Intermediate phase-enhanced Ostwald ripening for the elimination of phase segregation in efficient inorganic CsPbIBr₂ perovskite solar cells

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ABSTRACT Mixed halide perovskites with the ability to tune bandgaps exhibit attractive applications in tandem solar cells, building integrated photovoltaic and wavelength-tunable light-emitting devices. However, halide demixing under illumination or in the dark with a charge-carrier injection in both hybrid and inorganic perovskites results in bandgap instability and current-density-voltage (*J*-*V*) hysteresis, which can significantly hamper their application. Here, we demonstrate that halide segregation and *J*-*V* hysteresis in mixed halide inorganic CsPbIBr₂ solar cells can be effectively mitigated by introducing an intermediate phase-enhanced Ostwald ripening through the control of the chemical composition in the CsPbIBr₂ precursor solution. Excess amounts of either PbBr₂ or CsI are incorporated into originally even molar amounts of PbBr₂ and CsI precursor solutions. With the PbBr₂-excess, we observed an enlarged perovskite grain size, no detectable halide phase segregation at the grain boundaries nor the perovskite/TiO₂ interface, an increased minority carrier lifetime, a reduced *J*-*V* hysteresis, and an improved solar-cell performance. However, different CsI:PbBr₂ stoichiometric ratios were found to have different effects on the performance of the perovskite solar cell. The excessive lead phase is reactive with

the dimethyl sulfoxide (DMSO) in the precursor solution to form the Pb(I, Br)₂-DMSO complex and the quasi-two-dimensional (2D) CsPb₂(I, Br)₅, which are conducive to Ostwald maturation and defect extinction. Finally, the CsPbIBr₂ solar cell with a PbBr₂-excess precursor composition reaches a power conversion efficiency (PCE) of 9.37% (stabilized PCE of 8.48%) and a maximum external quantum efficiency of over 90%.

Keywords: solar cells, phase segregation, CsPbIBr₂, cathodoluminescence, transmission electron microscope

INTRODUCTION

Photoactive materials with the perovskite structure show great potential in the next-generation photovoltaics and optoelectronics. In particular, the ability to tune bandgaps with adjustments of the composition is one of the most attractive properties for their potential applications in tandem solar cells [1], building integrated photovoltaics [2], and wavelength-tunable light-emitting devices (LEDs) [3]. The bandgap of perovskite absorbers can be continuously tuned from approximately 1.2 to 2.3 eV by

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varying the composition of the ABX_3 formula, with A cations, such as methylammonium ($CH_3NH_2^+$), formamidinium ($CH(NH_2)_2^+$), and cesium (Cs^+); B cations such as tin (Sn^{2+}) and lead (Pb^{2+}); and halides, such as iodide (I^-), bromide (Br^-), and chloride (Cl^-), as the X anion [4,5]. However, both hybrid and inorganic perovskites with a large bandgap are subject to bandgap instability due to halide demixing under illumination or in the dark with charge-carrier injection [6–9]. Halide segregation can prevent the achievement of spectrally stable LED devices [10] and, also, potentially enhance ion migration and alter the electric-field gradients within the solar cell, negatively influencing the performance and stability of the device [8,11–14].

Halide segregation within an initially perfect single crystal, such as $CsPbI_{3-x}Br_x$, is not energetically favorable as a large lattice mismatch exists between the iodide-rich and bromide-rich phases [15]. However, near a defect, such as a grain boundary (GB), the lattice mismatch may be more easily accommodated with a lower energy penalty. Furthermore, the formation energy of the point defects at the GBs, and the film's surfaces can be much lower than that in the grain interiors [16,17]. In our previous study, cathodoluminescence (CL) was employed to further reveal the nanoscale halide phase segregation in inorganic $CsPbIBr_2$, in which the iodide-rich $CsPbI_{1+x}Br_{2-x}$ phases were identified to segregate at the GBs [8]. The crystalline defects, typically halide vacancies and interstitials, promoted halide migration and segregation by providing low-energy migration pathways that could potentially lead to current-density-voltage ($J-V$) hysteresis [17–19]. Furthermore, a free carrier trapped at the defective GBs with a low bandgap, such as the iodide-rich phase of $CsPbI_{3-x}Br_x$, could greatly increase the recombination rate [20].

Therefore, it is important to understand the relationship between the phase segregation and the crystalline defects to further improve the performance and stability of the perovskite solar cells (PSCs). The $CsPbI_{3-x}Br_x$ inorganic perovskites exhibit better structural stability than the hybrid perovskites under electron beams, enabling analysis of the relationship between the phase segregation and the defects' details by advanced electron microscopy techniques [17,21–24]. Furthermore, $CsPbI_{3-x}Br_x$ inorganic perovskites are more thermally stable than hybrid perovskites; thus, they have attracted increasing amounts of attention for their photovoltaic and light-emitting properties [7,25–33].

In this paper, we attempt to improve the quality of the $CsPbIBr_2$ crystal to suppress the halide segregation to

achieve a photo-stable material [15,18]. Excess amounts of $PbBr_2$ or CsI were incorporated into the inorganic $CsPbIBr_2$, prepared from originally even molar amounts of $PbBr_2$ and CsI . We found that the $PbBr_2$ -excess composition favored the formation of $Pb(I, Br)_2$ -dimethyl sulfoxide (DMSO), and quasi-two-dimensional (2D) $CsPb_2(I, Br)_5$. These intermediate phases greatly enhanced the Ostwald ripening, reducing the interface energy and increasing the mass transportation of the constituents for $CsPbIBr_2$ crystal growth [34,35]. A significantly larger grain size and a lower defect density were achieved by compositional engineering *via* the $PbBr_2$ -excess composition. Therefore, no halide phase segregation was detected at the GBs nor the perovskite/ TiO_2 interfaces, and there was an increased minority carrier lifetime, a reduced $J-V$ hysteresis, and an improved solar-cell performance. In contrast, the CsI -excess did not improve the properties of the $CsPbIBr_2$ PSCs in any way.

EXPERIMENTAL SECTION

Materials

Unless specified otherwise, all the materials were purchased from either Alfa Aesar or Sigma-Aldrich and used as received. Spiro-OMeTAD (2,2',7,7'-tetrakis (*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene) was purchased from Luminescence Technology Corp.

Device fabrication

A dense TiO_2 blocking layer was first deposited on a clean fluorine-doped tin oxide (FTO) glass by spray pyrolysis at 450°C, using a bis(isopropoxide)-bis(acetylacetonate)titanium(IV) solution. After cooling to room temperature, the substrate was cut into smaller pieces of approximately 1 cm².

A concentration of 0.7 or 1 mol L⁻¹ $CsPbIBr_2$ in a DMSO precursor solution was then prepared from CsI and $PbBr_2$, at a molar ratio of 1:1 for the stoichiometric, 1.05:1 for the CsI -excess, and 1:1.05 for the $PbBr_2$ -excess compositions. A compact $CsPbIBr_2$ film was spin-coated onto a TiO_2 -coated FTO substrate by the gas-assisted method in which dry argon (Ar) gas at 40 psi (1 psi = 6.895 kPa) was blown over the film's surface for 30 s, once the spinning speed reached 1000 r min⁻¹. The films were then annealed at 320°C for 20 min in a tube furnace with an Ar atmosphere. Subsequently, 25 µL of the spiro-OMeTAD solution (prepared by dissolving 41.6 mg of spiro-OMeTAD in 0.5 mL of chlorobenzene and adding 7.5 µL of a stock solution of 520 mg mL⁻¹ of lithium bis(trifluoromethylsulphonyl)imide in acetonitrile) and

16.9 μL of 4-*tert*-butylpyridine was coated onto the CsPbIBr_2 film by spin-coating at 3000 r min^{-1} for 30 s in a glove box filled with nitrogen. Finally, an 80-nm gold layer was deposited by thermal evaporation to form the complete device.

CL characterization

CL characterization was performed using an FEI Nova NanoSEM 450 scanning electron microscope (SEM) equipped with a Delmic SPARC CL System. The CsPbIBr_2 films for CL characterizations were deposited on a typical substrate used for photovoltaic devices [24], consisting of layers of TiO_2 , FTO, and glass. Before the CL characterization, the CsPbIBr_2 films were kept in a dark vacuum chamber for more than 10 min to avoid unintended light-induced phase segregation. All of the CL mappings were recorded from the previously unexposed regions of the sample, except when specifically indicated. The CL measurements were carried out under electron-beam-accelerating voltages of 2 and 5 kV. A fresh cross-section was created by direct mechanical cleaving just before loading the sample into the SEM chamber for cross-sectional CL mapping.

At the electron-beam-acceleration voltage of 2 kV, the CL intensity mapping through the photomultiplier tube (PMT) was obtained with a resolution of 1024×1024 pixels ($\sim 11 \text{ nm}$ on each side) and a dwell time of 300 μs per pixel, while the CL spectral maps were obtained with a dwell time of 200 ms per pixel. The electron-beam current was fixed at 440 pA.

At the electron-beam-acceleration voltage of 5 kV, the CL-PMT maps were obtained with a resolution of 1024×1024 pixels ($\sim 11 \text{ nm}$ on each side) and a dwell time of 50 μs per pixel, while the CL spectral maps were obtained with a dwell time of 10 ms. The electron-beam current was fixed at 799 pA.

Photoluminescence

The photoluminescence (PL) spectra were collected by a confocal microscope system (WITec, alpha 300R) in ambient conditions. The CsPbIBr_2 samples were excited using a 532-nm laser source. The time-resolved PL (TRPL) decay traces were measured using a time-correlated single photon counting (TCSPC) technique on a Micro Time 200 (Picoquant) microscope, by 470-nm laser excitation at a 1 MHz repetition rate and detection through a bandpass pass filter ($582 \pm 75 \text{ nm}$). The excitation power density was 300 mW cm^{-2} . The PL decay traces measured by the TCSPC were well fitted with a bi-exponential function:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right), \quad (1)$$

where $I(t)$ was the time-dependent PL intensity, τ_1 and τ_2 were the lifetimes of the fast and the slow decay components, respectively, and A_1 and A_2 were the corresponding amplitudes. From this, we defined the effective lifetime as [36]

$$\tau_{\text{eff}} = (A_1 \tau_1 + A_2 \tau_2) / (A_1 + A_2). \quad (2)$$

Solar-cell performance characterizations

Current-voltage characterization was performed using a solar simulator (Oriel) fitted with a filtered 1000 W xenon lamp to replicate AM 1.5, 100 mW cm^{-2} conditions. The illumination of the light source was calibrated using a silicon reference cell (Peccell Technologies) with a color filter to minimize the spectral mismatch between the calibration diode and the PSC. The J - V response was recorded using a Keithley 2400 source meter. The solar cells were masked with a non-reflective metal aperture of 0.16 cm^2 that defined the active area of the device. The J - V measurements were carried out with a scan rate of 100 mV s^{-1} from the forward bias to the short-circuit (reverse scan) and from the short-circuit to the forward bias (forward scan). The external quantum efficiency (EQE) measurements were performed using a 150 W xenon lamp (Oriel) fitted with a monochromator (Cornerstone 260). The EQE photocurrents were recorded under the short-circuit conditions using a Keithley 2400 source meter. The monochromatic photon flux was quantified *via* a calibrated silicon cell (Peccell Technologies).

Other characterizations

The perovskite samples for X-ray diffraction (XRD) were prepared on the TiO_2 -coated FTO-glass substrates and analyzed using a D2 PHASER (Bruker Corp.). Fourier transform infrared (FTIR) spectra were recorded with an Agilent Technologies Cary 630 spectrometer. The CsPbIBr_2 samples were deposited by spin-coating onto glass substrates and were scratched for analysis.

RESULTS

Crystal growth *versus* composition

Chemical composition engineering has already exhibited a significant influence on crystal growth, defect passivation, and solar-cell performance in hybrid perovskites [37,38]. Stoichiometric hybrid organic-inorganic perovskites can be achieved from a non-stoichiometric pre-

cursor solution since the excess organic cations are removed during annealing due to their volatile nature [38]. In contrast, due to the superior thermal stability of the inorganic components, excess CsX (X = I, Br) or PbX₂ are retained after annealing by the formation of secondary phases such as Cs₄PbX₆ and CsPb₂X₅, according to the phase diagram of PbBr₂-CsBr [39]. Compared with the hybrid perovskites, this more complicated phase diagram provides improved prospects for using compositional engineering to control the crystal growth process and, thereby, to improve the generation, transportation, and collection of free carriers, as well as the recombination in inorganic perovskites. Therefore, we first studied the effect of the precursor chemical composition on the CsPbIBr₂ crystal growth and the microstructure evolution during thermal annealing. (Hereafter, “CsI-excess” and “PbBr₂-excess” refer to excess of CsI or PbBr₂, respectively, being incorporated into originally even molar amounts of PbBr₂ and CsI precursor solution.)

The conversion from the precursor to the crystallized CsPbIBr₂ film was monitored morphologically, compositionally, and crystallographically by SEM, FTIR, and *in-situ* heating XRD, as shown in Fig. 1. All three compositions showed almost identical average grain sizes (<100 nm), after annealing at 70°C for 10 min. The *in-situ* heating and *ex-situ* XRD spectra in Fig. 1a and Fig. S1 prove that these small grains were mainly the “black phase” orthorhombic CsPbIBr₂ perovskite with XRD peaks at 15°, 21.2°, and 30.1°, corresponding to the {110}, {200}, and {220} planes [29]. The FTIR spectra for all three compositions indicated the existence of Pb(I, Br)₂·DMSO, showing a peak at ~900–1000 cm⁻¹ that corresponded to the S=O stretching vibration of the Pb(I, Br)₂·DMSO adduct, as shown in Fig. 1b [40–42].

As the annealing temperature was increased to 175°C and was maintained as such for 5 min, the average grain size of the CsPbIBr₂ increased to a few hundred nanometers for all three precursor compositions. The large CsPbIBr₂ crystals were grown at the expense of smaller ones, consistent with Ostwald ripening [34,35] (Ostwald ripening is a phenomenon observed in solid solutions or liquid sols that describes the change of an inhomogeneous structure over time, i.e., small crystals or sol particles dissolve and are redeposited onto larger crystals or sol particles). Ostwald ripening is driven by the reduction in the total surface free energy resulting from the enlarging grain size. It has been reported that DMSO released from the Pb(I, Br)₂·DMSO adduct in the CsPb(I, Br)₃ precursor film can greatly facilitate mass transport, enhancing the Ostwald ripening and defect annihilation

in the CsPb(I, Br)₃ [43,44] through the following reaction:

$$\text{Pb(I, Br)}_2 \cdot \text{DMSO} \rightarrow \text{Pb(I, Br)}_2 + \text{DMSO}. \quad (3)$$

However, as the annealing time was extended to 20 min (at 175°C), the crystal growth of the CsI-excess samples almost finished, while the stoichiometric and PbBr₂-excess samples kept growing. This was consistent with the fact that DMSO had been fully removed in the CsI-excess sample, while traces of DMSO could still be seen in the other two compositions after annealing at 175°C for 5 min (Fig. 1b).

After annealing at 175°C for 20 min, DMSO had been fully removed from all these three compositions, as suggested in Fig. 1b. Therefore, DMSO-assisted sintering could not explain the further crystal growth of the CsPbIBr₂ in the stoichiometric and the PbBr₂-excess samples. In the stoichiometric and the PbBr₂-excess samples, it was evident that the small crystals dispersed at the GBs had gradually merged into the growing CsPbIBr₂ large crystals with increasing temperature or time (Fig. 1a). This indicated that the growth of the CsPbIBr₂ crystals might have been further enhanced by these small crystals after the DMSO were fully evaporated. The CL spectra proved the existence of Pb(I, Br)₂ and CsPbIBr₂ in these small crystals, which showed a much lower CL intensity compared with the large CsPbIBr₂ crystals in Figs S2 and S3.

As the annealing continued, the residual small crystals migrated together and combined into larger crystals, which showed much darker secondary electron (SE) contrast in the SEM images collected at an acceleration voltage of 2 kV (Fig. 1a). In Fig. 2a, the energy dispersive spectrometer (EDS) results prove that the CsPb₂(I, Br)₅ grains (grains labeled as 1–3) showed much darker SE contrast than the CsPb(I, Br)₃ grains (grains labeled as 4–6). However, as the acceleration voltage for the SEM image increased from 2 to 10 kV, the contrast of the CsPb₂(I, Br)₅ and CsPb(I, Br)₃ grains became almost the same. Therefore, SEM at the low-acceleration voltage (2 kV) is an effective way to identify the distribution of CsPb₂(I, Br)₅ secondary phases. The existence of CsPb₂(I, Br)₅ was also identified by the *in-situ* heating XRD with a peak position at 11.3°, corresponding to the (001)_t orientation of the tetragonal CsPb₂(I, Br)₅ phase [45] (throughout this manuscript, the subscripts “t” and “o” denote indexing in the tetragonal and orthorhombic phases, respectively). The CsPb₂(I, Br)₅ phase was formed due to the following reaction:

As the annealing temperature increased to 240°C, the

Figure 1 (a) SEM images, (b) FTIR, and (c) *in-situ* heating XRD of the CsPbI₂Br thin films with the precursors of stoichiometric, CsI-excess, and PbBr₂-excess compositions at elevated annealing temperatures. The FTIR for the DMSO reference in (b) is obtained from reference [42]. The scale bars in the SEM images are 1 μ m. These SEM images are collected with an electron-beam-acceleration voltage of 2 kV. The samples for the FTIR are in the form of powder scratched from the deposited CsPbI₂Br films.

Pb(I, Br)₂ was fully converted to the CsPb₂(I, Br)₅ phase, as proved by the *in-situ* heating XRD analysis. However, after annealing at 320°C for 20 min, the CsPb₂(I, Br)₅ phase in the stoichiometric sample completely disappeared in both the SEM and the *in-situ* heating XRD. In contrast, in the PbBr₂-excess samples, the CsPb₂(I, Br)₅ phase was still present. From the observation above, it can be seen that the CsPb₂(I, Br)₅ and the CsPb(I, Br)₃ were mutually convertible. The small CsPb(I, Br)₃ crystals were

first converted to CsPb₂(I, Br)₅ when the excess Pb(I, Br)₂ was available. As the annealing temperature further increased, the CsPb₂(I, Br)₅ reacted with the remaining Cs(I, Br) to form CsPb(I, Br)₃, according to the following reaction:

Phase segregation versus composition

PL is a sensitive tag, identifying the phase segregation

Figure 2 (a–d) Investigation of the chemical composition of the photo-inactive phase in the PbBr₂-excess CsPbIBr₂ film. (a, b) SEM images with the same region in the PbBr₂-excess CsPbIBr₂ film with the electron-beam-acceleration voltages of 2 and 10 kV, respectively. (c, d) SEM image and CL-PMT map for the PbBr₂-excess CsPbIBr₂ film at the electron-beam-acceleration voltage of 2 kV, respectively. (e–h) Investigation of the photo-inactive phase evolution during the crystal growth of the PbBr₂-excess CsPbIBr₂ film at an annealing temperature of 170°C for 5 min (e, f), and 320°C for 20 min (g, h). (f, h) CL-PMT mapping corresponding to the SEM images of (f) and (g), respectively. (i, j) Chemical compositions obtained by EDS corresponding to the numbered points in (a, b) and (g, h), respectively. The scale bars are 3 μm.

with the formation of a strong red-shifted PL peak that was first reported by Hoke *et al.* [6]. Light-induced phase segregation was observed in the stoichiometric and CsI-excess CsPbIBr₂ samples, in which the PL spectra of these perovskites developed a new, red-shifted peak at 640–680 nm under constant 1-sun illumination in 100 s, as shown in Fig. S4a. This suggested that the CsPbIBr₂ segregated into two phases: an iodide-rich minority domain (CsPbI_{1+x}Br_{2-x}) and a bromide-rich majority domain (CsPbI_{1-x}Br_{2+x}) [31]. In contrast, the PbBr₂-excess sample showed much better stability under continuous laser exposure with the single PL peak remaining at ~585 nm, corresponding to the original CsPbIBr₂ phase;

this is also suggested by the plane view CL spectra maps in Fig. S5 (see Supplementary Discussion for the detailed analysis).

Cross-sectional CL mapping was employed to further reveal the influence of the TiO₂/perovskite interfacial defects on the phase segregation; this is not a well-studied phenomenon. We present CL maps of cross-sections of the CsPbIBr₂ films with stoichiometric, CsI-excess, and PbBr₂-excess precursor compositions, as shown in Fig. 3. The layered structure sequences in all these cross-sectional figures are the same as Fig. 3a (layers from top to bottom: CsPbIBr₂/c-TiO₂/transparent conducting oxide (TCO)). In both the stoichiometric and CsI-excess films,

Figure 3 The CL-PMT intensity mapping (labeled as PMT) and spectrum mapping (labeled as chromatic) used to investigate the phase segregation in the cross-section of the CsPbIBr₂ film (a) CsI-excess, (b) at stoichiometric, and (c) PbBr₂-excess compositions, using an electron-beam-acceleration voltage of 5 kV. All the scale bars are 1 μ m. The CL spectra corresponding to the circled region labeled in the CL spectrum are shown in the right figure of each composition. The color code in the CL spectral map indicates the wavelength of the emitted light, with the red regions having a longer emitted light wavelength than the green regions and the brightness indicating the emitted light intensity.

phase segregation took place not only at the film's surface but also throughout the whole depth of the film. More importantly, the iodide-rich phases tended to segregate at the TiO₂/CsPbIBr₂ interface, which could only be directly observed by the CL cross-sectional mapping. Even within the same single crystal, the emission from the iodide-rich phase increased from the film's surface to the TiO₂/CsPbIBr₂ interface (from Region 1 to Region 3 in Fig. 3a, c), indicating that an increasing amount of the iodide-rich phase was segregated at the interface. The CsPbIBr₂ with an excess of PbBr₂ showed a more uniform emission-peak wavelength, indicating that the phase segregation was inhibited across the depth of the film, as shown in Fig. 3c. However, the CL spectra from a series of regions adjacent

to the TiO₂/CsPbIBr₂ interface showed the CL peak position slightly shifting to longer wavelengths, suggesting a slightly higher iodine concentration at the interface. To summarize, the iodide-rich phases tended to segregate at the defects, such as the GBs and the heterojunction interfaces. Phase segregation can be greatly inhibited by adjusting the CsPbIBr₂ precursor solution composition with a slight PbBr₂ excess.

J-V hysteresis versus composition

It was also observed that the precursor chemical composition had a significant influence on the performance of the CsPbIBr₂ inorganic PSCs, as shown in Fig. 4. In the CsPbIBr₂ prepared with CsI-excess, a power conversion

Figure 4 *J-V* curves of CsPbIBr₂ inorganic PSCs with the precursors of (a) stoichiometric, (b) at CsI-excess, and (c) at PbBr₂-excess compositions. The *J-V* curves were recorded under different scan conditions (reverse, from forward bias to short-circuit, and forward, from short-circuit to forward bias; scan speed, 100 mV s⁻¹). The precursor solution's molar concentrations and compositions are shown in the legend of each figure.

efficiency (PCE) of 7.70% was achieved in a reverse *J-V* scan, while a much-reduced efficiency of 4.02% was derived when scanned from the short-circuit to the forward bias, as shown in Table 1. It was clear that the CsPbIBr₂ PSCs prepared with CsI-excess exhibited a strong hysteresis in the *J-V* scan measurements, with a hysteresis index (HI) of 33%, as defined by Equation (1) [46]:

$$HI = \frac{PCE_{reverse} - PCE_{forward}}{PCE_{reverse}} \times 100\%. \quad (6)$$

However, the CsPbIBr₂ PSC prepared with PbBr₂-excess exhibited a much lower HI of 10.9%, with a PCE of 7.35% from the reverse *J-V* scan and 6.55% from the forward *J-V* scan. The average HI of the PbBr₂-excess PSCs (19.2%) was also much lower than that of the solar cells prepared with stoichiometric (46.5%) and with the CsI-excess (42.7%) precursor compositions, as shown in

Table S1. Therefore, the hysteresis of the inorganic CsPbIBr₂ PSCs was greatly reduced by the introduction of the PbBr₂-excess.

By increasing the precursor's molar concentration from 0.7 to 1 mol L⁻¹, the film thickness increased from ~300 to ~380 nm, which resulted in the average short-circuit current density (*J*_{SC}) of all three compositions increasing from ~9 to ~10 mA cm⁻², as shown in Table 1. Meanwhile, the average open circuit voltage (*V*_{OC}) also increased, stemming from a reduced pin-hole density, as shown in Fig. S6. However, the precursor composition did not influence the *J-V* hysteresis of the PSCs.

Consequently, the PSC with the precursor's molar concentration of 1 mol L⁻¹ and the composition of PbBr₂-excess showed the highest PCE of 9.37% in a reverse *J-V* scan, while a PCE of 7.94% was measured from the for-

Table 1 The photovoltaic device parameters of the best-performing CsPbIBr₂ solar cells with the precursor concentrations of 0.7 and 1 mol L⁻¹ and the compositions of the stoichiometric, CsI-excess, and PbBr₂-excess

Concentration composition	<i>J-V</i> scanning direction	<i>V</i> _{OC} (mV)	<i>J</i> _{SC} (mA cm ⁻²)	Fill factor	PCE (%)	HI (%)
0.7 mol L ⁻¹ Stoichiometric	Reverse	1123	9.67	0.628	6.82	63.78
	Forward	1044	9.56	0.247	2.47	
1 mol L ⁻¹ Stoichiometric	Reverse	1148	10.39	0.598	7.13	57.78
	Forward	1119	10.34	0.26	3.01	
0.7 mol L ⁻¹ CsI-excess	Reverse	1222	9.43	0.668	7.7	33.3
	Forward	1250	9.45	0.434	5.13	
1 mol L ⁻¹ CsI-excess	Reverse	1233	10.45	0.608	7.83	44.83
	Forward	1224	10.04	0.352	4.32	
0.7 mol L ⁻¹ PbBr ₂ -excess	Reverse	1199	9.22	0.665	7.35	10.9
	Forward	1205	9.02	0.603	6.55	
1 mol L ⁻¹ PbBr ₂ -excess	Reverse	1254	10.5	0.712	9.37	15.3
	Forward	1276	10.48	0.594	7.94	

ward J - V scan, as seen in Table 1, resulting in a stabilized PCE of 8.48%, as shown in Fig. S7a. It also showed a very broad EQE plateau of over 90% between 400 and 570 nm, as shown in Fig. S7b. The J_{SC} value obtained by integrating the overall EQE agreed well with that seen in the J - V curve.

DISCUSSION

From the above results, it is clear that a higher $PbBr_2$:CsI ratio is advantageous for the formation of $Pb(I, Br)_2$ ·DMSO and $CsPb_2(I, Br)_5$ intermediate phases, greatly enhancing the Ostwald ripening of $CsPb(I, Br)_3$ [47]. Consequently, the average grain sizes of the stoichiometric, $PbBr_2$ -excess, and CsI-excess compositions were ~ 0.6 , ~ 0.3 , and ~ 1.5 μm , respectively. The intermediate-phase-enhanced Ostwald ripening of the $CsPb(I, Br)_3$ could be divided into two phases.

At the low temperature ($\leq 175^\circ C$), the Ostwald ripening of the $CsPb(I, Br)_3$ was dominantly accelerated by the $Pb(I, Br)_2$ ·DMSO adduct that was formed as a result of the coordination of the Lewis acid $Pb(I, Br)_2$ and the Lewis bases DMSO with lone-pair electrons [48]. However, the iodine atom in the CsI contained lone-pair electrons that were ready to couple with the $Pb(I, Br)_2$ by the formation of a more thermally stable $CsPbIBr_2$ phase than the $Pb(I, Br)_2$ ·DMSO adduct [49]. Therefore, increasing the $PbBr_2$:CsI ratio in the precursor solution resulted in the formation of a larger amount of $Pb(I, Br)_2$ ·DMSO adduct, which retarded the release of DMSO. With a higher $PbBr_2$:CsI ratio, the $CsPbIBr_2$ crystal growth and defect annihilation period were greatly elongated, and a significantly larger $CsPbIBr_2$ grain size could be achieved by the trace amount of DMSO released at $175^\circ C$.

At the high temperature ($>175^\circ C$), all the DMSO had been fully removed, and the crystal growth of the $CsPbIBr_2$ was further assisted by the $CsPb_2(I, Br)_5$ intermediate phase. The crystal growth of the $CsPb_2(I, Br)_5$ tended to extend onto the substrate's surface, which resulted from its 2D structure composed of Cs^+ cations sandwiched between the $Pb_2Br_5^-$ layers, as shown in Fig. 5h [50]. The $CsPb_2(I, Br)_5$ exhibited anisotropic 2D growth with the $Pb_2Br_5^-$ layers parallel to the substrate's surface with the 001_t direction normal to the substrate [51]. Therefore, the $CsPb_2(I, Br)_5$ phases in the stoichiometric and $PbBr_2$ -excess samples showed a preferred orientation at 001_t , as was shown in both the *in-situ* XRD and the selective area electron diffraction (SAED) pattern in Figs 1c and 5d. However, the tetragonal $CsPb_2(I, Br)_5$ at the 001_t direction and the orthorhombic $CsPb(I, Br)_3$ at

the 110_o direction exhibited greater structural similarity than both the experimental and theoretical simulations, as shown in Fig. 5a–g. In particular, these two phases shared almost identical crystal structures during annealing at $320^\circ C$ since all the circulated spots completely disappeared when the orthorhombic 110_o -oriented $CsPbIBr_2$ phase converted to a tetragonal or cubic structure [52]. The Ostwald ripening of the 110_o -oriented $CsPbIBr_2$ phase was greatly enhanced by means of a quasi-2D 001_t -oriented $CsPb_2(I, Br)_5$ intermediate phase to achieve a large lateral grain size. Consequently, the $CsPbIBr_2$ exhibited a preferred- 110_o orientation, as shown in both the XRD and the SAED patterns in Figs 1c and 5d, respectively.

Therefore, the intermediate phases introduced by the $PbBr_2$ -excess composition greatly enhanced the Ostwald ripening of the $CsPbIBr_2$, facilitating the crystal growth and defect annihilation. Therefore, the halide segregation was eliminated, the minority carrier lifetime was improved (Fig. S4b and Table S2), and the J - V hysteresis of the $CsPbIBr_2$ PSC was reduced.

However, by further increasing the $PbBr_2$:CsI ratio from 1.05 to 1.2, an average $CsPbIBr_2$ grain size of ~ 3 μm was achieved with a 20% excess of $PbBr_2$ in the precursor solution, as shown in Fig. S8b. However, it also introduced an increasing amount of $CsPb_2(I, Br)_5$, which was photo-inactive with no CL emission, as shown in Fig. 2g, h. This result is consistent with the findings of the work by Dursun *et al.* [50] that intrinsic $CsPb_2Br_5$ is an indirect bandgap material that does not exhibit an appreciable intrinsic PL. Therefore, further increasing the $PbBr_2$:CsI ratio leads to a decrease in the short-circuit current density of the solar cells, as shown in Fig. S8d.

CONCLUSIONS

In conclusion, we have demonstrated that the perovskite precursor chemical composition plays an important role in enhancing the crystal growth, reducing the defects, and mitigating the segregation of halides, as well as the J - V hysteresis of inorganic $CsPbIBr_2$ PSCs. Adding an excess of $PbBr_2$ to the $CsPbIBr_2$ precursor solution was found to be beneficial in reducing the GB density, increasing the minority carrier's lifetime, and finally, eliminating segregation and reducing the J - V hysteresis. Preparing the precursor solution at stoichiometric or with CsI-excess composition resulted in the opposite effects. These results directly prove that the phase segregation and the J - V hysteresis resulted from the trap states in the perovskite layer, which can be greatly reduced by controlling the $CsPbIBr_2$ crystal growth process. The higher $PbBr_2$:CsI

Figure 5 (a, b) Bright field TEM images of the $\text{CsPbI}_2\text{Br}_2$ and $\text{CsPb}_2(\text{I}, \text{Br})_5$ grains in the PbBr_2 -excess film. (c, d) The experimental SAED patterns taken from the circled regions in (a, b), respectively. (e, f) The calculated SAED patterns of CsPbBr_3 at the 110_o zone axis and the CsPb_2Br_5 at 001_t zone axis, respectively. (g) The calculated pattern from the overlap of (e) and (f). The circled spots in (g) will disappear when CsPbBr_3 is converted from the orthorhombic to the tetragonal and the cubic phases. (h) The atomic model for the CsPb_2X_5 ($\text{X} = \text{I}$ and Br) preferentially growing at the 001_t direction normal to the substrate. The scale bars are: (d, e) 500 nm, and (f, g) 2.5 nm^{-1} .

ratio benefited the formation of the $\text{Pb}(\text{I}, \text{Br})_2\cdot\text{DMSO}$ and the quasi-2D $\text{CsPb}_2(\text{I}, \text{Br})_5$ intermediate phases, which greatly enhanced the Ostwald ripening, and thus improved the crystallinity of the $\text{CsPbI}_2\text{Br}_2$ photo absorber. Due to the similarity in the crystal structure, these results obtained from the inorganic $\text{CsPbI}_2\text{Br}_2$ perovskite could provide guidance for the understanding and the removal of some of the issues concerning phase segregation and hysteresis in organic-inorganic mixed halide hybrid perovskites.

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- Al-Ashouri A, Köhnen E, Li B, *et al.* Monolithic perovskite/silicon tandem solar cell with >29% efficiency by enhanced hole extraction. *Science*, 2020, 370: 1300–1309
- Zuo L, Shi X, Fu W, *et al.* Highly efficient semitransparent solar cells with selective absorption and tandem architecture. *Adv Ma-*

- ter, 2019, 31: 1901683
- Quan LN, García de Arquer FP, Sabatini RP, *et al.* Perovskites for light emission. *Adv Mater*, 2018, 30: 1801996
- Shi B, Duan L, Zhao Y, *et al.* Semitransparent perovskite solar cells: From materials and devices to applications. *Adv Mater*, 2020, 32: 1806474
- Yang TCJ, Fiala P, Jeangros Q, *et al.* High-bandgap perovskite materials for multijunction solar cells. *Joule*, 2018, 2: 1421–1436
- Hoke ET, Slotcavage DJ, Dohner ER, *et al.* Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics. *Chem Sci*, 2015, 6: 613–617
- Beal RE, Slotcavage DJ, Leijtens T, *et al.* Cesium lead halide perovskites with improved stability for tandem solar cells. *J Phys Chem Lett*, 2016, 7: 746–751
- Li W, Rothmann MU, Liu A, *et al.* Phase segregation enhanced ion movement in efficient inorganic $\text{CsPbI}_2\text{Br}_2$ solar cells. *Adv Energy Mater*, 2017, 7: 1700946
- Braly IL, Stoddard RJ, Rajagopal A, *et al.* Current-induced phase segregation in mixed halide hybrid perovskites and its impact on two-terminal tandem solar cell design. *ACS Energy Lett*, 2017, 2: 1841–1847

- 10 Kim HP, Kim J, Kim BS, *et al.* High-efficiency, blue, green, and near-infrared light-emitting diodes based on triple cation perovskite. *Adv Opt Mater*, 2017, 5: 1600920
- 11 Duong T, Mulmudi HK, Wu YL, *et al.* Light and electrically induced phase segregation and its impact on the stability of quadruple cation high bandgap perovskite solar cells. *ACS Appl Mater Interfaces*, 2017, 9: 26859–26866
- 12 Shao Y, Fang Y, Li T, *et al.* Grain boundary dominated ion migration in polycrystalline organic-inorganic halide perovskite films. *Energy Environ Sci*, 2016, 9: 1752–1759
- 13 Wei J, Zhao Y, Li H, *et al.* Hysteresis analysis based on the ferroelectric effect in hybrid perovskite solar cells. *J Phys Chem Lett*, 2014, 5: 3937–3945
- 14 Seol D, Jeong A, Han MH, *et al.* Origin of hysteresis in $\text{CH}_3\text{NH}_3\text{-PbI}_3$ perovskite thin films. *Adv Funct Mater*, 2017, 27: 1701924
- 15 Rehman W, McMeekin DP, Patel JB, *et al.* Photovoltaic mixed-cation lead mixed-halide perovskites: Links between crystallinity, photo-stability and electronic properties. *Energy Environ Sci*, 2017, 10: 361–369
- 16 Yuan Y, Wang Q, Huang J. Ion migration in hybrid perovskite solar cells. In: Park NG, Grätzel M, Miyasaka T (eds.). *Organic-Inorganic Halide Perovskite Photovoltaics*. Cham: Springer, 2016: 137–162
- 17 Barker AJ, Sadhanala A, Deschler F, *et al.* Defect-assisted photo-induced halide segregation in mixed-halide perovskite thin films. *ACS Energy Lett*, 2017, 2: 1416–1424
- 18 Knight AJ, Wright AD, Patel JB, *et al.* Electronic traps and phase segregation in lead mixed-halide perovskite. *ACS Energy Lett*, 2019, 4: 75–84
- 19 Ruth A, Brennan MC, Draguta S, *et al.* Vacancy-mediated anion photosegregation kinetics in mixed halide hybrid perovskites: Coupled kinetic Monte Carlo and optical measurements. *ACS Energy Lett*, 2018, 3: 2321–2328
- 20 Samu GF, Janáky C, Kamat PV. A victim of halide ion segregation. How light soaking affects solar cell performance of mixed halide lead perovskites. *ACS Energy Lett*, 2017, 2: 1860–1861
- 21 Milosavljević AR, Huang W, Sadhu S, *et al.* Low-energy electron-induced transformations in organolead halide perovskite. *Angew Chem Int Ed*, 2016, 55: 10083–10087
- 22 Klein-Kedem N, Cahen D, Hodes G. Effects of light and electron beam irradiation on halide perovskites and their solar cells. *Acc Chem Res*, 2016, 49: 347–354
- 23 Yuan H, Debroye E, Janssen K, *et al.* Degradation of methylammonium lead iodide perovskite structures through light and electron beam driven ion migration. *J Phys Chem Lett*, 2016, 7: 561–566
- 24 Bischak CG, Sanhira EM, Precht JT, *et al.* Heterogeneous charge carrier dynamics in organic-inorganic hybrid materials: Nanoscale lateral and depth-dependent variation of recombination rates in methylammonium lead halide perovskite thin films. *Nano Lett*, 2015, 15: 4799–4807
- 25 Liang J, Wang C, Wang Y, *et al.* All-inorganic perovskite solar cells. *J Am Chem Soc*, 2016, 138: 15829–15832
- 26 Marshall KP, Walker M, Walton RI, *et al.* Enhanced stability and efficiency in hole-transport-layer-free CsSnI_3 perovskite photovoltaics. *Nat Energy*, 2016, 1: 16178
- 27 Fu Y, Zhu H, Stoumpos CC, *et al.* Broad wavelength tunable robust lasing from single-crystal nanowires of cesium lead halide perovskites (CsPbX_3 , X = Cl, Br, I). *ACS Nano*, 2016, 10: 7963–7972
- 28 Kulbak M, Cahen D, Hodes G. How important is the organic part of lead halide perovskite photovoltaic cells? Efficient CsPbBr_3 cells. *J Phys Chem Lett*, 2015, 6: 2452–2456
- 29 Ma Q, Huang S, Wen X, *et al.* Hole transport layer free inorganic $\text{CsPbI}_2\text{Br}_2$ perovskite solar cell by dual source thermal evaporation. *Adv Energy Mater*, 2016, 6: 1502202
- 30 Ripolles TS, Nishinaka K, Ogomi Y, *et al.* Efficiency enhancement by changing perovskite crystal phase and adding a charge extraction interlayer in organic amine free-perovskite solar cells based on cesium. *Sol Energy Mater Sol Cells*, 2016, 144: 532–536
- 31 Sutton RJ, Eperon GE, Miranda L, *et al.* Bandgap-tunable cesium lead halide perovskites with high thermal stability for efficient solar cells. *Adv Energy Mater*, 2016, 6: 1502458
- 32 Eperon GE, Paternò GM, Sutton RJ, *et al.* Inorganic caesium lead iodide perovskite solar cells. *J Mater Chem A*, 2015, 3: 19688–19695
- 33 Swarnkar A, Marshall AR, Sanhira EM, *et al.* Quantum dot-induced phase stabilization of $\alpha\text{-CsPbI}_3$ perovskite for high-efficiency photovoltaics. *Science*, 2016, 354: 92–95
- 34 Varlamov S, Dore J, Evans R, *et al.* Polycrystalline silicon on glass thin-film solar cells: A transition from solid-phase to liquid-phase crystallised silicon. *Sol Energy Mater Sol Cells*, 2013, 119: 246–255
- 35 Shen Z, Zhao Z, Peng H, *et al.* Formation of tough interlocking microstructures in silicon nitride ceramics by dynamic ripening. *Nature*, 2002, 417: 266–269
- 36 Chen W, Wen X, Latzel M, *et al.* Nanoscale characterization of carrier dynamic and surface passivation in InGaN/GaN multiple quantum wells on GaN nanorods. *ACS Appl Mater Interfaces*, 2016, 8: 31887–31893
- 37 Jeon NJ, Noh JH, Yang WS, *et al.* Compositional engineering of perovskite materials for high-performance solar cells. *Nature*, 2015, 517: 476–480
- 38 Moore DT, Sai H, Tan KW, *et al.* Crystallization kinetics of organic-inorganic trihalide perovskites and the role of the lead anion in crystal growth. *J Am Chem Soc*, 2015, 137: 2350–2358
- 39 Cola M, Massarotti V, Riccardi R, *et al.* Binary systems formed by lead bromide with (Li, Na, K, Rb, Cs and Tl)Br: A DTA and diffractometric study. *Z für Naturforschung A*, 1971, 26: 1328–1332
- 40 Yang WS, Noh JH, Jeon NJ, *et al.* High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science*, 2015, 348: 1234–1237
- 41 Yin G, Zhao H, Jiang H, *et al.* Precursor engineering for all-inorganic CsPbI_2Br perovskite solar cells with 14.78% efficiency. *Adv Funct Mater*, 2018, 28: 1803269
- 42 A Awadhia, SL Agrawal. Structural, thermal and electrical characterizations of PVA:DMSO: NH_4SCN gel electrolytes. *Solid State Ionics*, 2007, 178: 951–958
- 43 Lee JW, Kim HS, Park NG. Lewis acid-base adduct approach for high efficiency perovskite solar cells. *Acc Chem Res*, 2016, 49: 311–319
- 44 Zai H, Zhang D, Li L, *et al.* Low-temperature-processed inorganic perovskite solar cells via solvent engineering with enhanced mass transport. *J Mater Chem A*, 2018, 6: 23602–23609
- 45 Zhang X, Xu B, Zhang J, *et al.* All-inorganic perovskite nanocrystals for high-efficiency light emitting diodes: Dual-phase $\text{CsPbBr}_3\text{-CsPb}_2\text{Br}_5$ composites. *Adv Funct Mater*, 2016, 26: 4595–4600
- 46 Duong T, Wu YL, Shen H, *et al.* Rubidium multication perovskite with optimized bandgap for perovskite-silicon tandem with over 26% efficiency. *Adv Energy Mater*, 2017, 7: 1700228

- 47 Li J, Zhang H, Wang S, *et al.* Synthesis of all-inorganic CsPb₂Br₅ perovskite and determination of its luminescence mechanism. *RSC Adv*, 2017, 7: 54002–54007
- 48 Jeon NJ, Noh JH, Kim YC, *et al.* Solvent engineering for high-performance inorganic-organic hybrid perovskite solar cells. *Nat Mater*, 2014, 13: 897–903
- 49 Zhang S, Wu S, Chen W, *et al.* Solvent engineering for efficient inverted perovskite solar cells based on inorganic CsPbI₂Br light absorber. *Mater Today Energy*, 2018, 8: 125–133
- 50 Dursun I, De Bastiani M, Turedi B, *et al.* CsPb₂Br₅ single crystals: Synthesis and characterization. *ChemSusChem*, 2017, 10: 3746–3749
- 51 Wang KH, Wu L, Li L, *et al.* Large-scale synthesis of highly luminescent perovskite-related CsPb₂Br₅ nanoplatelets and their fast anion exchange. *Angew Chem Int Ed*, 2016, 55: 8328–8332
- 52 Rodová M, Brožek J, Knížek K, *et al.* Phase transitions in ternary caesium lead bromide. *J Thermal Anal Calorimetry*, 2003, 71: 667–673

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Author contributions Li W, Rothmann MU, Ethridge J, Bach U, and Cheng YB conceived and designed the experiment. Li W and Zhu B carried out the sample preparation and solar-cell fabrication. Li W, Rothmann MU, Choo YY, and Liu A conducted the CL characterization. Li W, Zhu B, and Choo YY carried out the XRD analysis. Chen W and Wen X characterized the TRPL decay traces. Pai N conducted the FTIR analysis. All authors contributed to the discussion of the results and the writing of the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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中间相促进CsPbIBr₂晶体生长以消除高效无机钙钛矿太阳能电池的卤素相分离

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摘要 混合卤化物钙钛矿材料由于易于调整光学带隙, 在叠层太阳能电池、光伏建筑一体化和波长可调的发光器件等方面显示出诱人的应用前景。然而, 混合卤化物钙钛矿材料在光照或电荷注入的条件下, 卤素离子会产生相分离, 从而影响光学带隙的稳定性和器件性能, 严重阻碍其应用前景。本文中, 我们将过量PbBr₂或CsI加入到最初等化学计量比的PbBr₂和CsI前驱体溶液中。当PbBr₂过量时, 我们观察到CsPbIBr₂钙钛矿晶粒尺寸增大, 晶界和CsPbIBr₂/TiO₂的异质结界面处的卤化物相分离得到抑制; 少数载流子寿命增加, 电流密度-电压(*J*-*V*)滞后减弱, 太阳能电池性能提高。然而当CsI过量时, 所观察到的结果与前者恰恰相反。这是因为在前驱体溶液中加入过量PbBr₂, 有利于形成Pb(I, Br)₂·DMSO络合物和准二维CsPb₂(I, Br)₅中间相, 大大促进了CsPbIBr₂晶体的生长和缺陷的消除。因此, 通过控制CsPbIBr₂前体溶液中的化学成分, 引入中间相, 促进晶体的生长, 从而有效缓解混合卤化物无机CsPbIBr₂太阳能电池中的卤化物相分离和器件的*J*-*V*迟滞。制备的CsPbIBr₂太阳能电池的最高光电转化效率达到9.37%(稳态效率达到8.48%), 最大外量子效率超过90%。