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# Thermally Regulated Energy Loss in Dion–Jacobson Perovskite Solar Cells

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Quasi-2D perovskite solar cells (PSCs), with impressive stability and tunable optoelectronic properties, have become a promising alternative to 3D PSCs. However, the lack of understanding about rationally promoting the film quality of 2D perovskites has significantly undermined their power conversion efficiency (PCE). Herein, a thermally induced crystallization strategy to process the Dion-Jacobson (DJ) 2D perovskite films based on (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> (n = 5) afforded by thermal treatments is reported, realizing high-quality perovskite films with increased crystallinity and dense structure. The photovoltaic performance of PSCs improved by thermal treatments is found to be mainly attributed to the significantly suppressed nonradiative recombination, more efficient charge generation, and restricted interfacial charge accumulation. As a result, the optimal device processed with thermal treatments produces a high open-circuit voltage of 1.21 V and a PCE of over 17.6% with suppressed energy loss down to 0.42 eV. Moreover, the treated devices without encapsulation show a satisfactory stability with <20% PCE degradation after 1000 h under maximum power point tracking. The demonstrated strategy in this work offers a promising route for the performance enhancement of 2D DJ PSCs toward realistic energy conversion applications.

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## DOI: 10.1002/solr.202200636

# 1. Introduction

Metal halide perovskites have attracted tremendous attention due to their excellent optoelectronic properties, which include long carrier diffusion lengths, high absorption coefficients, high defect tolerances, tunable bandgaps, and a capacity for ambipolar charge transport.<sup>[1–5]</sup> The certified power conversion efficiency (PCE) of perovskite solar cells (PSCs) has rapidly increased to as high as 25.7%.<sup>[6]</sup> However, the practical application of perovskites remains limited by the inherently poor stability of their hybrid organicinorganic frameworks, especially under long-term moisture, heat, and illumination stresses.<sup>[7–9]</sup> Recently, reducing the dimensionality of perovskites from 3D to lower dimensionality has been found to be an effective approach for enhancing the stability.<sup>[10–12]</sup>

By introducing the large cation which

could cut along the crystallographic planes <100> of the 3D perovskite structure, layered perovskites, which are also referred as 2D perovskites, have been conceptually achieved.<sup>[13]</sup> Due to the hydrophobicity and high binding energy, 2D perovskites show superior stability.<sup>[14,15]</sup> Among 2D perovskites, the Ruddlesden–Popper (RP) phase and the Dion–Jacobson (DJ) phase have gained substantial attention recently.<sup>[16–20]</sup> The DJ structure contains a single divalent interlayer spacer cation, while the RP phase features two monovalent spacer cations. In comparison with RP perovskites, the short interlayer distance and absence of van der Waals gap in DJ perovskites, which benefit the charge separation/transport, light harvesting, and stable crystal structure, offer the potential for high conversion efficiency and stability in DJ-phase PSCs.<sup>[21,22]</sup>

In pursuit of efficient and stable 2D perovskite PSCs, it is critical to manipulate the film formation process to prepare high-quality perovskite films. Examples can refer to the preparation process of 2D RP perovskite films, such as the hot-casting deposition,<sup>[23,24]</sup> solvent engineering,<sup>[25,26]</sup> tailoring composition and ligands.<sup>[18,27]</sup> The hot-casting process, additive engineering, solvent engineering and selection of ligands, have also been involved to improve the quality of the 2D DJ perovskite. Liu et al. found that the fast removal of the solvent from PDMA-based DJ perovskite solution via hot casting or antisolvent dripping resulted in a more uniform thickness distribution of





quantum wells, and an optimal PCE of 15.81% was achieved.<sup>[19]</sup> Chen et al. presented a multifunctional additive strategy for preparing high-quality MA-free DJ quasi-2D perovskite films, demonstrating that the CDTA modification could control the phase distribution, enlarge the grain size, and modulate crystallinity and crystal orientation.<sup>[28]</sup> It was reported by Liu et al. that stable 2D DJ PSCs were achieved by developing thiophene-based aromatic spacers as well as device engineering.<sup>[20]</sup> Thereafter, they found that the 2D DJ perovskite using TTDMA spacer with extended  $\pi$ -conjugation length exhibited high film quality, large crystal size, and preferred crystal orientation with boosted PCEs.<sup>[29]</sup>

Normally, an annealing process right after the deposition of precursor films is necessary for the preparation of perovskite films, which aims to promote solvent evaporation and perovskite crystallization. As a simple, robust, and general method, the annealing process has shown potential for controlling the crystallization and layer orientation in 2D perovskites. For instance, Loo et al. reported on solvent-vapor annealing as a general postdeposition strategy to induce strong vertical orientation across the broad classes of 2D perovskite films.<sup>[30]</sup> Despite this, in case of thermal annealing, a fixed annealing temperature is often adopted based on empirical estimation or fast device screening, while the impacts of different thermal energies induced to the perovskite have been ignored. Moreover, energy loss analysis is an impressive procedure to understand the working principle of the solar cells, which could help to comprehend where the lost energy went and how to improve the PCE of the photovoltaic cell.<sup>[31]</sup> The radiative efficiency of the typical PSC, which has the bandgap of 1.55 eV, is 31.5% according to the Shockley-Queisser limit under AM1.5G illumination conditions.[32,33] The open-circuit voltage ( $V_{oc}$ ) of the reported 2D DJ PSCs is generally lower than 1.2 V,<sup>[34]</sup> except for the example demonstrated by Chen et al. based on PMA-based DJ PSCs.<sup>[35]</sup> It indicates that the voltage loss in 2D DJ PSCs is considerable, at least, compared with 3D PSC counterparts. However, to the best of our knowledge, in-depth investigations of the influence of thermal treatment on the properties of DJ-phase perovskites are yet lacking.

In this work, we report a thermally assisted crystallinity strategy through applying thermal annealing to (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films to obtain regulated crystallization and boosted the photovoltaic performance of DJ 2D-phase PSCs. With this method, high-quality DJ 2D perovskite films with increased crystallinity and dense structures have been realized. The relationships between the induced thermal energies and resultant modifications on the perovskite film quality and  $V_{oc}$  loss were discussed. It was found that the optimal device (based on the films processed with an annealing temperature of 120 °C) yielded a high  $V_{\rm oc}$  of 1.21 V and a PCE over 17.6% with a low energy loss of 0.42 eV. In addition, the treated devices without encapsulation showed a satisfactory stability with <20% PCE degradation after 1000 h under maximum power point (MPP) tracking. The photovoltaic performance of PSCs improved by thermal treatments is mainly attributed to the significantly suppressed nonradiative recombination, efficient charge generation/separation, and inhibition of interfacial charge accumulation. This work provides a promising strategy for improving the key figure of merits of 2D DJ-phase PSCs toward realistic photovoltaic applications.

## 2. Results and Discussion

The structure of our quasi-2D BDA-based PSCs is shown in **Figure 1**a, which is composed of ITO/PTAA/perovskite/ $C_{60}$ /BCP/Ag. Here, PTAA and  $C_{60}$ /BCP were adopted as hole-transporting layer (HTL) and electron-transporting layer (ETL), respectively. Owing to the appropriate high occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO) of both PTAA and  $C_{60}$ , photon-generated electrons and holes in perovskite films could efficiently transport to ETL and HTL. Figure 1b shows the cross-section scanning electron microscope (SEM) images of PSCs based on (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> active layer where the interfaces between different layer components are well resolved.

In this study, perovskite precursor solution was spin-coated at a constant substrate temperature during the whole spin procedure. After film deposition, different annealing temperatures (100, 110, 120, 130, and 140 °C, respectively) were applied based on which the evolution of crystallization was assessed. With (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> device optimization, we turned to the best photovoltaic characteristics, as shown in Figure 1c. The corresponding device parameters are summarized in Table 1. All the devices exhibit the negligible hysteresis effect as the I-V curves of forward and reverse scanning direction are nearly overlapped. The  $V_{oc}$ , short-circuit current ( $I_{sc}$ ), and fill factor (FF) simultaneously exhibit an increasing tendency with the processing temperature (up to 120 °C), followed by a decreasing trend, with further increasing the temperature, leading to a peak PCE of 17.61%. Considerable enhancements of  $V_{oc}$  and  $J_{sc}$  were observed on the device processed at film annealing temperature of 120 °C. To further confirm the reliability of conversion efficiency of our devices, the maximum power output of champion device was carried out, as shown in Figure S1, Supporting Information. The stabilized PCE shows flat tendency over 17%. The statistics of PCE and  $V_{oc}$  of devices (Figure S2, Supporting Information) demonstrate the significant difference of the photovoltaic performance for solar cells processed with various annealing temperature. The annealing process at 100 and 110 °C was prolonged to study the effects of annealing time on devices performance (Figure S3, Supporting Information). It was found that a prolonged annealing time hardly contributed to the increase of conversion efficiency, which highlighted the significant influence of annealing temperature on device performance. Demonstrated in Figure 1d are the external quantum efficiency (EQE) spectra of devices based on (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films processed by different annealing temperatures, which confirm the validity of the Jsc results obtained from the J-V curves. Apparently, the EQE curves of devices with respectively low film annealing temperature present higher value in the short-wavelength region, while those with respectively high annealing temperature exhibit higher value in the longwavelength region, where the photocurrent originates from the absorbed photons in 3D or higher *n*-value components.<sup>[36]</sup> In addition, with the increase in annealing temperature, the perovskite films show a redshift onset photoresponse edge, which is beneficial to broadband light absorption.

We performed long-term stability tests of PSCs prepared with different film annealing temperatures from 100 to 140 °C. The normalized PCE under MPP tracking (under nitrogen

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**Figure 1.** a) Energy diagram of quasi-2D (BDA) (MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskites alongside different charge-transporting layers. b) Cross-section SEM image of DJ 2D PSCs based on (BDA) (MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> active layer. c) *J*–V characteristics of the champion (BDA) (MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> PSCs under AM 1.5G solar irradiation. d) EQE spectra of champion (BDA) (MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> PSCs. e) MPP tracking of unencapsulated (BDA) (MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> PSCs tested in nitrogen-purged glovebox under 1 sun illumination at  $40 \pm 5$  °C.

Table 1. Champion photovoltaic parameters obtained from the reverse scans of devices based on quasi-2D (BDA) (MA)\_4Pb\_5I\_{16} perovskite films processed with different annealing temperature.

Annealing temperature	V <sub>oc</sub> [V]	∫ <sub>sc</sub> [mA·cm <sup>−2</sup> ]	FF [%]	Efficiency [%]	Stability at T <sub>80</sub> MPP [h]
100 °C	1.19	14.28	66.90	11.37	24
110°C	1.19	17.73	73.39	15.48	450
120 °C	1.21	18.21	79.92	17.61	>1000
130 °C	1.14	17.91	78.38	16.00	150
140 °C	1.08	15.83	77.10	13.18	25

environment, at 40  $\pm$  5 °C) as a function of aging time is shown in Figure 1e. The device processed with the film annealing temperature of 120 °C is most stable, which maintains 80% of the

initial conversion efficiency after 1000 h. For comparison, the efficiency of the device processed with 110 °C shows a relatively large linear reduction during aging. Apart from the above two conditions, the other devices exhibit poor stability in the first 100 h. These results give strategy for enhancing the stability of PSCs under illumination through adjusting the film annealing temperature.

As the photovoltaic properties of PSCs earlier are significantly different, it is necessary to explore the property changes in the perovskite films processed under various annealing temperature conditions and reveal the related mechanism. To understand the structure evolution of quasi-2D (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films, X-ray diffractometry (XRD) measurement was performed. **Figure 2**a shows the XRD patterns of perovskite films processed with different annealing temperatures. Two dominant peaks are observed at the diffraction angles of 14.44° and 28.71° in these samples, which correspond to the (111) and (202) lattice planes

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**Figure 2.** a) XRD patterns of  $(BDA)(MA)_4Pb_5I_{16}$  perovskite films processed with different annealing temperatures. b) Schematic illustration of the (111) and (202) lattice planes of  $(BDA)(MA)_4Pb_5I_{16}$  perovskites. c) FWHM of (111) and (202) lattice planes as a function of annealing temperature from 100 to 140 °C.

of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite, respectively. The schematic diagram of the (111) and (202) lattice planes of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite is exhibited in Figure 2b. The full-width at halfmaximum (FWHM) values for both (111) and (202) lattice planes as a function of annealing temperature are summarized in Figure 2c. Both FWHM<sub>(111)</sub> and FWHM<sub>(202)</sub> reduce gradually upon increasing the annealing temperature from 100 to 120 °C, remaining constant for higher annealing temperature. These results imply that the crystalline quality of perovskite films improves with the increase in annealing temperature and becomes optimal with temperatures above 120 °C.

To explore more details about the effect of annealing temperature on the crystallinity and orientation of quasi-2D (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films, the grazing-incidence wide-angle X-ray scattering (GIWAXS) measurement was performed. The results are shown in **Figure 3**a–e. Obvious Bragg diffraction spots of (111) and (202) lattice planes on the patterns are observed. The emergence of diffraction spots rather than diffraction rings confirms the high crystallinity of as-prepared quasi-2D perovskite films. The GIWAXS patterns for lower annealing temperature of 100 and 110 °C exhibit series-wide and continuous Debye–Scherrer diffraction spots, indicating a more isotropic distribution of scattering intensity. This phenomenon points to randomly orientated grains inside the perovskite films processed by low annealing temperature. On the contrary, the Bragg spots become more discrete and sharper in films

annealed at higher annealing temperature (120, 130, and 140  $^{\circ}$ C), which implies the improvement of both crystallinity and orientational homogeneity.

Figure 4a-e shows the SEM surface images of quasi-2D (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films processed with different annealing temperatures. The corresponding atomic force microscope (AFM) images are shown in Figure 4f-j. As the annealing temperature increases, the perovskite grains change their morphology from round shape to angular shape, accompanied with the size increase. The results indicate the crystallinity improvement of perovskite films afforded by increasing the annealing temperature. However, holes and pins are emerged in films processed with the temperature above 130 °C, which implies the reduction of film compactness and the increase of defects. Because of the formation of hole defects usually accompanied with the change of surface roughness and elementary composition, the AFM and energy-dispersive spectroscopy (EDS) measurements were both performed to analyze the morphology and composition difference. The root mean square (RMS) roughness and the atoms proportion of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films processed under various annealing temperature conditions are provided in Figure 4f-j and S4a, Supporting Information, respectively. It is seen that the RMS roughness increases from 11.9 to 27.3 nm monotonously by increasing the annealing temperature. The atomic ratio of I/Pb shown in Figure S4b, Supporting Information, first decreases and then adversely increases with ADVANCED SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com



Figure 3. GIWAXS patterns of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films processed with different annealing temperatures: a) 100 °C, b) 110 °C, c) 120 °C, d) 130 °C, and e) 140 °C.



**Figure 4.** SEM and AFM surface images of various (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> DJ 2D perovskite films processed with different annealing temperatures: a,f) 100 °C, b,g) 110 °C, c,h) 120 °C, d,i) 130 °C, and e,j) 140 °C. The red circles in (d) and (e) mark the holes that existed in films. Corresponding RMS roughness of perovskite films is provided in the inset text of (f–j).

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increasing annealing, showing an approximate value of 3.60 for samples annealed with 120 °C. The valley value is the closest to the stoichiometry of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> (I/Pb = 3.20), which indicates the formation of an ideal perovskite structure.<sup>[37]</sup> Meanwhile, the atomic ratio of C/N drops sharply for samples processed with annealing temperature of 120 °C. Owing to the fact that the atomic ratio of C/N of MAAc solvent is higher than that of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films, the decrease can be ascribed to the efficient evaporation of MAAc solvent. Therefore, the hole defects generated at annealing temperature above 130 °C may be the result of fast solvent evaporation, which can cause the increase of RMS roughness at the same time.

To further find out the photophysical origin for the optimal device performance at film annealing temperature of 120 °C, the optical properties of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskites were investigated in detail. **Figure 5a** demonstrates the UV–vis absorption spectra of perovskite films processed with different annealing temperatures. The obvious multiple peaks are assigned to the DJ perovskite phases in different *n*-values. Moreover, when the annealing temperature increases, the absorbance of perovskite films exhibits a redshift characteristic, which is in accordance with the EQE spectra. The steady-state photoluminescence (PL) spectra of perovskite films excited from front and back sides are exhibited in Figure 5b,c, respectively. It is seen that the PL spectra show nearly no peaks for the quantum wells of n = 1, 2, 3, and 4 no matter the use of front or back excitation. The reason can be attributed to the uniform structure from top to bottom of

the entire perovskite films.<sup>[38]</sup> Regular redshift of PL peaks from 764 to 770 nm is observed by elevating the annealing temperature, indicating the decreased bandgap of DJ perovskite films. In addition, the PL intensity improves gradually as the annealing temperature increases from 100 to 120 °C, indicating the reduction of defect states in perovskite films, which is in good agreement with the XRD and GIWAXS analysis. The maximum PL intensity is observed at 120 °C, implying the improvement of film quality and the reduction of defects.

According to the XRD analysis before, the crystallinity of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films processed under annealing temperatures of 120, 130, and 140 °C is close to each other as the FWHM of (111) and (202) main lattice planes is approximately the same. Despite this, the SEM and AFM results unambiguously confirm the growth of crystalline grains and the multiplication of hole defects in perovskite films with the annealing temperature increased. Therefore, it is concluded that the approximately same crystallinity of perovskite films at high annealing temperature above 130 °C is the result of balance between the improved grain size and the increased defect density. As the steady-state PL spectra have shown obviously different peak intensities for 120, 130, and 140 °C, it is speculated that the defects in samples prepared at higher annealing temperature are easier to induce nonradiative charge recombination and therefore lead to the intensity decrease above 130 °C.

To directly reveal the recombination lifetime of the as-prepared quasi-2D perovskite films, time-resolved PL



Figure 5. a) UV-vis absorption spectra of  $(BDA)(MA)_4Pb_5I_{16}$  perovskite films processed with different annealing temperatures. b,c) Steady-state PL spectra of the corresponding perovskite films excited from front and back sides, respectively. d) TRPL spectra for the corresponding perovskite films.

(TRPL) decay characterization based on quartz substrates was carried out. The corresponding results are exhibited in Figure 5d. One can find that the TRPL traces display a biexponential decay profile, of which the faster decay lifetime  $\tau_1$  and slower decay lifetime  $\tau_2$  can be extracted according to the formula below.<sup>[38]</sup>

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$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$
(1)

where *I* is the PL intensity and  $A_1$  and  $A_2$  the scaling factor. The calculated results are summarized in Table S1, Supporting Information. In general, the fast and slow decay processes originate from the trap-assisted recombination and bimolecular recombination of photogenerated carriers in active layer, respectively.<sup>[39,40]</sup> The largest  $\tau_1$  and  $\tau_2$  decay time is obtained at 120 °C, which reveals the suppression of both the trap-assisted and bimolecular recombination in perovskite films. The average PL lifetime  $\tau_{ave}$  is also estimated with the equation below.<sup>[38]</sup>

$$\tau_{ave} = \frac{\sum_{i=1}^{n} A_i \tau_i^2}{\sum_{i=1}^{n} A_i \tau_i}$$
(2)

where  $A_i$  and  $\tau_i$  represent the scaling factor and decay time, respectively. The calculated value is provided in Figure 5d. The largest  $\tau_{ave}$  at 120 °C confirms the optimal film quality, which is consistent with the steady-state PL analysis.

To obtain solid evidence on the change of charge recombination in perovskite films upon annealing, light intensitysolar-rrl.com

dependent I-V measurement was performed, as demonstrated in **Figure 6**a. Through the calculation of the slope from  $V_{oc}$ -light intensity plot, the diode ideality factor (IF) of devices can be extracted. In general, a slope approaching  $2k_{\rm B}T/q$  with IF = 2  $(k_{\rm B}T/q$  represents the thermal voltage) corresponds to a dominant Shockley-Reed-Hall (SRH) recombination process in the presence of defects or traps,<sup>[41,42]</sup> while a slope with IF = 1implies that the second-order bimolecular recombination dominates without charge trapping.<sup>[17]</sup> From the results, it is seen that the IF for our devices based on perovskite films annealed at different temperature all exhibits values less than 2. The slope with annealing at 120 °C is 1.25  $k_{\rm B}T/q$ , which is the smallest among all the samples. Moreover, the IF of devices decreases significantly by increasing the annealing temperature from 100 to 120 °C, indicating the suppression of SRH recombination in perovskite films. The further increase of IF by raising the annealing temperature from 120 to 140 °C implies the increased proportion of SRH recombination, which promotes nonradiative recombination and therefore causes the PL intensity decrease above 130 °C (Figure 5b,c).

Figure 6b depicts the dark J-V characteristics of electron-only devices based on (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films processed with different annealing temperatures from 100 to 140 °C. Obvious transition from the linear behavior at low bias (ohmic region) to the trap-filling current (TFC) region fingerprinted of a stronger voltage dependence can be observed. Based on the voltage ( $V_{tr}$ ) determined by the transition from



**Figure 6.** a) Light intensity-dependent  $V_{oc}$  of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> PSCs processed with different annealing temperatures. b) Dark *J*–V characteristics of electron-only devices based on processed perovskite films. c,d) TPC and TPV decay kinetics measured on PSCs in different film annealing conditions, respectively.

ohmic to TFC region, the trap density ( $N_{\rm trap}$ ) can be calculated by the formula.<sup>[43,44]</sup>

$$N_{\rm trap} = \frac{2\varepsilon_0 \varepsilon_{\rm r} V_{tr}}{qL^2} \tag{3}$$

where  $\varepsilon_0$  is the vacuum dielectric constant,  $\varepsilon_r$  the relative dielectric constant of perovskites ( $\approx 25$ ), *q* the elemental charge, and *L* the thickness of the active layer. The calculated  $N_{\text{trap}}$  at annealing temperatures of 100, 110, 120, 130, and 140 °C is  $5.49 \times 10^{15}$  $5.30 \times 10^{15}$ ,  $4.84 \times 10^{15}$ ,  $5.69 \times 10^{15}$ , and  $6.93 \times 10^{15} \, \mathrm{cm^{-3}}$ , respectively. One can find that the trap density first reduces and then increases upon the increased film annealing temperature. This analysis points to the minimum defect density in perovskite films processed at annealing temperature of 120 °C, which is beneficial to the suppression of SRH recombination. In the higher-bias regime, the space-charge-limited current (SCLC) region with the quadratic voltage dependence is also shown in Figure 6b. According to Mott-Gurney law, the electron mobility  $\mu_e$  of perovskite films can be extracted from the fitted plots.<sup>[17]</sup> As the mobility is mainly influenced by the scattering of both lattice and defects,<sup>[45]</sup> the largest value of  $\mu_e$  at 120 °C shown in Figure 6b reflects the lowest defect density, which corresponds to the smallest  $N_{trap}$ . Therefore, the number of mobile charges upon irradiation increases and the largest Jsc is obtained under this condition.

Considering the enhancement of electron transport and the suppression of SRH recombination through adjusting the annealing temperature, it is believed that the ability of charge extraction should be improved. To clarify this, both transient photocurrent (TPC) and transient photovoltage (TPV) measurements based on these solar cells were performed, of which the results are shown in Figure 6c,d. As expected, the champion device with film annealing temperature of 120 °C exhibits the shortest charge sweepout time ( $\tau_{ext}$ ), suggesting a more efficient charge separation and a less interfacial charge accumulation via recombination. The recombination lifetime ( $\tau_{rec}$ ) detected at open-circuit condition by TPV measurement also manifests the most effective retardation of interfacial carrier recombination in devices, associated with the longest  $\tau_{\rm rec}$  of 7.1 µs. As a result, the enlarged  $J_{sc}$  and  $V_{oc}$  of devices are both obtained under the 120 °C film annealing condition (Figure 1c). Moreover, it has been reported that the ratio of  $\tau_{\rm ext}$  and  $\tau_{\rm rec}$  ( $\tau_{\rm ext}/\tau_{\rm rec}$ ) is partly related to the FF of PSCs.<sup>[17]</sup> According to the established balance between charge extraction and recombination, the decrease of  $\tau_{\rm ext}/\tau_{\rm rec}$  reflects the equilibrium shift to the former process, which would benefit the reduction of carrier loss and the improvement of FF. In this context, the highest FF at 120 °C can be explained by the smallest  $\tau_{\rm ext}/\tau_{\rm rec}$ , which is in good agreement with the device performance shown in Table 1.

In light of the high  $V_{\rm oc}$  (1.21 V) in the champion cell, we further investigated the details of energy loss ( $\Delta E_{\rm loss}$ ) in these (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> devices and the results are given in **Table 2**. The schematic diagram for energy loss is shown in Figure S5, Supporting Information. Generally speaking, the  $\Delta E_{\rm loss}$  equals the sum of three parts described as follows.<sup>[46]</sup>

$$\Delta E_{loss} = E_g - qV_{oc} = (E_g - qV_{oc,SQ}) + q\Delta V_{oc,rad \ below \ gap} + q\Delta V_{oc,nonrad} = \Delta E_1 + \Delta E_2 + \Delta E_3$$
(4)

**Table 2.** Voltage loss-relevant parameters determined on various  $(BDA)(MA)_4Pb_5I_{16}$  DJ 2D PSCs processed with different film annealing temperatures.

Annealing temperature	E <sub>g</sub> [eV]	$\Delta E_1$ [eV]	$\Delta E_2$ [eV]	$\Delta E_3$ [eV]	V <sub>oc,cal</sub> [V]	V <sub>oc</sub> [V]	EQE <sub>EL</sub>
100 °C	1.627	0.276	0.014	0.149	1.189	1.192	$3.21\times10^{-3}$
110°C	1.626	0.276	0.014	0.146	1.188	1.191	$3.60\times10^{-3}$
120°C	1.625	0.276	0.021	0.129	1.201	1.206	$6.85\times10^{-3}$
130°C	1.619	0.274	0.025	0.174	1.145	1.139	$1.19\times10^{-3}$
140 °C	1.595	0.273	0.013	0.201	1.107	1.080	$\rm 4.23 \times 10^{-4}$

where  $\Delta E_1$  represents the energy difference between the bandgap edge  $E_g$  and  $qV_{oc}$  in the SQ limit ( $V_{oc,SQ}$ ), which is mainly dependent on the bandgap  $E_g$  of the active layer.  $\Delta E_1$ resembles each other in our devices prepared by different film annealing temperatures as the bandgaps are approximately the same. The radiative loss  $\Delta E_2$  represents the additional radiative recombination derived from the absorption below the bandgap. To clarify this, the Fourier-transform photocurrent spectroscopy (FTPS) was performed to evaluate the sub-band absorption, as shown in Figure S6, Supporting Information. It is seen that all the annealing-treated devices exhibit no obvious subgap absorption, indicative of the suppression of radiative recombination below the bandgap.<sup>[47]</sup> Therefore, small  $\Delta E_2$  is obtained for our PSCs. The third part  $\Delta E_3$  represents the nonradiative recombination loss and correlates directly with the external radiative efficiency of electroluminescence (also expressed as EQE<sub>EL</sub>, shown in Figure S7, Supporting Information), following the equation  $\Delta E_3 = -k_B T \ln(EQE_{EL})$ .<sup>[48]</sup> It becomes apparent that the variation of  $\Delta E_3$  is the main part causing the differentiated energy loss and  $V_{oc}$  values (see Table 2). The smallest  $\Delta E_3$  of 0.129 eV at the film annealing temperature of 120 °C results in the highest calculated  $V_{oc}$  ( $V_{oc,cal}$ ) of 1.201 V, which approaches the actual  $V_{\rm oc}$  value of 1.206 V. Due to this, an impressive Voc of 1.21 V is achieved, reflected by the smallest  $\Delta E_{\rm loss}$  of 0.42 eV, which benefits from effective suppression of nonradiative recombination. Given that the trap states can also serve as the nonradiative recombination center, it is concluded that the highest V<sub>oc</sub> of the champion device is associated with the smallest  $N_{\text{trap}}$ . Our combined results highlight the effectiveness of applying appropriate thermal treatments in reducing the defect states, mediating the crystallization, suppressing the voltage loss, and boosting the eventual photovoltaic performance of DJ 2D PSCs.

## 3. Conclusion

In summary, we have demonstrated a thermally induced crystallinity strategy through adjusting the annealing temperature of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films to boost the photovoltaic performance of DJ-phase 2D PSCs. With this method, high-quality DJ 2D perovskite films with enhanced crystallinity and compact structures were obtained at the annealing temperature of 120 °C, which led to an impressive  $V_{oc}$  of 1.21 V and PCE of 17.61% of 2D DJ-phase PSCs based on BDA organic spacers (n = 5). The





unencapsulated device also showed a satisfactory stability with the PCE degradation <20% for over 1000 h under MPP tracking. The optimal performance of PSCs was found to be mainly ascribed to the significant suppression of SRH recombination, efficient charge separation, and restricted interfacial charge accumulation. Further analysis confirmed that the enhanced  $V_{oc}$  was dominated by the suppression of nonradiative recombination, reflected by the smallest energy loss of 0.42 eV. This work provides a promising strategy for improving the key figure of merits of 2D DJ-phase PSCs toward realistic photovoltaic applications.

## 4. Experimental Section

*Materials*: PbI<sub>2</sub> (99.999%), MAI (99.8%), BDAI<sub>2</sub> (99.5%), methylamine acetate (MAAc) ionic liquid (99.9%), PTAA (Mn: 15 000–25 000), C<sub>60</sub> (99.5%), and BCP (99.0%) were purchased from Xi'an Polymer Light Technology Corp. DMF (99.9%). DMSO (99.9%) and toluene (99.8%) were purchased from Aldrich. All reagents and solvents were used as received without any further purification.

Synthesis: BDAI<sub>2</sub>, MAI, and PbI<sub>2</sub> with a molar ratio of 1:4:5 were mixed in DMF, DMSO, and MAAc ionic liquid solvent ( $V_{DMF}/V_{DMSO} = 0.7:0.3$ ,  $V_{\text{DME+DMSO}}/V_{\text{MAAc}} = 0.7:0.3$ ) and stirred at 70 °C for 8 h to prepare 0.75 м (BDA) (MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> precursor solution. The ITO/glass substrate was cleaned by successive sonication in detergent, deionized water, acetone, and isopropyl alcohol and then dried by nitrogen flow. After that, the ITO substrates were treated by oxygen plasma for 15 min. 40  $\mu L$  of PTAA solution (1.5 mg mL<sup>-1</sup> in toluene) was spin coated on ITO at 5000 rpm for 30 s, followed by annealing at 100 °C for 10 min in glove box filled with N<sub>2</sub>. The PTAA/ITO glass substrate was kept at a constant substrate temperature and 50 µL of perovskite precursor solutions were applied and spin coated at 4000 rpm for 30 s. Directly thereafter, the as-prepared precursor films were annealed at different temperatures (100, 110, 120, 130, and 140 °C) for 10 min. The whole deposition and annealing process of perovskite films was carried out in air atmosphere. The relative humidity in air was 25-40% while preparing the perovskite films in our experiments. Subsequently, C<sub>60</sub> and BCP films with 30 and 8 nm, respectively, were deposited by thermal evaporation. Finally, 100 nm Ag electrode was evaporated using a metal shadow mask. The active area of each device was 4 mm<sup>2</sup>.

Characterization: J-V characteristics of DJ PSCs and electron-only devices were measured using a Keithley 2400 SourceMeter under nitrogen atmosphere. The solar cells were tested under irradiation of AM 1.5G by an AAA solar simulator calibrated by a standard Si reference cell. The electrononly devices were tested in the dark. The EQE spectra were measured by a EnliTech external quantum measurement system (QE-R3011) in the spectral range of 300-850 nm. A field-emission SEM (Hitachi SU-8220) was used to characterize the surface and cross-section morphology of perovskite films and solar cells. The composition of the samples was measured by EDS attached on the SEM. The instrument used an electron beam accelerated at 3-5 kV, enabling operation at a variety of currents. XRD patterns were measured by a Rigaku D/MAX-TTRIII3 (CBO) X-ray diffractometer equipped with a push-plug Gobel mirror and a monochromatic  $CuK\alpha$  $(\lambda = 1.5405 \text{ Å})$  radiation source. GIWAXS measurements were performed on a Xenocs Xeuss SAXS/WAXS beamline system based on an X-ray wavelength of 0.6887 Å. AFM topographic images were captured by Bruker MultiMode 8 microscope in the tapping mode. UV-vis spectrometer (PerkinElmer Lambda 650/850/950 UV-vis spectrophotometer) was used to measure the absorbance spectra of perovskite films. HORIBA Fluorolog-III spectrofluoroemeter equipped with a diode laser  $(\lambda = 510 \text{ nm})$  for excitation was carried out to measured the steady-state PL spectra and TRPL spectra in the steady and transient mode, respectively. TPC and TPV were measured by applying a 488 nm solid-state laser (Coherent OBIS CORE 488LS) with a pulse width of  $\approx$ 30 ns. The photocurrent and photovoltage traces were recorded by a mixed domain oscilloscope (Tektronix MDO3032) through converting the registered voltage drop across  $2\Omega$  and  $10 M\Omega$  resistor in series, respectively. FTPS measurement was performed at a Vertex 70 from Bruker Optics. A Keithley 2400 SourceMeter was used for supplying voltages and recording injected current, and a Keithley 485 picoammeter was used for measuring the electroluminescence intensity.

# **Supporting Information**

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

# Acknowledgements

J.C. and B.W. contributed equally to this work. This work was financially supported by the National Key Research and Development Program of China (2017YFA0206600), the National Natural Science Foundation of China (nos. 21922505 and 21773045), the CAS Instrument Development Project (no.YJKYYQ20190010), and the Strategic Priority Research Program of Chinese Academy of Sciences (no. XDB3600000). Y.Z. thanks the financial support from the National Natural Science Foundation of China (nos. 21875012 and 21674006).

# **Conflict of Interest**

The authors declare no conflict of interest.

## Data Availability Statement

Research data are not shared.

## **Keywords**

defect suppression, energy losses, solar cells, thermal induction, 2D Dion–Jacobson perovskites

Received: July 13, 2022 Revised: August 26, 2022 Published online:

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