**Introduction**

Perovskite photovoltaics (PV) is one of the fastest growing optoelectronic technologies.\(^1\)–\(^7\) The ability to deposit these abundant materials with large area solution processing techniques has the potential to make perovskites viable for low-cost production.\(^8\)–\(^10\) Typical perovskite thin films in devices are fabricated by depositing mixtures of dissolved organic and inorganic precursor salts and annealing to form polycrystalline films. Despite these relatively crude solution processing methods (in comparison to methods to grow traditional inorganic solar absorbers), these materials exhibit exceptional optoelectronic properties suggesting a remarkable defect tolerance. For example, perovskite films show sharp absorption edges,\(^11\),\(^12\) long carrier diffusion lengths\(^13\) and high luminescence quantum efficiencies,\(^14\) suggesting they are clean semiconductors with low densities of sub-gap trap states.\(^15\) These properties directly translate to excellent photovoltaic figures-of-merit (FOM), with record device efficiencies currently reaching 22.1%.\(^7\)

Researchers have investigated several engineering methods to further optimize perovskite film morphology and improve their performance.\(^3\),\(^16\),\(^17\) Thermal engineering is the most widely studied approach, which aims to elucidate the optimal combination of annealing temperature, annealing time, atmospheric conditions and temperature profiles.\(^16\),\(^18\)–\(^20\) For most perovskite materials, the anneal temperature is critical for optimized conversion of the as-coated precursor material into...
a crystallized perovskite film but annealing for too long may cause degradation.\textsuperscript{16,21,31} Thus, studying how the photovoltaic performance of a perovskite solar cell evolves with time during the anneal is crucial in thermal engineering. However, to do so, one needs to pre-anneal and complete the device stack, then measure current–voltage (\(JV\)) sweeps \textit{ex situ} in multiple solar cells for different annealing periods,\textsuperscript{16,23,24} which would take an unfeasible amount of time.

In-depth complementary measurements are also needed to understand the trends of FOM profiles vs. annealing time. Synchrotron Grazing Incidence X-ray diffraction (GI-XRD) techniques have shed light on several aspects of the precursor to perovskite conversion including degradation, phase transformations, degree of crystallinity, and distribution of crystal sizes and orientation.\textsuperscript{16,25–31} Fast 2D detectors and high intensity X-ray beams have allowed \textit{in situ} studies during the formation, crystallization, and degradation of perovskite films in Grazing Incidence Wide Angle X-ray Scattering (GI-WAXS) geometry.\textsuperscript{21,22,31,32} Data obtained from \textit{in situ} GI-XRD measurements can be used to interpret FOM profiles of perovskite solar cells vs. anneal time. A direct relationship between the photovoltaic performance and the structural properties can only be established when photovoltaic and structural measurements are performed simultaneously in a working solar cell. However, top layers above the perovskite film in a standard perovskite solar cell would interfere with the GI-XRD measurement when compared to a bare perovskite film, and even then it is again unfeasible to fabricate and anneal at different time periods several solar cells and then measure their diffraction patterns \textit{ex situ}.

In this work, we explore the performance of perovskite solar cells during the formation of the perovskite from the earliest stages of its conversion from the precursor phase to the fully formed perovskite phase and during its degradation. This is achieved by leveraging the concept of interdigitated back-contact (IBC) solar cells, in which the electron and hole selective electrodes are co-positioned on the backside of the cell in an interdigitated fashion. Unlike conventional planar heterojunction solar cells, with the IBC architecture, optical transmission losses caused by the top contact can be avoided as the photoactive layer is directly exposed to light. In this work, the main advantage of IBC perovskite solar cells is that the perovskite layer represents the final step of the device fabrication. Since the perovskite film is not blocked by any capping layer, \textit{in situ} annealing can be performed without compromising the perovskite conversion. At the same time, the perovskite film is directly accessible by an X-ray beam in GI-WAXS geometry. Here, we use the IBC structure to simultaneously acquire photovoltaic and GI-WAXS measurements \textit{in situ} during the anneal to directly investigate the relationships between the figures-of-merit of a solar cell and its structural properties. We investigate two state-of-the-art benchmark perovskite materials for processing under ambient conditions (MAPbI\(_3\), MA = methylammonium) prepared from MAI: PbCl\(_2\) and two additives (HI or PbI\(_2\)). We spin-coat these solutions on the IBC architecture and show that even in the earliest stages of conversion of precursors to perovskite we achieve remarkably high open-circuit voltages, suggesting that the defect tolerance appears at an early stage in the conversion process. In contrast, the current continues to rise until the precursor conversion is complete and there is a continuous pathway for collecting charges. We show analogous trends in the FOM of planar heterojunction solar cells fabricated from MAI: PbCl\(_2\) with HI and annealed \textit{ex situ}. We further observe analogous high photovoltages before the full perovskite conversion for a variety of perovskite systems including (1) MAPbI\(_3\) prepared from MAI: PbAc\(_2\),\textsuperscript{21} (2) the triple mixed cation Cs\(_{0.5}\)(MA\(_{0.17}\)FA\(_{0.83}\))\(_{0.95}\)Pb\(_{0.83}\)(Br\(_0.17\))\(_3\) \(\text{FA} = \text{formamidinium}\),\textsuperscript{33} and (3) the mixed cation (FAI)\(_{1.0}\)(MA\(_{0.38}\)Br\(_{0.62}\))\(_{1.1}\)(PbI\(_2\))\(_{0.20}\).\textsuperscript{34} Our work elucidates the direct connection between the clean semiconductor behaviour of perovskite materials and their structural properties. To the best of our knowledge, this is the first report of simultaneous photovoltaic and GI-WAXS measurements of solar cells performed \textit{in situ} during formation of the perovskite absorber layer.

### Results and discussion

We custom-designed a setup to directly monitor the structural properties of perovskite films and their photovoltaic performance during the fabrication of an interdigitated back contact (IBC) solar cell \textit{in situ} and \textit{in operando} (Fig. 1a). Briefly, measurements were performed at the XMAS beamline (ESRF, Grenoble, France) using an annealing chamber with regulated temperature control mounted on a diffractometer and a white LED mounted above the sample to give a similar photon flux to solar illumination conditions \((\sim 100 \text{ mW cm}^{-2}\)) at the sample position. The substrates employed here are interdigitated ITO substrates with a channel length of 100 \(\mu\text{m}\). Electron- and hole-selective electrodes were obtained by electrodepositing electrodes with TiO\(_2\) and PEDOT, respectively (Fig. 1a).\textsuperscript{35} The substrate was spin-coated in air with a perovskite precursor solution and immediately mounted within 20 \(s\) on the sample stage (hotplate) pre-set at a specific temperature (isothermal measurements). \(JV\) curves under dark and light conditions and Grazing Incidence Wide Angle X-ray Scattering (GI-WAXS) diffraction patterns under dark conditions were acquired every \(\sim 54.4 \text{ s}\) during the anneal process for \(\sim 3 \text{ h}\). The typical measurement procedure consisted of a continuous loop of the following: (1) measure one GI-WAXS pattern (light off, X-ray on); (2) measure one current–voltage (\(JV\)) sweep (light off, X-ray off); (3) measure \(JV\) sweep (light on, X-ray off). The setup and the measurement procedure described here is also illustrated in the movie shown in ref. 52.

In Fig. 1 we show a summary of the measurements performed on an IBC solar cell spin-coated with a precursor solution made of MAI: PbCl\(_2\) \((2.95:1 \text{ M})\) with HI additive \((1\%)\) in dimethylformamide (DMF), which is a recipe able to produce high performance solar cells in the ambient conditions employed here.\textsuperscript{10,36} The perovskite-coated IBC solar cell (IBC130) was annealed at 88.2 °C (measured at the sample surface) under \(N_2\) atmosphere to minimise X-ray beam damage. The as-coated film
undergoes a three-stage evolution: (i) precursor phase conversion into perovskite phase, (ii) perovskite crystallization, (iii) perovskite degradation into lead iodide.\textsuperscript{31,32,26,27} Diffraction patterns collected at the beginning of the anneal only display the characteristic crystalline precursor phase (Fig. 1b), which reaches a maximum intensity after \(~15\) min from the beginning of the anneal. The \((100)\) perovskite peak, belonging to the pseudo-cubic \(z\)-phase,\textsuperscript{37,38} gradually increases in intensity after \(~10\) min and reaches a maximum value after \(~62\) min. The primary product of the perovskite degradation, \(\text{PbI}_2\), appears after \(~70\) min and increases throughout the anneal (Fig. 1c). Line profiles azimuthally integrated over the entire image are plotted in Fig. 1e and display the evolution of four precursor peaks, the perovskite peak and the \(\text{PbI}_2\) peak in the \(q = [0.74 1.24]\ \text{Å}^{-1}\) range. The full sequence of GI-WAXS images and extracted data are shown in the movie for S130 shown in ref. 53.

The \(J\)V sweeps in Fig. 1d were performed across a \(100\) \(\mu\text{m}\) channel length. Measurements under light conditions show a rectifying behaviour and display a low photocurrent at the beginning of the anneal, with a gradual increase until \(~90\) min, a maximum photocurrent of \(0.18\) mA cm\(^{-2}\), and a progressive reduction throughout the anneal. \(J\)V sweeps under dark conditions show a rectifying behaviour with negligible current density (see the movie for S130 shown in ref. 53 for a comparison between dark and light sweeps). Measurements on interdigitated ITO substrates without PEDOT and TiO\(_2\) displayed photocurrents two orders of magnitude smaller than that of a coated device in the first 14 min of the anneal (see the movies for S28 and S29 shown in ref. 54 and Fig. S2, ESI\textsuperscript{†}). However, after 14 min no photocurrent was detected. The opto-electrical properties of IBC perovskite solar cells with a channel length of \(100\) \(\mu\text{m}\) are comparable to the measurements shown in an earlier work using a channel length of \(4\) \(\mu\text{m}\) (Fig. S3, ESI\textsuperscript{†}).\textsuperscript{35} The fact that working devices can be obtained using a channel length exceeding the carriers diffusion lengths was predicted by Pazos-Outón et al., who interpreted this as the effect of photon recycling, which boosts the ‘diffusion’ length of electrons and holes.\textsuperscript{35} Measurements performed on IBC solar cells with gaps ranging from \(50\) \(\mu\text{m}\) to \(200\) \(\mu\text{m}\) did not show any clear trend in the FOM vs. channel length (Fig. S4 and S5, ESI\textsuperscript{†}), suggesting that larger gaps would be required to observe clearer differences in the photovoltaic performance.

To better compare the opto-electrical measurements with the structural data, we calculate the areas under the most intense precursor peak (\(\sim0.85\) \(\text{Å}^{-1}\)), the perovskite peak, and the \(\text{PbI}_2\) peak, and plot them vs. the annealing time. These peak integrals represent the degree of crystallinity (i.e. amount of scattering crystals) of the three phases and are compared to the normalized figures-of-merit (FOM) extracted from reverse \(J\)V sweeps measured during the anneal in Fig. 2. Absolute values of the FOM and \(J\)V sweeps are available in the movie for S130 shown in ref. 53.

The short circuit current density \((J_{sc})\) starts from a negligible value at the beginning of the anneal (\(~3\) min) and seems to follow a growth dynamics similar to that of the perovskite peak. It reaches a peak of \(0.18\) mA cm\(^{-2}\) after \(90\) min, decreases, and
The current peaks only when all of the precursors have been converted to perovskite. While the voltage peaks when surrounded by passivating dielectric material, the current only peaks when there is a continuous path for charge collection. When the current and perovskite signal peak, the perovskite grains will impinge upon each other and this is likely to introduce crystal defects at the boundaries, responsible for non-radiative recombination and hence a reduction in $V_{oc}$. The reduction of chloride ions (MACl), which sublimate during the precursor to perovskite conversion,\(^{25}\) could be the reason why the $V_{oc}$ reduces after reaching a peak.

To confirm whether the structural and FOM trends are interdependent, we performed analogous measurements by annealing other IBC solar cells at different temperatures: 83.8 °C (IBC S142), 92.5 °C (IBC S129), and 96.8 °C (IBC S128). Diffraction patterns, structural data, and FOM for these devices are available in the movies for S142, S129, S128 shown in ref. 55–57 and in Fig. S7–S9 (ESI†). As the annealing temperature is varied, the trend dynamics of both the FOM and the peak integrals shift together with time (Fig. S10–S13, ESI†). Particularly, the trends mentioned above for IBC S130 are also observed in IBC S142, S129, and S128. This confirms that the opto-electrical properties are directly correlated with the structural properties measured by GI-WAXS. The structural data from the IBC solar cells annealed at different temperatures can be used to assess the perovskite crystallization kinetics with the Johnson–Mehl–Avrami (JMA) model.\(^{16,21,22}\) We calculate an activation energy for crystallization ($\sim 89$ kJ mol\(^{-1}\)) slightly higher than the one reported by Barrows et al. ($\sim 85$ kJ mol\(^{-1}\))\(^{22}\) and by Moore et al. ($\sim 86$ kJ mol\(^{-1}\))\(^{21}\) (Fig. S14 and Table S3, ESI†). This minor difference could be due to the fact that the IBC solar cells discussed here are annealed under nitrogen atmosphere, which slows down the crystallization, and/or have HI as an additive. However, this is partially counterbalanced by the fact that the perovskite films reported here are $\sim 200$ nm thinner than the ones reported by Barrows et al., which would speed up the crystallization.

These results reveal several fascinating insights. The reasonably high voltages through many of the early stages of the conversion suggests that we have a relatively clean semiconductor from the very beginning. The moderate voltage at the start of the anneal, where we have predominantly a pure precursor phase and solvent, suggests that we first form a percolative pathway for charge transport at this earliest point in time. The photovoltage peaks at a point in time when much of the precursor material has not yet been converted to perovskite, is consistent with a self-passivation of perovskite defect states by amorphous material including precursors (PbI$_2$, PbCl$_2$).\(^{39,40}\)

The multiple oscillations in the $J_{sc}$ and $V_{oc}$ trends in Fig. 2b are not visible in the structural data, suggesting that they are not related to structural changes in the perovskite crystal. IBC S132 was prepared as IBC S130, with the exception that GI-WAXS and JV measurements were performed every 10 min, instead of every 54.4 s, corresponding to a reduction in the X-ray and light dose. As shown in the movie for S132 in ref. 58 and Fig. S15 (ESI†), a reduction in the data sampling period does not seem to mitigate the oscillations in the short circuit current density. IBC S116 was prepared as IBC 132, with the
difference that the GI-WAXS patterns were integrated for a longer period (10 s instead of 1 s) and that \( J_{sc} \) and \( V_{oc} \) were statically measured without applying any bias. In this case \( J_{sc} \) and \( V_{oc} \) appeared significantly smoother without noticeable oscillations (see the movie for S116 shown in ref. 59 and Fig. S16, ESI†). We then increased the GI-WAXS and static \( J_{sc} \) and \( V_{oc} \) sampling time on another IBC solar cell (S117) back to 54.4 s. The increased X-ray and light dose did not result in oscillations in \( J_{sc} \) and \( V_{oc} \) (see the movie for S117 shown in ref. 60 and Fig. S17, ESI†). These measurements suggest that the oscillations could be related to changes in ionic accumulation at the electrodes induced by the \( JV \) sweeps, potentially related to the release of excess \( \text{MACl} \) from the surface. Note that these oscillations do not affect the general trend of the figures-of-merit.

To address whether the bias applied during the \( JV \) sweeps could influence the dynamics of the perovskite film during the anneal, we compare the peak integrals extracted from the GI-WAXS measurements performed on IBC S132 (\( JV \) sweeps) and IBC S116 (static \( J_{sc} \) and \( V_{oc} \) measurements). The trends of the perovskite peak match almost perfectly in the initial phase (Fig. S19, ESI†) and thus, if any structural change takes place as an effect of the applied bias, this is not measurable with our GI-WAXS setup. After reaching a maximum value at \( \sim 63 \) min in IBC S116 (10 s integration time), the intensity of the perovskite peak reduces due to the higher X-ray dose.

Perovskite films can be damaged by prolonged exposure to X-rays and light. X-ray damage is visible as a yellow stripe (PbI\(_2\)) that spreads from the beam footprint position (Fig. S18, ESI†). The emergence of the PbI\(_2\) signal and the decrease in the perovskite signal after \( \sim 70 \) min from the beginning of the anneal, is mainly due to beam damage (Fig. 2a), which exacerbates the natural perovskite decomposition into PbI\(_2\) due to the loss of the organic component for extended anneal.\(^{41}\) When the GI-WAXS sampling rate was reduced from one measurement every 54.4 s (IBC S130) to one measurement every 10 min (IBC S132), a much lower PbI\(_2\) signal was recorded during the anneal. Since the X-ray beam footprint is limited to a small area of the solar cell, beam damage has a limited effect on the degradation of the figures-of-merit. However, the FOM are strongly affected by continuous exposure to light (cf. IBC S115 with S113 in Fig. S19, ESI†). X-ray beam and light damage are further discussed in the ESI† along with comparisons between samples exposed to different X-ray and light doses (Fig. S19, ESI†). We also find that the FOM parameters increase faster with longer light exposure over the initial periods (Fig. S19, ESI†). This is likely related to a photo-induced reduction in trap density (\textit{i.e.} photo-brightening effects),\(^{42}\) which is in turn related to photo-induced ion migration processes and could be further exaggerated with residual oxygen and moisture molecules in the precursor film.\(^{40,43}\)

As already elucidated in a recent report on spray-coated and spin-coated perovskites from MAI: \( \text{PbCl}_2 \; (3:1) \) on both \( \text{Si/SiO}_2 \) and \( \text{Si/SiO}_2/\text{PEDOT:PSS} \) substrates, the annealing process is characterized by the rotation and lattice contraction and expansion of both perovskite and precursor crystallites.\(^{27}\) The grain evolution is evident from the change in the scattering vector position of the diffraction spots populating the diffraction rings of the GI-WAXS patterns during the \textit{in situ} anneal.\(^{27}\)

From the sequences of GI-WAXS images of all the IBC solar cells reported in this work (see the movie shown in ref. 52) we observe again that the diffraction spots from single crystallites move in the reciprocal space during the anneal, which is an indication of grain rotation and lattice contraction/expansion. By reducing the sampling rate from 54.4 s down to 11 s (see the movie for S131 shown in ref. 61) the moving diffraction spots can be observed in a clearer way.

To establish whether IBC solar cells fabricated and measured \textit{in situ} during the anneal show performance dynamics similar to standard solar cells fabricated \textit{ex situ}, we prepared a series of planar heterojunction solar cells and annealed them \textit{ex situ} for different periods. Compact \( \text{TiO}_2 \) was deposited via spray-pyrolysis onto FTO substrates, followed by a spin-coated \( \text{TiO}_2 \) mesoporous layer. The perovskite layer was spin-coated onto this mesoporous layer and annealed at \( \sim 97 \) °C for various periods (1–180 min). Doped (Li-TFSi and \( t \)BP) Spiro-OMeTAD was spin-coated onto the perovskite layer before an 80 nm gold electrode was thermally evaporated.

Fig. 3a shows a comparison between the normalized \( J_{sc} \) of the planar solar cells and two IBC solar cells annealed at \( \sim 97 \) °C. On the first IBC device (S128) we performed simultaneous electrical measurements and GI-WAXS measurements every 54.4 s. The electrical measurements consisted of a forward \( JV \) sweep under dark (18 s) followed by a reverse \( JV \) sweep under light (18 s). In the GI-WAXS measurement under dark the IBC was exposed to the X-ray beam for 1 s. On the second IBC device (S105) we performed static \( J_{sc} \) and \( V_{oc} \) measurements under light (6 s), without applying any bias and without exposing the IBC to the X-ray beam. The \( J_{sc} \) follows the same initial trend for the two architectures and reaches a peak after 20–30 min. This peak roughly corresponds to the instant when the perovskite film has fully converted and reached the maximum crystallization point (Fig. 3c). The first IBC device (S128) undergoes a sudden drop in the \( J_{sc} \) after 22 min caused by a relatively high light dose. We observe an analogous but less pronounced decay in the second IBC device (S105) thanks to the lower light dose and the absence of applied bias. The planar solar cells show a relatively stable performance after the first 20 min. Prolonged annealing for 3 hours shows no statistically significant reduction in performance (see absolute values in Fig. S20, ESI†). As discussed above, trends similar to the ones displayed by the planar solar cells were observed in IBC solar cells by reducing the \( J_{sc} \) and \( V_{oc} \) sampling rate to 10 min (IBC S142, S130, S129). However, this data is only available for lower temperatures.

Fig. 3b shows a comparison between the normalized \( V_{oc} \) of the planar solar cells and the two IBC solar cells annealed at \( \sim 97 \) °C. The three profiles all show a relatively high open circuit voltage at the beginning of the anneal similarly to what we observed in the earlier discussion. In the first IBC solar cell (S128) the \( V_{oc} \) shows a trend that is similar to the \( J_{sc} \), although it reaches a peak when the peak intensity of the precursor phase...
equals the intensity of the perovskite phase (Fig. 3b). The FF in the IBC solar cells behaves in a very different way compared to the planar solar cells, and is characterized by a sudden drop within the first 10 min of the anneal (Fig. S21, ESI†). The FF in IBC devices when fabricated using a different precursor route equals the intensity of the perovskite phase (Fig. 3b). The FF in the IBC solar cells behaves in a very different way compared to the planar solar cells, and is characterized by a sudden drop within the first 10 min of the anneal (Fig. S21, ESI†). The FF in IBC devices when fabricated using a different precursor route.

The illustrated measurements suggest that the figures-of-merit of IBC solar cells fabricated and measured in situ during the anneal follow dynamics comparable to that of standard planar solar cells. This implies that IBC solar cells can provide a fast and low-cost route for optimizing perovskite materials requiring thermal annealing treatments, while preserving the features of the standard solar cells. The dataset presented for the planar solar cells is the result of the fabrication of 40 devices, each made of 4 usable pixels, i.e. solar cells. The time required for the entire fabrication and measurements was about 30 h. This was necessary to provide acceptable statistics, resulting in reasonably smooth trends of the average values of the figures-of-merit. We can imagine that such a trend would represent the behaviour of a hypothetical planar solar cell measured in situ during the anneal. On the other hand, the fabrication and measurement of a single IBC solar cell would require ∼3.5 h. The figures-of-merit extracted in situ are clearly smoother than the ones extracted for the planar solar cells, because adjacent points of the trend lines are measured on the same device. Furthermore, the integration of simultaneous GI-WAXS measurements with the opto-electrical measurements of IBC solar cells fabricated in situ during the anneal, gives the opportunity to relate the figures-of-merit to the structural properties. We note that we also see similar results for our IBC devices when fabricated using a different precursor route (MAI : PbCl₂ with PbI₂ additive), suggesting that the results we show can be generalised (see Fig. S23 and ESI† for discussion).

**Conclusion**

In summary, we investigate the performance of perovskite solar cells during the formation of the perovskite starting from the earliest stages of its conversion from the precursors and solvent to the fully formed perovskite and during its degradation employing simultaneous Grazing Incidence Wide Angle X-ray Scattering and current–voltage measurements on films annealed in situ and deposited on interdigitated back-contact substrates. This suite of analyses allows establishing a direct correlation between the crystallographic and photovoltaic properties of working solar cells. The remarkably clean semiconductor behaviour of perovskites is evidenced by the high photovoltages measured at the first stages of perovskite conversion from precursors, at the percolation threshold for bulk conductance. Open circuit voltages reach maximum value before the precursor has fully converted into perovskite, when the fraction of precursor and perovskite crystals are comparable. Short circuit currents and power conversion efficiencies follow a trend similar to that of the perovskite
peak intensity extracted from the GI-WAXS measurements. We have shown that the behaviour of the figures-of-merit versus annealing time of IBC devices compares well with analogous profiles of conventional planar heterojunction solar cells, and that our results can be generalised to other perovskite precursor routes. The measurement strategy followed in this work is not limited to perovskite materials and will be of interest for any processable photovoltaic technology requiring thermal annealing.

Materials and methods

IBC substrates

Interdigitated ITO substrates were purchased from Ossila Ltd (code S162) and were sonicated in acetone and isopropanol and dried with N2. The TiO2 and polyethyleneoxythiophene (PEDOT) electrodeposition were performed in a similar manner as already reported in Pazos-Outo´n et al.35 The TiO2 electrodeposition on electrodes 6–10 (see Fig. S1, ESI†) was done in a single compartment using three-electrode electrochemical cell consisting of an Ag/AgCl reference electrode, a Pt counter electrode, and the ITO substrate as the working electrode.46 The deposition bath contained 0.01–1 M of TiOSO4 (Sigma-Aldrich), H2O2 (Sigma-Aldrich), and NH4NO3 (Sigma-Aldrich), and it was kept at a temperature of 10 °C.47 Crystalline anatase TiO2 films were obtained by applying −1.05 V for 800 s (versus Ag/AgCl) and subsequently heating the coated substrates at 300 °C for 1 h in air. On the remaining ITO electrodes (1–5), PEDOT was deposited through electropolymerisation using a three-electrode configuration consisting of an Ag pseudo-reference electrode, a Pt counter electrode, and the ITO substrate as the working electrode.48 The deposition bath consisted of a solution 0.01 M 3,4-ethylenedioxythiophene (EDOT) monomer (Sigma-Aldrich) in 1.0 M of LiClO4 (Acros Organics) electrolyte in propylene carbonate (Sigma-Aldrich). The anodic polymerisation was carried out at 1.25 V (versus Ag) for 1 s.

Perovskite precursor solutions

MAI:PBCl2 + HI. The perovskite precursor solution consisted of a blend between 395 mg of CH3NH3I (MAI) and 234 mg of PBCl2 (2.95 : 1 mol), diluted in DMF (630 mg mL−1). Hydrogen iodide (HI) was added into the solution (1 vol%). Addition of HI results in continuous perovskite films and more efficient solar cells compared to bare MAI:PBCl2.10,36 The as-prepared solution was used for preparing the planar solar cells, however the IBC solar cells required a much thinner perovskite layer. For this reason, the solution was further diluted twice in DMF. The final perovskite solution was filtered and kept at 70–75 °C prior to spincoating. For the planar solar cells the solution was spincoated at 2000 rpm for 45 s under ambient conditions. For the IBC solar cells the solution was spincoated onto a preheated substrate (from a hotplate at 100 °C) at 2000 rpm for 45 s under ambient conditions.

MAI:PBBr2 + PBBr2. MAI:PBBr2 (3 : 0.98 mol) with PBBr2 (0.5 vol%) was dissolved in DMF (42.2 wt%). The solution was diluted twice in DMF and spin-coated at 2000 rpm for 45 s under ambient conditions. The presence of a trace amount of PbI2 induces a homogenous distribution of MAPbI3 seed crystals during the film formation. The seeds subsequently grow to yield a highly crystalline film with enhanced optoelectronic properties.49

MAI:PBAc2. MAI:PBAc2 (3 : 1 mol) was dissolved in DMF (40 wt%) (all materials were purchased from Sigma-Aldrich or Acros Organics and were used as received).31 The perovskite solution was spincoated at 2000 rpm for 60 s under ambient conditions.

C50.4(MA0.17FA0.83)0.35PbI2(0.88Br0.17). The organic cations were purchased from Dyessel; the lead compounds from TCI; Dimethylformamide (DMF), cesium iodide from Sigma Aldrich. The triple cation lead mixed halide perovskite precursor solution was prepared by dissolving 1 M FAI, 1.1 M PbI2, 0.2 M MABr, 0.2 M PbBr2 in a 4 : 1 (v : v) mixture of anhydrous DMF : DMSO and 1.5 M stock solution of CsI in DMSO was added to above solution in 5 : 95 volume ratio.33 The perovskite solution was then spin coated at 6000 rpm 30 s under ambient conditions. During the second step, 50 μL of chlorobenzene was dripped on the spinning substrate 10 s prior the end.

(FAI)2a(MABr)3b(PBBr2)1−a(PBBr2)2−b. The organic cations were purchased from Dyessel; the lead compounds from TCI; dimethylformamide (DMF), cesium iodide from Sigma Aldrich. The mixed cation lead mixed halide perovskite precursor solution44 was prepared by dissolving FAI (215 mg), MABr (28 mg), PbI2 (634 mg), PbBr2 (92 mg) in a 4 : 1 (v : v) mixture of anhydrous DMF : DMSO. The perovskite solution was then spin coated in two steps: 1000 rpm for 10 s followed by 6000 rpm for 35 s under ambient conditions. During the second step, 70 μL of anisole was dripped on the spinning substrate 5 s prior the end.

Planar heterojunction solar cells fabrication and characterization

TEC 8 and 10 glass substrates (XOP glass) were etched with zinc powder and 4 M HCl prior to sonication in Helmanex detergent solution, deinonised water, and IPA. Substrates were transferred to a hotplate and heated to 450 °C for spray pyrolysis of compact titanium oxide. 1.72 mL of titanium disopropoxide bis(acetylactonate) (Sigma 325252) was diluted with IPA to 20 mL. This solution was then sprayed onto the substrates via a handheld spray gun (Draper 09709) with a nitrogen feed at 30 psi. Substrates were coated every 30 s until all the precursor was used and left to sinter for 30 min. Dyessel 18-NRT mesoporous paste was diluted to 22% weight in ethanol and spin coated onto the substrates at 2000 rpm. These were then transferred to a hotplate to be sintered for 1 h at 450 °C. The perovskite ink was prepared and spin-coated as described above. Spiro-OMeTAD solution (Ossila) was prepared at a concentration of 96.6 mg mL−1 in chlorobenzene. This solution was then doped with the following quantities of dopant per 1 mL of spiro-OMeTAD solution: 30 μL Li-TFSI (175 mg mL−1 in acetonitrile), 10 μL TBP, and 20 μL of FK-209 (175 mg mL−1 in acetonitrile). The doped spiro-OMeTAD solution was then spin coated at 2000 rpm onto the annealed perovskite films. Finally, an 80 nm gold electrode was...
evaporated in an Edwards Auto 306 bell-jar evaporator at a pressure of $\sim 10^{-6}$ mbar. All solution-processed layers were deposited under ambient conditions. Devices were characterised by measuring $JV$ curves with a Keithley 237 source measure unit under AM 1.5 simulated solar irradiance (Newport 92251A-1000). Each device consisted of six $4 \text{ mm}^2$ pixels. Due to defects associated with edge pixels these were ignored leaving four usable pixels per device. Devices were illuminated through a shadow mask with an aperture of $0.026 \text{ cm}^2$ and scanned from $-1.2 \text{ V}$ to $1.2 \text{ V}$ at a speed of $0.4 \text{ V s}^{-1}$. Performance metrics were calculated from the reverse scan.

**Beamline setup**

The beamline setup illustrated here represents an evolution of the setup detailed in ref. 27. A fixed-exit, water-cooled, double crystal Si(111) monochromator was used to monochromatize the X-ray beam coming from a bending magnet ($E_c = 9.8 \text{ keV}$). The X-ray energy was tuned to $10 \text{ keV}$ ($1.2398 \text{ Å}$) and a Rh-coated toroidal mirror was used to focus the monochromatic beam horizontally and vertically. The beam flux was $\sim 5 \times 10^{10} \text{ photons s}^{-1}$ at the sample position. The original beam spot size was $500$ (horizontal) $\times 400$ (vertical) $\mu \text{m}^2$ at the sample position. We employed a set of motorized slits (Huber, Germany) immediately before the sample to have a better defined footprint in the vertical direction. The final beam spot size with slits was $300$ (horizontal) $\times 115$ (vertical) $\mu \text{m}^2$. The beam footprint extended $300 \mu \text{m}$ horizontally and throughout the entire length of the IBC substrate.

**Annealing chamber**

The sample stage consists of a thin polished copper hotplate. A temperature controller regulates the hotplate temperature with a thermocouple mounted on its surface and two cartridge heaters. On top of the hotplate, a polyether ether ketone (PEEK) structure holds two gold plated screws acting as electrical probes, which are connected to a multimeter. The electrical contacts pressing against the IBC substrate provided mechanical stability and good thermal contact with the hotplate. A white LED is mounted on the ceiling of the annealing chamber at about 6 cm from the sample stage giving a similar photon flux to solar illumination conditions ($\sim 100 \text{ mW cm}^{-2}$) at the sample position. The annealing chamber is illustrated in Fig. S1 (ESI†) and in the movie shown in ref. 52.

**X-Ray measurements**

The IBC substrate coated with PEDOT and TiO$_2$ was mounted on the hotplate preset at a specific temperature. The temperature was not changed during the measurements. The hotplate was pre-aligned with an IBC substrate before the actual device was mounted on it. The polished hotplate and the pressure exerted by the electrical probes on the substrate allowed keeping a good and repeatable alignment. However, because the actual device was not aligned small deviation from the actual incident angle could be present. While this has a negligible effect on GI-WAXS measurements, it has prevented us from performing GI-SAXS measurements, where small misalignments greatly affect the measured diffraction patterns. The time between the end of the spin-coating and the beginning of the GI-WAXS and $JV$ measurements was about 3 min, and therefore data between 0 and 3 min is not available in the plots shown in this work. Measurements were performed at an out-of-plane incident angle of $z_i \approx 0.3^\circ$ corresponding to a penetration depth of $\sim 140 \text{ nm}$.

**Current–voltage sweeps**

Current–voltage sweeps were performed with a Keithley 2401 source meter. Forward and reverse $JV$ sweeps were performed from $-0.2 \text{ V}$ to $1 \text{ V}$, and from $1 \text{ V}$ to $-0.2 \text{ V}$, respectively. In both cases the voltage step was $0.01 \text{ V}$, resulting in 120 points per sweep. At each voltage step, the bias was held constant for 50 ms (delay) before measuring the current. Solar cells were not pre-biased before the $JV$ sweep. The power of the white LED used for the $JV$ sweeps under illumination was tuned with an irradiance meter (91159V, Newport, USA) to give an approximate irradiance of $100 \text{ mW cm}^{-2}$. The $JV$ sweeps and the light switch were remotely controlled via a SPEC macro from the beamline control cabin. For the calculation of the short circuit current and the PCE we employed an active area of $0.0396 \text{ cm}^2$, defined by the total area of the interdigitated electrodes facing each other (Fig. S32, ESI†).

**X-ray diffraction analysis**

Data processing was performed with the MATLAB software (GI-WAXS GUI) described in our previous works. Azimuthally integrated line profiles were extracted from the ‘cake slice’ between $\chi = 7^\circ$ to $\chi = 89^\circ$ in steps of $\sim 0.51^\circ$ (160 line profiles at different $\chi$) (Fig. S33, ESI†). In order to obtain an accurate estimate of the peak integrated intensities, we first removed the baseline from line profiles and then fitted the precursor, perovskite, and PbI$_2$ with multiple Gaussians. The peak integrals discussed throughout the text are the integrals of the fitted peaks.

**Author contributions**

M. A. and S. L. conceived the experiments. M. A. fabricated the IBC substrates, performed the measurements at the beamline, and analysed the data. O. B. took care of the setup at the beamline. J. B. fabricated the planar solar cells. J. B., M. A. J., M. H., S. M. prepared the precursor solutions. M. A. J. helped optimizing the electrodes deposition and precursor solution concentration. L. Y. O., M. H., J. E. M., and C. G. helped with the measurements at the beamline. P. T. designed a key component of the annealing chamber. S. L. was the main investigator of the measurements at the synchrotron, managed the project, and wrote the software for the data analysis. All authors discussed the results and contributed to the manuscript.

**Conflicts of interest**

There are no conflicts to declare.
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Notes and references


52 https://youtu.be/ZSUug00lsyU.
53 https://youtu.be/ZSUug00lsyU#t=2m17s.
54 https://youtu.be/ZSUug00lsyU#t=3m07s.
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56 https://youtu.be/ZSUug00lsyU#t=4m09s.
57 https://youtu.be/ZSUug00lsyU#t=4m58s.
58 https://youtu.be/ZSUug00lsyU#t=6m07s.
59 https://youtu.be/ZSUug00lsyU#t=6m48s.
60 https://youtu.be/ZSUug00lsyU#t=7m09s.
61 https://youtu.be/ZSUug00lsyU#t=10m05s.