Efficient Thermally Evaporated $\gamma$CsPbI$_3$ Perovskite Solar Cells

Zongbao Zhang, Ran Ji, Martin Kroll, Yvonne J. Hofstetter, Xiangkun Jia, David Becker-Koch, Fabian Paulus, Markus Löfler, Frederik Nehm, Karl Leo,* and Yana Vaynzof*

Thin-film deposition by thermal evaporation offers many advantages, yet in the field of perovskite photovoltaics solution-processed devices significantly outperform those fabricated by thermal evaporation. Here, high-quality $\gamma$CsPbI$_3$ perovskite layers by coevaporation of PbI$_2$ and CsI with a small amount of phenylethylammonium iodide (PEAI) are deposited. It is demonstrated that the addition of PEAI into the perovskite layers leads to a preferred crystal orientation and a far improved microstructure, with columnar domains that protrude throughout the film’s thickness. This is accompanied by a reduced density of defects as evidenced by the increase in photoluminescence and decrease in Urbach energy as compared to reference CsPbI$_3$ films. Photovoltaic devices based on the PEAI containing perovskite layers reach up to 15% in power conversion efficiency, thus surpassing not only the performance of reference CsPbI$_3$ devices, but also that of most solution-processed PEAI containing inorganic CsPbX$_3$ (X = Cl, Br, I) perovskite solar cells. Importantly, encapsulated thermally evaporated perovskite devices maintain their performance for over 215 days, demonstrating the stabilizing effect of PEAI on thermally evaporated CsPbI$_3$.

1. Introduction

Organic–inorganic hybrid perovskites have aroused increasing attention due to their excellent photophysical properties.[1,2] The power conversion efficiency (PCE) of perovskite solar cells (PSCs) has grown from 3.8% to 25.5% in the past decade, which is comparable with the best silicon and chalcogenide devices.[3–4] To accelerate the commercialization of perovskite solar cells, the processing of the perovskite photoabsorber should be compatible with established deposition techniques in the semiconductor industry. The physical vacuum deposition process, which is commonly used for the fabrication of organic light-emitting diodes for display and lighting applications, is an industrial-grade deposition method that allows the sequential deposition of functional materials to form the desired multilayered structure. The utilization of this method for the deposition of perovskite materials is challenging, complicated by the need to co-deposit several precursors from multiple sources while precisely controlling their deposition rates in order to obtain a high-quality perovskite film of the desired stoichiometric composition.[7] However, thermal evaporation of perovskites offers many advantages over alternative methods based on solution-processing, in particular for industrial-scale production.[8] Some of these advantages include the high purity provided by the sublimed materials, accurate and simple control over the layer thickness and the ease of uniform deposition over large areas.[9–11] Moreover, the solvent-free nature of this deposition method offers further advantages, such as freedom of substrate selection, low temperature annealing, or even no annealing treatment needed for perovskite formation and finally noteworthy benefits in terms of sustainability of PSCs.[7,12,13]

The first demonstration of solar cells with thermally deposited CH$_3$NH$_3$PbI$_3$–Cl$_x$ perovskite active layer was by Snaith and co-workers, reaching an efficiency of 15%, which, at the time, was comparable with the solution-processed PSCs.[14] The seminal work by Bolink group who reported vacuum-deposited n-i-p and p-i-n MAPbI$_3$ PSCs reaching over 20% efficiency was a strong trigger motivating researchers to investigate thermal evaporation as an alternative method to solution processing.[15] Very recently, Bruno and her team combined vacuum deposition, interfacial optimization, and surface treatment, demonstrating MAPbI$_3$ PSCs (small areas) and mini-modules (21 cm$^2$ active area) achieving record PCEs of 20.28% and 18.13%, which shows the great potential of these devices for integration in industrial applications.[16]

Despite the progress made in the field of thermally evaporated perovskite solar cells, their performance still lags far behind the performance of the state-of-the-art solution-processed PSCs. To bridge this gap, the processing of perovskite films should follow the rules for all high-performance PSCs: a high-quality film on a high-quality substrate with a high-quality buffer layer and a high-quality contact. Therefore, in this work we focus on the deposition of high-quality perovskite films using thermal evaporation in order to improve the PCEs of perovskite solar cells.
behind that of their solution-processed counterparts. In fact, many high-performance thermally evaporated PSCs are still based on methylammonium lead triiodide (MAPbI₃) due to the complexity of forming multication mixed halide compositions and the difficulty in controlling the crystallization process of thermally evaporated perovskites. One of the most severe limitations is that many optimization strategies, such as ion exchange,[15] intermediates synthesis,[16] antisolvent strategies,[17,18] ionic liquids, and other additives,[19–22] the introduction of macromolecular ligands to form 2D structures,[23,24] etc., are widely used in solution-processing of perovskites, but are not applicable to the evaporation-process because of the fundamental differences in the film formation between the two types of methods: the precursors need to be sublimated at high-temperature and the entire deposition process takes place under high-vacuum environment. Thus, it is imperative to develop strategies to improve the perovskite film quality, which are suitable for the thermal evaporation process of perovskite materials. Recently, one such approach has been developed by Liu and co-workers. The authors demonstrated that an atmosphere controlled annealing process of thermally evaporated CsPbI₃ solar cells enables high photovoltaic performance reaching a power conversion efficiency of up to 16%.[25] While this is a noteworthy achievement, the high annealing temperature of 350 °C does not only increase the energy cost of fabricating such devices, but also limits their potential application on, for example, flexible substrates.[26]

In this work, we precisely control the crystallization process of γ-CsPbI₃ perovskite[27,28] by co-evaporating small amounts of the ammonium salt phenethylammonium iodide (PEAI) alongside CsI and PbI₂. We show that a stable γ-phase is formed at a low temperature of 100 °C, which indicates that the formation energy of γ-CsPbI₃ is reduced with the addition of PEAI. The PEAI containing thermally evaporated γ-CsPbI₃ perovskite films exhibit a far better film microstructure and a preferential crystal orientation. The addition of PEAI enhances the (0 0 2) and (0 0 4) orientation and suppresses the (1 1 0) and (2 2 0) orientation, which prompts crystallization of uniform and ordered grains that protrude throughout the entire film’s thickness. Consequently, the defects in the PEAI containing γ-CsPbI₃ layers are substantially reduced. This decrease in defect density leads to a lower nonradiative recombination in the devices, resulting in an open-circuit voltage ($V_{oc}$) of 1.1 V and a PCE of 15% for the optimized devices. Moreover, this performance surpasses that reported for solution-processed PEAI containing γ-CsPbI₃ PSCs[23] based on the same composition, illustrating that thermally evaporated PSCs can compete and even outperform most PSCs deposited from solution. Finally, we demonstrate the enhancement in the stability of the PEAI containing γ-CsPbI₃ PCSs, which maintain >90% of their initial performance after 215 days of exposure to dim light at room temperature. These findings demonstrate a facile approach to fabricate stable and efficient PSCs using thermal deposition processes and provide a promising method for precisely controlling the crystallization of vacuum-deposited perovskites.

2. Results and Discussion

2.1. Properties of Thermally Evaporated γ-CsPbI₃ Perovskite Films

To investigate the properties of the thermally evaporated γ-CsPbI₃ perovskite thin films, a series of thin films with increasing amounts of PEAI were deposited by thermal evaporation (Figure 1a). In our experiments, first a reference CsPbI₃ sample was prepared by coevaporation of only the inorganic components, i.e., CsI and PbI₂. The PEAI containing samples (Figure 1b) were then fabricated by co-evaporating PEAI, while maintaining the deposition parameters of CsI and PbI₂ unchanged to those of the reference CsPbI₃. In analogy to solution-processing, this would mean the addition of a small amount of PEAI into the standard precursor solution of CsPbI₃, rather than replacing a certain fraction of CsI with PEAI. The additional amount of PEAI in each sample is denoted by its volume/volume percentage v/v%. This v/v% can be converted to a molar ratio and these values are summarized in Table S1 (Supporting Information) for the PEAI v/v% investigated in this study. After the deposition, the layers are annealed at 100 °C for 3 min.

The microstructure of the evaporated films was examined by scanning electron microscopy (SEM) and representative images are shown in Figure 2. The reference CsPbI₃ sample shows a range of domain sizes which are hard to distinguish due to lack of contrast at the boundaries of these domains. The addition
of 0.5% PEAI introduces some changes in the microstructure with the appearance of small pinholes. 5% and 10% PEAI samples, on the other hand, show a highly compact film with small distinguishable domains. The microstructure of the 20% PEAI sample is similar, however with some larger domains visible at the surface. We note that the SEM images shown in Figure 2 are of perovskite layers evaporated on glass, so to examine the microstructure on solar cell substrates (i.e., glass/Indium tin oxide (ITO)/Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), we imaged the 0% and 10% PEAI samples fabricated on those substrates as well (Figure S1, Supporting Information). We find that the samples exhibit a very similar microstructure on both types of substrates and are generally very uniform, as expected from thermally evaporated layers (Figure S2, Supporting Information). To examine the microstructure in the direction of charge transport, cross-sectional SEM images were collected on the reference CsPbI₃ sample (i.e., 0%) and the 10% PEAI sample. The reference sample shows that many small domains constitute the film, with dozens of boundaries in the charge transport direction. On the other hand, the 10% PEAI sample shows a far more columnar structure of domains, with most domains protruding throughout the entire film thickness.

Considering the structural changes observed in surface and cross-sectional SEM images, we next evaluated the crystallinity of the films by X-ray diffraction (Figure 3). The reference CsPbI₃ film shows γ phase diffraction peaks with particularly strong (0 0 l) and (1 1 0) Bragg reflections. The addition of 0.5% PEAI suppresses the (1 1 0) and (2 2 0) reflections, which now appear with a lower intensity than in the reference sample. These reflections are completely suppressed upon further increasing the PEAI content, resulting in only (0 0 2) and (0 0 4) diffraction peaks which are gradually shifted to slightly lower values of 2θ, similar to what has been reported for solution-processed CsPbI₃ perovskites that contain small amounts of PEAI. The fact that (1 1 0) and (2 2 0) reflections are suppressed by the addition of PEAI suggests that its coevaporation leads to a change in the orientation of the perovskite crystalline domains such that only growth along (0 0 l)-planes is preferred during the deposition of the film. This observation is in agreement with the columnar domain structure observed in the cross-sectional SEM. It is noteworthy that the inclusion of PEAI in solution-processed was not shown to suppress (1 1 0) and (2 2 0) orientation, which suggests that the crystallization processes during the solution and evaporation deposition are different. Importantly, the preferential orientation of the perovskite domains along the (0 0 l)-planes is also observed for films deposited on solar cell substrates (Figure S3, Supporting Information). We note that we do not observe diffraction peaks that are directly associated with 2D perovskites at low 2θ range (Figure S4, Supporting Information). This is not surprising in light of the very small amount of PEAI introduced into our samples (Table S1, Supporting Information), which results in the diffraction patterns being dominated by the inorganic γ phase CsPbI₃ network.

To investigate whether PEAI is indeed incorporated into the samples during the coevaporation procedure, we performed X-ray photoemission spectroscopy (XPS) depth profiling measurements on the 0% and 10% PEAI samples, in particular tracking the evolution of the C1s spectra as a function of depth since the PEAI molecule contains carbon, while the other perovskite precursors do not (Figure S5, Supporting Information). In the case of the reference sample, a strong C1s signal is only observed at the surface of the sample and is associated with adventitious carbon. In the bulk of the film, however, no carbon signal is observed throughout the 1800 s long etching experiment (the full film thickness). On the other hand, the 10% PEAI sample shows a small, but constant C1s signal tracking the evolution of the C1s spectra as a function of depth since the PEAI molecule contains carbon, while the other perovskite precursors do not (Figure S5, Supporting Information). We note, however, that the surface XPS scan of the 10% PEAI sample reveals excess of PEAI on the surface of the sample. This is evident by the presence of a N1s signal which constitutes ~2.5 atomic % of the sample. In the bulk of the film, the N signal is too low to be detected, since the C/N ratio in PEAI is 8.1, and the atomic % of C is only ~3%, the expected N amount
is thus <0.4%, which is too low to be detected by XPS for an element with a low cross section like nitrogen. We believe that this surface excess is formed during the postannealing step as we observe it for all the PEAI containing samples (Figure S6 and Table S2, Supporting Information).

The effect of PEAI addition on the absorption of the films is very subtle. Figure 4a displays the UV–vis spectra collected on these samples, which show only a very minor increase in the bandgap of these films. Photoluminescence (PL) measurements, on the other hand, reveal a far greater effect (Figure 4b).

The emission spectra appear slightly shifted to lower wavelengths—in agreement with the very small bandgap increase (Figure S7, Supporting Information)—however, the biggest difference is observed in the intensity of the PL, which significantly increases with increasing amounts of PEAI. This increase in PL intensity demonstrates that the electronic quality of the PEAI containing perovskite layers is significantly enhanced, suggesting a far lower density of traps that can lead to non-radiative recombination. This is in agreement with the changes in the layers’ microstructure, in which fewer domain

Figure 3. Left: X-ray diffraction diffractograms measured on reference CsPbI₃ (0%) and PEAI containing perovskite with increasing amounts of PEAI (0.5%, 5%, 10%, and 20%). Right: Zoom-in diffractograms displaying only the (0 0 2), (1 1 0), (0 0 4), and (2 2 0) diffraction peaks.

Figure 4. a) UV–vis absorption spectra and b) photoluminescence emission spectra of reference CsPbI₃ (0%) and PEAI containing perovskites with increasing amounts of PEAI (0.5%, 5%, 10%, and 20%).
boundaries are present in the vertical direction of charge transport. Increasing the PEAI amount to 40 v/v%, which corresponds to a molar ratio of 12%, results in a further blueshift of the PL spectrum (Figure S8a, Supporting Information) and the appearance of small contributions from 2D perovskites with \( n = 1, 2, 3 \) which are highlighted in Figure S8b (Supporting Information). In the case of samples with a lower PEAI content, no peaks associated with 2D perovskites are observed.

### 2.2. Photovoltaic Performance and Stability

To characterize the photovoltaic performance of the films in solar cells, they were incorporated into devices with an inverted architecture of glass/ITO/PTAA/perovskite/[6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM)/bathocuproine (BCP)/Ag (Figure 1b). The optimal thickness of the CsPbI\(_3\) perovskite layers was found to be 500 nm (Figure S9, Supporting Information). The perovskite layers were annealed for 3 min at 100 °C, which was found to lead to highest photovoltaic performance (Figure S10, Supporting Information). These conditions were kept unchanged for all devices. The photovoltaic performance of the devices is summarized in Figure 5a–d. Reference CsPbI\(_3\) devices showed a rather poor performance, reaching a PCE of \( \approx 2–3\% \), slightly lower than previously reported for thermally evaporated CsPbI\(_3\) layers that were annealed at 350 °C and integrated in a standard device architecture. The low performance is related to the low short-circuit currents (\( J_{SC} \)) and fill factors (FF) of the devices. The \( V_{OC} \) is broadly distributed with an average of 0.9 V, suggesting significant nonradiative losses are present in the reference devices, in agreement with the low photoluminescence of these layers and their poor microstructure. Gradually increasing the amount of PEAI from 0.5% to 10% leads to a significant improvement in the photovoltaic performance. In particular, the \( J_{SC} \) and FF of the devices are dramatically enhanced, reaching on average \( 17 \) mA cm\(^{-2} \) and 78%, respectively. This is accompanied by an increase in the \( V_{OC} \) of the devices. Further increasing the PEAI amount to 20% leads to further enhancement in \( V_{OC} \) up to a maximum of 1.14 V, however the \( J_{SC} \) and FF are greatly reduced, resulting in a PCE only slightly better than the CsPbI\(_3\) reference. This suggests that larger amounts of PEAI, while still resulting in high quality perovskite films with low recombination losses, hinder charge transport in the perovskite active layer thus resulting in lower photocurrent and overall photovoltaic performance.[32]

The highest performing device was obtained for 10% PEAI, reaching an impressive PCE of 15%, far superior to the champion CsPbI\(_3\) devices with a PCE of 3.17%. Figure 5e displays the external quantum efficiency (EQE) spectra of both these champion devices, demonstrating the greatly improved photocurrent generation in the PEAI containing perovskite solar cell. The current density–voltage (\( J–V \)) characteristics of the two devices are shown in Figure 5f. The devices exhibit near-negligible hysteresis, with a stabilized power output of 14.38% for the champion 10% PEAI perovskite device (Figure S11, Supporting Information). This performance is among the highest previously reported for thermally evaporated CsPbX\(_3\) solar cells based on p-i-n structure (Table S2, Supporting Information).[37–42]

### Figure 5.

Photovoltaic performance parameters: a) \( V_{OC} \), b) \( J_{SC} \), c) FF, and d) PCE distributions of reference CsPbI\(_3\) (0%) and PEAI containing CsPbI\(_3\) perovskite with increasing amounts of PEAI (0.5%, 5%, 10%, and 20%) solar cells. Each boxplot is based on \( \approx 50 \) solar cells of each type. e) EQE spectra and f) \( J–V \) characteristics of champion reference CsPbI\(_3\) (0%) and CsPbI\(_3\) with 10% PEAI device, g) MPP tracking of reference 0% and 10% PEAI solar cell for 20 h.
Importantly, this performance also surpasses that of most solution-processed PEAI containing CsPbI₃ perovskites that reached a maximum PCE of 13.65% and a stabilized power output of 13.29%.²¹ Figure 5g shows the maximum power point (MPP) tracking of both the reference 0% and 10% PEAI devices over a period of 20 h. The photovoltaic performance parameters for champion devices of each kind are provided in Table 1 and the PCE distribution of 500 solar cells with 10% PEAI is shown in Figure S12 (Supporting Information).

| v/v % of PEAI | Scan direction | V<sub>OC</sub> [V] | J<sub>SC</sub> [mA cm<sup>−2</sup>] | FF [%] | PCE [%] |
|---------------|----------------|----------------|-----------------|------|-------|
| 0%            | Forward        | 1.02           | 5.81            | 49.38| 2.94  |
|               | Reverse        | 1.02           | 5.41            | 57.30| 3.17  |
| 0.5%          | Forward        | 1.06           | 12.59           | 43.30| 5.76  |
|               | Reverse        | 1.07           | 12.86           | 50.43| 6.94  |
| 5%            | Forward        | 1.08           | 17.50           | 65.63| 12.43 |
|               | Reverse        | 1.08           | 17.60           | 70.19| 13.40 |
| 10%           | Forward        | 1.09           | 17.33           | 77.52| 14.62 |
|               | Reverse        | 1.09           | 17.33           | 79.41| 15.00 |
| 20%           | Forward        | 1.12           | 7.88            | 47.22| 4.17  |
|               | Reverse        | 1.14           | 8.28            | 55.09| 5.22  |

Our earlier observation of excess PEAI at the surface of the PEAI containing perovskite layers raises an important question regarding the function of the PEAI in improving the device performance, i.e., is it the surface excess of PEAI that leads to enhanced performance due to passivation of surface defects? To explore this option, we fabricated photovoltaic devices in which a CsPbI₃ layer was evaporated first, and then capped with a thin layer of PEAI evaporated solely on the surface of the perovskite film and then annealed. The performance of the devices is shown in Figure S13 (Supporting Information). The results show that evaporating a separate layer of PEAI at the surface does not lead to an improvement in the photovoltaic performance, with a minor increase in V<sub>OC</sub>, but much lower J<sub>SC</sub> and FF in devices with a surface PEAI layer. SEM imaging reveals that evaporating PEAI on the top of CsPbI₃ results in an inhomogeneous film (Figure S14a, Supporting Information), very different to the PEAI excess formed at the surface of coevaporated PEAI containing films (Figure 2). While the evaporated surface PEAI layer indeed resulted in increased photoluminescence (Figure S14b, Supporting Information)—consistent with the small improvement in V<sub>OC</sub>—its presence is not sufficient to lead to the type of performance improvement we observe in the coevaporated solar cells. Next, we investigated the effect of removing the PEAI surface layer from 10% PEAI coevaporated perovskite films. In this case, we utilized the Ar cluster etching source that was earlier used for XPS depth profiling in order to gently etch the surface PEAI layer off the perovskite sample. After this step, the layers were completed with the remaining solar cell layers (i.e., PCBM, BCP, and Ag) and characterized (Figure S15, Supporting Information). We find that etching of the surface PEAI layer does not significantly alter the performance of the photovoltaic devices, thus suggesting that it is the introduction of PEAI into the bulk of the film during coevaporation that is key for improving the performance of the solar cells.

To investigate the origin of the improved photovoltaic performance, we focus on characterizing solely the CsPbI₃ reference devices and those with an optimal PEAI content (i.e., 10% PEAI). To evaluate the charge recombination processes in these devices, we performed transient photovoltage (TPV) and light intensity-dependent V<sub>OC</sub> measurements. TPV experiments monitor the decay of charges that are generated by a weak laser pulse in devices that are held under open-circuit conditions using a background white light bias. As can be seen in Figure 6a, the PEAI containing perovskite devices exhibit a longer charge recombination lifetime than reference devices, indicating that charge recombination is strongly suppressed in these devices. In agreement with these results, light intensity dependent V<sub>OC</sub> measurements (Figure 6b) show that PEAI containing perovskite solar cells exhibit an overall lower trap-assisted recombination, as the slope measured for the reference CsPbI₃ device (1.36 KT q<sup>−1</sup>) is reduced to 1.06 KT q<sup>−1</sup> for the 10% PEAI devices.

Photothermal deflection spectroscopy (PDS) is a powerful tool to examine the electronic quality of perovskite films and quantify the energetic disorder present in the layers. As can be seen in Figure 6c, the 10% PEAI perovskite layers result in a sharper absorption edge than reference CsPbI₃ films. Correspondingly, the Urbach energy extracted from the PDS measurements is decreased from 25.7 meV for reference films to 17.3 meV for 10% PEAI layers. This decrease in energetic disorder is consistent with a reduced density of traps in the PEAI containing perovskite layer. Photoluminescence lifetime measurements (Figure 6d) confirm this observation as the lifetime of the 10% PEAI perovskite films is enhanced as compared to that of reference CsPbI₃ layers.

While all these results suggest that a reduced density of traps in 10% PEAI perovskite films leads to a suppression of nonradiative recombination, a direct measurement of this can be obtained by operating the solar cells as light-emitting diodes and measuring their electroluminescence quantum efficiency (ELQE). The EL emission spectra of the devices are shown in Figure 6e and the ELQE as a function of the applied voltage is shown in Figure 6f. We observe that the ELQE of the 10% PEAI perovskite devices is enhanced by approximately a factor of 20 in comparison to the reference solar cells at each voltage. The nonradiative voltage losses (ΔV<sub>nonrad</sub>) can be calculated via the equation²⁴,²⁵

\[
\Delta V_{\text{nonrad}} = -\frac{k_B T}{q} \ln(\text{ELQE})
\]  

where k<sub>B</sub> is the Boltzmann constant, T is the temperature, and q is the elementary charge. The ΔV<sub>nonrad</sub> of the 10% PEAI perovskite devices is decreased by 0.077 V, in comparison to the reference solar cells, which is in excellent agreement with the enhancement in V<sub>OC</sub> described previously (from 1.02 V to 1.09 V). We note that the increase in bandgap observed in the optical measurements shown in Figure 4 is far too small in comparison to the observed increase in V<sub>OC</sub>, and thus can be eliminated as a contributing factor.
While the enhanced performance of thermally evaporated PEAI containing CsPbI₃ perovskite solar cells is highly promising for their future exploitation in industrial applications, the long-term stability of the devices is also critically important. We monitored the performance of encapsulated photovoltaic devices, in which the ambient atmosphere should not affect the perovskite active layer, surrounding organic extraction layers and electrodes. As can be seen in Figure 7, reference CsPbI₃ devices quickly deteriorate in their performance preserving ≈20% of their initially low PCE, even with an encapsulation. Perovskite solar cells with 10% PEAI, on the other hand, exhibit an essentially unchanged photovoltaic performance, even after 215 days, which suggests that the devices show a significantly enhanced storage stability.

Next, we investigated the thermal stability and photostability of the devices. The former was evaluated by tracking the PCE of 0% and 10% PEAI solar cells at 80 °C (Figure S16, Supporting Information). We observe that the 10% PEAI perovskite devices maintained approximately 60% of their initial efficiency after 120 h, while reference devices degraded completely already after 7 h. To examine the photostability of the devices, their performance was tracked upon continuous illumination at 1 sun (Figure S17, Supporting Information). The reference devices degraded quickly and converted to the δ-phase with no photovoltaic performance after 30 h. On the other hand, the 10% PEAI devices maintain ≈80% of their initial performance after 165 h. These studies confirm the superior stability of PEAI containing CsPbI₃ perovskite solar cells over reference CsPbI₃ devices.
3. Conclusion

To summarize, we report on the fabrication of efficient and stable $\gamma$-CsPbI$_3$ perovskite photovoltaic devices by thermal evaporation. We demonstrate that the incorporation of PEAI leads to a significantly improved microstructure with columnar grains and a preferred crystalline orientation. The PEAI containing perovskite layers exhibit suppressed radiative recombination losses due to a reduced density of traps. Consequently, highly efficient devices with a maximum PCE of 15% with an enhanced stability are demonstrated, opening the route for mass production of $\gamma$-CsPbI$_3$ perovskite solar cells by thermal evaporation.

4. Experimental Section

Materials: ITO coated glass substrates were bought from PsiOTech Ltd. PCBM (99.5%) was purchased from Solenne BV. PTAA and BCP (99.99%, trace metals basis) were obtained from Solenne BV and Sigma-Aldrich, respectively. PbI$_2$ (99.999%, trace metals basis), CsI (99.999%, trace metals basis), and PEAI (98%) were obtained from Sigma-Aldrich. All materials were used as received without purification.

Perovskite Film Deposition: Substrates for film deposition were ultrasonically cleaned with 2% Hellmanex detergent, deionized water, acetone, and isopropanol and transported to a vacuum chamber (CreaPhys GmbH, Germany) from a nitrogen-filled glovebox. Subsequently, the PTAA-coated substrates were transferred to the vacuum chamber for evaporation. By monitoring the rates of three sources, the films of different thickness and PEAI concentration could be obtained. Next, PCBM (20 mg mL$^{-1}$ in chlorobenzene) was dynamically spin-coated at 2000 rpm for 30 s followed by annealing at 100 °C for 3 min. Finally, a BCP (0.5 mg mL$^{-1}$ dissolved in isopropanol) hole-blocking layer was deposited onto the substrates at 4000 rpm for 30 s, following by an 80 nm thermally evaporated Ag cathode (Mantis evaporator, base pressure of 10$^{-7}$ mbar). The thickness of the PTAA and BCP layers were determined using X-Ray Reflectivity (XRR) measurements (Figure S18, Supporting Information) to be ($4.09 \pm 0.04$) nm and ($1.245 \pm 0.0005$) nm, for PTAA and BCP, respectively. The as-prepared photovoltaic devices were sealed/encapsulated in a glovebox using an UV-hardened epoxy glue and a transparent clean encapsulation glass. The encapsulation was found to significantly increase the environmental stability of the devices (Figure S19, Supporting Information).

Photovoltaic Device Fabrication: Prepatterned ITO substrates were ultrasonically cleaned with 2% Hellmanex detergent, deionized water, acetone, and isopropanol, followed by 10 min oxygen plasma treatment. PTAA (15 mg mL$^{-1}$ in toluene) was spin-coated on the clean substrates with 4000 rpm, 30 s and annealed at 100 °C for 10 min in a nitrogen-filled glovebox. Subsequently, the PTAA-coated substrates were transferred to the vacuum chamber for evaporation. By monitoring the rates of three sources, the films of different thickness and PEAI concentration could be obtained.

Photovoltaic Device Characterization: EQE spectra of the devices were recorded using the monochromatic light of a halogen lamp from 400 nm to 800 nm and the reference spectra were calibrated using an NIST-traceable Si diode (Thorlabs), J–V characteristics of solar cells under a solar simulator (Abet Sun 3000 Class AAA solar simulator, AM 1.5 conditions) were recorded using a computer controlled Keithley 2450 source measure unit. The incident light intensity was calibrated via a Si reference cell (NIST traceable, VLSI) and tuned by measuring the spectral mismatch factor between the real solar spectrum, the spectral response of the reference cell and the perovskite devices. All devices were scanned from short circuit to forward bias (1.2 V) and reverse with a rate of 0.025 V s$^{-1}$. No treatment was applied prior to measurements. The active area for all devices was 4.5 mm$^2$.

Scanning-Electron Microscopy: A SEM (Gemini 500, (ZEISS, Oberkochen, Germany)) with an acceleration voltage of 3 kV under 5–6 × 10$^{-4}$ mbar was utilized to obtain the surface and cross-sectional SEM images using the in-lens mode.

X-Ray Diffraction: XRD patterns were measured in ambient air by using a Bruker Advance D8 diffractometer equipped with a 1.6 kW Cu-Anode ($\lambda = 1.54060$ Å) and a LYNXEYE_XE_T 1D-Mode detector. The scans (2theta–Omega mode, 2$\theta$ = 10°–30°, step size 0.05°, 0.5 s per step) were measured in a parallel beam geometry with a height limiting slit of 0.2 mm.

UV–Vis Absorption and Photoluminescence Measurements: A Shimadzu UV-3100 spectrometer and Horiba FluoroMax-3 (excitation wavelength, 467 nm) were utilized in the ultraviolet–visible (UV–vis) absorbance and spectroscopic recording, respectively.

PDS: PDS measurements were performed following the previously developed procedure.[46–48] In short, the perovskite films on quartz substrate were mounted in the signal enhancing liquid (Fluorinert FC-770) filled quartz cuvette inside a N$_2$-filled glovebox. Then, the samples were excited using a tunable, chopped, monochromatic light source (150W xenon short arc lamp with a Cornerstone monochromator), and probed using a laser beam (635 nm diode laser, Thorlabs) propagating parallel to the surface of the sample. The heat generated through the absorption of light changes the reflective index of the Fluorinert liquid, resulting in the deflection of the laser beam. This deflection was measured using a position sensitive-detector (Thorlabs, PDP900A) and a lock-in amplifier (Amatec SR7230) and is directly correlated to the absorption of the film.

Time-Correlated Single Photon Counting (TCSPC): A TCSPC setup contained of a 375 nm laser diode head (Pico Quant LDHDC375), a PMA Hybrid Detector (PMA Hybrid 40), a TimeHarp platine (all PicoQuant),
and a Monochromator SpectraPro HRS-300 (Princeton Instruments). Perovskite films on quartz were excited with the 375 nm laser diode and then the emission was collected by the PMA hybrid detector. The pulse width is ~44 ps, power is ~3 mW, the spot size is ~1 mm², and the excitation fluence is ~0.132 J m⁻². The lifetimes were evaluated using deconvolution algorithms of FluorFit (PicoQuant).

TPV: For TPV measurements, an LED light (Thorlabs TO-1 3/4, λ = 465 nm) was pulsed by a function generator (Agilent/Keysys 33510B) and focused on the devices. An oscilloscope (Picoscope 5443A) was utilized to measure the TPV signal.

**Electroluminescence Measurement**: The devices were mounted in an integrating sphere (Labsphere Inc.). The current–voltage characteristics were recorded using a Keithley 2450 source-measure unit. An integrating sphere (Labsphere Inc.). The current–voltage characteristics were recorded using a Keithley 2450 source-measure unit. At the same time, a scientific grade spectrometer (Ocean Optics QE65PRO) was used to record the emitted light spectra and converted them to luminance. The optical system (spectrometer, integrating sphere, and coupling optical fiber) was calibrated via a calibrated light source (Ocean Optics HL-2000-CAL).

**UPS and XPS**: The samples were transferred to an ultrahigh vacuum chamber (ESCALAB 250Xi by Thermo Scientific, base pressure: 2 × 10⁻¹⁰ mbar) for UPS and XPS measurements. UPS measurements were carried out using a He discharge lamp (hv = 21.2 eV) and a pass energy of 2 eV. XPS measurements were carried out using an XPS monochromated Al Kα source (hv = 1486.6 eV) and a pass energy of 20 eV. Depth profiling and PEAI surface etching was performed using an argon cluster ion beam with large argon clusters (Ar₂₀₀) and an energy of 4 keV generated by a MACCIS dual mode ion source. During XPS depth profiling, the etching spot size was (2.5 × 2.5) mm² and the XPS measurement spot size was 650 μm. In case of PEAI surface removal experiment, the surface of the entire sample area (1.2 × 1.2) cm² was etched.

**Supporting Information**

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

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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**Keywords**

PEAI, perovskite, solar cells, thermal evaporation, γ-CsPbI₃

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