Phase Segregation Enhanced Ion Movement in Efficient Inorganic CsPbIBr₂ Solar Cells

Wei Li, Mathias Uller Rothmann, Amelia Liu, Ziyu Wang, Yupeng Zhang, Alexander R. Pascoe, Jianfeng Lu, Liangcong Jiang, Yu Chen, Fuzhi Huang, Yong Peng, Qiaoliang Bao, Joanne Etheridge, Udo Bach,* and Yi-Bing Cheng*

1. Introduction

Organic–inorganic hybrid perovskite solar cells with mixed cations and mixed halides have achieved impressive power conversion efficiency of up to 22.1%. Phase segregation due to the mixed compositions has attracted wide concerns, and their nature and origin are still unclear. Some very useful analytical techniques are controversial in microstructural and chemical analyses due to electron beam-induced damage to the “soft” hybrid perovskite materials. In this study photoluminescence, cathodoluminescence, and transmission electron microscopy are used to study charge carrier recombination and retrieve crystallographic and compositional information for all-inorganic CsPbIBr₂ films on the nanoscale. It is found that under light and electron beam illumination, “iodide-rich” CsPbI₁₋ₓBrₓ phases form at grain boundaries as well as segregate as clusters inside the film. Phase segregation generates a high density of mobile ions moving along grain boundaries as ion migration “highways.” Finally, these mobile ions can pile up at the perovskite/TiO₂ interface resulting in formation of larger injection barriers, hampering electron extraction and leading to strong current density–voltage hysteresis in the polycrystalline perovskite solar cells. This explains why the planar CsPbIBr₂ solar cells exhibit significant hysteresis in efficiency measurements, showing an efficiency of up to 8.02% in the reverse scan and a reduced efficiency of 4.02% in the forward scan, and giving a stabilized efficiency of 6.07%.
segregation is more obvious in mixed halide perovskite film[6] which can greatly influence solar cell performance, especially hysteresis in current density–voltage (J–V) measurements.[7] Moreover, microstructures within PSC devices, such as grain boundaries,[7] interfaces[8] are playing important roles in ion migration and thus greatly affecting solar cell device performance. However, how the halide phases are spatially segregated is still not well studied due to lack of high resolution microstructural evidences.

Electron microscopy has provided valuable guidance for the development of solar cell materials such as Si, CdTe, CIGS, and others.[9] However, the organic–inorganic hybrid perovskites are extremely fragile under electron beam illumination and can undergo morphological, compositional, and structural degradation.[10] This greatly limits the use of electron microscopy to probe the morphology, microstructure, elemental composition, crystal structure, and electronic properties of the hybrid materials at the micro or the nanoscale.[11] Although low dose techniques can reduce the damage rate,[10c,11,12] the use of high dose techniques, such as atomic resolution imaging or chemical mapping are limited due to the possible influence of electron beam-induced artifacts.[12]

Inorganic perovskites are more thermally stable, and have as such attracted more and more attention for their photovoltaic and light emitting properties.[6b,11] Furthermore, inorganic perovskites are significantly more electron-beam stable. Therefore, detailed microstructural analyses of inorganic perovskites, such as CsPbI₃, CsPbBr₃, and CsSnI₃, can not only offer useful insights into these inorganic perovskite solar cells, but potentially also provide guidance for better understanding other perovskite materials[10b,12], including the hybrid perovskite solar cell materials.

Cubic phase α-CsPbI₃ (black phase) has a bandgap of 1.73 eV, the narrowest bandgap of all cesium lead halides. However, it tends to convert to a non-photoactive orthorhombic phase (yellow phase) at temperatures lower than the cubic to orthorhombic phase transition temperature of 300 °C.[13,14] By alloying with bromide, a lower phase transition temperature can be achieved, but a higher bromide to iodide ratio leads to a significant increase in the band gap. This limits the short circuit current of mixed halide cesium lead PSCs when used in single-junction configurations.[13b,h] CsPbIₓBrₓ (with x ≥ 0.7) has a bandgap of 1.82 eV achieved a record device power conversion efficiency of 11.8% among inorganic perovskite solar cells.[15] By further increasing Br to I ratio, CsPbBr₂ shows a significantly reduced phase transition temperature of around 100 °C[14] and a balanced band-gap of around 2.05 eV,[14] which allows for it to be used as the top cell in a tandem solar cell.[16] Ma et al. reported a CsPbBr₂ thin film cell reaching a PCE of 4.7%.[14] Recently, Lau et al. in the same group further improved the PCE to 6.3% by using a two-step preparation method.[17]

In this work, a gas-assisted method is used to form CsPbBr₂ composition dissolved in dimethyl sulfoxide (DMSO) was prepared by mixing CsI and PbBr₂ precursors in a 1:1 molar ratio. In order to improve the film coverage on the substrate, a gas-assisted method, initially developed to increase the nucleation rate of grains in the CH₃NH₃PbI₃ system,[18] was utilized to achieve a uniform CsPbBr₂ film. Subsequent annealing at 320 °C for 20 min resulted in a highly crystallized cubic CsPbBr₂ thin film as shown in Figure S1 (Supporting Information). Planar CsPbBr₂ solar cells were fabricated with the following configuration: glass/FTO/c-TiO₂/CsPbBr₂ (~300 nm)/Spiro-OMeTAD/Au. The J–V curves, external quantum efficiency spectra, and stabilized power output (SPO) of the best performing planar CsPbBr₂ solar cells are presented in Figure 1 (see Table 1 for the photovoltaic device performance parameters). A PCE of 8.02% has been achieved with the planar champion cell in a reverse J–V scan while a much-reduced efficiency of 4.02% is derived when scanning from short-circuit to forward bias, so finally a stabilized efficiency of 6.07% is achieved. The best planar device also shows a very broad external quantum efficiency (EQE) plateau of over 80% between 400 and 570 nm, as shown in Figure 1c. The Jₘ value obtained by integrating over the EQE agrees well with the one seen in the J–V curve.

It should be noted that the CsPbBr₂ PSCs tested here exhibit a rather strong hysteresis in the J–V scan measurements with a hysteresis index of around 47% as defined by Equation (1)[19].

\[
\text{Hysteresis index} = \frac{\text{PCE}_{\text{reverse}} - \text{PCE}_{\text{forward}}}{\text{PCE}_{\text{reverse}}} \tag{1}
\]

Nowadays, more and more studies support the hypothesis that hysteresis is attributed to accumulated ions near the...
interfaces between the perovskite/hole transportation material and the perovskite/electron transportation material.

The accumulation of ions results from the migration of halide ions/interstitials driven by an external electrical bias, leading to a shift in the effective work function at the respective electrodes. This shift in work function screens the applied voltage, and changes the charge collection efficiency, which results in the observed $J-V$ hysteresis.\(^{[7]}\)

Halide ion separation may also influence the $J-V$ hysteresis in CsPb(I\(_{1-x}Br_x\))\(_3\) ($0 < x < 1$) solar cells. Beal et al. reported that phase separation occurs under illumination in CsPb(I\(_{1-x}Br_x\))\(_3\) materials when $x$ is $>0.4$. CsPbBr\(_2\) ($x = 0.67$) falls into this category, while CsPbI\(_2Br\) ($x = 0.33$) does not.\(^{[4b]}\) Such a light-induced phase segregation has been identified by PL spectroscopy at one-sun illumination condition in our CsPbIBr\(_2\) films, as shown in Figure S2 (Supporting Information).

We also calculated the hysteresis index of published CsPb(I, Br\(_3\)) solar cells as shown in Table S1 (Supporting Information). By utilizing a similar planar configuration of c-TiO\(_2\)/CsPb(I, Br\(_3\))\(_2\)/Spiro-OMeTAD, phase stable CsPbBr\(_3\)(Br\(_x\)I\(_{1-x}\)) materials such as CsPbI\(_3\) and CsPbI\(_2Br\) show much lower hysteresis index than the phase unstable CsPbIBr\(_2\) (the hysteresis indexes have been reported to be 25.1% for CsPbI\(_3\),\(^{[13a]}\) 20.4% for CsPbI\(_2Br\),\(^{[13b]}\) and 43.8% for CsPbBr\(_2\) PSCs). Halide phase segregation is undoubtedly accompanying, and more likely promoting, I\(^-\) and Br\(^-\) migration in CsPbIBr\(_2\) films, thus enhancing hysteresis. Crystal defects such as grain boundaries also play important roles in ion migration, since ion migration at the grain boundaries is greatly enhanced and dominates the $J-V$ hysteresis. Therefore, it is of great importance to understand how the phase is segregated spatially in the CsPbIBr\(_2\) film, in order to better understand the strong hysteresis in planar CsPbIBr\(_2\) solar cells.

In order to study how the halide phases segregate, we studied CsPbIBr\(_2\) deposited on a typical substrate used for photovoltaic devices,\(^{[11]}\) consisting of layers of TiO\(_2\), FTO, and glass. Before CL characterization, the CsPbIBr\(_2\) film was kept in the dark vacuum chamber for more than 10 min to avoid unintended light-induced phase segregation. All of the CL mappings were recorded from previously unexposed regions of the sample, except when specifically indicated.
The generation volume of electron–hole pairs (EHPs) by CL is controlled by the electron beam accelerating voltage. Monte Carlo simulations were used to predict the generation volume within the CsPbIBr₂ film for acceleration voltages of 2 and 5 kV, as shown in Figure S3 (Supporting Information). At 2 kV, the generation volume of EHPs is mainly confined to the film surface, while at 5 kV it penetrates to the whole film thickness. Phase segregation at the CsPbIBr₂ film surface was initially studied by using a low electron beam accelerating voltage at 2 kV and a beam current of 440 pA. The emitted luminescent photons were captured by a high-numerical-aperture parabolic mirror above the sample and detected by a photomultiplier tube (PMT) to obtain a panchromatic CL image. An SEM image and PMT map obtained in the same region of the sample are shown in Figure 2a,b. It is evident that all the GBs show higher CL intensity compared with the grain interiors (GIs). Even at very low incident electron beam dose conditions, with an electron beam current of 29 pA, a higher CL intensity at the GBs is still evident. This is clear in the PMT mapping image shown in Figure S4 (Supporting Information), which was obtained by keeping the accelerating voltage and the dwell time the same as for the 440 pA measurements.

In order to further analyze the reason for the enhanced CL intensity at the GBs, CL spectrum mapping was also performed. Spectrum mapping differs from PMT mapping in that not only is the overall CL intensity information collected, but the wavelengths of the emitted photons are resolved through a spectrometer and collected by a spectral camera. Figure 2c–e shows the CL spectrum maps obtained, with a pixel size of 40 nm × 40 nm and a dwell time of 200 ms, which is 667 times longer than that used for PMT mapping. The color in Figure 2e is divided into green and red regions by different spectrum windows of 530–590 nm (Figure 2c) and 590–640 nm (Figure 2d), respectively. Figure 2f reveals the CL spectrum for the area inside a CsPbIBr₂ grain (GI, area ① in Figure 2e) and its grain boundary (GB, area ② in Figure 2e), marked in the white circles in Figure 2e. Compared to the GI CL spectrum peak of 585 nm, the peak of the GBs is redshifted to 610 nm. The GI peak is consistent with the original PL peak position for the CsPbIBr₂ before light-induced phase segregation, as shown in black curve of Figure S2a (Supporting Information). The GB peak position, which is in the range of a segregated CsPbIBr₂ phase after light exposure, indicates the formation of an iodide-rich phase at the boundaries.

Figure 2 represents the first high resolution CL mapping-based evidence of chemical segregation of an iodide-rich mixed halide phase at the grain boundaries. Although these iodide-rich phases at the GBs only take up a small volume fraction, they dominate the PL spectra because of photogenerated carriers relaxing into lower energy states and thus predominately emitting from the lowest bandgap phases (the iodide-rich phases, in this case). Therefore, the iodide-rich domains act as carrier traps, concentrate and facilitate radiative electron–hole recombination. It is believed that the free energy of a semiconductor in the excited state can be reduced when the charge carriers are able to migrate to the low bandgap phase. Therefore, in both PMT mapping and CL spectrum mapping with the electron beam acceleration voltage at 2 kV, the CL intensity at the grain boundaries is much higher than that in the grain interiors.

Figure 3 shows CL spectrum maps of the CsPbIBr₂ thin film, with the accelerating voltage increased to 5 kV. At 5 kV, not all the GBs exhibit higher CL intensity as it was observed at an acceleration voltage of 2 kV. However, heterogeneity of the CL intensity is still observed in the PMT image in Figure 3b.
in which "cluster-like" phases show higher CL intensity than other regions. To further analyze the reason for the varied CL intensity in different regions, CL spectrum mapping was again performed in the square region marked in Figure 3a. Figure 3c,d shows CL intensity mapping in the spectrum window of 530–630 and 630–730 nm, respectively. Figure 3e covers the whole spectrum window from 530 to 730 nm in which the color indicates the wavelength of the emitted light wavelength with a following order: red > green > blue while the stronger brightness reveals a higher CL intensity. CL spectrum mapping reveals the intragrain heterogeneity. As shown in Figure 3e, the CL peak position of the grain interior region ① is consistent with the original PL peak position of the CsPbIBr2 before light-induced phase segregation. However, the CL peak of the grain boundary region ③ exhibits a shoulder peak in the wavelength region from 650 to 700 nm which indicates the formation of an iodide-rich phase. The most striking features in Figure 3e are the regions ② and ④ where the CL intensity is much higher than in other regions. More importantly, the CL peak position of region ④ is clearly redshifted to 692 nm, which is almost the same as the PL peak position for a pure CsPbl3 phase[4b,13h] and 606 nm, respectively. By increasing the electron beam acceleration voltage to 5 kV, the generation volume of the electron–hole pairs extends to the bulk of the film, which potentially results in a poorer spatial resolution in the CL map. Therefore, the CL spectra in region ② contain two peaks, the one with a lower wavelength peak position, corresponding to the formation of a bromide-rich phase, and the other with a higher wavelength peak position, corresponding to the iodide-rich CsPbI1-xBrx phase. Although the creation of iodide-rich domains must be accompanied by the creation of a bromide-rich phase in the films,[4b] the bromide-rich region is difficult to be identified in the PL spectrum since the emission from the bromide-rich region is significantly weaker (nearly 2 orders of magnitude weaker) than that from the iodide-rich region.[21]

The microstructure of the CsPbIBr2 solar cell device is further analyzed by TEM characterization (Figure 4), using an electron acceleration voltage at 200 kV, and a cross-section lamella prepared by focused ion beam (FIB). Columnar CsPbIBr2 grains are observed in the bright-field TEM image of Figure 4a. The selected area electron diffraction (SAED) pattern corresponding to the circular region in Figure 4a suggests a single crystal CsPbIBr2 grain exists through the whole ~300 nm thickness of the perovskite layer. This SAED pattern is consistent with the [014] zone-axis. There is no indication of damage to the crystal structure of the inorganic CsPbIBr2 after FIB milling and 200 kV electron beam illumination in the TEM, suggesting that this material is much more stable under electron/ion-beam irradiation than hybrid organic–inorganic perovskites.[22]

In order to analyze the elemental distribution after the electron beam-induced phase segregation, an energy dispersive spectroscopy (EDS) line scan was also performed across the GB shown in the CsPbIBr2 film. The scanning direction is marked by the red arrow in both the bright field and the high-angle annular dark-field (HAADF) images in Figure 4a,b, and the corresponding EDS line scan results for iodide and bromide, and cesium and lead are shown in Figure 4c,d, respectively. The iodide-rich phase and the bromide-rich phase, separated by the grain boundary, are clearly revealed by the EDS line scan in Figure 4c. On the other hand, the lead and cesium concentrations are largely similar across the grain boundary.

In the CsPbIBr2 film, phase segregation and ion migration mutually influence each other. The easy ion migration enables the phase segregation in the CsPbIBr2[6] CsPbX3 compounds...
Phase segregation and the accompanying ion migration have a great influence on the performance of CsPbIBr₂ solar cells, particularly through J–V hysteresis. In this study, we first utilize a low electron acceleration voltage of 2 kV in Figure 2 to study the phase segregation on the film surface, which tends to have a high vacancy density, greatly speeding up ion migration. Grain boundaries are 2D defects in which the density of vacancies is much higher than that in the grain interior, due to crystallographic misorientation or misfit, dangling bonds, or tensile strain of grains.[6] The formation energy of point defects at grain boundaries can thus be much lower than that in the grain interiors.[6] Therefore, the iodide-rich phase segregates at the grain boundaries, which becomes more obvious on the film surface possibly facilitated by a rapid surface transport of vacancies. Grain boundaries have an important role in dominating and facilitating the ion migration, resulting in the J–V hysteresis in the polycrystalline PSCs. Due to the phase segregation at the grain boundaries, it can generate a higher density of mobile ions.[6] These negatively charged mobile ions may pile up at the perovskite/TiO₂ interface resulting in the formation of larger injection barriers and hampering electron extraction and lead to a more severe J–V hysteresis.[8,25] At higher electron acceleration voltage, such as 5 kV as seen in Figure 3 and 200 kV in Figure 4, the phase segregation is studied in the bulk of the film, which extends to the CsPbBr₂/TiO₂ interface. “Cluster-like” iodide-rich phases are observed in both CL mapping and the TEM elemental mapping. Similar iodide-rich perovskite nanodomains, on a length scale of up to a few hundred nanometers, have been reported in a mixed cations and mixed halides perovskite (FAPbI₃)₀.₈₅(MAPbBr₃)₀.₁₅ as well.[5] The formation of “cluster-like” iodide-rich phases might be related to the defects on the CsPbBr₂/TiO₂ interface. These interfacial defects greatly influence charge carrier recombination,[26] charge injection/extraction and thus solar cell J–V hysteresis.[8]

Phase segregation might reduce achievable voltages due to the low band gap iodide-rich phase, limiting the overall obtainable voltage.[4a] However, it has been proposed that such phase segregation, ultimately leading to a “bulk-heterojunction,” could be beneficial for perovskite solar cells.[3] In our study, due to intragrain defects, particularly at grain boundaries and at the film interfaces, phase segregation causes enhanced ion migration, leading to a much stronger J–V hysteresis.[7,8] Therefore, a stronger J–V hysteresis is observed in our CsPbBr₂ solar cells than other solar cells of the stable CsPb(IₓBr1−ₓ)₃ family with a similar planar architecture configuration.

Modifying the TiO₂ surface by incorporation of Cl atoms[26] or applying a fullerene electron transport layer[16,15,27] has been shown to result in a lower density of interfacial trap state and a significant reduction in J–V hysteresis. As shown in Table S1 (Supporting Information), J–V hysteresis can also be greatly reduced by inserting a mesoporous TiO₂ between c-TiO₂ and the CsPbBr₂/TiO₂ interface. “Cluster-like” iodide-rich phases are halide-ion conductors, and halide ions can move easily due to the low activation energies of the halide-ion vacancies.[23] On the other hand, phase segregation also enhances ion migration. Br⁻, with its smaller ionic radius, moves more readily than I⁻ throughout the crystal, resulting in strain in the perovskite crystal lattice.[6] Moreover, mixed halide alloys are probably less stable thermodynamically due to immiscibility between the two components, which can cause phase separation, and generate a higher density of mobile ions.[6]

Light and defects are two important factors that influence both phase segregation and ion migration. Under light illumination, the photoexcited electrons will become trapped at the vacancies in the perovskite film, such as on the film surface, at grain boundaries and interfaces, etc. This trap filling would perturb the system and create internal electric fields that induce halide migration, as suggested by photo-induced halide redistribution theory by deQuilettes et al.[24] After stopping illumination, the trapped electrons recombine with holes, and thus the electric field created by the electrons trapped in the vacancies is removed. The concentration gradient allows bromide and iodide ions to migrate back to their equilibrium position and return to a single phase of well-mixed material.[44] Therefore, a reversible, light-induced transformation in CsPbBr₂ is observed by the PL spectrum as shown in Figure S2c (Supporting Information).

Figure 4. Elemental distribution in the CsPbIBr₂ film bulk resulting from phase segregation. a) Bright-field (BF) and b) high-angle annular dark-field (HAADF) 200 keV TEM images of the same cross-sectional area of the CsPbBr₂ solar cell prepared by FIB. In the inset of (a), the SAED pattern at the [014] zone-axis is obtained from the area in the red circle in (a), showing the grain is a single crystal of the cubic phase. EDS line scans taken along the arrow from right to left in (b) for c) iodide and bromide and d) cesium and lead. The scale bars in (a) and (b) are 500 nm.
perovskite layers, which greatly enlarges the interface between the electron collection layer and the light absorber to facilitate the electron collection efficiency. The similar results were also observed in our mesoporous CsPbBr3 solar cells with the following configuration: glass/ FTO/c-TiO2/mp-TiO2/CsPbBr3/Spiro-OMeTAD/Au. The J–V curves, external quantum efficiency spectra, and SPO of the best performing planar CsPbBr3 solar cells are presented in Figure S5 in the Supporting Information (see Table S2 in the Supporting Information for the photovoltaic device performance parameters). A PCE of 6.64% has been achieved with the mesoporous champion cell in a reverse J–V scan while a similar efficiency of 6.2% is derived when scanned from short-circuit to forward bias, so finally a stabilized efficiency of 6.25% is achieved which is higher than that of the champion planar device.

It has been found that the photoactive CsPbBr3 black phase gradually converts to a photoinactive yellow phase with time when exposed to a humid air condition (22 °C, relative humidity ~45%, room light exposure) as shown in the transmission optical microscope images in Figure S6a (Supporting Information), and at the same time all the solar cell parameters are also degraded as shown in Figure S6b and Table S3 (Supporting Information). Therefore, a proper device encapsulation is necessary in applications to avoid such unfavorable phase transition.

3. Conclusions

To summarize, we have observed iodide-rich phase segregation near grain boundaries, as well as the formation of “clusters” in the bulk of CsPbBr3 film. This spatial distribution also has a great influence on the ion migration. Concentrated mobile ions generated by phase segregation can migrate quickly alone grain boundaries and finally pile up at the CsPbBr3/TiO2 interface resulting in the formation of larger injection barriers and hampering electron extraction. This can exacerbate the current density–voltage hysteresis in inorganic CsPbBr3 perovskite solar cells. These results could provide guidance for understanding organic–inorganic hybrid perovskites with mixed halides suffering from the same photostability issues, for which electron microscope studies of the microstructure are strongly limited by material instabilities under the electron beam.

4. Experimental Section

Materials: Unless specified otherwise, all materials were purchased from either Alfa Aesar or Sigma-Aldrich and used as received. Spiro-OMeTAD (2,2’,7,7’-tetraakis (N,N-diphenylamino) -9,9’-spirobifluorene) was purchased from Luminescence Technology Corp.

Device Fabrication: A dense TiO2 blocking layer was first deposited on clean FTO glass by spray pyrolysis at 450 °C, using a bis(isoproxydioxymethyl)-bis(acetylacetone)tellurium(IV) solution. After cooling to room temperature, the substrate was cut into smaller pieces of around 1 cm². For the mesoporous structure, the thin mesoporous TiO2 layer was deposited by spin-coating 30 µL of the TiO2 nanoparticle solution at 11 000 rpm for a period of 60 s. The mesoporous TiO2 film was then dried at 150 °C for 15 min, and subsequently sintered at 500 °C for 30 min.[19] A 0.7 µL, 45 wt% CsPbBr3 in DMSO precursor solution was then prepared from CsI and PbBr2, in a molar ratio of 1:1, and spin coated onto the TiO2 layer. For the conventional spin-coating method, the solution was first spun at 500 rpm for 50 s, then at 1000 rpm for 30 s. For the gas-assisted method, dry argon gas at 40 psi was blown over on the film surface for 30 s once the spinning speed reached 1000 rpm. The films were then annealed at 320 °C for 20 min in a tube furnace with an Ar atmosphere. Subsequently, 25 µL of spiro-OMeTAD solution (prepared by dissolving 41.6 mg spiro-OMeTAD in 0.5 mL chlorobenzene, and adding 7.5 µL of a stock solution of 520 mg mL⁻¹ lithium bis(trifluoromethylsulphonyl)imide in acetonitrile and 16.9 µL 4-tert-butylpyridine) was coated on the CsPbBr3 film by spin-coating at 3000 rpm for 30 s. Finally, an 80 nm gold layer was deposited by thermal evaporation to form the complete device.

Cathodoluminescence Characterization: CL characterization was performed using an FEI Nova NanoSEM 450 SEM equipped with a Delmic SPARC cathodoluminescence System. CL measurements were carried out for the CsPbBr3 polycrystalline thin film on a c-TiO2 coated FTO glass substrate at room temperature (298 K) under accelerating voltages of 2 and 5 kV. The electron beam generation volume in the CsPbBr3 film with an electron beam acceleration voltage of 2 and 5 kV are shown in Figure S3 (Supporting Information). They were simulated by the Monte Carlo method of electron trajectory using the CASINO software.[20]

TEM Characterization: An FIB system (FEI 3D Quanta Nanolab FIB/SEM) was used to prepare cross-sectional TEM lamellae. To protect the lamellae area from excessive beam damage during the focused ion beam milling, a Pt layer of 200 nm followed by one of ~1 µm were deposited on the area of interest by electron beam and FIB, respectively, prior to the FIB cross-section preparation. The lamellae were cut to around 1 µm in thickness by 30 kV Ga⁺ ions with an ion beam current of ~1–6 nA, before being removed from the bulk sample using in situ lift-out, and then attached to the Omniprobe semiring. Final thinning was performed with 30 kV Ga⁺ ions, with an ion beam current of 0.1 nA followed by cleaning with 5 keV Ga⁺ ions, with a beam current as low as 50 pA. An FEI Tecnai G2 F20 TEM operated at 200 kV and equipped with an EDS detector was used for TEM, selected area diffraction images, and the chemical element distribution analysis.

Solar Cell Performance Characterizations: Current–voltage characterization was performed using a solar simulator (Oriel) fitted with a filtered 1000 W xenon lamp to replicate AM1.5, 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 perovskite solar cell. The J–V response was recorded using a Keithley 2400 source meter. The solar cells were masked with a nonreflective surface when exposed to a humid air condition (22 °C, 45% relative humidity). The perovskite samples were excited using a 532 nm laser source. Alpha 300R) in ambient conditions. The perovskite samples were excited using a 532 nm laser source. PL spectra were collected by a confocal microscope system (WiTeC, alpha 300R) in ambient conditions. The perovskite samples were excited using a 532 nm laser source.

Other Characterizations: X-ray diffraction perovskite samples were prepared on TiO2-coated FTO-glass substrates, and analyzed using a D2 PHASER (Bruker Corp.).

Supporting Information

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

This work was financially supported by the Australian Government through the Australian Renewable Energy Agency (ARENA), Australian Centre for Advanced Photovoltaics (ACAP), and ARC Centre of Excellence in Exciton Science (ACEX). The authors acknowledge use of facilities within the Monash Centre for Electron Microscopy. This research used equipment funded by Australian Research Council grants: LE0882821, LE111000223, and LE140100104. This work was performed in part at the Melbourne Centre for Nanofabrication (MCN) in the Victorian Node of the Australian National Fabrication Facility (ANFF). The authors would thank Dr. Yiqiang Chen for indexing selective area electron diffraction pattern.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

cathodoluminescence, hysteresis, inorganic perovskite solar cells, ion movement, phase segregation

Received: April 6, 2017
Revised: May 5, 2017
Published online: