Mixed-halide mixed-cation hybrid perovskites are among the most promising perovskite compositions for application in a variety of optoelectronic devices due to their high performance, low cost, and bandgap-tuning capabilities. Instability pathways such as those driven by ionic migration, however, continue to hinder their further progress. Here, an operando variable-pitch synchrotron grazing-incidence wide-angle X-ray scattering technique is used to track the surface and bulk structural changes in mixed-halide mixed-cation perovskite solar cells under continuous load and illumination. By monitoring the evolution of the material structure, it is demonstrated that halide remixing along the electric field and illumination direction during operation hinders phase segregation and limits device instability. Correlating the evolution with directionality- and depth-dependent analyses, it is proposed that this halide remixing is induced by an electrostrictive effect acting along the substrate out-of-plane direction. However, this stabilizing effect is overwhelmed by competing halide demixing processes in devices exposed to humid air or with poorer starting performance. The findings shed new light on understanding halide de- and re-mixing processes and their impact on device longevity. These operando techniques allow real-time tracking of the structural evolution in full optoelectronic devices and unveil otherwise inaccessible insights into rapid structural evolution under external stress conditions.

1. Introduction

Halide perovskites of the form $ABX_3$—where $A$ is a monovalent cation (e.g., methylammonium (MA), formamidinium (FA), cesium (Cs)); $B$ is a divalent cation (e.g., lead (Pb), tin (Sn)); and $X$ is a halide (e.g., iodine (I), bromine (Br))—are revolutionizing the field of optoelectronic devices. This is evidenced by the power conversion efficiency of single junction perovskite solar cells (PSCs) increasing from 3.8% to certified values of 25.5% in just over a decade, and by the external quantum efficiency of record perovskite light-emitting diodes reaching over 20%.[1] These results are driven, among other properties, by their bandgap tunability,[2,3] low non-radiative recombination rates,[4] good tolerance to defects,[5,6] long carrier diffusion lengths,[7,8] and low exciton binding energies.[9] The most widespread and reproducible PSCs, leading to moderate stability under device operation, typically employ alloyed compositions with mixed A-site cations (FA, MA, and/or Cs) and halides (I and Br).[10] The wide family of halide perovskites and the devices they are based on are nevertheless sensitive to a number of degradation pathways,[11-14] such as photoinduced[15,16] and bias/current-induced[17,18] ionic migration and phase segregation. Ionic migration particularly affects the halide components of the films due to their higher diffusion coefficients and lower activation energies.[19,20] This segregation effect is particularly exacerbated in moisture- and oxygen-rich atmospheres,[11] and it has been observed to be one of the primary culprits of hysteresis effects in current–voltage (IV) scans of suboptimal PSCs.[21,22] Migrating halides segregating into phases rich in a single halide[23,24] lower the effective bandgap ($E_g$) and open-circuit voltage ($V_{oc}$) of the device. This is due to the lowest $E_g$ domains acting as recombination sites to which carriers funnel down to via downhill energetic gradients.[25,26] This segregation effect is particularly exacerbated in moisture- and oxygen-rich atmospheres,[21] and it has been observed to be one of the primary culprits of hysteresis effects in current–voltage (IV) scans of suboptimal PSCs.[27,28] Furthermore, it has been reported that the presence of mechanical[29-31] or chemical[32,33] (i.e., ionic component size-induced) structural strain may play a key role in inducing or suppressing this halide segregation. It has in fact been observed that X-site alloying fractions below particular threshold values (generally, a Br-content lower than ≈20% on the X-site in mixed I:Br systems) show greatly reduced photoinduced halide segregation...
compared to higher Br-fractions and that this threshold can be increased by the application of compressive strain, reducing the miscibility gap of X-site alloyed halide perovskites. This is especially interesting when considering the reported electrostrictive effect (i.e., mechanical lattice deformation under applied electric field, resulting in an internal mechanical strain) of halide perovskites. A global understanding of the interplay between mechanisms influenced by stressors in an operating device, including light, bias, and atmosphere, is essential to fully understand the stability of mixed-composition PSCs.

Here, we develop an operando variable-pitch grazing-incidence wide-angle X-ray scattering (GIWAXS) technique to track the effect of applied illumination and bias on the structure and on halide segregation in state-of-the-art triple-cation FA$_{0.79}$MA$_{0.16}$Cs$_{0.05}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ PSCs. This strategy, together with ex- and in-situ photoluminescence (PL) measurements, allows us to simultaneously correlate changes in the bulk and in the surface structure of the perovskite absorber to the device performance over time under operation. We show that light- and bias-dependent effects under continuous operation lead to shifts in diffraction peaks of the absorber, consistent with an apparent compressive mechanical strain acting on the lattice and overall better halide mixing, and an associated stable device performance. However, the stability imparted from halide remixing is overwhelmed if the device is operated in humid air, where halide demixing and segregation dominates. Further studies on a poorer quality device with higher series resistance also show halide demixing correlating with subsequent rapid device performance losses dominating the changes, even when operated in inert atmosphere. This study highlights the competition between halide mixing and demixing processes, how sensitive this balance is to initial device quality and operating conditions, and how this will impact expected service lifetime of PSCs. The work also provides a platform for monitoring changes under device operation conditions, leading to systematic and focused mitigation of problematic degradation mechanisms in halide PSCs and other optoelectronic devices.

2. Results and Discussion

We fabricate devices with a glass/indium-doped tin-oxide (ITO)/SnO$_2$/perovskite/Spiro-OMeTAD/Au architecture (see Note S1, Supporting Information for device details and statistics). Figure 1a shows the operando GIWAXS experimental setup.

![Figure 1](https://www.advancedsciencenews.com)

**Figure 1.** a) Experimental setup of operando GIWAXS measurements. b) Current–voltage (IV) curves of the good device (normalized to 0 min $I_{sc}$) at the start and end of the recorded inert operation (the approximate temporal location of IV curve probing is indicated by the respectively colored circles in (c)). The dotted black curve shows the initial power–voltage characteristics. The vertical dotted line indicates the applied voltage. c) Normalized temporal current trend of the good device during inert atmosphere operando GIWAXS testing. The yellow shaded area represents inert atmosphere operation. d–g) Temporal evolution of the bulk (220)/(004) perovskite peak in the out-of-plane (OOP) and in-plane (IP) direction during inert atmosphere operation of the good device, where the peaks are normalized to their individual maximum. The OOP and IP directions are highlighted in shaded green areas in the 2D diffractograms in (d) and (f), respectively. The reference measurement before any operation or illumination is labeled R and is artificially enlarged for visualization purposes. The peak centroids are reported as blue squares, also indicating the instances of GIWAXS probing. The beginning and end of the illuminated timeframe are indicated by the red dashed lines. Outside of these lines, the device is not in operation. The diagrams in the panels show the orientation of the probed crystal planes and their final evolution. A selection of the respective diffractograms is reported in Figure S4, Supporting Information.
We use a variable-pitch stage to selectively probe the bulk of the perovskite layer and the perovskite/top transport layer interface (hereby termed “surface”), simultaneously monitoring the device performance under combined electrical bias and illumination. We use a shallow (0.15°), and a steep pitch angle (0.65°) to respectively probe the surface (i.e., the first few nanometers) and the bulk (i.e., the entirety) of the perovskite absorber layer (see Experimental Section). The use of a synchrotron radiation probe allows us to rapidly acquire measurements with very short exposure times (1 s) to track real-time changes in the crystal structure and detect eventual trace amounts of impurity phases in the device. The utilized X-ray radiation at 24 keV is able to penetrate the thin gold contacts of our devices (see Note S1, Supporting Information). In Figure S1, Supporting Information, we show the 2D GIWAXS diffractograms of our device as acquired in the dark, in pristine conditions, at short-circuit (i.e., 0 V), before any applied illumination or biasing. The corresponding full-quadrant radially integrated GIWAXS diffractograms are shown in Figure S2, Supporting Information. We index the diffraction patterns according to a tetragonal unit cell.[34] We note we also identify small fractions of PbI₂ in the pristine diffractograms due to the addition of excess PbI₂ to the precursor solution for the fabrication of highly efficient cells.[14,35]

Current–voltage (IV) curves of the device designed for in operando GIWAXS measurements at initial operation (Figure 1b, black curve) show the maximum power point to be near 0.8 V. We conservatively operate our device at a voltage bias \( V_{\text{bias}} = 0.5 \text{ V} \) in order to always bias it at \( V_{\text{bias}} < V_{\text{oc}} \) regardless of possible \( V_{\text{oc}} \) degradation during operation. From here onward, “operation” denotes a condition of 0.5 V forward bias and simultaneous 1-sun equivalent illumination. “Not in operation” denotes a condition of 0 V (i.e., short-circuit) bias in the dark (i.e., illumination off). We also define a reference condition, labeled \( R \) in the figures, collected with the device in the dark at 0 V (i.e., short-circuit), before any operando measurements were carried out.

We then continuously operate the device for 150 min in inert atmosphere. A quasi-stable current trend is observed (Figure 1c), consistent with the pre-/post-operation IV curves (Figure 1b) showing only a small drop in short-circuit current \( (I_{\text{sc}}, \text{to } 94 \% \text{ of initial}) \) and \( V_{\text{oc}} \) (to 97% of initial) over this period of operation. We hereby refer to this device as “good device.” We show the corresponding temporal evolution of the GIWAXS radially integrated (220)/(004) perovskite peak in the out of plane (OOP; Figure 1d,e) and inplane (IP; Figure 1f,g) directions for the bulk of the absorber layer (see Figure S3, Supporting Information for surface, and Figure S4, Supporting Information for a selection of the corresponding 2D, and integrated diffractograms). In these and following figures, the reported times indicate the time elapsed since first putting the device under operation.

At 0 min, we observe a shift of the (220)/(004) peak to smaller scattering angles (i.e., larger d-spacing) with respect to the reference diffractogram R in both OOP (Figure 1e) and IP (Figure 1g) directions once in operation. Assuming a volumetric thermal expansion coefficient of \( -1.57 \times 10^{-4} \text{ K}^{-1} \), the cell volumetric changes are found to correspond to changes in temperature of \( \Delta T \approx 16 \text{ K} \) and \( =12 \text{ K} \) in the OOP and IP direction, respectively.[36] We also estimated \( \Delta T \) by using the XRD peak of the gold electrode as an in situ thermometer, indicating a temperature increase in the \( \approx 2–14 \text{ K} \) range (see Note S2, Supporting Information). This range is consistent with the calculated change in temperature in both the OOP and IP direction, and we therefore ascribe the perovskite peak shifts at 0 min primarily to temperature effects.

After the initial shift at 0 min, the (220)/(004) OOP peak gradually shifts to larger q-values (i.e., smaller d-spacing) during operation for 150 min (Figure 1e). In contrast, the IP peak does not show significant changes during device operation (Figure 1g and Figure S5, Supporting Information). On the surface (Figure S3 and figure S5, Supporting Information), the effects in the two directions are qualitatively similar to the bulk observations.

We note we also observe similar trends in other perovskite peaks (Figure S6, Supporting Information). Probing slightly steeper pitch angles with respect to the one utilized for the surface, and therefore probing deeper below the surface and into the bulk, also reveals similar trends (Figure S7, Supporting Information). We also note that after relaxation (i.e., 30 min not in operation, at time point 180 min) the perovskite peaks in the IP direction shift back to their dark reference position, while in the OOP direction the relaxed peaks still retain the shifting to higher angles incurred during operation. Importantly, we note that illumination-only and bias-only operation modes do not induce noticeable changes in the structure (Figure S8, Supporting Information), indicating that our observations are due to the combination of both illumination and bias.

We again put the same device under operation in inert atmosphere, and after a further 10 min we now stress it by introducing, in situ, a humid air atmosphere (relative humidity: \( \approx 60–70\% \)). The operando current trend of the device under operation is shown in Figure 2a. During this operation, we observe a rapid decrease in current to 12% of its initial (i.e., 0 min) value, and the IV curves show degradation in the \( I_{\text{sc}}, V_{\text{oc}}, \) and fill factor parameters (Figure 2b). In Figure 2c,d we report the temporal trends of the radially integrated GIWAXS diffractogram around the (220)/(004) OOP and IP bulk perovskite peak (see Figure S9, Supporting Information for surface, and Figure S10, Supporting Information for a selection of the corresponding 2D, and integrated diffractograms). In all, we observe the same initial peak shifting to lower q-values upon illumination as we observed in Figure 1 (attributed to temperature shifts). However, after this initial lattice expansion, the peaks now undergo a pronounced shift over a period of 30 min to smaller scattering angles in both IP and OOP directions and all probing depths as the device is operated in humid air (Figure S11, Supporting Information), in stark contrast to the behavior observed in inert atmosphere. We note we also observe similar trends in other perovskite peaks (Figure S12, Supporting Information) and probing angles (depths) (Figure S13, Supporting Information). A bare film illuminated over time in humid air for the same illumination dosage shows noticeable peak splitting, a clear sign of halide segregation[21] (Figure S14, Supporting Information). We ascribe the milder peak shifting of our device under the same conditions, compared to the bare film, to the encapsulation effect provided by the transport layers and electrodes present on the device. These results suggest that
The current of the illuminated device held at 0.5 V in inert atmosphere (Figure 1) quickly degrades in operando to 9% of its initial value after 120 min under operation; this behavior is in stark contrast to the trend of the current in the better starting device in Figure 1. The IV curves in Figure 3a show this to be a result of a severe $I_{sc}$ degradation, as well as some $V_{oc}$ loss. The evolution of the (220)/(004) OOP peak centroid moved to 185 min, for visualization purposes. The peak centroids are reported as blue squares, also indicating the instances of GIWAXS probing. The beginning and end of the illuminated timeframe are indicated by the red dashed lines. Outside of these lines, the device is not in operation. The diagrams in the panels show the orientation of the probed crystal planes and their final evolution. A selection of the respective diffractograms is reported in Figure S17, Supporting Information.

We now directly compare in Figure 4a,b the operando (220)/(004) OOP and IP bulk perovskite peak centroid positions of the good (black) and defective (red) devices at the start and end of the investigated periods of operation. After operation in inert conditions, the OOP peak position of the good device is located at larger scattering angles compared to its initial position at the start of the inert operation, while the corresponding IP peak is relatively unaffected. Complementary ex situ PL measurements on a device of comparable performance operated under similar inert conditions show negligible changes in the PL peak position before and after operation (Figure 4c—see Figure S21, Supporting Information).
An electrostrictive effect on lead halide perovskite devices tested ex situ). Nanometer-scale spatial halide heterogeneity has been shown even in highly efficient spincoated mixed-halide perovskites. Furthermore, it has recently been shown that the application of compression on mixed-halide perovskites widens the available miscibility window. An electrostrictive effect on lead halide perovskite films has also been previously reported. An application of such an effect on the film in an absorber layer could therefore lead to an increased intermixing of the halides when starting from a partially segregated starting film composition. We therefore propose that the combined action of the applied bias and illumination in operation activates an electrostrictive effect along the OOP direction, leading to a remixing of the halide species along it (Figure 4d, “stable biased”). We exclude operation-induced strain-only effects as the primary cause of the observed peak shifts as such an effect would likely be relieved upon removal of bias and illumination, whereas the persistent shift of the observed GIWAXS peaks to higher scattering angles in the OOP direction even after extended relaxation without operation is consistent with ionic redistribution (Figure 4a, b, Dark3). Furthermore, we expect local areas maintaining their initial halide composition, including slightly lower bandgap regions, to still persist, to which carriers funnel onto even in the remixed configuration, thus consistent with the observed quasi-stable PL emission position during operation. We propose that an electrostrictive effect compressing the lattice, inducing halide remixing, leads to processes retaining well-mixed halide compositions and thus helps stabilize the operation by hindering phase segregation. We propose that the IP peak position remains stable throughout operation due to a combination of a rigid substrate interfacing directly with these planes, and a photoinduced gradient of halide ions in the OOP direction thus modifying the diffracting lattice planes to a greater extent along the OOP direction. We note we see similar trends even when narrowing the azimuthal integration window (Figure S22, Supporting Information). Future work will be needed to identify and understand the precise origin of these effects, including exploring how electrostrictive and ferroelastic effects influence these phenomena.

Once the initially good device is operated in humid air, on the other hand, we observe the shifted OOP peak position returning close to its initial value (Figure 4a, b, Dark3); the IP peak also undergoes shifting to smaller angles this time, but only during operation (Figure 4d, “unstable biased”). Complementary PL studies on a device of comparable performance run under similar conditions now show a largely red-shifted emission peak (Figure 4c and Figure S21, Supporting Information). The shifting of the GIWAXS peaks to lower angles while the current is degrading, together with the correlated PL red-shift, are interpreted as signatures of halide segregation (demixing); this is also observed in bare films (Figure S14, Supporting Information). These observations are consistent with reports showing that halide segregation is exacerbated in the presence of oxygen and moisture. Therefore, in this situation the segregation effects outcompete any effects which otherwise maintain halide mixing. Finally, we observe at least partial current (and PL) recovery in the complementary ex situ PL device studies after full degradation and relaxation (Figure S21, Supporting Information), and in the operando device (Figure S23, Supporting Information) after relaxation of the humid-air-operated device for 15 min, suggesting some level of halide backward diffusion and remixing during relaxation in the dark.

The peak shifting of the defective device toward smaller angles suggests that this device also undergoes phase segregation (Figure 4d, direct transition from “initial” to “unstable biased”). We speculate that the high series resistance in the device leads to additional heating that further exacerbates segregation under illumination, though further studies would be needed to verify this. The noticeable increase in full-width at half-maximum in the bulk (220)/(004) perovskite peak (Figure S24, Supporting Information) also suggests some degree of absorber layer degradation or amorphization, possibly attributed to this additional heating, which in turn hinders charge extraction.

Finally, we observe that the peak positions (in both directions) of the good and of the defective device after post-degradation relaxation (Figure 4a, b, Dark, for the good device, and Dark, for the defective device) are similar. We therefore propose that the perovskite layers reach a terminal partially halide-segregated
composition that is common to both devices, close to the reported miscibility limit of mixed I:Br perovskites, as evidenced by the final post-degradation perovskite peak positions of both devices.

This phase segregation, whether induced by atmospheric or heating effects, is detrimental to device performance and stability as it leads to a reduction of the effective $V_{oc}$ and $J_{sc}$. These processes result from the creation of I-rich phases and the recombination of charges in these domains as charges funnel down to them due to preferential band alignments. Moreover, exaggerated phase segregation negates any beneficial effects of carrier diversion away from traps that takes place in mixed configurations.

We note that a beneficial halide remixing proved here via a multimodal characterization approach can coexist with the light-induced beneficial lattice expansion reported for comparable pure-iodide systems, as both effects could be convoluted on the observed GIWAXS patterns. This interplay further highlights the complex nature of the properties that different phases invoke in mixed-halide perovskite systems.

Further work should explore approaches to maximize the compression-induced remixing to outcompete unwanted segregation effects, including tweaking absorber compositions, utilizing passivation additives, and exploiting the mechanical properties of contact layers and interfaces. This work will require exploration of these approaches whilst still maintaining high starting efficiency, establishing an important optimization compromise. Furthermore, strategies incorporating native compressive stresses in the perovskite active layer could be conceptualized in order to hinder their phase segregation tendencies, hence extending their expected lifespan and efficiency.

3. Conclusion

Through correlated GIWAXS, PL, and current measurements, we show that illuminated biasing in inert atmosphere of mixed-halide perovskite devices induces remixing of the halide population in the out-of-plane direction of the absorber layer. We propose that this effect occurs due to an electrostrictive effect inducing a compressive strain in the out-of-plane direction. Compressive strain has been reported to increase the miscibility window of mixed-halide perovskite films, as well as effects of carrier diversion away from traps that takes place in mixed configurations.

4. Experimental Section

Perovskite Precursor Solutions

- Reduced (thin) electrode thickness devices: the perovskite solution was prepared by dissolving PbI$_2$ (1.15 m), PbBr$_2$ (0.2 m), formamidinium iodide (FAI, 1.09 m), and methylammonium bromide (MABr, 0.2 m) in a mixed solvent of N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) with 4:1 ratio. CsI solution in DMSO (5 vol.%, 1.5 m) was then added to the mixed perovskite solution. These devices were prepared according to a methodology for highly efficient perovskite solar cells reported by Saliba et al.

- Full (normal) electrode thickness devices and thin films: the perovskite solution was prepared by dissolving PbI$_2$ (1.1 m), PbBr$_2$ (0.22 m), FAI (1 m), and MABr (0.2 m) in a mixed solvent of DMF:DMSO with 4:1 ratio. CsI solution in DMSO (5 vol.%, 1.5 m) was then added to the perovskite solution.

Device and Thin Film Fabrication

- Reduced (thin) electrode thickness devices:
  - Good device: the SnO$_2$ particle solution was diluted in deionized water and was sonicated for 15 min before use. 2, 2’, 7, 7’-Tetrakis[N, N-di-(4-methoxyphenyl)aminol] 9, 9’-spirofluorene (Spiro-OMeTAD), 72.3 mg solution was prepared by dissolution in chlorobenzene (1 mL). 4-Tert-butylpyridine (tBP), lithium bis(trifluoromethane)sulfonamide (LiTFSI), and tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) trifluoromethane sulfonimide (FK 209 Co(III) TFSI) were added in the Spiro-OMeTAD solution with a 3.3, 0.05, and 0.5 molar ratio concentration with respect to Spiro-OMeTAD. To form a thin Spiro-OMeTAD layer (50 nm), the solution was then diluted with chlorobenzene with a 1:3 volume ratio. ITO substrates 12 × 12 mm$^2$ were cleaned by sequentially sonicationing them in a Decon 90, deionized water, acetone, and isopropanol bath for 15 min each time. The dried ITO substrates were then treated in UV ozone for 15 min. The diluted SnO$_2$ solution was spin-coated on the ITO substrates at 3000 rpm for 30 s and was then annealed at 150 °C for 30 min in air. After cooling down, the substrates were immediately transferred to an inert glovebox. The perovskite solution was spin-coated on the substrates according to a two-step spin-coating protocol: 1) 2000 rpm for 10 s, and 2) 6000 rpm for 20 s. 5 s before the end of the spin-coating process, chlorobenzene (100 μL) was dropped on the perovskite. The perovskite films were then annealed at 100 °C for 60 min. After annealing, Spiro-OMeTAD was spin-coated on the perovskite layer at 6000 rpm for 30 s. Finally, gold (20–25 nm) contacts were deposited by vacuum deposition.
  - Defective device: [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was dissolved in chlorobenzene (20 mg mL$^{-1}$) and heated at 75 °C for 2 h. Bathocuproine (BCP) was dissolved in isopropanol (0.5 mg mL$^{-1}$) and sonicated for 30 min. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA, 2 mg mL$^{-1}$) was dissolved in chlorobenzene, and poly[(9,9-bis(30-([N,N-dimethyl-N-ethylammonium(propyl)-2,7-fluorene)]-alt-2,7-(9,9-diocetylfluorene)]) dibromide (PFN-P2), 0.5 mg mL$^{-1}$) was dissolved in methanol. The PFN-P2 solution was sonicated for 30 min. ITO substrates 12 × 12 mm$^2$ were cleaned by sequentially sonicationing them in a Decon 90, deionized water, acetone, and isopropanol bath for 15 min each time. The dried ITO substrates were then treated in UV ozone for 15 min. The PFN-P2 solution was spin-coated on the PTAA layer at 5000 rpm for 30 s. The substrates were then immediately transferred to an inert glovebox. The perovskite deposition followed the same protocol as described above for the good device. After annealing, PCBM...
was spin-coated on the perovskite layer at 1200 rpm for 30 s. The BCP was dynamically dropped on the PCBM layer during spin-coating at 2000 rpm for 30 s. Finally, silver (20–25 nm) contacts were deposited by vacuum deposition.

- **Full (normal) electrode thickness devices**: Spiro-OMeTAD (72 mg) solution was prepared by dissolution in chlorobenzene (1 mL), doped with tBP (28.8 µL), Li-TFSI (17.5 µL, 520 mg mL⁻¹ in acetonitrile) and FK 209 Co(III) TFSI (28.8 µL, 300 mg mL⁻¹ in acetonitrile). ITO substrates 12 × 12 mm² (15 L), doped with tBP (28.8 L, 520 mg mL⁻¹) were cleaned by sequentially sonicating them in a Decon 90, deionized water (3x), and isopropanol bath for 10 min each time. The substrates were dried with a nitrogen gun and subsequently O₂-plasma etched for 5 min using a radio-frequency plasma source. The SnO₂ precursor (15% in H₂O colloidal dispersion) was diluted in deionized water, and was subsequently spin-coated on the substrates at 3000 rpm for 30 s. The substrates were annealed at 180 °C for 30 min. After cooling down, the substrates were immediately transferred to an inert glovebox. The perovskite solution was spin-coated on the substrates according to a two-step spin-coating protocol: 1) 1000 rpm for 10 s, and 2) 6000 rpm for 35 s. 10 s before the end of the spin-coating protocol, chlorobenzene (100 µL) was dropped on the perovskite. The perovskite films were then annealed at 100 °C for 40 min. After annealing, Spiro-OMeTAD was spin-coated on the perovskite layer at 4000 rpm for 20 s. Finally, gold (80 nm) contacts were deposited with a rate of 0.03 nm s⁻¹ for the initial 10 nm, and then 0.1 nm s⁻¹ until the target thickness was reached.

- **Thin films**: Glass substrates were cleaned by sonication in acetone and isopropanol for 30 min, and were then further cleaned with O₂-plasma treatment for 10 min. The perovskite solution was spin-coated on the glass substrates according to a two-step spin-coating protocol: 1) 1000 rpm for 10 s, and 2) 4000 rpm for 30 s. 10 s before the end of the spin-coating protocol, chlorobenzene (100 µL) was dropped on the perovskite. The perovskite films were then annealed at 100 °C for 40 min. After annealing, Spiro-OMeTAD was spin-coated on the perovskite layer at 4000 rpm for 20 s. Finally, gold (80 nm) contacts were deposited with a rate of 0.03 nm s⁻¹ for the initial 10 nm, and then 0.1 nm s⁻¹ until the target thickness was reached.

**Ex Situ Device Characterization**

- **Full (normal) electrode thickness devices**: the photocurrent density–voltage (JV) curve measurements were performed with illumination from a 450 W Oriel xenon lamp with a Schott K113 Tempax sunlight filter (Präzisions Glas und Optik GmbH, Germany) to adjust the emission spectrum to the AM 1.5 standard. The intensity of the lamp was calibrated by an Si reference diode with a Schott KG-3 infrared cut-off filter to 1-sun intensity (100 mW cm⁻²) curve measurements were performed with illumination from a xenon lamp (Abet Sun 2000 Solar Simulators, AAB class) at 1 sun intensity (100 mW cm⁻², AM 1.5G). The light intensity was calibrated by a reference Si diode with a KG5 filter. The device performance was recorded with a Keithley 2636A, controlled by a home-built LabVIEW program. The JV curves were scanned from 1.2 to 0 V (reverse scan) and 0 to 1.2 V (forward scan) with a step size of 50 mV. Both forward and reverse scan were conducted with a scanning rate of 100 mV s⁻¹. The solar cell active area was 4.5 mm², defined by the mask. All the devices were measured in air without encapsulation.

- **Reduced (thin) electrode thickness devices**: the photocurrent density–voltage (JV) curve measurements were performed with illumination from a xenon lamp (Abet Sun 2000 Solar Simulators, AAB class) at 1 sun intensity (100 mW cm⁻², AM 1.5G). The light intensity was calibrated by a reference Si diode with a KG5 filter. The device performance was recorded with a Keithley 2636A, controlled by a home-built LabVIEW program. The JV curves were scanned from 1.2 to −0.1 V (reverse scan) and −0.1 to 1.2 V (forward scan) with a step size of 20 mV and a delay time of 100 ms. Both forward and reverse scan were conducted with a scanning rate of 100 mV s⁻¹. The solar cell active area was 8.75 mm², defined by the mask. All the devices were measured in air without encapsulation.

**GIWAXS**: The measurements were performed at the I07 beamline of the Diamond Light Source facility in Didcot, United Kingdom. The beam energy was 10 keV for bare film and 24 keV for full device measurements. 24 keV was used for the latter in order for the X-rays to penetrate the metal electrodes, as the device was operated with illumination impinging on the thin gold metal contact rather than on the customary glass backside. The bare films were measured with a pitch angle of 0.30°. The good device was measured with pitch angles of 0.15° (surface), 0.20°, 0.30°, and 0.65° (bulk). The defective device was measured with pitch angles 0.10° (surface)—note shallower pitch angle for surface measurements due to silver electrodes), 0.15°, 0.30°, and 0.65° (bulk). The surface pitch angles were chosen such as to be below the critical angles of the gold and silver electrodes at 24 keV. This ensured that the X-rays only penetrated the electrodes as evanescent waves for the surface measurements, thereby only probing the first few nanometers of the perovskite layer. The measurement chamber was continuously flushed with dry He gas or artificial humid air at 3 L min⁻¹. Humidity was introduced by bubbling the gas flow through a water-filled container. The levels of relative humidity were <5% for dry He, and 60–70% for humid air conditions. Illumination of bare films was achieved by a 532 nm laser mounted inside of the chamber. Illumination of full devices was achieved by a 532 nm laser placed outside of the chamber, incoupling into a non-polarization-maintaining optical fiber, and then outcoupling into the chamber onto the devices via a laser outcoupler. <0.3 sun (30 mW cm⁻²) illumination for bare films was achieved by powermeter calibration. Illumination for full devices was calibrated to yield ~1-sun equivalent (100 mW cm⁻² equivalent) illumination via monitoring of the device current. The devices were mounted on a custom-made pitch-tilting stage in order to allow surface- and bulk-sensitive measurements, as well as their electrical probing. 0.5 V forward biasing was achieved via a computer-controlled Keithley 2450 sourcemeter, which also allowed IV collection. Postprocessing of the GIWAXS diffractograms and baseline correction was carried out in DAWN and OriginPro software. A mask was applied by discarding all negative intensity values (these correspond to the detector grid gaps, in order not to be counted in the integration). The device GIWAXS measurements were calibrated in OriginPro by q-value and intensity normalization of the scattering pattern to the q = 2.15 Å⁻¹ ITO reference peak individually for each pitch angle and full- or half-quadrant integration (note the defective device surface diffractograms at 0.10° pitch angle were calibrated using the 0.15° pitch angle calibration values due to the excessively low intensity of the ITO reference peak at this pitch angle). Out-of-plane integrations were carried out integrating the 0 ≤ χ ≤ 45° interval, while in plane integrations were carried out in the 45° ≤ χ ≤ 90° intervals, where y is the azimuthal angle, and 0° and 90° correspond to the qₓ and qᵧ axes, respectively.

**Photoluminescence**

- **Ex situ device operating measurements**: the photoluminescence was acquired with devices placed in a dry N₂ flow. Note this flow could not guarantee a completely inert atmosphere. The “stable” measurement reports a negligible change in photoluminescence. A completely inert atmosphere would have produced an even smaller change, and can therefore be considered representative. The full current degradation (unstable) measurement can also be considered representative of a full degradation experiment in humid air as humidity and oxygen were nevertheless present in the testing atmosphere, therefore only delaying/reducing any humid-air-induced observed effects rather than completely suppressing them, as observed. The illumination source for photovoltaic operation was a ~0.75 ± 0.25-sun-equivalent (75 ± 25 mW cm⁻²-equivalent) 532 nm laser (the laser is vertically polarized, but it reaches the device through a non-polarization-maintaining optical fiber and laser outcoupler, making the incident excitation unpolarized). For photoluminescence spectra acquisition, the intensity was 75 ± 25-sun-equivalent. 0.5 V forward biasing was achieved via a Keithley 2450 sourcemeter. The photoluminescence was collected via a coupling lens and a multimode fiber, and detected with an OceanOptics Maya2000 Pro fixed-grating spectrometer. The exposure time was 100 ms. All photoluminescence measurements were averaged through 10 exposures. The peak positions were derived...
by Gaussian fitting of the peaks after Jacobian transformation to energy scale.

- **GIWAXS in situ measurements of bare films**: the photoluminescence was acquired with bare films under a ~0.3-sun (30 mW cm⁻²) 532 nm laser as illumination source. The photoluminescence was collected via a coupling lens and a multimode fiber, and detected with an OceanOptics Maya2000 Pro fixed-grating spectrometer. The exposure times were 5 s for measurements in dry He and 0.5 s for measurements in humid air.

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

**Acknowledgements**
The authors acknowledge the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (HYPERION, grant agreement No. 756962), and the Engineering and Physical Sciences Research Council (EPSRC) (grant agreement No. EP/R023980/1, EP/TO2030X/1, EP/S030638/1 and EP/V027131/1). E.R. was partially supported by an EPSRC Departmental Graduate Studentship. R023980/1, EP/T02030X/1, EP/S030638/1 and EP/V027131/1. S.D.S. also acknowledges funding from the Lloyd’s Register Foundation. M.A. acknowledges funding from the European Union’s Horizon 2020 research and innovation programme, the Marie Skłodowska-Curie actions (grant agreement No. 841386) under the European Union’s Horizon 2020 research and innovation programme. S.D.S. also acknowledges funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (HYPERION, grant agreement No. 756962), and the Engineering and Physical Sciences Research Council (EPSRC) (grant agreement No. EP/S030638/1). A.A. acknowledges the Royal Society for funding. R. Prasanna, A. Gold-Parker, T. Leijtens, B. Conings, A. Babayigit, H.-G. Boyen, M. F. Toney, M. D. McGehee, J. Am. Chem. Soc. 2017, 139, 11117.

**Conflict of Interest**
S.D.S. is a co-founder of Swift Solar, Inc.

**Data Availability Statement**
The data that support the findings of this study are openly available in Apollo - University of Cambridge Repository at https://doi.org/10.17863/CAM.86897.

**Keywords**
diffraction, electrostriction, perovskites, photosegregation, photovoltaics

Received: March 8, 2022
Revised: July 11, 2022
Published online:

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