Phase Transition Control for High Performance Ruddlesden–Popper Perovskite Solar Cells

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Ruddlesden–Popper reduced-dimensional hybrid perovskite (RDP) semiconductors have attracted significant attention recently due to their promising stability and excellent optoelectronic properties. In this study, the RDP crystallization mechanism in real time from liquid precursors to the solid film and how the phase transition kinetics influences phase purity, quantum well orientation, and photovoltaic performance are investigated. This finding reveals an important template-induced nucleation and growth of the desired (BA)2(MA)3Pb4I13 phase, which is achieved only via direct crystallization without formation of intermediate phases. As such, thermodynamically perpendicular crystal orientation and high phase purity can be obtained. However, the formation of intermediate phases, including PbI2 crystals and solvate complexes, slows down intercalation of ions and increases nucleation barrier, leading to formation of multiple RDP phases and orientation randomness. These insights enable to obtain high quality (BA)2(MA)3Pb4I13 films with preferentially perpendicular quantum well orientation, high phase purity, smooth film surface, and improved optoelectronic properties. The resulting devices exhibit high power conversion efficiency of 12.17%. The results of this work should help guide the perovskite community to better control Ruddlesden–Popper perovskite structure and further improve optoelectronic and solar cell devices.

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reduced-dimensional (2D and quasi-2D) metal-halide perovskites (RDPs) $A_nA'_nM_nX_{3n+1}$, where $A$ and $A'$ are cations, $M$ is metal, and $X$ is halide, are becoming a new target of perovskite-based research. These materials, unlike graphene or other conventional 2D systems, can be grown from solution, which then allows for a remarkable tunability for structure and properties of the materials through the appropriate use of functional organic molecules and relaxed size restrictions, such that they provide not only high performance optoelectronic properties in contrast to 3D perovskites, but also high stability to light irradiation and chemical erosion.

Recent work demonstrates that for RDPs, there exists an intrinsic mechanism for dissociation of the excitons to long-lived free carriers provided by layer-edge states (LESs) when $n$ is larger than 2. This means fabricating solar cells from polycrystalline films with high purity and proper crystal grain sizes to allow balanced exciton diffusion to LESs and charge transport is one of the key factors to guarantee that charges can be separated and collected efficiently. In a recent breakthrough, perpendicular (out-of-plane) growth of perovskite crystals between electrodes was established by several groups as another key factor to allow efficient out-of-plane charge carrier transport in the 2D perovskites. Interestingly, the crystal growth is found to be highly dependent upon the solution-processing conditions. For example, casting $(BA)_2(MA)_3PbI_4$ solution on the hot substrate facilitates a strongly out-of-plane texture of the crystallographic planes of the inorganic perovskite component, while casting on substrates maintained at room temperature does not. In addition to substrate temperature, the choice of solvent also plays an important role in determining texture. The $(BA)_2(MA)_3SnI_4$ slabs show an in-plane alignment of the crystallographic planes to the substrate when dimethyl sulfoxide (DMSO) is used as the solvent, but this orientation can be flipped to the perpendicular direction when $N,N$-dimethylformamide (DMF) is used instead. These findings in the literature point to a complex formation mechanism of RDPs which remains to be further clarified and understood in order to achieve the desired texture and physical properties.

Herein, through extensive in situ investigations, modeling, film and device characterizations, we elucidate the RDP crystallization mechanism during solution processing and identify the key bottlenecks that limit the RDP film properties and overall efficiency of solar cells. We demonstrate that highly crystalline RDPs with high phase purity, preferentially perpendicular crystal orientation and large grain size can be grown only by fast and direct transition from a disordered precursor solvate to the perovskite phase without formation of any intermediate phases. While, the indirect crystallization does not template RDP phases for nucleation and growth, leading to orientation randomness and phase impurity. We demonstrate this to result in high PCE of 12.17%, whereas the indirect crystallization through the solvate phase leads to PCE in the range of 3–8.8%.

The phase transition from precursor sol–gel to the perovskite phase occurs during the solution casting was probed in situ using time-resolved grazing incidence wide-angle X-ray scattering (GIWAXS), which provides a comprehensive picture of how solution-processing conditions modulate the kinetics and mechanism of the RDP crystallization. The influences of the phase transition on the morphology and optoelectronic properties are also investigated thoroughly to establish a process–structure–property–performance relationship for this exciting new class of perovskite semiconductors.

Thin films of the RDP $(BA)_2(MA)_3n-1PbI_{3n}$ ($n = 4$, $n$ is set by the ratio of precursors used for a given solution) were fabricated using a one-step spin-coating method reported previously. We set out to investigate the role of ink formulation and coating temperature on the formation, morphology, phase purity, texture, quantum well orientation, optoelectronic properties, and solar cell performance of films, since both these parameters are known to impact the solidification outcome of layered perovskites. The ink formulation was varied in terms of the choice and ratio of solvent mixtures, namely DMF and DMSO. Coating temperature was controlled by preheating the substrate and sample holder prior to spin coating. The solution was spin cast on a compact TiO$_2$ (c-TiO$_2$)-coated FTO glass substrate, followed immediately by thermal annealing at 100 °C for 10 min.

We begin by evaluating the photovoltaic performance of RDP films fabricated in the different conditions as outlined above. The solar cells were fabricated according to the glass/FTO/c-TiO$_2$/RDPs/spiro-OMeTAD/Au architecture (Figure 1a). The most common fabrication condition for RDP films consists of spin coating from a DMF solution on the room temperature substrate (abbreviated as DMF-25 °C). This yields poor device performance, which is consistent with previous reports. We recorded an average PCE of 3.09% and peak efficiency of 3.25% with $V_{oc}$ of 1.02 V, $J_{sc}$ of 9.25 mA cm$^{-2}$, and FF = 32.75% (Figure 1b). We then introduced DMSO into the DMF solution but kept the substrate temperature maintained at 25 °C with the aim of modifying the precursor phase through the formation of DMSO–PbI$_2$ intermediate phases which are known to assist the fabrication of 3D perovskite films. We found a solvent mixture with DMSO:DMF = 7:3 ratio (abbreviated as DMSO:DMF-25 °C) yields a significantly improved PCE with average 7.25% and peak efficiency of 8.54%. The enhancement of PCE is mainly ascribed to the large improvements in $J_{sc}$ and FF in contrast to the neat DMF sample, i.e., 14.02 versus 9.25 mA cm$^{-2}$ and 53.04% versus 35.75%, respectively. This improvement hints at significant differences in the film microstructure which we will investigate below. Encouraged by this, we increased the substrate temperature stepwise up to 150 °C by preheating prior to spin casting the solution. We found that device performance increases monotonically with temperature up to 90 °C (abbreviated as DMSO:DMF-90 °C), achieving a peak efficiency of 12.17% with $V_{oc}$ of 1.08 V, $J_{sc}$ of 19.45 mA cm$^{-2}$, and FF = 58.22% (Figure 1b and Table 1).

The measured external quantum efficiency (EQE) and the corresponding integrated $J_{sc}$ are plotted in Figure 1c. The integrated $J_{sc}$ is calculated to be 19.20 mA cm$^{-2}$, which is within 1.5% of the $J_{sc}$ measured under AM 1.5G standard irradiation.

Furthermore, both forward and reverse scans yield a negligible variation in $J–V$ characteristics, indicating low hysteresis. Further increasing the substrate temperature deteriorates all figures of merit, with PCE declining significantly to 0.63% at 150 °C (Table S1, Supporting Information). The device performance was further investigated by casting solution on the 90 °C substrate with different volume ratios of DMSO:DMF, confirming the optimum solvent mixture to be DMSO:DMF = 7:3 (Table S1, Supporting Information) for the RDP solar cells.
Figure 1. a) Schematic representation showing one-step spin coating (BA)$_2$(MA)$_3$Pb$_4$I$_{13}$ precursor solutions as well as device architecture and (BA)$_2$(MA)$_3$Pb$_4$I$_{13}$ crystal structure. b) $J$-V characteristics of solar cell devices based on the three cases DMF-25 °C, DMSO:DMF-25 °C, and DMSO:DMF-90 °C. c) External quantum efficiency (EQE) and the corresponding integrated short circuit current density ($J_{sc}$) for the best performing device obtained for the DMSO:DMF-90 °C case. d) $J$-V characteristics recorded from forward sweep (from $J_{oc}$ to $J_{sc}$) and reverse sweep (from $J_{sc}$ to $J_{oc}$) under AM 1.5G illumination showing negligible hysteresis.

The device results show that they are dependent upon solvent and substrate temperature, indicating that formation of the RDP films is significantly influenced. We investigated the film formation mechanism and its dependence on the above important parameters by performing time-resolved GIWAXS in situ during spin coating. Three distinct conditions examined include: DMF-25 °C, DMSO:DMF-25 °C, and DMSO:DMF-90 °C. The time evolutions of the diffraction features as a function of scattering vector $q$ and time, are illustrated in Figure 2 for the three cases. Representative 2D GIWAXS snapshots taken at the end of spin coating are shown in Figure S1a–c (Supporting Information). The integrated intensity traces during spin coating associated to reflection of the RDP phase ($q = 10.0$ nm$^{-1}$) are plotted in Figure S1d (Supporting Information). Intensity versus $q$ for the scattering features of the three as-cast films are plotted in Figure S1e (Supporting Information) and the pole figures showing the differences in broadness of the Azimuth angle are plotted in Figure S1f (Supporting Information).

In all the cases, we observed a scattering halo at low $q$ values (2.5–5.5 nm$^{-1}$) corresponding to disordered precursor colloidal sol–gel (Figure 2), similar to previous observations in 3D MAPbX$_3$ solutions. The scattering halo at low $q$ dynamically evolves toward larger $q$ values as the solvent evaporates. In the DMF-25 °C case (Figure 2a,d), the RDP phase ($q = 10$ nm$^{-1}$) forms upon solidification at 20 s. Previous investigations of solution casting MAI: PbCl$_2$ or MAI: PbI$_2$ from DMF have revealed the formation of MAI·PbI$_2$·DMF crystalline solvate. Crystal-solvate line solvates are also observed for the DMF-25 °C formulation, with relatively weaker scattering features located at $q = 3.9$ and 7.7 nm$^{-1}$ corresponding to the (BAI)-(MAI)-(PbI$_2$)·DMF and PbI$_2$·DMF respectively. The scattering intensity of the RDP phase increases continuously for a duration of 10 s from 20–30 s (Figure S1d, Supporting Information), implying predominant nucleation and growth during the period. While, the broad diffraction peak suggests small RDP crystals with wide distribution in size. The representative 2D GIWAXS snapshot under AM 1.5G illumination showing negligible hysteresis.

Table 1. Summary of the photovoltaic parameters of the devices based on the three distinct fabrication conditions. The photovoltaic parameters for other fabrication conditions are shown in Table S1 (Supporting Information).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Stage $T$</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
<th>PCE$_{max}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>25 °C</td>
<td>1.02 ± 0.01</td>
<td>9.25 ± 0.23</td>
<td>32.75 ± 0.45</td>
<td>3.09 ± 0.12</td>
<td>3.25</td>
</tr>
<tr>
<td>DMSO:DMF (7:3)</td>
<td>25 °C</td>
<td>0.97 ± 0.03</td>
<td>14.02 ± 1.02</td>
<td>51.04 ± 1.98</td>
<td>7.25 ± 0.91</td>
<td>8.54</td>
</tr>
<tr>
<td>DMSO:DMF (7:3)</td>
<td>90 °C</td>
<td>1.08 ± 0.01</td>
<td>19.20 ± 0.24</td>
<td>58.00 ± 1.22</td>
<td>12.04 ± 0.12</td>
<td>12.17</td>
</tr>
</tbody>
</table>

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taken at the end of spin coating exhibits orientation randomness for both the RDP phase and intermediate solvates (Figure S1, Supporting Information). It is important to note that, the formation of intermediate phase slows down intercalation of ions and significantly influences crystallization of the quantum wells. When the solvent evaporates out, the complexes become weakened, allowing organic cation (BA$^+$ and MA$^+$) intercalation with newly released PbI$_2$ or (BAI$^-$)(MAI$^-$)(PbI$_2$)$^-$DMF framework to form RDPs. Noteworthy, smaller-$n$ phases ($n < 4$) are more favorable during crystallization due to lower nucleation barrier.\cite{43} Thus, the final film would contain RDP quantum wells with various $n$ values (indeed, phase heterogeneity is observed by the end of thermal annealing as will be shown further). The RDP formation can therefore be described in the following chemical equations:

\begin{align}
\text{MAI} + \text{PbI}_2 + \text{BAI} + \text{DMF} \rightarrow (\text{BA})_n(\text{MA})_{n-1}\text{PbI}_{2n+1} + \text{DMF} \uparrow \tag{1}
\end{align}

\begin{align}
\text{BAI} \cdot \text{MAI} \cdot \text{PbI}_2 \cdot \text{DMF} \rightarrow \text{thermal annealing} \rightarrow (\text{BA})_n(\text{MA})_{n-1}\text{PbI}_{2n+1} \tag{2}
\end{align}

\begin{align}
\text{PbI}_2 \cdot \text{DMF} + \text{MAI} \rightarrow \text{thermal annealing} \rightarrow (\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{2n+1} + \text{DMF} \uparrow \tag{3}
\end{align}

It takes more than 80 s for the DMSO:DMF-25 °C system to solidify (Figure 2b,e and Figure S1d (Supporting Information)), much longer than the DMF system, thanks in part to the higher boiling point of DMSO compared to DMF (189 vs 152 °C, respectively). However, the DMSO:DMF-25 °C formulation does not yield the desired perovskite phase during solution casting. Instead, randomly oriented intermediate phases are formed including PbI$_2$ crystals ($q = 8.9$ nm$^{-1}$)\cite{40}, PbI$_2$·DMSO solvate ($q = 7.9$ nm$^{-1}$), and (BAI$^-$)(MAI$^-$)(PbI$_2$)$^-$DMSO solvate ($q = 3.7, 4.3, 4.8, 6.3$ nm$^{-1}$). The precursor-DMSO solvate is also observed in another separated work when solution casting MAPbI$_3$ from DMSO:GBL solvent mixture or neat DMSO.\cite{44} The scattering intensity of these solvate phases is much stronger in contrast to that for the DMF-25 °C case (Figure S1e, Supporting Information). A plausible explanation is that DMSO can form strong Lewis-base adducts with lead halide and strong hydrogen bonds with ammonium salts due to high polarity (7.2).\cite{43} In this scenario, the presence of large amount of DMSO further increases the nucleation barrier of the desired RDP phase.\cite{43} Therefore, $n < 4$ phases are remarkably favored when intermediate phases transfer to RDPs. Due to the BA$^+$ overconsumption for $n < 4$ RDPs, the left precursors would assemble to $n < 4$ RDPs or even 3D perovskite in the following period, leading to broader phase distribution in contrast to the DMF-25 °C case. The RDP formation can be thus described in the following chemical equations:

\begin{align}
\text{MAI} + \text{PbI}_2 + \text{BAI} + \text{DMSO} + \text{DMF} \rightarrow \text{BAI} \cdot \text{MAI} \cdot \text{PbI}_2 \cdot \text{DMSO} \tag{4}
\end{align}

\begin{align}
\text{BAI} \cdot \text{MAI} \cdot \text{PbI}_2 \cdot \text{DMF} \rightarrow \text{thermal annealing} \rightarrow (\text{BA})_n(\text{MA})_{n-1}\text{PbI}_{2n+1} + \text{DMF} \uparrow \tag{5}
\end{align}
In contrast to these 25 °C cases, the DMSO:DMF-90 °C formulation exhibits direct phase transition from precursor sol–gel to the RDP phase without appearance of any intermediate phases (Figure 2c,f). The solution quick solidifies at $\approx 2$ s due to fast evaporation of solvents (Figure S1d, Supporting Information). The perovskite phase forming at $\approx 2$ s continues to dynamically evolve over a period longer than 2 min (Figure S1d, Supporting Information). The quick and direct phase transition from precursor sol–gel to the RDP phase is ascribed to the fast nucleation of precursors at the preheated substrate.\textsuperscript{[46–48]} Once formed, these nuclei act as template and further growth will continue outward quite rapidly.\textsuperscript{[49]} This template-aided growth yields highly crystalline RDP phase during solution processing, as evidenced by the observations of quite narrow scattering peak (Figure S1e, Supporting Information) and high orientation of quantum wells (Figure S1f, Supporting Information). Another interesting feature appears to be that, in the absence of DMSO, solution-casting films from pure DMF on the preheated substrate leads to lower quality RDP phase, suggesting that DMSO participates in perovskite crystallization (see Figure S2 in the Supporting Information for more details). The direct phase transition can be described as

\[
\text{PbI}_2 + \text{MAI} + \text{BAI} \xrightarrow{\text{thermal annealing}} \rightarrow (\text{BA})_2 (\text{MA})_{n-1} \text{Pb}_n \text{I}_{3n+1} (n \geq 4)
\]

We sought to ascertain how the phase transition influences the state of films. The crystalline quality of the final films (after thermal annealing) was first investigated using ex situ GIWAXS diagnostics. The GIWAXS patterns for the three cases are shown in Figure 3a–c and the corresponding intensity versus $q$ for the diffraction features is plotted in Figure 3d. After thermal annealing, all intermediate phases are replaced by perovskite phase. Note that solvate phases have the opportunity to realign amid the solvent and dissolved ions, especially for the DMSO:DMF-25 °C case. This is evidenced by the fact that the (BAI)⋅(MAI)⋅(PbI$_2$)–DMF solvate is predominantly oriented randomly in the as-cast film, while the well钝 orientation in the final films is significantly improved (Figure 3b and Figure S1b (Supporting Information)).

Due to different phase transition mechanisms, the final films exhibit various phase impurity accordingly. We confirm the (BA)$_2$(MA)PbI$_3$ formation in all films based on crystallographic determinations from indexing the Bragg peaks observed from GIWAXS and high-resolution X-ray diffraction (XRD) data (Figure S3a–c, Supporting Information). The strong scattering peak at $q = 10.0$ nm$^{-1}$ corresponds to their (111) plane of orthorhombic structure. It is evident that the DMSO:DMF-25 °C film appears to be a mixture of multiple RDP phases with different n values. Both GIWAXS (Figure 3b,d) and high-resolution XRD patterns (Figure S3, Supporting Information) indicate existence of $n \leq 4$ phases, including the (020) plane of the (BA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ ($n = 2$, (BA)$_2$(MA)PbI$_3$) phase, the (002) plane of the (BA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ ($n = 1$, (BA)$_2$PbI$_3$) phase, the (040) plane of the (BA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ ($n = 2$, (BA)$_2$(MA)PbI$_2$) phase, and the (111) plane of the $n = 4$ phase. Larger-$n$ phases or even 3D perovskites coexist with the $n = 4$ phase, with the scattering arcs also located at $q = 10.0$ nm$^{-1}$. Contrary, smaller-$n$ phases are less observed for the DMF-25 °C film from GIWAXS and XRD patterns, indicating less phase heterogeneity. Importantly, there is lack of strong feature for $n < 4$ phases in the DMSO:DMF-90 °C film, implying high phase purity (Figure 3c and Figure S3 (Supporting Information)). However, this does not mean phase impurity does not absolutely exist, merely that multiple phases are not sufficient to be discerned.

The comparison of intensity versus $q$ for the perovskite diffraction features indicates significantly improved crystalline quality of RDPs in the presence of DMSO (Figure 3e). The crystal sizes calculated using Scherrer formula for the predominant (111) peak show $≈ 33.5$ nm, $≈ 62.4$ nm, and $≈ 71.1$ nm for the DMF-25 °C, DMSO:DMF-25 °C, and DMSO:DMF-90 °C cases, respectively. This suggests the growth of larger crystals in the DMSO-derived films. Since the RDP crystallization is highly sensitive to nucleation barrier and ion diffusion, the lower nuclei density and faster ion diffusion are expected when higher affinity DMSO is introduced.

The influence of phase transition on quantum well orientation was further investigated. The pole figures of the Azimuth angle shows three arcs along the same rings at 90°, 137°, and 160° (Figure 3f) for the DMF-25 °C case, indicating that quantum wells are randomly oriented in films. For the DMSO:DMF-25 °C case, the pole figures shows two arcs at the Azimuth angle of 90° and 170°, also suggesting orientation randomness. By contrast, the DMSO:DMF-90 °C film exhibits sharp, discrete Bragg spots at pole figure 90° without noticeable peaks along the same rings, indicating that the quantum wells are highly oriented with inorganic layers perpendicular to the substrate to form continuous charge-transport channels, allowing efficient charge transport in the vertical direction. This is likely one of origins that the device fabricated via direct crystallization shows much improved $J_{sc}$ as observed in Figure 1 and in previous work.\textsuperscript{[24]}

Computational analysis was further performed on the interface between RDP nuclei and TiO$_2$ substrate based on density functional theory (Figure 3g). To this end, orthorhombic (BA)$_2$(MA)PbI$_3$ slab was deposited onto TiO$_2$ slab under two forms: BA attached TiO$_2$ and MA attached TiO$_2$, representing the parallel orientation and perpendicular orientation conditions, respectively. These nuclei were placed in contact with 120 TiO$_2$ anatase $5 \times 3 \times 2$ slab, with a mostly exposed (101) surface. The optimized TiO$_2$ cell parameters are used throughout our calculations, and this supercell guarantees the distance between adjacent (BA)$_2$(MA)PbI$_3$ nuclei larger than 15 Å to ignore the coupling effect. The interfacial energy is evaluated as follows

\[
E_{b} = E_{\text{slab}} - E_{(\text{BA})_{2}(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}} - E_{\text{TiO}_2}
\]

After scalar-relativistic geometry optimization, the (BA)$_2$(MA)PbI$_3$/TiO$_2$ junction with parallel orientation exhibits a 0.5 eV interfacial energy which mainly comes from van der Waals force. In the perpendicular orientation case, bond
formation between iodine and under coordinated titanium is highly favored, which leads to a strong interfacial energy of 8.9 eV. This value is almost 18-fold higher in contrast to the parallel orientation case. One can therefore deduce from these theoretical results that the perpendicular orientation is highly preferential when the (BA)$_2$(MA)$_3$Pb$_4$I$_{13}$ nuclei form on TiO$_2$ substrate (also see Figure S4 in the Supporting Information for interfacial energies for RDP/TiO$_2$ with $n = 2$ and 1).

The film morphology was examined using scanning electronic microscopy (SEM) and atomic force microscopy (AFM). Cross-sectional SEM image of the DMF-25$^\circ$C sample exhibits a concrete film with densely packed grains (Figure 4a). Perpendicular growth of RDP planes is observed for the DMSO:DMF cases. Plan-view SEM and AFM provide more insights into surface quality. Uniform surface without large grain boundaries can be observed from SEM images for the three cases (Figure 4b); while the details when looking from AFM images suggest quite distinct surface (Figure 4c). The DMF-25$^\circ$C film is extremely rough (root-mean-square roughness (RMS) = 42.8 nm), with plane size of only 200–500 nm (Figure S5, Supporting Information). In contrast, crystalline planes are quite large (2–5 µm) for the DMSO:DMF-25$^\circ$C and −90$^\circ$C cases, with relatively higher smoothness for the latter (21.6 vs 16.2 nm, respectively). These results imply that film quality is much better when precursors directly crystallize to RDPs without formation of intermediate phases.

The difference of perovskite crystalline quality and morphology prompted further study into optoelectronic properties. The optical absorbance and photoluminescence (PL) spectra of the three films are illustrated in Figure 5a,b. Interestingly,
Figure 4. a) Cross-sectional scanning electronic microscopy (SEM) images of the RDP films. b) Plan-view SEM images of the RDP films. c) Atomic force microscopy (AFM) images of the RDP films showing root-mean-square roughness (RMS).

bandgap (E_g) absorption is more pronounced and sharper in the DMSO-derived films. In addition to the lowest bandgap absorption, higher energy absorption peaks at ≈570 and ≈607 nm corresponding to the n = 2 and 3 phases are also observed for all films.[50] Meanwhile, the E_g values determined using Tauc plot decrease from 1.71 ± 0.004 to 1.62 ± 0.002 and 1.62 ± 0.001 eV for the DMF-25 °C, DMSO:DMF-25 °C, and DMSO:DMF-90 °C films (Figure 3c). This finding clearly implies lower E_g as one of origins for higher J_o in the DMSO-derived devices.

PL spectra exhibit dominated peaks at ≈719 nm (1.72 eV), ≈772 nm (1.61 eV), and ≈762 nm (1.63 eV) for the DMF-25 °C, DMSO:DMF-25 °C, and DMSO:DMF-90 °C cases, respectively. Meanwhile, an additional peak at ≈624 nm (1.98 eV) associated to the n = 2 phase[50] is found for the DMF-25 °C and DMSO:DMF-25 °C films with higher intensity for the latter. Apparently, concomitant effects can be obtained based on optical absorbance and emission spectra: variation in phase purity and phase distribution. The DMF-25 °C and DMSO:DMF-25 °C films tend to form less pure quantum wells with broad phase distribution. The highest phase purity is achieved in the DMSO:DMF-90 °C film with n predominantly located at 4. This phenomenon agrees well with the aforementioned X-ray observations, as shown in Figure 3. Furthermore, we also observed a shift for the dominant peak resulting from phase transition difference. The redshift for the DMF-25 °C film is likely due to the existence of much larger-n phases or even 3D perovskite; while the blueshift of which for the DMF-25 °C case is mainly caused by the low crystal quality. The variation of PL linewidth for the dominant peak, which is related to the crystal quality of 3D perovskite,[5,6,11] is also studied for the three films (Figure 5c). The PL linewidth decreases from ≈100.94 to ≈74.38 and ≈70.93 meV for the DMF-25 °C, DMSO:DMF-25 °C, and DMSO:DMF-90 °C films, respectively. This finding therefore confirms again the highest crystal quality in the DMSO:DMF-90 °C film.

Time-resolved PL (TRPL) spectroscopy was used to investigate the carrier lifetime of RDP films on glass (Figure 5d and Table S2 (Supporting Information)). TRPL displays increased lifetimes (τ_avg) from 5.87 to 11.93 and 28.35 ns for the DMF-25 °C, DMSO:DMF-25 °C, and DMSO:DMF-90 °C films, respectively. We ascribed the longer lifetime in the DMSO:DMF-90 °C film to higher phase purity and less defects because of high textured film and high crystal quality, which is beneficial for suppressing the charge recombination. Contrary, lower carrier lifetime in the DMSO:DMF-25 °C film highlights the influence of appearance of n < 4 phases, because free carriers exist at the layer-edge states only for larger-n phases.[25] The results therefore establish that carrier lifetime of RDP films originates mainly from the intrinsic crystalline quality; while the phase purity is also playing a role.

The most interesting observation in the kinetics study finds that solution casting (BA)₉(MA)₃Pb₄I₁₃ precursors on the preheated substrate promotes a direct phase transition from disordered precursor sol–gel to the RDP phase without formation of intermediate phases. This phase transition is driven by the fast dissociation of precursor–solvent complexes at the solution/substrate interface. As such, crystallization via template-induced nucleation and growth leads to thermodynamically perpendicular quantum well orientation. Due to homogeneous distribution of large cation in the absence of intermediate phases, high purity quantum wells can be obtained for the desired RDP with phase distribution centered close to the expected n set by...
the precursor ratios. The strongly perpendicular alignment of quantum wells with high film quality and phase purity enable a more efficient carrier transport and long carrier lifetime, which result in a high J_{sc} and PCE (12.17%).

In contrast, intermediate phases are preferentially formed during slow film formation due to strong interactions of Lewis acid adduct[35] and hydrogen bond between solvent and precursors. Smaller-n RDPs with lower nucleation barrier are more readily formed when intermediate phases crystallize to RDPs. In this scenario, quantum wells with wide phase distribution are more favored, even though the molar ratio of used precursors is intended for a single phase. Likewise, the substrate does not template RDP phases for nucleation and growth. This is likely the primary reason that solution casting on the low temperature substrate yields poor quantum well orientation.[34] The poor quantum well orientation and low crystal quality for the DMF-25 °C film dramatically hinder charge mobility in the perpendicular direction and therefore yield a low J_{sc} and FF in devices.[34] Noteworthy, orientation and phase distribution of quantum wells vary, but other structural properties are comparable for the DMSO:DMF-25 °C film in contrast to the 90 °C case. Due to larger exciton binding energy, the smaller-n phases appearing in the DMSO:DMF-25 °C case hint a challenge in the exciton dissociation and carrier collection in devices.[24-25] With this in mind, it is easy to see our conclusions concerning synthesis of RDP members with pure phase and perfect quantum well orientation which is important for identifying the physical limits and exploring the interesting new physics.[31]

Overall, our results suggest the significant importance of phase transition during solution casting \((\text{BAI})_2(\text{MAI})_3\text{Pb}_4\text{I}_{13}\) perovskite. The phase transition kinetics observed here can be generally applied to the most A_{n}A_{m-1}M_{n}X_{n+1} RDP structures. We believe significant advances in understanding RDP formation and controlling phase purity, quantum well orientation, and film quality would direct RDPs toward more desirable optoelectronic properties and device performance.

**Experimental Section**

**Solution Preparation and Device Fabrication:** The perovskite solution (1.2 \text{ ml}) was comprised of BAI (99.5%, Xi’an Polymer Light Technology Corp.), MAI (99.5%, Xi’an Polymer Light Technology Corp.), and \(\text{PbI}_2\) (99.985%, Alfa Aesar) (2:3:4 molar ratio) in solvent mixture of DMF (99.9%, Aladdin) and DMSO (99.9%, Aladdin) with various solvent volume ratios. The spiro-OMeTAD solution was prepared by dissolving 90 mg spiro-OMeTAD, 22 \text{ µL} lithium bis(trifluoromethanesulfonyl) imide (99%, Acros Organics, 520 mg \text{ mL}^{-1}) in acetonitrile (99.7%, Alfa Aesar), and 36 \text{ µL} 4-tert-butylpyridine (96%, Aldrich) in 1 \text{ mL} chlorobenzene (99.8%, Aldrich). All the solutions were prepared under inert atmosphere. The FTO-coated glass substrates (2.5 cm \times 2.5 cm) was cleaned by sequential sonication in acetone, isopropanol, and ethanol for 30 min each and then dried under N\textsubscript{2} flow. The cleaned substrates were exposed...
to ultraviolet and ozone for 15 min before the solution casting. The spin coating was accomplished under inert atmosphere. The TiO₂ was prepared by chemical bath deposition with the FTO glass immersed in a TiCl₄ (CP, Sinopharm Chemical Reagent Co., Ltd.) aqueous solution with the volume ratio of TiCl₄:HO₂ equal to 0.0225:1 at 70 °C for 1 h. Coating temperature was controlled by preheating the substrate and sample holder prior to spin coating, followed by dropping 70 µL precursor solutions and spin coating at 5000 rpm for 30 s without delay. The films were then annealed at 100 °C for 10 min. The hole-transporting layer was deposited onto the light-absorbing layer by spin coating spiro-OMeTAD solution at 4000 rpm for 30 s followed by evaporation of 50 nm gold electrode on the top of the cell.

**Optical Metrology:** UV-visible absorption spectra were acquired on a PerkinElmer UV-Lambda 950 instrument. Steady-state PL (excitation at 510 nm) and TRPL (excitation at 510 nm and emission at 733–766 nm) were performed with Rudower Chaussee 29 (PicoQuant GmbH, Germany).

**AFM:** Topography images were acquired on Bruker Dimension ICON instrument.

**SEM:** A Hitachi SU-8020 field emission scanning electron microscope was used at an acceleration voltage of 1 kV for the top surface images and 2 kV for the cross-sectional SEM images.

**XRD:** XRD measurements were carried out in a θ–2θ configuration with a scanning interval of 2θ between 3° and 45° on a Rigaku Smart Lab (X-ray Source: Cu Kr; λ = 1.54 Å).

**GIWAXS:** GIWAXS measurements were performed at D-line at the Cornell High Energy Synchrotron Source (CHESS). The wavelength of the X-rays was 1.166 Å with a bandwidth Δλ/λ of 1.5%. The scattering signal was collected by Pilatus 200K detector, with a pixel size of 172 µm × 172 µm placed at 176.76 mm away from the sample position. The incident angle of the X-ray beam was at 0.25° and the integration time was 1 s.

**Solar Cell Characterizations:** Current–voltage characteristics were analyzed by a digital source meter (Keithley Model 2400) under ambient condition at room temperature. The light source was a 450 W xenon lamp (Oriel Instruments PV Reference Cell System Model 91150 V, Newport) to match the power output of the lamp to the AM 1.5G standard. All measurements were conducted through the sides.

**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.

**Keywords**

in situ diagnostics, phase transition, Ruddlesden–Popper perovskite, solar cells, solution processing


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