Route 4 in Figure 1a). The resultant OIHP thin films are expected to be

Figure 1. a) Schematics of different routes to prepare the WB-OIHP thin films; SEM images of the 0.8- γ B OIHP thin films: b) $\gamma = 0$, c) $\gamma = 2.5$, d) $\gamma = 5$, and e) $\gamma = 7.5$. f) XRD patterns, g) ultraviolet-visible absorption spectra, and h) TRPL decays of the 0.8- γ B OIHP thin films with $\gamma = 0, 2.5, 5$, and 7.5 .

overstoichiometric in FAX. The modified route indeed yields significantly improved photostability as compared to Route 3, as will be discussed later. To further verify the proposed role of excess FAX, we also prepared an OIHP thin film (denoted as 0.8-5D) using solution A and 5 vol% of $(\text{CsI})_{0.17}(\text{FAI})_{0.83}[\text{PbI}_2 + \text{FAI}]_{0.6}[\text{PbBr}_2 + \text{FABr}]_{0.4}$ (solution D additive). In this case, only excess FAX ($X = \text{I}$ and Br) and no $\text{Pb}(\text{SCN})_2$ is introduced in the precursor. It can be seen from Figure S3 of the Supporting Information that the OIHP thin film shows barely no change in the XRD intensity compared with the Route 1 prepared films, confirming that the improvement of the crystallinity in the 0.8- γ B films is assisted by $\text{Pb}(\text{SCN})_2$, not FAX.

After elucidating the role of different compositions in solution B, we varied the volume ratio of solution B in the parent precursor solution (solution A) and investigated how it affects the crystallinity, grain size and consequently the electronic properties of the perovskite films. The SEM images of the 0.8- γ B ($\gamma = 0, 2.5, 5$, and 7.5) OIHP thin films are shown in Figure 1b–e, which demonstrate the increase of the average grain size from ≈ 150 nm for 0.8-0B to ≈ 500 , ≈ 1000 , and ≈ 1300 nm for 0.8-2.5B, 0.8-5B, and 0.8-7.5B OIHP thin films, respectively. The XRD patterns (Figure 1f) indicate the highly enhanced crystallinity with the addition of solution B. The intensity of the main peaks at 14.20° and 28.59° is enhanced rapidly with the increasing of γ from 0 to 5 (Figure 1f), which corresponds well to the enlarged grain size (Figure 1b–e). However, when γ is further increased from 5 to 7.5, the XRD

peak intensity starts to drop (Figure 1f) although the grain size is further enlarged (Figure 1e). It is found that two new peaks at 12.74° and 25.72° arise with γ increased from 5 to 7.5 (Figure S4, Supporting Information). These two peaks correspond to PbX_2 ($X = \text{I}$ and Br) (Figure S1c), indicating incomplete conversion of PbX_2 ($X = \text{I}$ and Br) to perovskite. The perovskite formation proceeds likely in two steps, first initiated by PbX_2 ($X = \text{I}$ and Br) crystallization and then followed by the intercalation of organic ions into the PbX_2 ($X = \text{I}$ and Br) structure.^[26] The initial size of PbX_2 precipitate may increase with increasing γ and exceeds some critical value when γ increases to 7.5, making it difficult for the FA cations to efficiently intercalate to all reaction sites, thus resulting in incomplete conversion in 0.8-7.5B OIHP thin film.

The bandgap of the 0.8- γ B ($\gamma = 0, 2.5, 5$, and 7.5) OIHP films is determined to be ≈ 1.72 eV through the Tauc plots (Figure 1g). The absorption edge turns to be steeper with the addition of solution B, suggesting reduced lattice defects.^[31] Time-resolved photoluminescence (TRPL) measurement was performed on the OIHP films deposited on glass, and the results are shown in Figure 1h. The carrier lifetime is derived by fitting the exponential decay and the fitting details are provided in Figure S5 and Table S1 of the Supporting Information. It can be seen that the carrier lifetime is increased from 32.44 ± 0.16 ns for the 0.8-0B film to 55.88 ± 0.11 ns and 97.80 ± 0.77 ns for the 0.8-2.5B and 0.8-5B films, respectively, and it drops to 60.74 ± 0.14 ns for the 0.8-7.5B film. This trend in carrier lifetime

Figure 2. AFM measurement results for the WB-OIHP films with small-grain morphology (prepared without $\text{Pb}(\text{SCN})_2$) and large-grain morphology (prepared with $\text{Pb}(\text{SCN})_2$). AFM height images of a) small grain film without (W/O) excess FAX (0.8-0B), c) small grain film with (W/) excess FAX (0.8-5D), e) large grain film W/O excess FAX (0.8-5C), and g) large grain film W/ excess FAX (0.8-5B). c-AFM images of the corresponding b) small grain film W/O excess FAX (0.8-0B), d) small grain film W/ excess FAX (0.8-5D), f) large grain film W/O excess FAX (0.8-5C), and h) large grain film W/ excess FAX (0.8-5B). The c-AFM images are taken with a bias voltage of 2.5 V applied.

correlates well with the aforementioned modification effect in grain crystallinity and surface passivation. The structural disorder inside grain or at grain boundaries, in forms of vacancy or interstitial defects, has been shown to form detrimental charge trap states that may lead to trap-assisted nonradiative charge recombination.^[1,32,33] The improvement in crystallinity and the passivation of surface defects at grain boundaries can both contribute to improved carrier lifetime. However, when residual PbX_2 ($X = \text{I}$ and Br) starts to form, it may degrade the crystal quality of the perovskite around and leads to reduced carrier lifetime.^[26] Therefore, we attained the optimized y value to be 5 for good phase stability and long carrier lifetime.

To further confirm that excess FAX contributes to grain boundary modification, we performed atomic force microscope (AFM) and conductive AFM (c-AFM) measurements on the 0.8-0B, 0.8-5D, 0.8-5C, and 0.85-5B OIHP films, with the first two corresponding to small grains with and without excess FAX, and the last two corresponding to large grains with and without excess FAX. As shown in **Figure 2a–h**, for all four samples the current flow from the grain boundaries to the AFM tip is higher than the current flow from the grains to the tip. Among the four samples, the grain boundary current of the 0.8-5D and 0.8-5B thin films (i.e., the “FAX-excess” samples) is clearly larger than that of the 0.8-0B and 0.8-5C OIHP thin films (**Figure 2a–d**). The two observations both agree well with the previous c-AFM study on MAPbI_3 perovskite films with and without excess MAI,^[1] and suggest the presence of excess FAX at the grain boundaries and their passivation effect.

In order to examine the applicability of the grain engineering method on wider bandgap OIHPs, we fixed y to 5 and

extended the x value to 1.2, 1.5, and 1.8. We found all the x -5B ($x = 1.2, 1.5$, and 1.8) OIHPs show greatly improved grain size (**Figure S6a–f**, Supporting Information) and crystallinity (**Figure S6g–i**, Supporting Information) as compared with the corresponding samples prepared without addition of solution B. The bandgap of the x -5B ($x = 1.2, 1.5$, and 1.8) OIHP thin films are derived from the Tauc plots (**Figure S6j–l**, Supporting Information) to be 1.79, 1.86, and 1.93 eV, respectively.

We now examine the photostability of the WB-OIHP before and after different grain treatments. We monitored the photoluminescence (PL) spectra of the x - y B ($x = 0.8, 1.2, 1.5$, and 1.8 ; $y = 0$ and 5) OIHP thin films under continuous light soaking of a 405 nm laser with an intensity around 150 mW cm^{-2} . The left column of **Figure 3** illustrates the morphology characteristic of each sample. As shown in **Figure 3a**, the 0.8-0B (i.e., untreated, $x = 0.8$) OIHP thin film shows slight red-shift in the PL peak under continuous light soaking. With the increasing of x to 1.2, 1.5, and 1.8, an additional PL peak at a longer wavelength appears and becomes more and more prominent under continuous light soaking (**Figure 3b–d**), manifesting photoinduced phase segregation in these WB-OIHPs.^[19] It is apparent that the photostability of the untreated WB-OIHP thin films decays rapidly with the increase of bandgap (**Figure 3a–d**). By introducing excess FAX into the OIHP (second row of **Figure 3**), i.e., by adding solution D to the parent precursor solution to obtain x -5D ($x = 0.8, 1.2, 1.5$, and 1.8) OIHPs, we observed a much slower upraise of the low energy PL peak and thus suppressed phase segregation (**Figure 3e,f**). The photostability improvement is due to grain boundary passivation by excess FAX ($X = \text{I}$ and Br),^[20,26,28,29] which blocks the preferred path

Figure 3. PL spectra of the OIHP thin films monitored under continuous light soaking with a 405 nm laser with an intensity around 150 mW cm^{-2} over 5 min: a) 0.8-0B, b) 1.2-0B, c) 1.5-0B, d) 1.8-0B, e) 0.8-5D, f) 1.2-5D, g) 1.5-5D, h) 1.8-5D, i) 0.8-5C, j) 1.2-5C, k) 1.5-5C, l) 1.8-5C, m) 0.8-5B, n) 1.2-5B, o) 1.5-5B, and p) 1.8-5B. PL spectra of the OIHP thin films monitored under continuous light soaking with a 405 nm laser with an intensity equivalent to 1 sun (the intensities are 66.7 mW cm^{-2} , 60.0 W cm^{-2} , 54.9 W cm^{-2} , 51.3 W cm^{-2} for $x = 0.8, 1.2, 1.5$, and 1.8 , respectively) over 4 h: q) 0.8-5B, r) 1.2-5B, s) 1.5-5B, and t) 1.8-5B. The bandgap (E_g) values of the OIHP thin films are 1.72, 1.79, 1.86, and 1.93 eV for $x = 0.8, 1.2, 1.5$, and 1.8 , respectively, and the corresponding schematics of the film morphology are shown in the left column.

of ion migration and accordingly suppresses phase segregation.^[34,35] We also found that by just enlarging the grain size (corresponding to x -5C, $x = 0.8, 1.2, 1.5$, and 1.8) the photostability could also be improved (Figures 3i–l), which may be attributed to the reduced number of bulk grain defects and grain boundaries. Lastly, by using the solution B additive (corresponding to x -5B, $x = 0.8, 1.2, 1.5$, and 1.8), we combined large grain and FAX grain boundary-passivation (last two rows of Figure 3). The PL spectra of the resultant WB-OIHP thin films demonstrate barely no change under both short-period (5 min, 150 mW cm^{-2}) light-stress (Figure 3m–p) and extended-period

(4 h, intensity equivalent to 1 sun) light-stress (Figure 3q–t), except that the widest bandgap 1.8-5B sample showed a small PL peak red-shift after 4 h stressing. These results demonstrate the strong synergistic effects of crystallinity improvement and grain surface passivation in achieving high photostability. Furthermore, we stressed the x -0.5B ($x = 0.8, 1.2, 1.5$, and 1.8) samples under a 200 mW cm^{-2} white light illumination and at 85°C , and observed good thermal-photostability of the films, as shown in Figure S7a–d of the Supporting Information.

To find out how the crystallinity and photostability improvement are correlated with the PV performances of the

WB-OIHP thin films, we incorporated the films into an FTO/SnO₂/perovskite/spiro-MeOTAD/Au structure and measured the PV characteristics. The statistics of the solar cells prepared from ($\gamma = 0, 2.5, 5$, and 7.5) OIHP thin films are shown in Figure S8a–d of the Supporting Information, and the result demonstrates the optimal performance can be achieved at $\gamma = 5$, where the crystallinity, phase purity, and carrier lifetime are maximized. The PV performance of the solar cells prepared from x - γ B ($x = 0.8, 1.2, 1.5$, and 1.8 ; $\gamma = 0$ and 5) are summarized in Figure 4a–d. In general, as compared with the x -0B ($x = 0.8, 1.2, 1.5$, and 1.8) based solar cells, the x -5B ($x = 0.8, 1.2, 1.5$, and 1.8) based solar cells show much improved PV performances with small disparity of V_{oc} , FF, and PCE between the forward and backward scans. Importantly, the average V_{oc} of the x -5B ($x = 0.8, 1.2, 1.5$, and 1.8) based solar cells increases monotonically with the increasing bandgap, from (1.223 ± 0.014) V for bandgap of 1.72 eV (0.8 -5B) to (1.254 ± 0.019) V, (1.272 ± 0.019) V, and (1.286 ± 0.017) V for 1.79 eV (1.2 -5B), 1.86 eV (1.5 -5B), and 1.93 eV (1.8 -5B), respectively (Figure 4a). The champion devices prepared from x -5B ($x = 0.8, 1.2, 1.5$, and 1.8) show a V_{oc} /stable output efficiency combination of up to 1.244 V/18.60%, 1.284 V/16.51%, 1.296 V/15.01%, and 1.312 V/14.35%, for $x = 0.8, 1.2, 1.5$, and 1.8 OIHPs, respectively (Figure 4e,f). The loss-in-potential of these cells is lowest among the reported values for the same bandgap range. By contrast, the average V_{oc} of the untreated solar cells, i.e., x -0B OIHPs, does not manifest a bandgap dependence and exhibit similar V_{oc} constraint as previously reported WB-OIHPs in the similar bandgap range,^[9,36] most likely due to the photo-induced formation of the lower bandgap phase in these WB-OIHPs.^[19,20]

3. Conclusions

In conclusion, we have demonstrated a highly reproducible way of achieving high-quality and well-passivated wide-bandgap Cs_{0.17}FA_{0.83}PbI_{3-x}Br_x ($x = 0.8, 1.2, 1.5$, and 1.8) OIHPs through Pb(SCN)₂ assisted crystallization and FAX ($X = I$ and Br) grain boundary healing. Our results suggest the synergistic effects of the precursor additive in enhancing film crystallinity and grain size, reducing impurity and passivating grain boundaries. Accordingly, the carrier lifetime in the composition-optimized perovskite films shows a significant improvement, and the photoinduced phase segregation is greatly suppressed. In addition, the thermal-photostability is also improved in the films. Remarkably, the highly crystallized and well passivated WB-OIHP based solar cells show greatly reduced hysteresis and excellent photovoltaic performance. The average and maximum values of V_{oc} of the solar cells show monotonically increase with bandgap and exhibits low loss-in-potential in the 1.72 – 1.93 eV range. The stabilized output efficiencies of the champion solar cells reach 18.60%, 16.51%, 15.01%, and 14.35% for $x = 0.8, 1.2, 1.5$, and 1.8 OIHPs, respectively. This study not only elucidates the importance of combining crystallinity improvement and grain boundary passivation in achieving stable wide bandgap mixed halide perovskites, but also provides fabrication guidelines for realizing high performance perovskite-based tandem cells.

4. Experimental Section

Substrate Cleaning: Nippon Sheet Glass was cleaned by sonication in a 2% Hellmanex water solution for 30 min. After rinsing with deionized water and ethanol, the substrates were further cleaned with isopropanol, acetone, and isopropanol for 30 min, respectively. Then the substrates were dried and stored in a dry box with the humidity controlled under 30% RH.

Preparation of SnO₂ Films: The SnO₂ colloid precursor was obtained from Alfa Aesar (tin(IV) oxide, 15% in H₂O colloidal dispersion). Before use, the SnO₂ colloid precursor was mixed with water in a volume ratio of 1:5.67. The FTO substrates were treated by UV-Ozone for 15 min before depositing of SnO₂. Then the diluted SnO₂ colloid solution was spin coated onto FTO substrates at 3000 rpm for 30 s, and then baked on a hotplate in ambient air (humidity around 70% RH, temperature around 22 °C) at 120 °C for 10 min then at 180 °C for 30 min. After annealing the hotplate was turn down and the FTO substrates cooled down to room temperature naturally. Then the substrates were treated by UV-Ozone one more time for 15 min and were then transferred to glovebox.

Preparation of Perovskite Films: Solutions of (CsI)_{0.17}(FAI)_{0.83}(PbI₂)_{1-0.5x}(PbBr₂)_{0.5x} ($x = 0.8, 1.2, 1.5$, and 1.8) were prepared by mixing 0.17 M CsI (Dyesol), 0.83 M FAI (Dyesol), (1-0.5x) M PbI₂ (TCI, 99.999%), and 0.5x M PbBr₂ (TCI, 99.999%) in anhydrous DMF:DMSO 9:1 (v:v) and stirred overnight (denoted as solution A). Solutions of (CsI)_{0.17}(FAI)_{0.83}[Pb(SCN)₂ + 3FAI]_{1-0.5x}[Pb(SCN)₂ + 3FABr]_{0.5x} were prepared by mixing 0.17 M CsI (Dyesol), (3.83-1.5x) M FAI (Dyesol), 1.5x M FABr (Dyesol), and 1 M Pb(SCN)₂ (Sigma-Aldrich, 99.999%) in anhydrous DMF:DMSO 9:1 (v:v) and stirred overnight (denoted as solution B). Solutions of Pb(SCN)₂ was prepared by dissolving 1 M Pb(SCN)₂ (Sigma-Aldrich, 99.999%) in anhydrous DMF:DMSO 9:1 (v:v) and stirred overnight. Solutions of (CsI)_{0.17}(FAI)_{0.83}[Pb(SCN)₂ + 2FAI]_{1-0.5x}[Pb(SCN)₂ + 2FABr]_{0.5x} were prepared by mixing 0.17 M CsI (Dyesol), (2.83-x) M FAI (Dyesol), x M FABr (Dyesol), and 1 M Pb(SCN)₂ (Sigma-Aldrich, 99.999%) in anhydrous DMF:DMSO 9:1 (v:v) and stirred overnight (denoted as solution C). Solutions of (CsI)_{0.17}(FAI)_{0.83}[PbI₂ + FAI]_{1-0.5x}[PbBr₂ + FABr]_{0.5x} were prepared by mixing 0.17 M CsI (Dyesol), (1.83-0.5x) M FAI (Dyesol), 0.5x M FABr (Dyesol), (1-0.5x) M PbI₂ (TCI, 99.999%) 0.5x M PbBr₂ (TCI, 99.999%) in anhydrous DMF:DMSO 9:1 (v:v) and stirred overnight (denoted as solution D). The precursor solutions were spin-coated onto the glass or SnO₂/FTO substrates in a two-step procedure at 500 and 6000 rpm for 2 and 40 s, respectively. During the second step, 120 μ L of chlorobenzene was casted onto the substrates 3 s after the beginning of the second spinning step. The films were placed on a hotplate at 100 °C for 60 min. The preparation of perovskite thin films was performed in a N₂-purged glovebox.

Preparation of Hole Transport Layer and Au Electrode: The hole transport layer precursor was prepared by dissolving 72.3 mg spiro-MeOTAD (TRC, Canada), 28 μ L 4-tert-butylpyridine (Sigma-Aldrich, 96%) and 17.5 μ L bis(trifluoromethane)sulfonimide lithium salt (Sigma-Aldrich) solution (520 mg Li-TFSI in 1 mL acetonitrile) in 1 mL chlorobenzene. The precursor was then spin-coated on the perovskite layer at 4000 rpm for 30 s. The deposition of the hole transport layer was in dropbox. Then the solar cells were transferred to a box with dry air (humidity lower than 20% RH) for oxidation for 16 h. Finally, a 100 nm Au electrode layer was deposited under a vacuum of $<1 \times 10^{-4}$ Pa with a rate of 0.1 nm s⁻¹. The preparation of Au electrode was performed in a N₂-purged glovebox.

Measurement and Characterization: The film morphology was characterized using SEM (Quanta 400). The XRD patterns of the samples were recorded using a Rigaku RU-300 diffractometer equipped with Cu K α_1 irradiation ($\lambda = 1.5406$ Å). UV–vis absorption spectra were taken on a Hitachi U-3501 UV–vis–NIR spectrophotometer. TRPL measurements were performed by exciting the samples with the second harmonic (400 nm) of a mode-locked femtosecond Ti:sapphire laser with a repetition rate of 76 MHz (Mira 900, Coherent). The excitation density was reduced to be 1.4μ J cm⁻² by a neutral density filter. The spectra were detected using a Hamamatsu streak camera, working on

Figure 4. PV parameter statistics of the x -yB ($x = 0.8, 1.2, 1.5$, and 1.8 ; $y = 0$ and 5) OIHP thin film-based devices in forward and backward scans: a) V_{oc} , b) J_{sc} , c) FF, and d) PCE. e) $I-V$ curves of the champion cells with $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_{3-x}\text{Br}_x$ ($x = 0.8, 1.2, 1.5$, and 1.8) as light absorbers. f) Stable output efficiency of the champion cells of $\text{FA}_{0.17}\text{Cs}_{0.83}\text{PbI}_{3-x}\text{Br}_x$ ($x = 0.8, 1.2, 1.5$, and 1.8) stressed at 1.06, 1.08, 1.08, and 1.10 V under 1 sun illumination, respectively.

the single sweep mode. The repetition rate of excitation was reduced by a pulse picker. The AFM and conductive AFM images were taken by a commercial atomic force microscope (SPA-400, SII), equipped with Pt/Ir-coated Si tips (SCM-PIT-V2, Bruker) with a typical resonance frequency of 75 kHz and a spring constant of 3 N m⁻¹. All images were acquired with bias voltages of 2.5 V at a scan rate of 0.5 Hz. Positive

bias was applied to the substrate, while the tips were grounded. The current and topographic images were taken simultaneously in ambient conditions with the humidity controlled lower than 30% RH. The PL spectra were measured by a spectrometer of AvaSpec ULS2048 × 64 (Avantes), under the excitation of 405 nm light source with varied intensities. All the samples were encapsulated and measured in

ambient air. The photothermal stressing was conducted under a white LED with an intensity of around 200 mW cm^{-2} at 85°C . The current density–voltage (J – V) curves were measured under simulated AM 1.5 1 sun illumination (100 mW cm^{-2} , 94011A-ES, ABB). The light intensity was adjusted by means of a Newport calibrated Si solar cell (91150-KG5, Newport). The mismatch factor was calculated to be less than 2%. The active area of the solar cell is 0.0893 cm^2 defined by an aperture. The area was determined by an optical microscope. The forward J – V scans were measured from forward bias to short-circuit and the backward scans were from short-circuit to forward bias, both at a scan rate of 100 mV s^{-1} . A stabilization time of 5 s at forward bias of 1.35 V under illumination was performed prior to scanning. The stable output efficiency was measured by stressing the devices around the maximum power output point under 1 sun illumination in N_2 filled glovebox. EQE were measured with a Keithley 2400 Source Meter under monochromatic illumination generated by passing the light beam from a 250 W quartz tungsten halogen lamp into a Newport 74215 Oriol Cornerstone 260 1/4 m monochromator. A calibrated silicon diode with a known spectral response was used as a reference.

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.

Keywords

crystallinity, grain boundaries passivation, open-circuit voltage deficit, photostability, wide-bandgap perovskites

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- [1] D. Son, J. Lee, Y. J. Choi, I. Jang, S. Lee, P. J. Yoo, H. Shin, N. Ahn, M. Choi, D. Kim, *Nat. Energy* **2016**, 1, 16081.
- [2] F. Wang, W. Geng, Y. Zhou, H. H. Fang, C. J. Tong, M. A. Loi, L. M. Liu, N. Zhao, *Adv. Mater.* **2016**, 28, 9986.
- [3] N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo, S. I. Seok, *Nature* **2015**, 517, 476.
- [4] M. Saliba, T. Matsui, J. Seo, K. Domanski, J. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, *Energy Environ. Sci.* **2016**, 9, 1989.
- [5] M. Saliba, T. Matsui, K. Domanski, J. Seo, A. Ummadisingu, S. M. Zakeeruddin, J. Correa-Baena, W. R. Tress, A. Abate, A. Hagfeldt, *Science* **2016**, 354, 206.
- [6] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, 131, 6050.
- [7] http://nrel.gov/ncpv/images/efficiency_chart.jpg (accessed: April 2018).
- [8] F. Hao, C. C. Stoumpos, R. P. H. Chang, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2014**, 136, 8094.
- [9] J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, S. I. Seok, *Nano. Lett.* **2013**, 13, 1764.
- [10] G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz, H. J. Snaith, *Energy Environ. Sci.* **2014**, 7, 982.
- [11] D. P. McMeekin, G. Sadoughi, W. Rehman, G. E. Eperon, M. Saliba, M. T. Hörantner, A. Haghighirad, N. Sakai, L. Korte, B. Rech, M. B. Johnston, L. M. Herz, H. J. Snaith, *Science* **2016**, 351, 151.
- [12] G. E. Eperon, T. Leijtens, K. A. Bush, R. Prasanna, T. Green, J. T. Wang, D. P. McMeekin, G. Volonakis, R. L. Milot, R. May, *Science* **2016**, 354, 861.
- [13] D. Zhao, Y. Yu, C. Wang, W. Liao, N. Shrestha, C. R. Grice, A. J. Cimaroli, L. Guan, R. J. Ellingson, K. Zhu, *Nat. Energy* **2017**, 2, 17018.
- [14] M. T. Hörantner, T. Leijtens, M. E. Ziffer, G. E. Eperon, M. G. Christoforo, M. D. McGehee, H. J. Snaith, *ACS Energy Lett.* **2017**, 2, 2056.
- [15] K. A. Bush, A. F. Palmstrom, J. Y. Zhengshan, M. Boccard, R. Cheacharoen, J. P. Mailoa, D. P. McMeekin, R. L. Hoyer, C. D. Bailie, T. Leijtens, *Nat. Energy* **2017**, 2, 17009.
- [16] T. Duong, Y. Wu, H. Shen, J. Peng, X. Fu, D. Jacobs, E. C. Wang, T. C. Kho, K. C. Fong, M. Stocks, *Adv. Energy Mater.* **2017**, 7, 1700228.
- [17] T. Todorov, T. Gershon, O. Gunawan, Y. S. Lee, C. Sturdevant, L. Y. Chang, S. Guha, *Adv. Energy Mater.* **2015**, 5, 1500799.
- [18] A. Guchhait, H. A. Dewi, S. W. Leow, H. Wang, G. Han, F. B. Suhaimi, S. G. Mhaisalkar, L. H. Wong, N. Mathews, *ACS Energy Lett.* **2017**, 2, 807.
- [19] E. T. Hoke, D. J. Slotcavage, E. R. Dohner, A. R. Bowring, H. I. Karunadasa, M. D. McGehee, *Chem. Sci.* **2015**, 6, 613.
- [20] A. J. Barker, A. Sadhanala, F. Deschler, M. Gandini, S. P. Senanayak, P. M. Pearce, E. Mosconi, A. Pearson, Y. Wu, A. R. Srimath Kandada, *ACS Energy Lett.* **2017**, 2, 1416.
- [21] C. Yi, J. Luo, S. Meloni, A. Boziki, N. Ashari-Astani, C. Grätzel, S. M. Zakeeruddin, U. Röhrlisberger, M. Grätzel, *Energy Environ. Sci.* **2016**, 9, 656.
- [22] C. G. Bischak, C. L. Hetherington, H. Wu, S. Aloni, D. F. Ogletree, D. T. Limmer, N. S. Ginsberg, *Nano Lett.* **2016**, 17, 1028.
- [23] M. Hu, C. Bi, Y. Yuan, Y. Bai, J. Huang, *Adv. Sci.* **2015**, 3, 1500301.
- [24] W. Ke, C. Xiao, C. Wang, B. Saparov, H. S. Duan, D. Zhao, Z. Xiao, P. Schulz, S. P. Harvey, W. Liao, *Adv. Mater.* **2016**, 28, 5214.
- [25] Y. Yu, C. Wang, C. R. Grice, N. Shrestha, D. Zhao, W. Liao, L. Guan, R. Awai, W. Meng, A. J. Cimaroli, *ACS Energy Lett.* **2017**, 2, 1177.
- [26] T. J. Jacobsson, J. Correa-Baena, E. Halvani Anaraki, B. Philippe, S. D. Stranks, M. E. Bouduban, W. Tress, K. Schenk, J. Teuscher, J. Moser, *J. Am. Chem. Soc.* **2016**, 138, 10331.
- [27] F. Liu, Q. Dong, M. K. Wong, A. B. Djurišić, A. Ng, Z. Ren, Q. Shen, C. Surya, W. K. Chan, J. Wang, *Adv. Energy Mater.* **2016**, 6, 1502206.
- [28] M. Abdi-Jalebi, Z. Andaji-Garmaroudi, S. Caciovich, C. Stavrakas, B. Philippe, J. M. Richter, M. Alsari, E. P. Booker, E. M. Hutter, A. J. Pearson, *Nature* **2017**, 555, 497.
- [29] Y. Zhou, F. Wang, Y. Cao, J. P. Wang, H. H. Fang, M. A. Loi, N. Zhao, C. P. Wong, *Adv. Energy Mater.* **2017**, 7, 1701048.
- [30] F. Brivio, C. Caetano, A. Walsh, *J. Phys. Chem. Lett.* **2016**, 7, 1083.
- [31] S. De Wolf, J. Holovsky, S. Moon, P. Löper, B. Niesen, M. Ledinsky, F. Haug, J. Yum, C. Ballif, *J. Phys. Chem. Lett.* **2014**, 5, 1035.
- [32] M. L. Agiorgousis, Y. Y. Sun, H. Zeng, S. Zhang, *J. Am. Chem. Soc.* **2014**, 136, 14570.
- [33] S. M. Vorpahl, S. D. Stranks, H. Nagaoka, G. E. Eperon, M. E. Ziffer, H. J. Snaith, D. S. Ginger, *Science* **2015**, 348, 683.
- [34] Y. Shao, Y. Fang, T. Li, Q. Wang, Q. Dong, Y. Deng, Y. Yuan, H. Wei, M. Wang, A. Gruverman, *Energy Environ. Sci.* **2016**, 9, 1752.
- [35] Y. Yuan, J. Huang, *Acc. Chem. Res.* **2016**, 49, 286.
- [36] T. J. Jacobsson, J. Correa-Baena, M. Pazoki, M. Saliba, K. Schenk, M. Grätzel, A. Hagfeldt, *Energy Environ. Sci.* **2016**, 9, 1706.