High Efficiency Quasi-2D Ruddlesden-Popper Perovskite Solar Cells

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2D Layered Perovskites

Solution Processable Materials
The recent discovery that single-layer 2D perovskites can be prepared using solution processing techniques\(^1\) has been followed by enormous research into optoelectronic applications of 2D perovskites including light emitting diodes (LEDs),\(^2\) phototransistors,\(^3\) and solar cells.\(^4\)

Tunable Emission Wavelength
Photoluminescent 2D perovskites have an emission wavelength that changes depending on the layer thickness and the choice of amine and halide. We offer an excellent portfolio of the most popular 2D perovskite compositions for photoluminescence based devices.

Improved Moisture Stability
Solar cells fabricated with 2D perovskites have improved stability in moist air compared to 3D perovskites.\(^4\)

| Formula | Cat. No. | Layer Thickness | \((\text{RNH}_2)_n(\text{MeNH}_2)_m\text{Pb}_x\text{X}_{2-x}\) |
|---------|----------|-----------------|---------------------------------|
| \((\text{BA})_n\text{PbI}_n\) | 910961 | \(n=1\) | \(\text{Bu}\) | 1 | 1 |
| \((\text{BA})_n\text{PbBr}_n\) | 910953 | \(n=1\) | \(\text{Bu}\) | \(\text{Br}\) | 1 |
| \((\text{PEA})_n\text{PbI}_n\) | 910937 | \(n=1\) | \(\text{PE}\) | 1 | 1 |
| \((\text{PEA})_n\text{PbBr}_n\) | 910945 | \(n=1\) | \(\text{PE}\) | \(\text{Br}\) | 1 |
| \((\text{BA})_n(\text{MA})_m\text{PbI}_n\) | 912816 | \(n=2\) | \(\text{Bu}\) | 1 | 2 |
| \((\text{BA})_n(\text{MA})_m\text{PbI}_{10}\) | 912557 | \(n=3\) | \(\text{Bu}\) | 1 | 3 |
| \((\text{BA})_n(\text{MA})_m\text{PbI}_{43}\) | 914363 | \(n=4\) | \(\text{Bu}\) | 1 | 4 |
| \((\text{BA})_n(\text{MA})_m\text{PbI}_{16}\) | 912301 | \(n=5\) | \(\text{Bu}\) | 1 | 5 |

BA = n-butylammonium; PEA = 2-phenethylammonium; MA = methylammonium, Bu=n-butyl, PE=2-phenethyl

References:
1) Dau, L.; Wang, A. B.; Yu, Y.; Lai, M.; Kammenga, J.; Eaton, S. W.; Fu, A.; Bischak, C. G.; Ma, J.; Ding, T.; Ginsberg, N. S.; Wong, L-W.; Alivisatos, A. P.; Yang, P. Science 2015, 349, 1518. DOI: 10.1126/science.aac7660
2) Yuan, M.; Quan, L. N.; Cumin, R.; Walters, G.; Sabatini, R.; Vannor, O.; Hoogland, S.; Zhao, Y.; Bourdier, E. M.; Kanjanaboos, P.; Li, Z.; Kim, D. H.; Sargent, E. H. Nat. Nanotechnol. 2016, 11, 872. DOI: 10.1038/NNANO.2016.110
3) Shao, Y.; Liu, Y.; Chen, X.; Chen, C.; Serpengüzel, I.; Chen, Z.; Feng, X.; Kong, J.; Watanabe, K.; Iwai, K.; J. Mater. Chem. A. 2017, 5, 4220. DOI: 10.1039/c7ta04928k
4) Cao, D. H.; Stafstrom, C. C.; Farha, O. K.; Hupp, J. T.; Kanaan, M. G. J. Am. Chem. Soc. 2015, 137, 7043. DOI: 10.1021/jacs.5b03796

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High Efficiency Quasi-2D Ruddlesden–Popper Perovskite Solar Cells

Alessandro Caiazzo and René A. J. Janssen*

Quasi-2D Ruddlesden–Popper perovskites (RPPs) are promising candidates for stable and efficient solar cells. Even though photovoltaic devices based on these materials are still lagging behind traditional 3D perovskites, they have experienced a dramatic increase in power-conversion efficiency, recently reaching >20%. As knowledge develops, the toolbox of RPP researchers is steadily growing in terms of organic spacers, additives, and characterization methods. This review aims to describe the use of such a toolbox to achieve high efficiency solar cells. The use of additives, functionalized spacers, and novel fabrication techniques are explored to control morphology, crystallinity, interlayer interaction, and phase distribution. Moreover, methods to achieve the coveted phase purity in RPPs and its implications on both single- and multi-junction solar cells are discussed. By describing successful cases of high efficiency solar cells combined with in-depth knowledge of material properties, it is shown that there are still several open research questions that need exploring to further develop this fascinating class of perovskites.

1. Introduction

Perovskite solar cells have attracted enormous interest because of their steep increase in photovoltaic performances, from 4% in 2009 to 25.7% in 2020.[1] Such a photovoltaic “miracle” is due to the outstanding optoelectronic properties of this material: low exciton binding energy at room temperature, high absorption coefficient, high carrier mobility, ability to tune the bandgap of the material by changing its composition.[2] Multi-junction solar cells—consisting of a perovskite over a silicon solar cell or multiple perovskites—are also gaining interest because of their chance to overcome the detailed-balance limit of single absorbers and provide >30% power conversion efficiency (PCE).[3] Despite these advantages, perovskite solar cells suffer from instability when exposed to ambient air, high temperature, high relative humidity, and even light.[4] Because of this, layered 2D perovskites have appeared on the scene with the promise of improving the stability of the material.[5,6]

Traditional organic-inorganic hybrid perovskites possess an ABX₃ chemical structure that describes a three-dimensional (3D) framework. Here, A consists of an organic cation, such as formamidinium (FA) or methylammonium (MA), B is usually lead (Pb) or tin (Sn), and X is a halide ion, mostly iodide (I) or bromide (Br). The choice of organic cation for 3D perovskites is dictated by a geometric tolerance factor based on the radii of ions, which should be in the range of 0.8 and 1, meaning that cations that are too-small or too-large cannot be incorporated in the crystal lattice and cannot be used to make 3D perovskites.[11] When using larger cations, such as butylammonium (BA) or phenethylammonium (PEA), that cannot be accommodated in the 3D perovskite, the 3D framework can be sliced along the (100) plane direction to form a layered, 2D or quasi-2D perovskite.[7–9] The chemical formula of 2D and quasi-2D perovskites is \((R)_{m}A_{n-1}B_{n}X_{3n+1}\), where R represents the bulkier spacer. Monovalent or divalent ammonium or acetal ammonium spacers have been reported to form Ruddlesden–Popper (RP, \(m = 2\)) or Dion-Jacobson (DJ, \(m = 1\)) perovskites, respectively, where lead halide octahedral sheets are sandwiched between the larger organic cations (Figure 1).[10–13]

The number of octahedra between the spacers (which we will refer to as \(n\)-value) dramatically changes the optoelectronic properties of the materials. For example, a pure 2D \(n = 1\) perovskite possesses a bandgap energy \((E_g)\) of about 2.3 eV and a high exciton binding energy > 300 meV, whereas by increasing \(n\), the bandgap and exciton binding energy decrease to those of a 3D perovskite \((n = \infty)\).[12,14] As a result, for solar cell applications, \(n\)-values between 3 and 5 are often used to achieve an absorption spectrum that has reasonable overlap with the spectral solar irradiance and to avoid the excitonic nature of small-\(n\) perovskites.[14] Such perovskite structures are often referred to as quasi-2D perovskites.

While 3D perovskites are limited to a handful of A-site cations, namely MA, FA, and Cs, RP and DJ perovskites possess a chemical tuneability that is virtually boundless. A large variety of organic spacers has already been used for the formation of RP and DJ perovskites either as active layer or passivation layer.[15–18] Although clear structure-property relationships—one of the
main research questions for the field—are yet to be identified, the variety of spacers that can be employed makes this class of perovskites an interesting field of research with chance of impactful discoveries. Even though processing of lower-dimensional perovskites creates new challenges, such as tuning phase distribution and controlling crystal orientation, these perovskites show promise with a rapidly-increasing PCE, and enhanced stability compared to 3D perovskites, as we will discuss below.

In this review, we focus on Ruddlesden–Popper perovskites (RPPs), possessing a monovalent organic spacer, and refer the reader to other reviews for DJ perovskites.[18–20]. Even though DJ and RP phases share similar challenges regarding fabrication of high efficiency devices, such as crystal orientation and phase distribution, RPPs have been more investigated and represent a more mature field. Furthermore, RPPs have shown enhanced stability compared to DJ phases.[21] However, DJ perovskites also possess promising features. For instance, the presence of a divalent ammonium spacer leads to shorter distances between the inorganic layers of PbI2 compared to RPPs and provides better orbital overlap and enhanced charge transport. As a result, this class of materials is promising for optoelectronics devices, and we expect much more studies in the following years.[18]

1.1. Phase Distribution in RPPs

There is a competition between the crystallization of 2D, quasi-2D, and 3D perovskites when fabricating quasi-2D RP films. Take, for example, a precursor solution containing BA1, MAI, and PbI2 in the appropriate ratio to form a quasi-2D perovskite with \( n = 4 \). During solvent evaporation, crystallization can lead to (BA)\(_2\)PbI\(_4\) (2D), (BA)\(_2\)MA\(_{n-4}\)Pb\(_n\)I\(_{3n+1}\) structures with different \( n \)-values (quasi-2D), and MAPbI\(_3\) (3D).[22] Usually, a combination of all of these appears in the film, effectively forming a multidimensional perovskite with both 2D, quasi-2D, and 3D phases, and an average \( n \)-value of less than 4. The film crystallization usually starts as a 3D perovskite at the liquid-air interface and proceeds toward the substrate forming multiple quasi-2D and 2D phases.[23] As a result, there are two processes to analyze: a) phase distribution of structural phases with different \( n \)-values (mostly at the bottom) and b) vertical phase segregation of (quasi-)2D and 3D phases [Figure 2a].[24–26] Both are responsible for a bandgap gradient in the film that leads to ultrafast charge carrier migration from small-\( n \) to large-\( n \) phases (Figure 2b).[27] which makes the analysis of phase distribution experimentally challenging. For instance, photoluminescence (PL) spectra display emission peaks derive mostly from low-\( E_g \) perovskites (Figure 2c), making it impossible to quantify the phases through this routine technique.[28] Ultrastart transient absorption (TA) measurements are often better suited to determine how phases are distributed by measuring the absorption profile just after excitation in the span of hundreds of femtoseconds (Figure 2d).[26] Apart from optical measurements, phase distribution can also be analyzed by angle-dependent grazing-incidence wide-angle X-ray scattering (GIWAXS), where probing with angles lower than the critical angle provide information only of the film’s very top surface, while higher angles probe the whole thickness.[29] This method is independent of carrier migration and provides information also on the crystal orientation, which, as we will see below, is of crucial importance for charge transport in RPPs.

The reasons behind vertical phase distribution have been debated in the literature. It is thought that this process takes place already during the gel stage, which corresponds to the first seconds of the spin coating process and can be modulated via solvent-precursors interactions.[22,30] Liu et al. proposed that differences in cation diffusivity are behind the formation of vertical phase segregation, which is exacerbated at high temperatures or with large cations.[30] For example, they found that the flux of MA cations to the surface of the film is much higher than for BA, which explains the prevalent presence of MA at the top interface and the vertical 2D–3D gradient that is so often observed. Nevertheless, this diffusivity model could not explain the formation of phases of different \( n \)-values at the bottom. Recently, Hoffman et al. studied the mechanism behind phase distribution and analyzed the evolution of the perovskite precursors to the final crystal structures.[22] One finding was that intermediate phases need free molecules of MAI and BAI to form the final perovskite structures. Based on these results, our group demonstrated that the molecules’ availability to react and the resulting phase distribution at the bottom of the film depend on their interaction with solvents and co-solvents, pointing once more to the importance of studying precursor solutions to understand phase distribution.[20] Similarly, in a comprehensive study published by Quintero-Bermudez and co-workers, these large complexes of precursors and solvents were thought to provide a framework that facilitates the formation of quasi-2D and 2D RPPs.[27] Overall, the solvent was found to be crucial in determining the phase distribution and crystallinity.

Figure 1. Illustration of a) 2D, b) quasi-2D, and c) 3D perovskite crystal structure.
While 2D–3D graded perovskites, with 2D phases at the bottom, are by far the most common encountered in the literature, recent studies have also highlighted the possibility of obtaining reverse-graded 3D-2D perovskites. For example, by using cyclohexylmethylammonium iodide as spacer, Wei et al. have shown that it is possible to obtain films where the 3D perovskite is at the bottom.\(^{[31]}\) The authors demonstrated that such a gradient is optimal for solar cells in \(n-i-p\) configuration, obtaining a PCE of 15% with \(\text{TiO}_2\) and Spiro-OMeTAD as electron- and hole-transport layer, respectively.

Efforts have also been made by many groups to avoid phase distribution altogether and to achieve phase-pure perovskites. In a pioneering work published in 2016, Kanatzidis’ group fabricated phase-pure 2D and quasi-2D perovskites single crystals by exploiting the solubility difference of structural phases with different \(n\)-values.\(^{[12]}\) However, to deposit a perovskite film via spin coating, crystals still needed to be dissolved in a solvent such as DMF, which often compromises phase purity. Recently, butylammonium acetate (BAAc) has been proposed as an alternative precursor to the iodide salt to form phase-pure perovskites.\(^{[32]}\) We will describe the use of single crystals and acetate salts in Sections 2.4 and 3.1, respectively, and we will broadly discuss phase purity in Section 4.

### 1.2. Crystal Orientation

Compared to thin-film 3D perovskites,\(^{[33]}\) crystal orientation has a more profound effect on charge transport in thin-film RPPs because the bulky organic spacers in layered perovskites hinder the charge transport between layers. In this case, a vertical orientation of the RPP crystals is desirable to assure that the transport of charges between electron- and hole-transport layers at top and bottom is not negatively impacted (Figure 3a).\(^{[34]}\) While the analysis of vertical orientation is often reported in the form of GIWAXS measurements, an accurate representation of the RP microstructure is complicated, again, by the presence of multiple phases with various \(n\)-values. It is often reported in the literature that the appearance of \((0k0)\) diffraction planes in the out-of-plane direction represents the formation of parallel-oriented small-\(n\) phases. However, high efficiency RP cells are usually made of vertically oriented films that also contain a variety of structural phases. To carefully characterize which RP phases are formed in such films, one should look at the \((0k0)\) peaks in the in-plane direction, which unfortunately are often obscured by the substrate horizon in conventional GIWAXS equipment.\(^{[35]}\) As a result, an accurate characterization of the RPP phases present in the film is rarely provided and very often RPPs are described with a specific \(n\)-value even though little characterization is available on which phases are present. Because characterizing RPP films is difficult via both optical and crystallographic methods, these materials are often described by an average \(n\)-value (\(\langle n \rangle\)), based on the stoichiometry of the precursor solution) that implies the presence of multiple phases.

The mechanism behind vertical orientation has been investigated. As mentioned before, the crystallization of RPPs starts at the liquid-air interface. When studying a BA-based system, Chen and co-workers found that BA molecules are not able to form a monolayer at the liquid-air interface due to interaction...
with the solvent or due to complexion with PbI$_2$. This leads to a scenario where BA molecules are oriented parallel to such interface and vertical orientation of the perovskite crystals is favored. Once the nucleation at the liquid-air interface has started, a completely vertical orientation can be obtained if low supersaturation makes crystal growth preferred over additional bulk nucleation processes, which instead inevitably lead to a random orientation of the crystals. Apart from these studies, many groups have reported different processing techniques that can enhance vertical orientation, although they seldom report the underlying mechanism. Among these techniques are hot casting, spin coating with antisolvent, use of co-solvents, use of pressure and heat.

### 1.3. Stability of RPPs

Despite their lower efficiencies in solar cells compared to 3D perovskites, RPPs have attracted enormous interest in the perovskite research field because of their promise to improve the intrinsic and extrinsic stability of this material. In 2014, Smith et al. first reported the superior stability of a PEA-based RPP compared to MAPbI$_3$ when exposed to ambient humidity. More specifically, for at least 46 days the RPP displayed no changes in X-ray diffraction (XRD) patterns, while the 3D counterpart showed significant amounts of PbI$_2$. Later, Sargent’s group investigated the stability of the same RPPs via density functional theory (DFT) and found a 6-fold decrease of PEAI desorption rate compared to MAI, which significantly decreased the film decomposition. Furthermore, they analyzed the stability of the solar cells in function of the n-value and found a decrease in stability when increasing n, as expected. Nevertheless, a RPP with n = 10 still displayed higher-long term air stability compared to MAPbI$_3$. Overall, lower n-values have typically led to solar cells with poorer efficiency but higher stability, thus the recently-observed drastic increase in PCE of RPPs with n between 3 and 5 makes this class of material extremely promising.

Recently, RPP solar cells with efficiency > 18% have been published, which all display enhanced stability compared to traditional 3D perovskites. To visualize such enhancement, we selected a few studies with the highest reported PCEs in which the stability of RPPs was compared with that of 3D perovskites (Figure 4). Most of the shelf-life studies were in the range of 500–1000 h and showed a PCE loss > 60% for 3Ds and < 20% for RPPs. It is worth mentioning that most data was obtained by storing a solar cell in relative humidity (RH) between 25 and 65% and measuring PCE at different points in time. Stability measurements at high temperature, instead, were often performed in an N$_2$-filled glovebox or low-humidity atmosphere. Finally, even though we analyzed only a few reports, we note that all followed different, sometimes arbitrary, procedure to evaluate stability. As a result, it is impossible to establish which RPP, in terms of composition or phase purity, possesses higher stability. Applying a consistent method to evaluate stability and to effectively compare results among the literature is thus necessary.

As mentioned before, RPPs possess a large chemical tunability because of the number of organic spacers that can be used. Changes in molecular stacking, crystallinity, charge transport properties impact the stability of the solar cells as well, apart from their efficiency. A comparison between 2-(methylthio)ethylammonium (MTEA) and BA, for example, has indicated better stability for MTEA when exposed to air and under heat stress conditions. Formation of PbI$_2$ was inhibited under these conditions when using MTEA, because S-S inter-spacer interactions provide stabilization of the RPP framework against humidity and heat. Fluorination of PEA in the para position has also been shown to improve the thermal stability of the perovskite layer compared to non-fluorinated PEA, whereas halogenation of PEA with F, Cl, and Br improved stability towards humidity. Similar findings have recently been published for fluorinated benzylammonium (FBZA). Zhang et al. reported that fluorination of PEA affects the phenyl-ring stacking, which is parallel slip-stacked in F-PEA and edge-to-face in PEA. The better stacking allows for maximization of π-orbital overlap and leads to better charge transport and stability. The A site plays a relevant role in stability as well. FA-based quasi-2D...
Solar cells based on 3D perovskites have experienced a steep increase in photovoltaic performance during the last >10 years. Nowadays, solar cells with efficiency > 20% are the norm, and multiple publications have recently demonstrated efficiencies > 25%.\textsuperscript{58-60} Similarly, RPPs have improved from less than 4% in 2014 to > 21% in 2021 (Figure 5). Despite significant less work on RPPs compared to 3Ds, this class of solar cells has experienced a steeper enhancement in performance in the last decade. Furthermore, while most high efficiency 3D perovskites are developed in n-i-p configuration, RPPs are broadly used in p-i-n solar cells, which are more suitable for multijunction applications. With further developments, RPPs have the potential to be stable and efficient perovskites for such applications.

The introduction of new fabrication methods, the use of new additives and spacers, and a more thorough understanding of crystallization mechanism, vertical orientation, and phase purity are behind this substantial increase of PCE in RPPs. Together with PCE, the toolbox of RPP researchers is also steadily growing in terms of fabrication methods to use or molecules to employ as additives or spacers. Furthermore, as RPPs represent a complex and multifaceted system, such a toolbox now also contains a broad variety of characterization techniques, among others GIWAXS, confocal PL microscopy, dynamic light scattering (DLS), ultrafast TA, all of which will be discussed. This review aims to describe successful methods of fabricating high efficiency solar cells based on RPPs amongst such a plethora of options. We will discuss the impact of molecular and additive engineering and new fabrication methods on both film properties, such as crystal orientation and phase distribution, and solar cell properties, such as charge transport and photovoltaic performance.

With this work, we summarize where this field is currently standing, and which research questions need answering to reduce the gap between 3D and RP perovskites and to further develop this exciting field.

### 2. Molecular and Additive Engineering

RPPs show an outstanding structural variety compared to traditional 3D perovskites because of the possibility to use an enormous assortment of organic spacers. The organic spacer in 2D and quasi-2D perovskites does not only slice the perovskite framework but also has important consequences on the optoelectronic and crystalline properties of the material, such as bandgap energy, charge transport, molecular packing, and phase distribution, that can be tuned to achieve higher PCEs. For the readers who desire a more fundamental understanding of the changes induced by different organic spacers, we refer to a broad review that was recently published by Kanatzidis’ group.\textsuperscript{17} Apart from molecular changes in the spacer structure, the field of RPPs has also experienced an extensive use of additives to induce modifications in film morphology, crystal orientation, or overall crystallization process.

In this section, we analyze some successful examples of molecular and additive engineering in high efficiency RPP solar cells, where chemical changes at the molecular level and induced changes of the film properties have led to enhanced photovoltaic performances (i.e., PCE > 14%).

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**Figure 5.** Evolution of power conversion efficiency (PCE) over time for 3D (from NREL\textsuperscript{[9]} and RP perovskites. For the latter, a brief description of the materials and fabrication method is given. References are the following: PEA,\textsuperscript{[41]} hot casting,\textsuperscript{[37]} Cs doping,\textsuperscript{[63]} MACI precursor,\textsuperscript{[62]} assisted crystal growth,\textsuperscript{[46]} and 4FPEA,\textsuperscript{[41]}
2.1. Fluorinated Spacers

The use of fluorinated functional groups has been successfully applied to organic solar cells with improvements in both film morphology and device efficiency. Likewise, as RPPs might benefit from the tunability of spacers’ chemical structure, multiple groups synthesized and used fluorinated organic spacers in quasi-2D perovskite solar cells (Table 1). Such spacers possess different dipole moments, molecular size, and solubility compared to non-fluorinated ones, leading to differences in phase distribution that can be exploited to achieve high efficiency devices. Wang et al. studied a series of halogenated PEAs and thoroughly characterized both the surface of the films and their distribution of phases. Fluorination of PEA (4FPEA) (Figure 6a) was found to increase crystallinity and grain size and to suppress the formation of \( n = 1 \) phases, as observed via ultrafast transient absorption (TA) measurements (Figure 6c), which are usually detrimental for device performance because of its parallel orientation that inhibits charge transport along the vertical direction. Furthermore, while they still exhibited a 2D–3D gradient with small-\( n \) phases at the bottom, 4FPEA-based films possessed a higher content of large-\( n \) phases compared to PEA-based films, which is instead favorable for the cells’ performance. In contrast, due to the lower solubility of 4BrPEA and 4ClPEA, small-\( n \) phases nucleated at an early stage of film formation when using such spacers, leading to a phase distribution drastically shifted towards 2D and, as a result, to low PCE. By using 4FPEA (\( n = 4 \)) in combination with MACl and PbCl\(_2\) as additives, the authors reported a PCE of 18.1% with open-circuit voltage (\( V_{\text{OC}} \)) of 1.21 V and short-circuit current density (\( J_{\text{SC}} \)) higher than 19 mA cm\(^{-2}\).

### Table 1. Solar cell parameters for high-efficiency RPPs fabricated with fluorinated organic spacer cations.

| RPP                  | Method\(^a\) | \( J_{\text{SC}} \) [mA cm\(^{-2}\)] | \( V_{\text{OC}} \) [V] | FF [-] | PCE [%] | Ref.    |
|---------------------|--------------|--------------------------------------|--------------------------|--------|---------|---------|
| (4FPEA)\(_2\)MA\(_3\)Pb\(_4\)I\(_3\) | H.C., Add.   | 19.04                               | 1.21                     | 0.78   | 18.10   | [47]    |
| (4FPEA)\(_2\)MA\(_3\)Pb\(_4\)I\(_3\) | Add.         | 19.00                               | 1.16                     | 0.79   | 17.34   | [48]    |
| (4FPEA)\(_2\)MA\(_3\)Pb\(_4\)I\(_3\) | H.C.         | 17.50                               | 1.08                     | 0.8    | 15.2    | [64]    |
| (4FPEA)\(_2\)MA\(_3\)Pb\(_4\)I\(_3\) | Add.         | 18.00                               | 1.06                     | 0.76   | 14.5    | [65]    |
| (4FPEA)\(_2\)FA\(_3\)Pb\(_5\)I\(_3\) | Add., A.S.   | 20.54                               | 1.13                     | 0.74   | 17.37   | [54]    |
| (4FPEA)\(_2\)FA\(_3\)Pb\(_5\)I\(_3\) | H.C., Add.   | 22.45                               | 1.18                     | 0.79   | 21.07   | [43]    |
| (4FPEA)\(_2\)MA\(_3\)Pb\(_4\)I\(_3\) | H.C., Add.   | 18.75                               | 1.20                     | 0.83   | 18.67   | [45]    |
| (4FPEA)\(_2\)MA\(_3\)Pb\(_4\)I\(_3\) | H.C., Add.   | 17.14                               | 1.23                     | 0.80   | 16.82   | [52]    |

\(^a\)H.C. = hot casting, Add. = additives used in the precursor solution, A.S. = antisolvent, FF = fill factor.

Figure 6. a) Chemical structure of PEA\(^+\) and 4FPEA\(^+\). Reprinted with permission. Copyright 2021, Wiley VCH. b) Chemical structure of PhFA and 4FPhFA with corresponding dipole moment. Reprinted with permission. Copyright 2021, American Chemical Society. c) Ultrafast transient absorption of PEA- and 4FPEA-based RPPs. Circled area (left plot) represents the ground state bleaching of \( n = 1 \), which is suppressed in 4FPEA. Reprinted with permission. Copyright 2021, Wiley VCH. d) External quantum efficiency (EQE) spectra and PCE statistical distribution of pure MA, FA-MA, and pure FA RPP based on 4FPEA. Reprinted with permission. Copyright 2021, Wiley VCH. e) Schematic representation of the spin coating process where MAPbCl\(_3\) seeds are formed during the gel stage. Reprinted with permission. Copyright 2021, Wiley VCH.

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compared to PEA (1.98 vs 1.26 D) with reduced dielectric confinement and exciton binding energy.[66] This, in combination with better intermolecular packing of the organic spacers, provided a PCE of (4FPEA)2MA2PbI6 to 17.3% with $V_{OC}$ of 1.16 V and $J_{SC}$ of 19 mA cm$^{-2}$. Overall, PCEs $>14\%$ have been reached also by other groups by using the same organic spacer, usually in combination with additives, such as NH$_4$SCN.[64,65]

As explained above, 4FPEA possesses a higher dipole moment compared to PEA, which is important for decreasing the exciton binding energy. A way to increase even further such dipole moment is to functionalize a FA cation with a bulky functional group, such as a fluorinated phenyl group. This strategy was first adopted by Dong et al., who functionalized FA with a thiophene group, and recently by another group who used a chlorinated phenyl group.[69,66] Li et al. reported the use of PhFA (Ph = phenyl) and 4FPhFA (Figure 6b) for MA-based RPPs and achieved efficiencies up to 17.37%. Interestingly, they also associated the enhanced hydrogen bonding between the fluorinated spacer and the [PbX$_6$]$_4$- framework with increased stability of the perovskite layer, showing that FA spacers are a suitable way to both decrease the PCE gap between 3D and RPPs and to further enhance their stability. It is useful to notice, however, that stability was measured in very mild conditions, namely room-temperature and N$_2$ atmosphere.

The use of FAPbI$_4$ in the 3D perovskite field has led solar cells to new highs in efficiency, because of its lower bandgap energy and less significant voltage losses. Although the use of FA in RPPs has been limited to a handful of studies, it has shown great promise in enhancing photovoltaic performances.[67] A recent study has reported a record efficiency of 21.07% by using 4FPEA as organic spacer in a FA-based RPP.[68] Shao and co-workers used a combination of 4FPEA and FA as A cation to push the efficiency from 17% (pure MA) to 21% (pure FA) (Figure 6d). To ensure the formation of α-phase, MACl and PbCl$_2$ were used as additives in a 1:1 ratio. By varying the concentrations, it was found that the presence of Cl induces the formation of MAPbCl$_3$ seeds during spin coating (Figure 6e), which act as nucleation points to assist the crystallization of 3D-like perovskite phases, thus suppressing the formation of n = 2 and facilitating charge transport. Even though no comparisons with non-fluorinated spacers were shown, this study currently presents the highest recorded PCE for an RPP and directs the research field towards FA-based perovskites for further improvements.

### 2.2. Multi-Spacer RPPs

Tuning the interlayers’ interaction can be achieved via engineering size, chemical structure, and functional groups of the organic spacer, but also by mixing multiple spacers. These different cations can act as co-spacers and create layered perovskites with a crystalline structure that, for example, differs in lattice spacing compared to the one-spacer RPP.[66] In 2019, Lian et al. introduced the use of a second spacer in a RPP solar cell by mixing BA and PEA.[69] To achieve good device performance, namely a PCE of 14.09% in a p-i-n device with poly(3,4-ethylendioxythiophene) polystyrene sulfonate (PEDOT:PSS) as hole transport layer (HTL) and phenyl-C$_{61}$-butyric acid methyl ester (PCBM) as electron transport layer (ETL), the authors indicated a stronger aggregation of the precursors in solution, measured via DLS, as a pre-requisite to achieve high-quality films with large crystal grains (Figure 7). This condition was successfully met when mixing two spacers, no matter their size or molecular shape, but efficiencies $>14\%$ were reached only with BA and PEA. More recently, a mixture of BA and PEA as organic spacers with the addition of a sulfobetaine zwitterionic additive has been successfully used to fabricate a solar cell with PCE of 17.04%.[70] The addition of this S=O containing additive has led to a more homogeneous phase distribution and an alleviated competition between MA and BA during the crystallization process because of its interaction with the perovskite precursors, proving that additive engineering to tune the colloidal properties of the precursor solution is a suitable strategy to improve solar cell performances. Liu et al. mixed BAI with bulky 1-naphthalenemethylammonium (NMA), showing the existence of a delicate equilibrium between enhanced interlayer interaction and vertical orientation, poor morphology, and formation of low-n phases.[71] Only after optimization of its concentration, an optimum was found with PCE of 14.21%. Another notable example of multiple spacers is provided by Long et al., who fabricated (BA$_{0.775}$GA$_{0.225}$)$_2$MA$_2$Pb$_3$I$_{10}$ by mixing BA and guanidinium (GA).[72] Interestingly, not only it did not change the phase distribution of the resulting RPP, but the addition of GA displayed accelerated energy transfer from n = 3 to n = 4 and 5 phases, which was shown to be beneficial for exciton dissociation and charge extraction, and enhanced crystallinity and crystal orientation. In an n-i-p configuration, the authors reported a high $V_{OC}$ of 1.25 V and PCE of 14.47%. Similarly, an inverted device published elsewhere and based on (PEAO$_2$GaO$_{0.2}$)$_2$MA$_3$Pb$_3$I$_{16}$ reached 15.27% efficiency.[71]

Overall, the use of multiple spacers is a facile way to improve the quasi-2D perovskite film quality and solar cell efficiency. PCEs obtained through such method are in the range of $\approx14\%$ with improvements to $\approx17\%$ achieved with the use of additives (Table 2). Furthermore, despite having investigated the impact of a second spacer on the crystalline structure of a RPP, the underlying mechanisms behind the improvement in efficiency still need to be understood and require further study.

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**Figure 7.** The use of multiple spacers induces aggregation in the precursor solution, which results in decreased nucleation sites and larger grains. Reprinted with permission.[69] Copyright 2021 Wiley VCH.
Table 2. Solar cell parameters for high-efficiency multi-spacer RPPs.

| RPP                     | Methodd | JSC [mA cm⁻²] | VOC [V] | FF [-] | PCE [%] | Ref. |
|-------------------------|---------|--------------|---------|--------|---------|------|
| (PEA₂GA₂)₃MA₃Pb₁₁₃    | H.C., Add. | 17.24        | 1.17    | 0.75   | 15.27   | [73] |
| (BA₂GA₂)₂MA₃Pb₁¹₀      | A.S.    | 16.20        | 1.25    | 0.71   | 14.47   | [72] |
| (BA₂nMA₂)₂MA₃Pb₁₁₃     | H.C.    | 17.54        | 1.12    | 0.72   | 14.21   | [71] |
| (BA₂PEA₂)₃MA₃Pb₁₁₃     | H.C.    | 16.74        | 1.10    | 0.77   | 14.09   | [69] |
| (BA₂FA)₃MA₃Pb₁₁₃       | H.C., Add. | 18.88        | 1.19    | 0.75   | 17.04   | [70] |

d) H.C. = hot casting, Add. = additives are used in the precursor solution, A.S. = antisolvent.

2.3. Additive Engineering

Methylammonium chloride (MACl) is extensively used both in RP and 3D perovskite film fabrication as a valuable salt to improve device performances.[24] As such, this additive has become part of the toolbox of the 2D perovskite researcher to optimize film deposition (Table 3). In fact, apart from the examples described below, which focus specifically on the use of MACl, numerous other works referenced in this review make use of this additive in their baseline spin coating recipe. While MACl acts as stabilizer of the α-phase and as crystallization rate modifier in FAPbI₃ perovskites,[60,75] it also has a large impact on the vertical orientation and the distribution of RPP phases with different n-values. Zheng et al. investigated these effects by fabricating BA₂MA₃Pb₁₁₃ films via drop-casting (see Section 3.2 for more information about this fabrication method) and calculated specific changes in n-values when doping the perovskite with MACl.[76] They found that MACl facilitates the formation of small-n perovskites and, as a result, increases the n-value of the 3D-like phases that are inevitably formed during crystallization (Figure 8a). Tuning the amount of MACl is important to find an optimal spot where the small-n phases provide a passivation effect without aggregating and forming quasi-2D domains with limited charge transport. Overall, by adding 6% MACl, solar cells fabricated in the p-i-n configuration reached 14.6% PCE. Apart from being used as additive, MACl has been also employed as the main precursor instead of or with MAI. For instance, Lai et al. introduced 2-thiophenemethylammonium (TMA) as organic spacer in an <n> = 3 RPP and found a higher degree of vertical orientation (Figure 8c), suppressed formation of n = 2 and parallel oriented small-n phases (Figure 8b), and overall higher performance (15.42% PCE) when using a mixture of MACl/MAI (0.5/0.5) as perovskite precursor.[56] A similar suppression of n = 2 phases was reported also by using PbCl₂ another Cl source, leading to a 15.08% p-i-n BA-based solar cell.[77] MACl was additionally used as the only MA source by Yang et al., who found that the n-value needed to be optimized in the range of non-integer values to achieve the right balance between the precursors, in this case PbI₂ MACl, and 3-bromobenzylammonium iodide (3BrBZAI).[62] Additionally, this work displayed that also small-n phases can orient vertically, thus favorably for charge transport, under the right conditions of film fabrication (in this article, hot casting). The peak efficiency for solar cells based on this material was 18.2%, with an impressive VOCl of 1.23 V.

Thiocyanate salts, usually NH₄SCN, have also been used as additives for RPPs to induce vertical orientation in the films, usually in combination with chlorides (NH₄Cl, MACl, etc.).[65,80-82] Just as MACl is a volatile specie that leaves the film during thermal annealing,[83] also SCN⁻ forms volatile HSCN and is not expected to remain in the film after thermal treatment. Recently, the use of NH₄SCN and HCl as co-additives led to an improvement of optoelectronic properties of (BA₂)n(FAMA)₃Pb₁₃ that resulted in a PCE of 16.45%.[38] Pb(SCN)₂ has also shown

Table 3. Solar cell parameters for high-efficiency RPPs fabricated with additives.

| RPP             | Methodd | JSC [mA cm⁻²] | VOC [V] | FF [-] | PCE [%] | Ref. |
|-----------------|---------|--------------|---------|--------|---------|------|
| (BA₂)₂MA₃Pb₁₁₃  | D.C., Add. | 19.00        | 1.11    | 0.64   | 14.60   | [76] |
| (TMA₂)₂MA₃Pb₁₁₀ | A.S., Add. | 18.89        | 1.07    | 0.76   | 15.42   | [50] |
| (BA₂)₂MA₃Pb₁₁₃  | H.C., Add. | 20.24        | 0.99    | 0.75   | 15.08   | [77] |
| (3BrBZAI)₂MA₃Pb₁₁₃| H.C., Add. | 18.22        | 1.23    | 0.81   | 18.20   | [62] |
| (BA₂)₂(FAMA)₃Pb₁₁₃| A.S., Add. | 19.34        | 1.11    | 0.77   | 16.45   | [38] |
| (PPA₂)₂MA₃Pb₁₁₀  | Add.    | 17.60        | 1.20    | 0.72   | 15.20   | [84] |
| (TMA₂)₂FA₃Pb₁₁₃  | PACC    | 23.39        | 1.07    | 0.76   | 19.06   | [44] |
| (TMA₂)₂FA₃Pb₁₁₀  | PACC    | 20.17        | 1.05    | 0.79   | 16.72   | [49] |
| (BA₂)₂MA₃Pb₁₁₃  | H.C., Add. | 21.38        | 1.12    | 0.75   | 18.04   | [78] |
| (BA₂)₂MA₃Pb₁₁₃  | H.C., Add. | 18.52        | 1.20    | 0.83   | 18.48   | [79] |
| (BA₂)₂MA₃Pb₁₁₃  | Add., S.A. | 18.67        | 1.18    | 0.75   | 16.48   | [87] |

d) D.C. = drop casting, H.C. = hot casting, Add. = additives are used in the precursor solution, A.S. = antisolvent, PACC = precursor organic salts-assisted crystal growth, S.A. = solvent vapor annealing, PPA = propargylammonium.
promise in enhancing film morphology and charge carrier mobility while reducing non-radiative recombination. The use of this additive has been reported to push the PCE of a solar cell based on propargylamine spacer to 15.20%, whereas the pristine film stopped at 12.15%.[84] Additives have also been used in antisolvents in a process called precursor organic salt-assisted crystal growth (PACG).[49] Among the highest efficiencies in RPPs, we mention a study on (TMA)$_2$FA$_4$Pb$_5$I$_{16}$ based solar cells by Lai et al. that makes use of such method to achieve 19.06% PCE with an outstanding $J_{SC}$ of 23.39 mA cm$^{-2}$.[44] This method consists of using an antisolvent solution containing an organic spacer, 4-(trifluoromethyl)benzylammonium iodide in the case mentioned above, that is poured onto the spinning substrate during spin coating. The fluorinated spacer is incorporated in the crystal lattice and induces changes in the film properties, resulting in a higher degree of vertical orientation, reduced trap density, faster charge collection, and enhanced hydrophobicity. Interestingly, this is one of the few examples of FA-based RPPs, which confirms the advantage when shifting to FA to achieve lower bandgaps and higher PCEs, as mentioned already in Section 2.1.

Finally, among the plethora of additives used, the usually undesired water has also played a role in increasing RPP efficiency. The addition of 2 vol% of H$_2$O was found to benefit the performances of both MA-based and CsFAMA-based RPP with BA as organic spacer ($\leq \alpha \leq 5$), which reached PCEs of 16.52 and 18.04%, respectively.[78] This provides a good example of how additive-precursors interactions might tune the perovskite crystallization and its phase distribution. In fact, the authors found that the formation of MAI-H$_2$O hydrate in the presence of water, as demonstrated by nuclear magnetic resonance (NMR) measurements and DFT, effectively inhibits the formation of MAPbI$_3$. This alleviates the competition between the crystallization of 2D and 3D phases, making a more uniform energetic landscape, as indicated in the confocal PL mappings that visualize the spatial distribution of n-values (Figure 8d), and increasing $J_{SC}$ compared to the control devices. Similarly, in work published by our group, it was shown that co-solvents impact the availability of perovskite precursors to react, leading to drastic changes in phase distribution.[29] As a result, it seems that the discovery and development of new additives or co-solvents might be a key factor in controlling the crystallization kinetics to achieve films with an optimized distribution of n-values or with phase purity.

Water seems to also have a role in determining the efficacy of other additives, such as NH$_4$Cl, as it facilitates the deprotonation of NH$_4^+$ and its release from the film when fabricated in air. Yang and co-workers studied the use of some ammonium additives: NH$_4$Cl, NH$_4$I, and NH$_4$I$_x$Cl$_{1-x}$.[79] They found that NH$_4$Cl prefers to adsorb on vertical-oriented (202) planes, meaning that during crystallization the (111) planes are exposed for secondary nucleation and grow faster. On the contrary, NH$_4$I adsorbs on (111), facilitating the crystallization of (202) planes and accelerating perovskite formation. This result agrees well with the findings of our group on the role of NH$_4$I in controlling the crystallization and phase purity of CsFAMA-based RPPs, showing that NH$_4$I promotes the formation of the 3D phase and increases the film’s absorption, while NH$_4$Cl shifts the phase distribution towards the 2D phase, leading to lower PCEs.[29] Authentication of the proposed mechanisms requires further studies, but these findings open new avenues for the development of additives that can be tailored to control the crystallization process and optimize the performance of RPPs.
planes that are favorably oriented. However, this positive effect is hindered by the slow deprotonation rate of NH₄⁺ by atmospheric H₂O (because of the low vapor pressure of HCl compared to HCl) that allows crystallization to be completed only during thermal annealing, leaving space to homogeneous nucleation and disruption of the vertical crystal growth of the film. The authors found a solution by using a mixed I and Cl additive, NH₄I₂Cl₀.₅, which led to enhanced vertical orientation, crystallinity, and reduction of defects. By fabricating in air a device based on (PEA)₂MA₃Pb₄I₁₃, a resulting PCE of 18.48% was obtained, with a Voc of 1.20 V and an outstanding FF of 83.39% (Figure 8e). Overall, while the fabrication of 3D perovskites usually takes place in N₂-filled gloveboxes to avoid the presence of water and oxygen, RPPs have shown potential with regards to being fabricated in ambient air, with important consequences for upscaling.⁷⁰,⁸₅,⁸₆

2.4. Phase Pure RPPs via Acetate Salts

Although previous works described here have reached high efficiencies in solar cells, all these studies failed in making a phase pure RPP. High-efficiency devices often consist of both quasi-2D and 3D perovskite phases, with small-n values being avoided to favor charge transport along the vertical direction and large-n being mostly the cause of enhanced efficiency. In a recent article, Liang et al. reported the formation of phase pure RPPs by using an ionic liquid precursor, namely butylammonium acetate (BAAc) (Figure 9a).¹¹₂ As proof of phase purity, the PL spectra of the films fabricated with BAAc display an emission peak precisely around the bandgap energy of the corresponding n-phase (Figure 9c), whereas the films fabricated with BAI as precursor consist of emission from multiple phases (Figure 9b,d). The perovskite precursor solution plays an important role in determining the phase purity of the corresponding film. In fact, this solution is often a complex mixture of colloidal particles with sizes ranging from nanometers to micrometers. In this regard, the use of acetate creates a solution with a narrow size distribution, around 0.6 nm, because of the interaction between Pb⁺² and Ac⁻ (Figure 9e). Overall, it seems that in presence of BAAc there is gelation of a uniformly distributed intermediate phase and subsequent crystallization of a phase pure quantum well with the evaporation of solvents and methylammonium acetate (MAAc). Apart from describing its formation mechanism, the authors fabricated an n-i-p device with SnO₂ as ETL, BA₂MA₃Pb₄I₁₃ as active layer, and Spiro-OMeTAD as HTL, and achieved 16.25% PCE and a record-Voc of 1.31 V. The external quantum efficiency (EQE) spectrum also shows an impressive phase purity with a steep onset at ~660 nm (Figure 9f). Surprisingly, such a high efficiency was obtained even though the phase pure films displayed a high degree of parallel orientation with respect to the substrate.

Several reports have shown the use of another ionic liquid, methylammonium acetate (MAAc), as solvent for perovskite precursors, including an 18.06% PCE solar cell fabricated with a RPP based on 2-(methylthio)ethylamine hydrochloride and a 3D MAPbI₃.⁵¹,⁸₈ With regards to the RPP, however, the focus was set mainly on the enhanced interaction between the organic spacers due to S-S bonds, which enabled good charge transport and high stability, and not on the use of MAAc as solvent. Nevertheless, the study represents an important milestone in high efficiency RPPs.

Phase pure RPPs have been up to now the holy grail of low-dimensional perovskites. If reproduced by multiple labs, among other applications, these materials could be integrated into tandem solar cells, where bandgap tuning without the use of high amounts of bromide ions is highly needed to avoid halide phase segregation.⁹⁰ More about phase purity will be discussed in Section 4.

![Figure 9](https://www.advenergymat.de)
3. Fabrication Methods

Apart from the numerous organic spacers or additives that can be synthesized for RPPs, various fabrication methods have been used over time to reach higher PCEs. In this section, we aim to describe some successful examples. However, we will not consider routine changes in the deposition technique as a different fabrication method. For instance, differences between room-temperature spin coating, hot casting, and use of antisolvents will not be treated in detail, even though they have been shown to change device performance considerably. Such techniques have now become routine methods to optimize the deposition of high-quality perovskite layers. Instead, we will highlight a few more remarkable changes in the fabrication method, such as the use of single crystal precursors, drop casting, or even thermal treatment of complete devices.

3.1. RPPs from Single Crystal Precursors

In 2016, Kanatzidis’ group published an extensive work on the synthesis and characterization of phase pure RP single crystals based on the BA spacer.[12] This method makes use of the different solubilities of RP with different n-values to achieve selective crystallization of a specific phase. For example, in a HI/H₃PO₄ solvent mix, larger-n phases are more soluble than small-n phases. As a result, BA is always used as a limiting reagent and in sub-stoichiometric amounts to achieve the desired phase. This method has been used extensively in the literature to form RP crystals with a reasonably high phase purity (Figure 10a). The next step to make RPP films is to dissolve the crystals in a solvent, usually DMF, and then proceed with spin coating and thermal annealing. This was firstly reported by Tsai et al., who hot-casted a BA <n> = 4 layer and achieved a PCE of around 12% for a p-i-n device.[37] The main issue with this process is that usually the phase purity of RPs is lost once the crystals are dissolved, meaning that when probing the phase distribution in the resulting film, multiple quantum well structures are found instead of a uniform distribution around a specific n-value.

In a recent work, Sidhik et al. investigated how to exploit single crystals to retain phase purity in quasi-2D perovskite films, and by using optimized and relatively phase pure BA₂MA₂Pb₃I₁₀ they achieved a PCE of 17.1% and a Vₜₚ of 1.20 V.[91] Their method consisted of dissolving single-crystals in DMF, with the addition of a small amount of MACl.
authors found striking differences between the crystallization of perovskites when powder precursors are dissolved in solution or when “parent” crystals are used. In the latter, the precursor solution contains particles of 200 nm average size (Figure 10b) that effectively act as memory seeds and around which nucleation takes place (Figure 10c), whereas in the former only particles < 1 nm were observed and the nucleation appeared to start at the liquid-air interface. Even though with single crystal dissolution higher phase purity is achieved, the resulting films still contain phase impurities. While particle sizes were determined via DLS, crystallization was investigated via in-situ high-resolution microscopy, a technique barely used to explore perovskites. Nevertheless, the use of relatively phase pure films is not enough to achieve high efficiency. The same perovskite only reached an efficiency of 12.6% when using PEDOT:PSS as HTL, whereas NiOx improved its efficiency to the abovementioned value of 17.1%. This confirms the importance of HTL and ETL design; for which we refer the reader to extensive works published elsewhere.\(^\text{[93–95]}\)

Table 4. Solar cell parameters for high-efficiency RPPs fabricated by using several fabrication methods.

| RPP Method | Jsc [mA cm\(^{-2}\)] | Voc [V] | FF [\(\%\)] | PCE [%] |
|------------|----------------------|---------|-------------|--------|
| (BA\(_2\))\(_2\)MAPb\(_4\)I\(_8\) | S.C. (R.T., Add.) | 17.56 | 1.20 | 0.81 | 17.1 | [91] |
| (BA\(_2\))\(_2\)MAPb\(_4\)I\(_8\) | S.C. (H.C., Add.) | 19.23 | 1.14 | 0.68 | 14.9 | [96] |
| (TEA\(_2\))\(_2\)MAPb\(_4\)I\(_8\) | S.C. (H.C., Add.) | 15.85 | 1.23 | 0.725 | 14.68 | [92] |
| (TMA\(_2\))\(_2\)MAPb\(_4\)I\(_8\) | S.C. (A.S.) | 18.89 | 1.07 | 0.76 | 15.42 | [50] |
| (BA\(_2\))\(_2\)MAPb\(_4\)I\(_8\) | D.C. (Add.) | 19.0 | 1.11 | 0.64 | 14.6 | [97] |
| (BA\(_2\))\(_2\)MAPb\(_4\)I\(_8\) | D.C. | 18.8 | 1.14 | 0.69 | 14.9 | [98] |
| (iBA\(_2\))\(_2\)MAPb\(_4\)I\(_8\) | D.C. (N\(_2\)) | 18.3 | 1.15 | 0.77 | 16.0 | [76] |
| (BA\(_2\))\(_2\)MAPb\(_4\)I\(_8\) | SPA (H.C.) | 19.89 | 1.24 | 0.77 | 17.26 | [99] |
| (AA\(_2\))\(_2\)MAPb\(_4\)I\(_8\) | SPA (H.C.) | 18.57 | 1.24 | 0.80 | 18.42 | [100] |
| (BA\(_2\))\(_2\)MAPb\(_4\)I\(_8\) | SPA (H.C.) | 18.69 | 1.24 | 0.80 | 18.68 | [101] |

\(*\text{S.C., single crystal precursors; D.C, drop casting; SPA, slow post annealing; R.T., room-temperature spin coating; H.C., hot casting; Add., additives are used in the precursor solution; A.S., antisolvent; N\(_2\), blow drying; AA, n-amy lammonium; iBA, isobutylammonium.}\)

3.2. Drop Casting

Up to date, most of the processing methods for RPPs include spin coating, which is known not to be suitable for upscaling. There are, however, some notable examples of active layers fabricated via drop casting method (Table 4). This process consists of dropping a small volume of precursor solution onto a preheated substrate (usually at 50 or 60 °C) and is followed by diffusion, solvent evaporation, and crystallization (Figure 11a). Advantages of drop casting include easy up-scaling, via doctor blading to slot-die coating, and little to no waste of precursor solution.

In 2019, Zuo et al. fabricated BA\(_2\)MAPb\(_4\)I\(_8\) via drop casting in air and achieved a 14.9% PCE.\(^{[98]}\) The study highlighted the importance of substrate pre-heating to achieve vertical-oriented films with enhanced charge transport (Figure 11b,c) and the possibility of easily changing film thickness by simply varying the volume of the precursor solution used in the process. Later, the same group specialized in drop-casting and published a series of articles, in one of which they achieved a 16% solar cell by applying an N\(_2\) blow-drying process to (iBA\(_2\))\(_2\)MAPb\(_4\)I\(_8\) RPPs.\(^{[69,77]}\) Such process controlled the film thickness, increased the nucleation rate, and led to smoother films with smaller grains, which improved the morphology. The authors additionally fabricated solar cells via a roll-to-roll (R2R) processing on a flexible ITO/PET substrate, reaching 9.3% efficiency. This demonstrates that drop casting is a promising method to prepare for upscaling, even though more optimization is highly needed especially in terms of reduction of roughness, sheet resistance, or hydrophobicity of the PET/ITO flexible substrate.\(^{[102]}\)

3.3. Post-Annealing Treatments

The control of phase distribution and crystal alignment of quasi-2D perovskite phases is known to be crucial to fabricate high efficiency devices and avoid the detrimental effect of quantum wells on charge collection. While numerous studies tried to achieve such control via rapid-crystallization techniques, such as hot-casting or N\(_2\)-quenching, thus focusing
on the fabrication of the perovskite layer, several studies have investigated the impact of post-annealing treatments on complete devices (Table 4). In 2019, Wu et al. introduced for the first time a slow post-annealing (SPA) process, where the complete devices are kept at 60°C for 60 h in an N₂-filled glovebox.[103]

The SPA treatment introduced changes in the phase distribution gradient along the thickness of the film, introducing a finer alignment compared to the non-uniform gradient formed just during hot-casting (Figure 12). By applying this technique to hot-casted BA₂MA₃Pb₄I₁₃ in a p-i-n solar cell, the authors achieved 17.26% PCE with JSC of almost 20 mA cm⁻² and an impressive VOC of 1.24 V. Interestingly, applying SPA only on the perovskite layer did not enhance PCE as much as when treating the complete device, possibly because the slow annealing also promotes surface trap passivation by C₆₀, used as ETL. In later studies, the same group pushed the PCE to 18.42%[100] (15.78% before SPA treatment) and 18.68%[101] by using n-amylammonium (AA) iodide as organic spacer, which has a C₅ chain compared to C₄ for butylammonium. In both papers, differences in colloidal aggregation after thermal aging of the precursor solutions and strengthened self-assembly properties due to increased van der Waals interactions were thought to be behind the increase in efficiency. The SPA treatment was used to further enhance the PCE of their best devices.

Post-annealing methods can be an almost effortless way to push the PCE of RPPs closer to their 3D counterpart. Nevertheless, a careful reader must have now noticed that research on RPPs often leads to groups specializing in one specific technique or method. These methods are rarely directly reproduced by other groups in the community, leaving the question of whether their application is generalizable to other systems. More specifically, questions remain open for the SPA method, such as whether it is dependent on the choice of materials (electron/hole transport layer, electrodes) and perovskite composition. By including methods such as drop-casting and post-annealing treatment in this review, we encourage researchers in the field to evaluate their validity in a variety of systems.

4. Implications on Phase Purity and Use in Single- or Multi-Junction Solar Cells

Despite the high efficiency reached by many RPP-based solar cells, there are important considerations to make regarding the lower dimensional nature of such films. As mentioned before, phase purity has been a long-hunted objective in the RPP field and is a challenging task where both kinetics and thermodynamics aspects need to be tackled. A phase pure device would possess high bandgap and, consequently, VOC. In fact, polydispersity has been previously linked to voltage losses.[34] Solar cells based on phase pure BA₂MA₃Pb₄I₁₃ published by Liang et al. possess a VOC of 1.31 V, which is the highest value published in the literature.[32] Similarly, Sidik et al. reported a VOC of 1.20 V for relatively phase pure BA₂MA₃Pb₂I₉Pb, still quite high compared to other cells published in the literature, but lower than the abovementioned study and with a loss > 800 mV considering the bandgap of 2.1 eV associated with the pursued n = 3 perovskite, simply because of the presence of phase impurities with larger n-values.[90,104] Whether or not phase pure quasi-2D perovskites are needed will depend on their application. For example, in light-emitting diodes (LED) it is necessary to avoid emission at higher wavelengths from impurities,
Multi-junction solar cells require the use of wide-bandgap perovskite sub-cells with high $V_{OC}$, which might be quasi-2D in nature if phase purity is reproducibly achieved. Most work on wide-bandgap sub-cells in multi-junction devices, however, is currently based on traditional 3D mixed-halide perovskites, which undergo phase segregation under illumination, meaning that low-energy iodide-rich phases are formed once the solar cell is illuminated, providing a significant shift in bandgap energy and loss in photovoltaic performances. RPPs could provide the optimal bandgaps for such application; an $n = 3$ phase-pure iodide-based RPP would possess an optical bandgap of about 2 eV, which is ideal for a triple-junction perovskite solar cell. Presently, high-efficiency RPPs lack the high $V_{OC}$ required for this application because their dominant 3D (or large-$n$) nature leads to a decrease of $E_g$. In the case of a triple-junction solar cell, phase impurities in quasi-2D perovskite with reduced bandgap reduce the $V_{OC}$ (Figure 13c). Interestingly, this draws a parallel between the phase segregation issue in 3D mixed-halide perovskites and phase distribution in quasi-2D RPPs, which both potentially impact the field of multi-junction devices.

For applications in single-junction PV devices, however, phase purity seems not to be a pressing concern, and stability could become the key issue that RPPs try to improve. An example is the use of precursor organic salts-assisted crystal growth method (PACG) mentioned earlier to achieve high efficiency RPPs. In that study by Lai et al., the bandgap energy was calculated as 1.50 eV, which is comparable to the one of FAPbI$_3$, and the EQE spectrum displayed a large contribution at 800 nm. As the films were prepared with a nominal stoichiometry of $<n> = 5$, this suggests that the solar cell performances were dominated by 3D phases more than quasi-2D ones, which should instead have higher bandgap energy. Nevertheless, the authors demonstrated significantly enhanced environmental and thermal stability of the RPPs compared to FAPbI$_3$. As a result, further efforts to bring the PCEs of RPP-based solar cells close to the 3D counterpart, despite the presence of phase impurities, might lead to an easier path to commercialization because of their enhanced stability. In our view, such studies should put more focus on stability, apart from solar cell performances, which could eventually be the main reason why RPPs will be preferred over the (until now) more efficient 3D perovskites. Such focus should result in a deeper understanding of the degradation paths of RPPs and, additionally, in uniform testing conditions, so that it becomes easier to draw comparisons between different studies, as is well explained in the consensus statement for stability assessment that was recently published and signed by many researchers of the field.

Overall, a reproducible method to fabricate phase pure RPPs will be a breakthrough that will pave the way to numerous applications that expand well beyond photovoltaics. As a result, the research community is dedicating time and effort to accomplish this task via a variety of methods that include the use of solvents, additives, new spacers, and new fabrication methods.

5. Outlook

As more knowledge of Ruddlesden–Popper perovskites is developed, their efficiency in solar cell devices is slowly approaching the one of the 3D counterparts, although still lagging behind FAPbI$_3$-based solar cells. In this work, we discussed several studies where multiple strategies have been used to achieve efficiencies above ~14%. Most of the high-efficiency solar cells rely on the use of additives that have an impact on morphology, crystallinity, vertical orientation, phase distribution, and charge transport. The additives used are usually chlorides, such as MACl or NH$_4$Cl, or thiocyanates, such as NH$_4$SCN. In some works, an additional organic spacer is used as an additive to improve the abovementioned properties, either in the perovskite layer or even in the antisolvent solution. Interestingly, even for the less-common fabrication methods, such as drop casting or slow post-annealing of complete devices, the use of such additives was often a
prerequisite. Additive engineering is clearly an effective tool to achieve higher efficiencies, even though the mechanism behind the enhancement in efficiency is often not studied or explained. Just like using hot-casting and anti-solvents have become a routine optimization path for developing RPPs, it seems that the use of such additives is also approaching the same route. As such, in our view, more studies are needed to evaluate the generalizability of such systems and more importantly the unearthing underlying mechanisms.

Apart from additive engineering, tuning the interlayer interaction and the dielectric confinement has also proved to be an effective way to increase the PCE of RPPs. Fluorination is by far the most successful strategy described in the literature. Given the enormous structural variety that is achievable with RPPs, functionalization of organic spacers is still an unexplored territory that needs further developments. For a more thorough study of the impact of spacers on RPPs, we refer to the extensive review recently published by Li et al.[17]

The study of precursor solution will also be crucial in developing a reproducible method to form efficient, phase pure RPPs. Up to now, there are conflicting reports on the impact of colloidal particles size distribution. For example, when phase pure RPPs were obtained by dissolving previously synthesized single-crystals in a solvent, Sidhik et al. highlighted the importance of having particles of around 200 nm, or seeds, in solution.[91] Qin et al. improved phase purity by using toluene and H1 as co-solvent and additive, respectively, to boost the colloidal particles size up to 1500 nm.[92] On the contrary, phase pure perovskites fabricated with acetate salts were spin coated from a solution with an average particle size of 0.6 nm, which in that case was attributed to the interaction of Pb2+ and Ac− and was reported to be an important requirement to crystallize a single n-phase.[32] Overall, a more comprehensive study on the role of colloidal particle size is needed, as it seems that the precursor solution plays an even more major role in RPPs than in 3D perovskites.

Finally, there is a general difficulty in evaluating the phase purity of RPPs. For this purpose, more efforts are needed to characterize the phase distribution of high-efficiency RPPs and to find ways to effectively fabricate films with narrow phase distribution. As we have described above, high PCEs can result also from a large contribution from 3D perovskite phases, which are usually responsible for lower Voc and higher Jsc. For some applications, such as tandem solar cells, phase purity is a crucial concern, and improving it would definitely lead to breakthroughs in multi-junction photovoltaic devices. Single-junction solar cells, on the contrary, seem to show enhanced stability for highly efficient devices, even in the presence of phase impurities, hence a deeper understanding of the degradation paths of RPPs, together with further enhancements of PCEs, might be the key to lead perovskite solar cells closer to commercialization.

Overall, Ruddlesden–Popper perovskites have shown enormous potential and in just a few years a great amount of expertise has developed. Despite RPPs being often described as “more stable but less efficient” compared to traditional 3Ds, with this work we show that there is plenty of potential and room for further improvements of this fascinating class of materials.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D perovskites, perovskites, Ruddlesden–Popper, solar cells
[69] X. Lian, J. Chen, M. Qin, Y. Zhang, S. Tian, X. Lu, G. Wu, H. Chen, Angew. Chem. Int. Ed. 2019, 58, 9409.
[70] H. Zheng, T. Zhang, Y. Wang, C. Li, Z. Su, Z. Wang, H. Chen, S. Yuan, Y. Gu, L. Ji, J. Li, S. Li, ACS Appl. Mater. Interfaces 2022, 14, 814.
[71] C. Liu, R. Liu, Z. Bi, Y. Yu, G. Xu, H. Hou, Q. Wu, H. Yu, X. Xu, Sol. RRL 2021, 5, 2100495.
[72] M. Long, T. Zhang, D. Chen, M. Qin, Z. Chen, L. Gong, X. Lu, F. Xie, W. Xie, J. Chen, J. Xu, ACS Energy Lett. 2019, 4, 1025.
[73] J. Shi, X. Jin, Y. Wu, M. Shao, APL Mater. 2020, 8, 101102.
[74] K. Odysseas Kosmatos, L. Theofylaktos, E. Giannakaki, J. Phys. Chem. 2021, 10, 11731.
[75] J. Qin, C. Kuang, H. Wang, Y. Wang, X. Liu, S. Bai, M. Li, T. C. Sum, Z. Hu, W. Zhang, F. Gao, Adv. Mater. 2019, 31, 1904243.
[76] J. Song, G. Zhou, W. Chen, Q. Zhang, J. Ali, Q. Hu, J. Wang, C. Wang, W. Feng, A. B. Djurišić, H. Zhu, Y. Zhang, T. Russell, F. Liu, Adv. Mater. 2020, 32, 2002784.
[77] L. Chao, T. Niu, Y. Xia, X. Ran, Y. Chen, W. Huang, J. Phys. Chem. 2019, 10, 11731.
[78] J. Xiao, C. Kuang, H. Wang, Y. Wang, X. Liu, S. Bai, M. Li, T. C. Sum, Z. Hu, W. Zhang, F. Gao, Adv. Mater. 2019, 31, 1904243.
[79] S. Díhidik, W. Li, M. H. K. Samani, H. Zhang, Y. Wang, J. Hoffmann, A. K. Fehr, M. S. Wong, C. Katan, J. Even, A. B. Marceli, M. G. Kanatzidis, J. Blanco, A. D. Mohite, Adv. Mater. 2021, 33, 2007176.
[80] Y. Qin, H. Zhong, J. J. Intemann, S. Leng, M. Cui, C. Qin, M. Xiong, F. Liu, A. K.-Y. Jen, K. Yoo, Adv. Energy Mater. 2020, 10, 1904050.
[81] V. M. le Corre, M. Stolterfoht, L. Perdigon Toro, M. Feuerstein, C. Wolf, L. Gil-Escrig, H. J. Bolink, D. Neher, L. J. A. Koster, ACS Energy Lett. 2019, 2, 6280.
[82] G. M. Arumugam, S. K. Karunakaran, C. Liu, C. Zhang, F. Guo, S. Wu, Y. Mai, Nano Select 2022, 2, 1081.
[83] S. Díhidik, Y. Wang, W. Li, H. Zhang, X. Zhong, A. Agrawal, I. Hadar, I. Spanopoulos, A. Mishra, B. Traroe, M. H. K. Samani, C. Katan, A. B. Marciel, J.-C. Blancon, J. Even, A. Kahn, M. G. Kanatzidis, A. D. Mohite, Cell Rep. 2021, 2, 100601.
[84] H. Li, X. Wang, T. Zhang, X. Gong, Q. Sun, H. Pan, Y. Shen, S. Ahmad, M. Wang, Adv. Funct. Mater. 2019, 29, 1903296.
[85] C. Zuo, A. D. Scully, W. L. Tan, F. Zheng, K. P. Ghigginio, D. Vak, H. Weerasinghe, C. R. McNeill, D. Angmio, A. S. R. Chesman, M. Gao, Commun. Mater. 2020, 1, 33.
[86] S. Shao, H. Duim, Q. Wang, J. Dong, S. Adjokatse, Cell Rep. 2021, 31, 1903889.
[87] Y. Wu, T. Yang, X. Li, T. Zhou, X. Zhang, S. Yue, J. Zhou, Y. Li, H. Wang, X. Shi, S. (Frank) Liu, K. Zhao, H. Zhou, Y. Zhang, Adv. Mater. 2019, 31, 1903889.
[88] Y. Wu, T. Yang, X. Li, N. Ahmad, X. Zhang, S. Yue, J. Zhou, Y. Li, H. Zhou, Y. Zhang, Adv. Funct. Mater. 2021, 31, 2107675.
[89] Y. Wu, X. Li, J. Zhou, J. Zhang, X. Zhang, X. Leng, P. Wang, M. Chen, D. Zhang, K. Zhao, S. Liu, H. Zhou, Y. Zhang, Adv. Energy Mater. 2019, 31, 1903889.
[90] Y. Lin, Y. Fang, J. Zhao, Y. Shao, S. J. Stuard, M. M. Nahid, H. Ade, Q. Wang, J. E. Shield, N. Zhou, A. M. Moran, J. Huang, Nat. Commun. 2019, 10, 3008.
[91] D. Ma, K. Lin, Y. Dong, H. Choubisa, A. H. Propple, D. Wu, Y.-K. Wang, B. Chen, P. Li, J. Z. Fan, F. Yuan, A. Johnston, Y. Liu, Y. Kang, Z.-H. Lu, Z. Wei, E. H. Sargent, Nature 2021, 599, 594.
[92] M. T. Hörantner, T. Leijtens, M. E. Ziffer, G. E. Eperon, M. G. Christoforo, D. M. McGehee, H. J. Snaith, ACS Energy Lett. 2017, 2, 2506.
[93] J. Wang, V. Zardetto, K. Datta, D. Zhang, M. M. Wiek, R. A. J. Janssen, Nat. Commun. 2020, 11, 5254.
[94] K. Xiao, J. Wen, Q. Han, R. Lin, Y. Gao, S. Gu, Y. Zang, Y. Nie, J. Zhu, X. Hu, H. Tan, Adv. Energy Lett. 2020, 5, 2819.
[95] Y. Han, S. Park, J. Wang, S. Jariwala, K. Lee, C. G. Bischak, S. Kim, J. Hong, S. Kim, M. J. Lee, D. S. Ginger, I. Hwang, Adv. Mater. Interfaces 2021, 8, 2107675.
[96] S. Shao, H. Duim, Q. Wang, B. Xu, J. Dong, S. Adjokatse, G. R. Blake, L. Protesescu, G. Portale, J. Hou, M. Saba, M. A. Loi, ACS Energy Lett. 2020, 5, 39.
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