Development of Efficient Wide-bandgap Perovskite Solar Cells with Composition and Interface Engineering

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South Dakota State University

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In 2015, I began my PhD journey. Since then, I never relaxed for a single day, even when on vacation; always looking forward to the day I would finish this long, exhausting journey. And now the day has arrived; I’m writing this acknowledgment, but not feeling joy, as I am already missing my lab, dear lab mates, faculty members, and my advisors.

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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\tau_r$</td>
<td>Charge lifetime</td>
</tr>
<tr>
<td>$\tau_t$</td>
<td>Charge transport time</td>
</tr>
<tr>
<td>$\mu$L</td>
<td>Microliter</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BA</td>
<td>Butylammonium</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered electron</td>
</tr>
<tr>
<td>C</td>
<td>Celsius</td>
</tr>
<tr>
<td>CIGS</td>
<td>Copper indium gallium selenide solar cells</td>
</tr>
<tr>
<td>CPD</td>
<td>Contact potential difference</td>
</tr>
<tr>
<td>CS-AFM</td>
<td>Current sensing atomic force microscopy</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>EA</td>
<td>Ethyl acetate</td>
</tr>
<tr>
<td>eV</td>
<td>Electron-volt</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive x-ray (spectroscopy)</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron transport layer</td>
</tr>
<tr>
<td>FA</td>
<td>Formamidinium</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
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<td>FF</td>
<td>Fill facto</td>
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FWHM Full width half maximum
GA Guanidinium
GB Grain boundary
GB Grain boundary
GBox Glove box
GI Grain interior
HTL Hole transport layer
IPA Isopropyl alcohol
ITO Indium doped tin oxide
$J_{sc}$ Short-circuit current density
KV Kilovoltage
$L_D$ Diffusion length
LED Light emitting diode
MA Methylammonium
mg Milligram
MHz Mega hartz
mL Milliliter
MWP Microwave processed
nm Nanometer
$N_t$ Trap density
$\text{PbX}_2$ Lead halides (X= I and Br)
PC Photoconductivity
PCE Power conversion efficiency
PL Photoluminescence
PMMA Poly (methyl methacrylate)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>PSC</td>
<td>Perovskite solar cell</td>
</tr>
<tr>
<td>PSK</td>
<td>Perovskite</td>
</tr>
<tr>
<td>PTAA</td>
<td>Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine</td>
</tr>
<tr>
<td>RMS</td>
<td>Route mean square</td>
</tr>
<tr>
<td>rpm</td>
<td>Rotation per minute</td>
</tr>
<tr>
<td>SCLC</td>
<td>Space charge limited current</td>
</tr>
<tr>
<td>SCR</td>
<td>Space charge region</td>
</tr>
<tr>
<td>SD</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SG</td>
<td>Secondary growth</td>
</tr>
<tr>
<td>SP</td>
<td>Surface potential</td>
</tr>
<tr>
<td>TFL</td>
<td>Trap-filled-limit-voltage</td>
</tr>
<tr>
<td>TIPC</td>
<td>Thermal induce phase control</td>
</tr>
<tr>
<td>TPV</td>
<td>Transient photovoltage</td>
</tr>
<tr>
<td>TPV</td>
<td>Transient photocurrent</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultra violet-visible</td>
</tr>
<tr>
<td>v/v</td>
<td>Volume/volume</td>
</tr>
<tr>
<td>V&lt;sub&gt;oc&lt;/sub&gt;</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>W</td>
<td>Watt</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ε₀</td>
<td>Permittivity</td>
</tr>
<tr>
<td>ε&lt;sub&gt;r&lt;/sub&gt;</td>
<td>Dielectric constant</td>
</tr>
<tr>
<td>Ω</td>
<td>Ohm</td>
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ABSTRACT

DEVELOPMENT OF EFFICIENT WIDE-BANDGAP PEROVSKITE SOLAR CELLS WITH COMPOSITION AND INTERFACE ENGINEERING

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Metal halide perovskites are considered the most promising solar energy technology because of their distinct properties, such as defect tolerance, low cost, easy fabrication due to solution-processibility, band tunability, etc. Due to these properties, the efficiency of perovskite solar cells reaches more than 25% and approaches the limit of single-junction within last few years. To increase the efficiency further in a more cost-effective way, double junction tandem solar cells with an efficient ‘top’ wide-bandgap cell is desired. But wide-bandgap perovskites still face some critical issues, such as poor morphology, smaller grain size, the formation of excessive lead halides, light-induced halide segregation, high surface recombination, etc. Higher bromide concentration in wide-bandgap perovskites causes charge-carrier traps/defects that can increase recombination rates reducing overall performance, stability and causing significant current density-voltage hysteresis. To develop a low-cost, stable, and highly efficient wide-bandgap perovskite, we have made efforts to understand these critical issues and solve them. Firstly, we designed a new composition of 1.78 eV quadruple cations \((\text{FA})_{0.79}\text{MA}_{0.16}\text{Cs}_{0.05}\text{Rb}_{0.05}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3\) wide-bandgap perovskite, where rubidium (Rb) is used to increase the grain size of the perovskite. We also developed a post-growth strategy known as secondary growth (SG) using guanidinium iodide to convert the excess lead halides to perovskites. Our CPD analysis using AFM indicated the type of defects in grain boundaries, and the nanoscale spatial mapping visualized and quantified the charge
carrier dynamics after the passivation of this wide-bandgap structure by Rb incorporation and performing SG treatment. The synergy of these two strategies increases the power conversion efficiency of the devices from 14.17% to 17.71%.

In our second project, we developed a facile crystallization technique utilizing poly(methyl methacrylate) (PMMA) to control the growth of our novel wide-bandgap perovskite. PMMA was applied on the surface of the perovskite film to slow down the crystallization and to lock the position of the perovskite components, which resulted in an excess lead halide free uniform perovskite film. Perovskite films using this strategy delivered superior electrical and optical properties with an efficiency of 18.18%.

Finally, we developed a rapid and cost-effective way to process our wide-bandgap perovskite using the microwave. After optimizing the microwave power and time, we achieved perovskite film with similar properties to the thermal annealing. Our microwave-processed film achieved a little higher efficiency than the thermal annealed devices with significantly reduced process time from ~1 hour to 90 sec.

Advanced characterization techniques conducted in these projects introduce an effective way to analyze grain boundary defects. Moreover, our developed novel wide-bandgap structure, defect passivation and crystallization strategies, and the low-cost fabrication method can provide a facile approach to realize efficient and more stable wide-bandgap devices to fabricate tandem structures.
CHAPTER 1 INTRODUCTION

1.1 Background

Global demand for energy is steadily increasing with time, and we are facing a major energy crisis due to this escalating energy demand. A significant part of this energy demand is fulfilled by the non-renewable traditional fossil fuels, such as, gas, coal, oil, etc. But burning fossil fuels can result in significant damage to our environment and bring severe health issues. Excessive use of these fossil fuels is depleting our resources and increases carbon dioxide at an alarming rate, which is responsible for global warming. Using fossil fuels at the present rate will bring major changes in our climate and affect the natural balance and impact the world economy in the future. To fulfill this energy demand and to minimize global warming, we need alternative energy sources.

All the renewable energy sources, for example, wind, solar, etc. are abundant in nature and produce zero-carbon. Renewable energy sources can play an important role to fulfill the energy demand sustainably. Among all the renewable energy sources, solar energy is considered the most promising renewable energy technology. The amount of energy we get from the sun in one hour is more than the entire world's annual energy consumption. If we can utilize sunlight energy efficiently and cost-effectively, we can run the entire world without affecting the environment. In 2019, U.S. electricity generation by solar energy was only 1.8% [1]. The lower usage of solar energy is the cost and low conversion efficiency of the present technologies. So, it is required to develop low-cost and highly efficient solar cells to adopt this technology extensively. In this context, perovskite solar cells (PSCs) are considered the most promising solar cell technology at present.
PSCs started their journey in 2009 with an efficiency of 3.9%. After a decade, the efficiency reaches more than 25%, which surpasses the multi crystalline Si and other photovoltaic technologies [2, 3] and approaches the theoretical limit of mono-junction solar cells. Double junction tandem solar cells with a top wide-bandgap top cell and bottom low-bandgap cell have been considered the most efficient way to achieve efficiency more than the single-junction solar cells. Perovskite is considered the most promising candidate to construct an efficient tandem structure due to its easy bandgap tunability. Perovskites have already been used to construct tandem structure with CIGS [4], silicon [5], and also to develop perovskite-perovskite tandem [6] solar cells. To construct such high-efficiency tandem structures, the fabrication of efficient wide-bandgap PSCs is crucial.

1.2 Perovskite solar cell
1.2.1 Introduction to perovskite
Perovskite is invented by a German scientist Gustav Rose in 1839, and named in honor of a Russian mineralogist Lev von Perovski. Perovskite (Figure 1a) indicates the Calcium titanate (CaTiO$_3$) or the material with a similar structure as CaTiO$_3$.

Figure 1. 1 Perovskite crystal on matrix found in nature.
Perovskite is just a crystal structure. Though we refer to them today as the name of the optoelectronic material, it is a tertiary crystal structure as it has three different components of the form ABX$_3$ as shown in figure 1a. The unit structure is defined by B and X octahedral shape, and it defines many properties of the crystal. Most perovskites are referred to as metal titanates. Now, the organic-metal hybrid perovskites were not really considered useful. Their semiconducting properties were not known until about 1994, when the first published photodetector used perovskite. In solar cells, they started being used in 2009.

![Perovskite Crystal Structure](image)

**Figure 1.** Organic metal halide perovskite crystal structure with different components

The organic-inorganic halide perovskites are relatively diverse. There are many components that can be incorporated into the crystal structure. Additionally, several other things can also be incorporated fully but in smaller amounts as dopants. So, the system can get relatively diverse with additional additives.
In ‘A’ site, the most common cations are methylammonium (MA), guanidinium (GA), formamidinium (FA), rubidium (Rb), cesium (Cs), etc. are used. Some other components, such as guanidinium (GA), potassium (K), sodium (Na) can also be used as dopants. In ‘B’ site, lead is the main component, unless it is a low bandgap material. For low-bandgap perovskite structure, tin (Sn) is used instead of lead. A combination of Sn and Pb is also being used in several structures. All halides are used in ‘X’ site, especially iodine (I) and bromine (Br). Fluorine (F) and chlorine (Cl) are also used to alter the morphology and stabilize the crystal structure.

1.2. Properties of perovskites

Perovskite has several interesting properties that make it a promising candidate in different applications, such as solar cells, LEDs, etc. These properties are the main reason behind the higher performance of perovskite solar cells within this short period. Some of the significant characteristics are described briefly below.

1.2.1. Defect tolerance in halide perovskites

Perovskites are solution-processable, which makes it a very simple and low-cost process. With this simple process, we are getting very high efficiency in PSCs. One of the primary reasons behind this superior performance is the defect tolerance characteristics of perovskite materials.

Several types of defects are observed in metal halide perovskites, as shown in figure 1.3. Figure 1.3a shows an ideal perovskite crystal structure, where ions are located in their equilibrium sites. As the perovskites are formed by annealing (negative temperature crystallization), the crystallization process is swift. Fast crystallization results in the formation of several types of defects in the crystal structure (Figure 1.3b-e). These defects are not only formed during the crystallization process but also with time.
under continuous illuminations. The volatile MA cation and iodide anion are responsible for the formation of defects. The most common defects in perovskite structure are vacancy, antisite, interstitial, Schottky, Frenkel, grain boundary, etc. Figures 1.3f and g show the real defects visible from the STM and TEM images.

Figure 1. 3 (a) Schematic of a perfect crystal structure; (b) Structure with defects; (c-e) microscopic configurations of different types of defects in the crystal; (f) STM images of
point/cluster defects in perovskite crystals; (g) Cross-sectional SEM image and the image inside the grain captured by TEM. Images were reprinted with permission from Ref. [7].

All the defects in perovskites can be categorized into two types: donor (positive) and acceptor (negative) defects. In figure 1.4a, the donor defects are colored blue, and the acceptors with red. The theoretical calculations showed that the point defects for MAPbI$_3$ perovskite are: interstitials [MA (MA$_i$), I (I$_i$), Pb (Pb$_i$)], vacancies [MA (V$_{MA}$), I (V$_I$), Pb (V$_{Pb}$)] and anti-sites [MA$_{Pb}$, MA$_{I}$, Pb$_{MA}$, Pb$_I$, I$_{MA}$, and I$_{Pb}$] [8, 9]. It is observed that majority of the defects are formed in the bands and are in the shallow energy level. The deep energy level defects, such as I$_{Pb}$, Pb$_{MA}$, I$_{MA}$, Pb$_I$, and Pb$_i$ do not contribute to high-density recombination (nonradiative) due to the high formation energy. The most common type of defects in perovskite crystals are shown in figure 1.4b.

The concept of defect tolerance is the overall charge neutrality of the structure. Within the perovskite structure, the self-regulation of cation and anion vacancies results in overall charge neutrality. It is performed by compensating for the loss of the ‘A’ cation by losing a ‘halide’ anion. Other semiconductors, for example, point defects in CdTe, have the energy level in the gap [7].

Defect tolerance does not mean defect immunity because all defects have consequences. The defect tolerant system shows less impact due to defects and preserves the functional properties of materials. Silicon has to be pure and perfect to get higher efficiency, but due to this defect tolerance, we can poorly handle perovskites and still get a competitive device efficiency [10-12].
Figure 1. 4 (a) Energy states (calculated) of point defects. Donor and acceptors are marked by blue and red color, respectively; (b) Point defects in perovskites crystal lattice;
(c) schematic of defect tolerant and defect intolerant structures; Illustration of how (d) shallow and (e) deep level traps impact the open-circuit voltage (Voc). Images were reprinted with permission from Ref. [7].

Figure 1.4c and d show how the shallow and deep level defects affect the open-circuit voltage of devices. It is seen from the figures that the shallow traps result in lower recombination processes due to the presence of defect sites within or near the bands. But the deep level defects result in Voc loss and nonradiative recombination, which is seen in figure 1.4e. It is also observed from Figures 1.4d and e that the charge carrier generated by illumination also affects the fermi level of adjacent charge transport layers [13-15].

1.2.2. 2 Optoelectronic properties

Metal halide perovskites have several superior optoelectronic properties. Perovskites are the direct bandgap material and have competitively a very high absorption coefficient. Due to these properties, a very thin layer of perovskite can absorb a sufficient amount of light for electricity conversion. In contrast, Si requires several micrometer thicknesses to produce a considerable amount of energy.

Unlike organic solar cell materials, perovskites have low binding energy in the range of 30-100 eV. These photogenerated electron-holes are free to move at room temperature and easy to extract at the charge transport layer interface.

Another essential property of perovskite is the long carrier lifetime. Charge carrier lifetime is very important for higher efficiency. Low charge carrier lifetime increases the chance of recombination. A higher charge carrier lifetime ensures a better chance to extract the charges. Perovskites show charge carrier lifetime in the range of microseconds.
1.2.2. Lightweight and flexible

Power per weight is a significant parameter to make lightweight devices. Among all the solar cell materials, perovskite shows the highest power per weight. Due to this excellent property, perovskite can be used in several critical applications. It can be used to make lightweight drones, aircraft, etc.

Figure 1.6a shows an ultrathin perovskite device on a PET substrate with a thickness of 1.4 µm. This perovskite solar cell was processed at 110 °C. The PCE of this device was ~12%, and the weight was 5.2 g/m². The power per weight was 23 Wg⁻¹,
which is the highest among all photovoltaic technologies [17], and the value is higher than double of the closest technology (figure 1.6b). They tested their solar cells to run a lightweight model aircraft with two modules with \(4 \times 8\) configurations (figure 1.6c and d).

Figure 1.6 (a) Schematic diagram of lightweight PSCs fabricated on a 1.4 \(\mu\)m thick PET substrate; (b) Power per weight data of major photovoltaic technologies; (c) the lightweight aircraft using the solar cells; (d) location of the module to run the dc motor of the propeller. Images were reprinted with permission from Ref. [17].

Perovskite thin films are also flexible and can be used to design flexible devices. As the process temperature of perovskite is much lower than the other solar cell materials, it can easily be deposited to flexible substrates. Several reports have shown the high performance of flexible solar cell devices. Figure 1.7 shows the performance of
flexible PSCs. It is observed from figure 1.7a that the efficiency was slightly changed after 1000 cycles at a 3 mm bending radius. After 2000 cycles, the PCE remained more than 90%. It indicates the stable efficiency of flexible perovskite solar cells.

Figure 1. 7 (a) Performance of flexible PSCs after 100 cycles at different bending radius; (b) Normalized power conversion efficiency at bending radius of 0.3 mm; (c) Stability of the unencapsulated devices at the inert environment. Images were reprinted with permission from Ref. [18].

1.2.2. 4 Processing

Metal halide perovskites can be processed from both solvent-free and solvent-based methods. In the solvent-free method, evaporation is used in a high vacuum. The non-solvent process is beneficial for not using hazardous solvents. But solvent-based
processes are fast and cost-effective. All perovskite materials can be dissolved in solvents. So, it is also solution-processable, which makes them a scale-up-friendly device structure. This allows roll-to-roll processing of perovskite devices. Figure 1.8a shows different deposition methods of perovskite thin film. All these processes are effective and can produce excellent efficiency but require optimization. Spin-coating is the most often used research lab method but does not meet the industrial needs to commercialize it. For commercialization, roll-to-roll processing is practical and desirable. Spray coating, slot die coating, screen printing, doctor blading, etc., can produce large areas and process perovskite due to solution processability [19-26]. Figure 1.8b [20] shows the schematic of the roll-to-roll processing of perovskites using the slot die coated gas-quenched lead halide layer on the ITO/ZnO coated PET substrate. This shows the faster processing of the perovskite module (Figure 1.8c) on flexible PET substrate. It is only possible due to low-temperature solution processing.

Compared to the traditional solar cells, which are processed at high temperatures, perovskites can be processed at low temperatures. Typically, perovskite solar cells can be processed at 100 °C or below. This low processing temperature makes perovskite a low-cost technology and can be used in different applications [27, 28]. That is why perovskite is much cheaper than Si or CIGS. A gigawatt-scale factory to produce PSC modules costs ten times cheaper than the cost to build a similar silicon-based solar factory.
1.2.2. Bandgap tunability of perovskites

One of the most incredible benefits of perovskite is the easy tunability by varying the components of ABX$_3$ (Figure 1.9b) structure. The bandgap can be varied from 1.15 to 3.06 eV by changing the ‘A’ [30, 31] and ‘B’ [32, 33] cations and halide anions [34]. Figure 1.9a shows the colloidal solution of CsPbX$_3$ perovskite at different percentages of halides when exposed to UV light [35]. The bandgap ranges from 1.77 eV to 3.06 eV.
The bandgap can be reduced more by replacing Cs with MA (Figure 1.9c). The bandgap can be reduced to 1.29 eV by simply replacing Pb with Sn in this structure. The trend does not follow a linear pattern [36, 37], and the lowest bandgap of 1.15 eV is found for MASn$_{0.8}$Pb$_{0.2}$I$_3$ [38]. The bandgap tuneability makes perovskites an ideal candidate for various applications, especially the wide-bandgap perovskites that can be used for making the tandem [39, 40], LEDs, photodetectors, etc. The ability to make wide-bandgap perovskites in the range of 1.65 eV to 1.9 eV makes perovskites a perfect candidate to make tandem structures with the existing technologies. These tandem structures can achieve higher efficiency exceeding the limit (Shockley-Queisser) of single junction SCs. Moreover, perovskite can be tuned from low-bandgap (1.2 eV) to high-bandgap, which makes it ideal to construct perovskite-perovskite tandem [41, 42].

Figure 1. 9 (a) Colloidal solution of CsPbX$_3$ when exposed to UV light with the structure of (b) ABX$_3$; (c) PL of the CsPbX$_3$ perovskite with different percentages of halides. Different amounts of Sn also vary MAPbI$_3$ perovskite in place of Pb. Images were reprinted with permission from Ref. [29]
1.3 Perovskite solar cell structure

The active perovskite layer is sandwiched between two charge transport layers as displayed in figure 1.10a. When the sunlight is exposed to the PSCs, it passes through the transparent electrode and charge transport layer and reaches the perovskite. Perovskite absorbs the light and generates excitons. As the exciton binding energy of perovskite is low, electrons and holes are free to move. It is required to separate the charge in the opposite direction before recombination to get electrical energy from the solar cells. This is done by the electron transport layers (ETL) and the hole transport layers (HTL) to extract the charges. These extracted electrons and holes are then connected to the external circuit by the electrodes.

![Working principle of PSCs.](image)

The function of ETL and HTL can be understood from the band diagram in figure 1.10b. The ETL is designed in such a way that it allows only electrons to pass and block the holes. On the other hand, HTL does the opposite, allowing holes to pass and blocks the electrons. In this way, electrons and holes are collected in opposite directions.
1.4 Recent trends in perovskite solar cell research

Figure 1.11a shows the best solar cell research efficiency chart. Figure 1.11b highlights the major solar cell technologies. CIGS solar cells started their journey in the 80’s, but the efficiency reached only 23.4%. On the other hand, PSCs reached 25.5% efficiency in the last 12 years, a similar efficiency to what Si solar cells achieved in the last 60 years. It indicates the prospect of PSCs. The efficiency of all these solar cell technologies reaches saturation. To improve the efficiency further, it is required to make a double junction tandem structure.

Tandem structured solar cells with a top wide-bandgap are considered as a proven route to achieving efficiency more than the Shockley-Queisser limit of a mono-junction. The double junction tandem solar cells model showed that an ideal wide-bandgap perovskite should be in the range between 1.65 to 1.9 eV depending on the rare cell bandgap [41, 43-46]. Perovskite bandgap tunability makes it perfect for enabling efficient double junction tandem devices. Perovskites have now been applied in tandem structure with CIGS [4], silicon [5], and low bandgap perovskite [6]. Perovskite-silicon tandem structure has already reached 29.15%, which is much higher than the single junction of all solar cell technologies. But this efficiency is much lower than the 40% theoretical limit of the double junction tandem. One of the primary reasons for this lower efficiency is the poor performance of the wide-bandgap PSCs. To enable an efficient tandem structure with higher efficiency, the production of efficient wide-bandgap PSC is crucial.
1.5 Challenges in wide-bandgap perovskite solar cells

The standard protocol adopted to achieve wider bandgap perovskite has been substituting iodide with bromide [47]. However, the Br-rich perovskites >20% present...
challenges with defects and phase segregation, which affects their performance and stability [44]. Trap densities, especially at the grain boundaries (GB), can significantly affect the charge recombination, extraction, and overall power conversion efficiency [48].

1.5.1 Poor morphology

Wide-bandgap perovskites result in poor morphology without any treatment. Dong et al. [49] reported that without any additives (FA$_{0.65}$MA$_{0.20}$Cs$_{0.15}$)Pb(I$_{0.8}$Br$_{0.2}$)$_3$ wide-bandgap perovskite showed poor morphology with pinholes (Figure 1.12a). After adding PEI, the morphology still showed lots of pinholes. A combination of PEAI and Pb(SCN)$_2$ was necessary for better morphology. Figure 1.12b shows the XRD pattern of the perovskites. It indicates that additive plays a vital role and affects the perovskite layer crystallinity. Without additives, wide-bandgap perovskites showed low crystallinity.

![Image](image.jpg)

Figure 1. 12 (a) SEM images and (b) XRD of wide-bandgap perovskite with and without additives. Images were reprinted with permission from Ref. [49].
1.5.2 Smaller perovskite grain size
Grain size has an essential role in the efficiency and stability of PSCs. Smaller grain size means larger grain boundaries which act as the defect sites. So, it is required to achieve larger grain sizes to reduce the defects and increase the performance of the solar cells. Smaller perovskite grain size is very familiar in wide-bandgap perovskites [49, 50]. Cong et al. [50] showed that the average grain size of FA$_{0.8}$Cs$_{0.2}$Pb(I$_{0.7}$Br$_{0.3}$)$_3$ wide-bandgap perovskite was only $169 \pm 53$ nm (Figure 1.13a). It was required to do further treatment to increase the grain size. They used Pb(SCN)$_2$ additives to increase the grain size, but it was not sufficiently large (Figure 1.13b). Finally, they had to do a solvent-annealing (SA) process to achieve larger perovskite grain sizes (Figure 1.13c).

Figure 1.13 SEM images of the perovskite thin films with different fabrication approaches. (a) no additives; (b) with 1.5% Pb(SCN)$_2$; (c) 1.5% Pb(SCN)2 and SA. Images were reprinted with permission from Ref. [50].

1.5.3 Excess lead halides (PbX$_2$)
Excess lead halides on the surface of the wide-bandgap perovskites are very common. Lead halides are nonconductive. The presence of PbX$_2$ on the surface hinders the charge flow from perovskite layer to the charge extraction layer. Moreover, this excess PbX$_2$ did not convert to perovskites which lowers the absorption of the light. Overall, less charge generation and extraction are visible from these excess lead halides. Several steps can remove excess lead halides. One of the easiest ways to do that is the
secondary growth treatment (SG), as shown in figure 1.14 [50]. Here, white spots in the SEM images indicate the excess lead halides (Figure 1.14a). Because of the non-conductive nature, lead halides appeared as white due to charge accumulation. After SG using guanidinium bromide, these white spots are not visible; indicating the conversion of excess lead halides to perovskites, as shown in figure 1.14b.

Figure 1.14 (a) Wide-bandgap perovskite film with excess lead halides (white spots in the SEM image); (b) SEM image of the perovskite film after SG treatment using guanidinium bromide. Images were reprinted with permission from Ref. [50].

1.5.4 Defects

Figure 1.15a shows the photoconductivity (PC) of Metal–MixAPbBr$_3$–Metal junctions, where MixAPbBr$_3$ is the lead tribromide mixed-cation (FA$_{0.85}$MA$_{0.1}$Cs$_{0.05}$)PbBr$_3$ wide-bandgap perovskite. The measurement was done at different light intensities. Data follows an exponent of $\gamma = 0.79 \pm 0.04$. The value of $\gamma$ indicates the type of recombination. If the value is 0.5, radiative bimolecular recombination occurs, whereas nonradiative recombination is indicated by the value of 1 [51]. The value of $\gamma$ in this wide-bandgap structure suggests one or more recombination centers under 1 sun. Figure 1.15b shows the TRPL decay with $\tau_1 < 10$ ns and a slow value of $\tau_2 < 90$ ns. This multiexponential decay in TRPL measurements is often
observed and indicates fast charge trapping into defects followed by bulk recombination. The initial PL amplitude is observed to level as $\phi 1.4$, indicating nonradiative recombination due to defects, [50] which is in agreement with the results in figure 1.15a.

Figure 1.15c presents the defect states distribution and the electronic transition ($\Gamma$) of the MixAPbBr$_3$ perovskite layer. In dark conditions, the defect level B is occupied, whereas A, C, and D are empty. It also indicates that defects C and D are closer to the conduction band supported by other groups [52]. Defects A and B are deep, which indicates the possibility of nonradiative recombination sites. These observations match with the result from the PC (Figure 1.15a) and TRPL data (Figure 1.15b).
Figure 1.15 (a) photoconductivity of the wide-bandgap perovskite layer at different light intensity; (b) TRPL data of the wide-bandgap perovskite using excitation light intensities. Images were reprinted with permission from Ref. [53].

### 1.5.5 Halide segregation

A common practice to enlarge the bandgap of the active perovskite is the addition of bromide (Br), replacing iodide (I). The higher Br concentration is responsible for halide segregation, also known as the Hoke effect [54, 55]. When the perovskite layer is subjected to light for an extended period, the iodine and bromine regions try to segregate. The possibility of segregation increases with the higher concentration of Br. As the I-rich region has a smaller bandgap, it acts as the trap states. This segregation affects the performance of the wide-bandgap perovskite. Figure 1.16 shows the PL spectra for different Br (25% and 40%) concentrations in Cs$_{x}$FA$_{1-x}$Pb(Br$_{y}$I$_{1-y}$)$_{3}$ perovskite. Figure 1.16b shows more pronounced halide segregation than 1.16a due to the lower Br amount. After 10 min at 0.1 sun 25% Br showed almost no shift, whereas 40% Br shifted to the lower bandgap region. At 10 sun, both showed the shift, but the shift in 40% is more than that with 25% Br. The open-circuit voltage monitored during the PL measurement indicated that the $V_{oc}$ loss with halide segregation (Figure 1.16c and d). More stable $V_{oc}$ was observed with lower Br compositions under illumination. This indicates that due to the larger Br content in wide-bandgap perovskite, perovskite shows poor performance due to the $V_{oc}$ loss under continuous illumination.
Recent advancements in wide-bandgap PSCs

‘A’ cation-combinations play a vital role in the properties of wide-bandgap perovskites. The lower performance of wide-bandgap perovskite is due to the higher percentage of Br because of the transition from trigonal to cubic structure due to the substitution of iodide with bromide. This phase change results in an amorphous phase near the transition which results in disorder and lower absorption. The phase change is also responsible for lower mobility [56].
This phase instability can be eliminated by replacing FA with Cs. Only FA does not show black perovskite phase at a higher concentration of Br (30% to 60%) due to phase transfer to cubic from trigonal. David et al. [56] studied the possibility of substituting FA partially for Cs to reduce the structural instability in the bromide rich perovskite. After performing this substitution, they achieve a structurally more stable 1.75 eV perovskite. They also tested the whole range of Br to I and found structural stability. It indicates that A cation plays a vital role in stabilizing Br-rich wide-bandgap perovskite.

Kevin et al. [44] developed a new composition of wide-bandgap perovskite using a lower Br content. As a higher Br concentration results in halide segregation and nonradiative recombination [57], the group achieved a similar bandgap using a higher cesium concentration instead of Br. A substantial increase in the bandgap was visible when the Br contents were between 11.25 to 30% (Figure 1.17). A very high Cs concentration is not suitable for the PSCs due to the lack of phase purity. But an average percentage of Cs (25%) with replacing Br (20%) gave the highest efficiency. It is observed that more than 20% is bad for the perovskite structure and can results in halide segregation.
Figure 1. The bandgap of Cs$_x$FA$_{1-x}$Pb(Br$_y$I$_{1-y}$)$_3$ perovskite layer at different concentrations of Br and Cs. Images were reprinted with permission from Ref. [44].

Several groups [49, 50] reported the benefit of implementing Pb(SCN)$_2$ to achieve higher wide-bandgap perovskite performance. Pb(SCN)$_2$ helps to grow bigger grain in perovskite, which is beneficial for better performance. It is found that the grain size gradually increases with higher amount of Pb(SCN)$_2$ as depicted in figure 1.18. Several groups also report a similar trend.

Cong et al. [50], in their work, reported that Pb(SCN)$_2$ is not enough to get the desired grain size of the perovskite. They also applied a solvent annealing process to get substantial grain sizes.

Figure 1.18 Effect of different Pb(SCN)$_2$ concentrations on the modification of grain size in (FA$_{0.65}$MA$_{0.20}$Cs$_{0.15}$)Pb(I$_{0.8}$Br$_{0.2}$)$_3$ wide-bandgap perovskite film. Images were reprinted with permission from Ref. [49].
Excess lead halides at the surface of the perovskite hinder the performance of the PSCs due to lower absorption and inefficient charge extraction. It is required to remove or convert these excess lead halides to perovskites to achieve higher efficiency. Removal of PbX₂ from the surface by solvent treatment is not feasible as the solvent that dissolves PbX₂ can also dissolve perovskite. Secondary growth (SG) using ‘A’ cation salt can readily react with PbX₂ and convert it to the perovskite phase. Most of the ‘A’ cation salts are easily dissolved in anhydrous IPA which is not that vulnerable to perovskite. Guanidinium bromide is applied as the SG treatment in wide-bandgap perovskite, which converted the PbX₂ to perovskite phase, results in a compositionally more uniform perovskite layer as shown in figure 1.14 [50].

Thermal annealing also plays an essential role in phase stability. Geunjin et al. [58] applied the thermal induce phase control (TIPC) strategy to get phase stability in wide-bandgap perovskite. They choose the well-known three cations FA₀.7₅MA₀.1₅Cs₀.1PbI₂Br wide-bandgap perovskite with a suitable bandgap of 1.73 eV for the experiment. They observed that a preferential growth of lead halides, observed from the XRD, can bring phase stability in the perovskite. To achieve that, they annealed the perovskite at 150 °C for the different periods. It is observed that the TIPC method did not change the perovskite bandgap, as evident from the steady-state PL data in figure 1.19. It is also evident from 1.19a that the peak position of the TIPC perovskite is not shifted after exposing to a laser beam for several minutes. A more intense PL peak indicates the defect passivation of the TIPC perovskites. It is also supported by the long carrier lifetime of the TRPL decay (Figure 1.19b). The consequence of defect passivation is reflected in the charge extraction from perovskite to the transport layer, which is shown
by the faster decay of the perovskite/SnO$_2$ layer (Figure 1.19c). Figure 1.19d-e also showed the fluorescence lifetime imaging microscope images (FLIM). It is evident from the histogram that the TIPC perovskite/SnO$_2$ has a lower lifetime than the control perovskite/SnO$_2$. It indicates better charge extraction of TIPC perovskite due to lower defects.

Figure 1. 19 (a) Steady-state and (b) TRPL data of wide-bandgap perovskite layer; (c) TRPL data of perovskite/SnO$_2$ layer; FLIM lifetime imaging and the lifetime histogram of perovskite/SnO$_2$ films, where perovskite is processed at (d) 100 °C and (e) 150 °C.

2D/3D perovskite structures have emerged as a very effective strategy to mitigate charge recombination in wide-bandgap perovskite, which results in a high value of $V_{oc}$. In the wide-bandgap structure of Cs$_{0.17}$FA$_{0.83}$Pb(I$_{0.6}$Br$_{0.4}$)$_3$, butylammonium (BA) increases the performance of the SCs, especially the $V_{oc}$. BA was deposited atop the perovskite layer and formed the 2D perovskite, which is confirmed by the XRD. XRD curve shows the distinct peak at around $\Delta2\theta = \sim 4.5^\circ$ (Figure 1.20). The thickness of the layer was around 2.0 nm. PL data confirmed nonradiative recombination in 2D/3D heterojunction and an increase in carrier lifetime.
Figure 1. 20 XRD pattern of the 2D/3D perovskite film with and without BABr atop Cs$_{0.17}$FA$_{0.83}$Pb(I$_{0.6}$Br$_{0.4}$)$_3$ at different concentrations; (b) XRD peaks at a lower angle; (c) Schematic of 2D/3D perovskite with relevant spacing.

The wide-bandgap perovskite used in the tandem structure with an efficiency of 29.15% focused on the interface of perovskite and the charge extraction layers [59]. The $V_{oc}$ loss in wide-bandgap structure is due to the halide segregation and nonradiative recombination at the interface [60]. The phase segregation can be halted by growing perovskite on a layer with efficient charge extraction and passivation capability. But passivation itself is not enough for better performance. To improve the charge extraction capability, a new HTL and a LiF layer in between perovskite and C$_{60}$ were used. The
developed HTL layer (named Me-4PACz) has a better charge extraction capability. The wide-bandgap perovskite showed an efficiency of ~20% with 84% FF. The same structure with PTAA HTL and without LiF showed only 18.2%. It indicates the importance of charge extraction ability to get higher efficiency in wide-bandgap perovskite.

1.7 Motivation and objectives
1.7.1 Motivation
Development of low-cost, efficient, and stable wide-band perovskite solar cells for tandem application to achieve efficiency beyond the Shockley-Queisser limit of single-junction solar cells.

1.7.2 Objectives
This dissertation aims to develop an efficient wide-bandgap perovskite with higher stability and lower fabrication cost. To achieve these goals, the following tasks have been performed:

- Designed a new quadruple cation 1.78 eV wide-bandgap structure
- Optimized the Rb cation compositions and process conditions to achieve the highest efficiency.
- Developed a secondary growth technique using GAI to passivate the grain boundaries and convert excess lead halides to perovskite.
- Performed several characterization methods to study the defects and the consequence of defect passivation after Rb incorporation and SG technique.
- Proposed a crystallization technique using PMMA to obtain defect passivated excess lead halide free perovskite film
• Studied the charge extraction and transport properties of PMMA-assisted crystalized perovskite thin films

• Developed a fast and cost-effective way to fabricate perovskite layer using the microwave heating technique.

• Optimized the power level and process time to achieve high-quality perovskite thin films.

• Fabricated wide-bandgap PSCs to study the performance of all the above methods.

1.8 Organization of the dissertation

Chapter 1 introduces perovskite crystal structure, properties, and the working principle of PSCs. This chapter also includes the challenges of wide-bandgap perovskite solar cells and the previous works addressing these issues. Finally, the motivation and objectives of this work are presented.

Chapter 2 discussed the experimental procedure of the perovskite solar cells. Besides all the characterizations, tools and techniques are described in detail.

Chapter 3 describes the design, optimization, and fabrication of the novel wide-bandgap perovskite solar cells. This chapter also shows vast characterization techniques to study the defects and the consequence of defect passivation.

Chapter 4 shows a facile crystallization technique of our novel wide-bandgap perovskite without excess lead halides and defects where PMMA was used to assist the crystallization process. Optimizations, improved properties of the perovskites, and the solar cell performance are also presented.
Chapter 5 includes the development of the efficient microwave-assisted fabrication of our wide-bandgap structure. This chapter shows the effect of microwave power and process time on the surface morphology and solar cells’ performance.

Chapter 6 is the summary of the dissertation and the proposed future work.
CHAPTER 2 EXPERIMENTAL TECHNIQUES

2. 1 Materials
Methylammonium iodide (MAI), methylammonium bromide (MABr), and formamidinium iodide (FAI) were purchased from Dyesol, lead iodide (PbI₂) was obtained from Alfa Aesar; and lead bromide (PbBr₂), cesium iodide (CsI), PTAA, rhodamine, guanidinium iodide (GAI) and ethyl acetate (EA) were obtained from Sigma Aldrich. Rubidium iodide (RbI) was purchased from abcr GmbH. PC₆₁BM and anhydrous isopropyl alcohol (IPA) were acquired from Nano-C and Fisher Scientific, respectively. All other solvents were purchased from Across and used as received.

2. 2 Substrate preparation
ITO-coated glass substrates with an area of 1.5 × 1.5 cm² were cleaned in several steps. First, the substrates were washed with detergent water, de-ionized water (two times), acetone, and isopropanol, sequentially for 20 min each. The substrates were then dried using a nitrogen (N₂) gun before use. The cleaned and dried ITO substrates were then treated by UV–O₃ for 25 min.

2. 3 Fabrication of wide-bandgap perovskite solar cells
All the perovskite layers were deposited by spin-coating except thermal evaporation of silver (Ag) electrode. Perovskite solar cell structure with corresponding layers are shown in the following figure:
2.3. 1 Hole transport layer (HTL) deposition

Before depositing the HTL, the perovskite layer was ozone-treated to increase the wettability of the substrate. PTAA (1.5 mg) was dissolved in toluene (1 mL) and immediately stirred for the whole night. We reused the PTAA stock solution for 3 weeks. Every time before depositing the PTAA layer, the stock solution was stirred for at least 1 hour. PTAA solution was dropped and spin-coated at 6000 rpm for 30 s on the ITO substrates, followed by thermal annealing at 100 °C for 10 min. We gradually increased the temperature of the hotplate to 100 °C. Before depositing the perovskite layer, DMF (30 µL) was dropped and spin-coated at 4000 rpm for 10 s to improve PTAA coated films' wettability.

2.3. 2 Perovskite precursor solution preparation

First, 1.5 M stock solutions of PbI₂, PbBr₂, CsI, and RbI were prepared using the appropriate amount. PbI₂ and PbBr₂ stock solutions were prepared in anhydrous DMF: DMSO 4:1 (v/v) by heating at 180 °C for 15 min. For CsI, anhydrous DMSO was used.
and heated at 150 °C for 10 min. RbI was dissolved in DMF: DMSO solvents without heating. In all the solutions, we added 5 mol% excess PbX₂ (X= I and Br).

**CsFAMA perovskite precursor** \[FA0.79MA0.16Cs0.05Pb(I0.6Br0.4)3\]

Appropriate amounts of FAI and MABr were added to the stock solutions of PbI₂, PbBr₂, CsI to prepare a 1.1 M precursor solution of CsFAMA perovskite.

**RbCsFAMA perovskite precursor** \[(FA_{0.79}MA_{0.16}Cs_{0.05})_{1-x}Rb_xPb(I_{0.6}Br_{0.4})_3\]

Different amount from RbI stock solution was added to the CsFAMA solution to make the RbCsFAMA precursor solution. The value of Rb in the RbCsFAMA composition were varied with the amounts x=0, 0.05 and 0.10. When a different amount of RbI was added, a similar amount of CsFAMA was taken out from the solution.

**RbCsFAMA-SG perovskite precursor**

Secondary growth (SG) treatment was done atop the RbCsFAMA perovskite layer. Secondary growth was done on top of the RbCsFAMA perovskite layer using GAI in IPA. Different amount of GAI (0, 1 and 2 mg) were used for the SG treatment.

### 2.3. 3 Perovskite layer deposition

DMF (30 uL) was spin-coated for 10 sec at 4000 rpm to increase the PTAA layer's wettability, and immediately the precursor solution of perovskite was dropped. The solution was spin-coated in two steps programs at 2000 and 6000 for 10 and 30 s, respectively. 200 uL of ethyl acetate (EA) was dripped 15 s before the end of the second spinning step. We followed the delayed annealing process where all the spin-coated films are kept in a covered Petri dish for 10 min and then annealed for 25 min at 100 °C on a pre-heated hot plate. After completing annealing, the perovskite films were cool down to ambient temperature before the next steps.
2.3.3. 1 Secondary growth

For SG, a different amount of guanidinium iodide per ml anhydrous IPA is dissolved. 150 uL of this solution is dropped on top of the RbCsFAMA perovskite layer at 5000 rpm for 25 s. Finally, the films were treated for 5 min at 100 °C. The temperature of the hot plate was gradually increased.

2.3. 4 Electron transport layer (ETL) deposition

Substrates were cooled down after annealing of the perovskite films. PC61BM (20 mg) in chlorobenzene (1 mL) was deposited at 2000 rpm for 40 sec, followed by annealing at 80 °C for 10 min. After cooled down, rhodamine (0.5 mg) in anhydrous IPA (1 mL) is deposited at 5000 rpm for 40 s. No annealing was done after that.

2.3. 5 Deposition of Ag electrode

Finally, 90 nm of the silver electrode was deposited by thermal annealing. It was done in a high vacuum. Crystal sensors monitored the thickness.

2. 4 Characterizations and measurement techniques

2.4. 1 Film characterizations

2.4.1. 1 UV-vis absorption spectra of perovskite

The absorbance of all the perovskite films was measured using the Agilent 8453 UV–visible Spectroscopy System. Chem station software was used for the measurement. The absorption ranged from 190 nm to 1100 nm. For the visible and the near-infrared range of light, a tungsten lamp was used. For the ultraviolet (UV) region, a mercury lamp was used. A monochromator is used to split the light at a different wavelength. UV-vis spectrum is used to know absorption, absorption coefficient, transmittance, bandgap, etc. Absorption spectroscopy follows the Beers Lambert law.

\[
\text{Absorbance (A)} = \log_{10} \left( \frac{I}{I_o} \right), \text{ where } I_o \text{ is the intensity of the light that falls, and } I \text{ is the light transmitted. The measurement procedure is shown in figure 2.2}
\]
Baseline correction was done by the PTAA coated ITO substrate before the measurement of the perovskite layer. After the blank measurement, the perovskite layer-coated films were loaded and measured. The software presented the absorption of only the perovskite layer by subtracting the blank.
2.4.1. 2 X-ray diffraction (XRD) spectrum

X-ray diffraction (XRD) was performed using Rigaku SmartLab with Cu Kα (1.54 Å radiation). For the measurement, the tube voltage and current of the x-ray were taken from 20 kV and 2 mA to 40 kV and 44 mA. We used the PB/PSA medium resolution with a 0.01 degree step size for the perovskite thin film. Perovskite film was placed on the sample holder's surface, and the intensity was recorded at 2θ. FWHM was calculated from the PDXL software. To get the PbX₂/perovskite area ratio, we calculated the PbX₂ and perovskite peaks area and then derived the ratio.

Figure 2. 2 Rigaku XRD spectroscopy.

2.4.1. 3 Scanning electron microscopy (SEM)

SEM is a potent instrument to conduct our research. The surface morphology of the perovskite thin films was analyzed using SEM. It is used to study the grain size,
morphology, presence of excess lead halides, and pinholes. For this purpose, backscattered electrons (BSE) are used. Using the EDX, we get the compositional analysis too. SEM images were captured using Hitachi S-4700 FESEM. We used 3 KV accelerating voltage with 2-3 mm working distance. No extra conducting layer was deposited for the measurement.

Figure 2. 3 Hitachi S-4700 Field Emission Scanning Electron Microscopy (FESEM) [62]

2.4.1.4 Profilometer

The thickness of the thin-films was measured using the Dektak 150 profilometer. It has a tip that moves on the film to measure the thickness of the film.
2.4.1. 5 Atomic force microscopy (AFM) measurements

AFM is used to perform several characterizations in our research. One of the essential characterizations is the topography image. From topography images, we came to know about several essential parameters, such as surface roughness, grain sizes, etc. For topography and phase images, Agilent 5500 AFM was used, as shown in figure 2.5.

The schematic of the AFM mechanism is shown in figure 2.6. It contains a nanometer-sized tip attached to the cantilever. A laser beam falls on the tip, and the tip's movement changes with the surface roughness. The laser beam is reflected from the tip, and the surface heights and roughness are detected by the photodiode which is then converted to the topographic image, as shown in figure 2.7. Both contact and the tapping mode can generate topography images. In our case, we used the tapping mode.
Figure 2. 5 Agilent 5500 scanning probe microscope.
Figure 2.6 Tapping mode of Atomic force microscope [63].

Contact mode AFM is used to measure the perovskite film's conductivity, known as current sensing AFM (CS-AFM) [64]. A Pt/Ir coated Si tip (Budget Sensors ContE-G; resonance frequency = ~14 kHz) was used to conduct the CS-AFM measurement. To avoid the perovskite layer damage, a small force controlled by the cantilever was applied. The conducting tip was in contact with the perovskite film and collected the charges to measure the current distribution on the surface. To collect the charges, a small bias was applied.

The measurement of the surface potential (SP) difference, also known as the contact potential difference (CPD), was conducted using the setup described in our previous work [65]. To map the topography and the SP measurement simultaneously, the AFM was equipped with MAC III controller (three lock-in amplifiers). A tip (multi 75Eg budget sensor) with illuminated white light was used.

2.4.1.6 Analysis of the defects in perovskite using CPD measurement

Figure 2.7 describes the concept of CPD measurement using the AFM tip. When the tip is in contact with the sample, electron flows from the sample to the tip due to the lower work function of the sample (in the present situation of figure 2.7) or vice versa. Electron flows to align the Fermi level. The flow of electron surface potential is created, which is then minimized by the external voltage source. The compensated voltage is equal to the CPD between the sample and the tip. CPD analysis can be used to study the defects and the trap states.
CPD depends on the work function difference of the sample and the tip, which is represented by the following equation:

$$CPD = \frac{\phi_{\text{sample}} - \phi_{\text{tip}}}{e}$$

If the CPD value is positive, the work function of the sample is higher than that of the tip. But if the CPD value is negative, the work function of the sample is low. Our study found negative CPD in the grain boundary (GB) compared to the grain interior. It indicates that GBs are more n-type than the Grains and act as the electron trap states, as shown in figure 2.8. It also acts as the hole blocking layer. GBs contain more defects than the grain and due to the more n-type nature at the GBs, we assume that the type of defects at the GBs are positive defects [67, 68]. We can say the defects are mostly due to halide vacancies as halide vacancies are the most common type of defects. Positive defects are most vernally than the negative type of defects as these act as the electron trap states. Electron trapping can result in a shunting path, which can reduce the $V_{oc}$ of the devices.
Figure 2. Negative CPD at the GBs act as the electron trap states. Images were reprinted with permission from Ref. [67]

2.4.1. 7 Nanoscale mapping of charge carrier dynamics

Defect passivation at the GBs can result in improved charge carrier dynamics in the perovskite layer. From CPD measurement, we confirmed the defect passivation of the perovskite layer. To understand the change in charge carrier properties after defect passivation, we have developed a nanoscale spatial mapping characterization technique, quantitively determining the charge carrier dynamics. Figure 2.9a shows the characterization setup. The real setup is shown in figure 2.10. We used 100 nm × 100nm for the measurement.

When the laser pulse hits the perovskite surface, the photogenerated charges are collected in two different conditions: short circuit (50 Ω) and open-circuit (1 MΩ) conditions, which is known as transient photocurrent (TPC) and transient photovoltage (TPV) measurements. These methods tell us about the charge transport time and carrier lifetime of the perovskite film at the nanoscale level, especially at the GBs.
The following mono-exponential decay model was used to calculate the charge carrier recombination lifetime and charge transport time.

\[ Y(t) = Y_0 e^{-\frac{t}{\tau}} \]

where \( \tau \) is the time constant representing charge carrier recombination lifetime \( \tau_r \) or charge transport time \( \tau_t \).

To calculate the diffusion length, \( L_D \), the diffusion coefficient was calculated using the carrier transport time \( (\tau_t) \) and active layer thickness \( (L) \).

\[ D_n = \frac{t^2}{2.35 \times \tau_t} \]

This diffusion coefficient was used to calculate the carrier diffusion length \( (L_D) \)

\[ L_D = \sqrt{D_n \tau_t} \]
Figure 2. 9 (a) Transient photo-response AFM (TP-AFM) instrumentation to measure perovskite film’s charge carrier dynamics at the nanoscale level. Here, the perovskite layer was illuminated with a green laser pulse, and the contact mode AFM did the measurement; (b) Device equivalent circuit of the TP-AFM measurement during TPV and TPC. Images were reprinted with permission from Ref. [69]
Figure 2. 10 Real TP-AFM setup in our lab.

2.4.1. 8 Calculations of defect density and filled trap state density

Defects and incomplete atomic bonding result in trap states at the GBs. These trap states capture the free charge carriers, which become electrically charged and generate a potential energy barrier blocking carriers' motion among crystallites. GB model from SP images can be used to calculate the charge carrier concentration. In this model, a GB corresponds to a surface with surface charges. Therefore, the net doping density ($P_{\text{net}}$) of perovskite can be calculated from the barrier height of band bending and the space charge region (SCR) with a width of $W_{\text{GB}}$ (Figure S10). The doping ($P_{\text{net}}$) and filled trap states density ($P_{\text{GB,trap}}$) are calculated by equations (1) and (2), respectively[70].
Figure 2. Calculation of $\Delta \varphi_{GB}$ and $W_{GB}$ from Gaussian fitted CPD distribution.

\[ P_{net} = \frac{2\varepsilon_o \varepsilon_r \Delta \varphi_{GB}}{e^2 W_{GB}^2} \quad (1) \]

\[ P_{GB,trap} = \frac{1}{e} \sqrt{8\varepsilon_o \varepsilon_r P_{net} \Delta \varphi_{GB}} \quad (2) \]

where $\varepsilon_o$ is the permittivity of free space, $\varepsilon_r$ is the dielectric constant of perovskite, $\Delta \varphi_{GB}$ is the barrier height of the band bending, $e$ is the elementary charge, and $W_{GB}$ is the width of the space charge region.

2.4.1.9 Photoluminescence measurement

Steady-state photoluminescence is used to measure the nonradiative recombination and the charge extraction capability at the active perovskite interface and the charge transport layers. These measurements were performed using FLS 920 fluorescence spectrophotometer. The perovskite layer is deposited on the glass without any charge transport layer (figure 2.12). As the photo-excited charges have to recombine with time, they generate photoemission in the case of direct bandgap material. But if the
perovskite layer has nonradiative recombination sites, the photo-emission is less. To get information about the charge extraction efficiency from perovskite to the charge extraction layer, we added ETL layer atop perovskite, as shown in figure 2.12. If the photo-emission is less, better charge extraction from perovskite to ETL.

Figure 2.12 Photoluminescence measurement of the perovskite layer.

2.4.1. Contact angle measurement
The contact angle was measured by using the instrument of VCA 2000 video contact angle system. The contact angle measurement was done using water.

2.4.2. Device characterizations
2.4.2.1 Current-voltage measurement
Solar cells were tested without encapsulation in ambient conditions using a Xenon arc lamp, as seen in figure 2.13. The light intensity was calibrated using a standardized silicon solar cell from NREL (S1133-14). All the measurement was done using 100 mW cm\(^{-2}\) (AM 1.5). The light was passed through the transparent ITO sites. All PSCs were characterized maintaining the same conditions using an Agilent 4155C semiconductor parameter analyzer. All the solar cells were measured with a metal mask to keep a fix active area of 0.0825 cm\(^2\). The measurement setup is shown in figure 2.13.
2.4.2. 2 EQE measurement

The external quantum efficiency (EQE) spectra were achieved using a Xenon lamp (Newport, Model 67005) and the monochromator (Newport, Model 74125). The monochromator generates wavelength with 0.35 nm accuracy. For EQE measurement, the wavelength was used from 350 nm to 800 nm with a 5 nm interval. Two lenses were used to focus the light on the cell. The data measured from the setup is compared with the standard calibrated EQE data of Hamamatsu photodiode (S1133-14) to get the EQE of the perovskite solar cells. The setup is shown in figure 2.14.
Figure 2. 14 Real lab set up of the EQE measurement.

2.4.2. 3 Transient photocurrent and photovoltage measurement

Transient measurements were conducted following the setup described in our previous paper [71]. The measurements were carried out using a OBB’s OL-4300 nitrogen laser coupled with a dye laser, which produced a 532 nm wavelength pulse for less than 1 ns. The transient response was recorded with an oscilloscope. The transient photocurrent was measured using a low input oscilloscope impedance of 50 Ω to simulate short circuit conditions. The transient photovoltage was measured by illuminating the perovskite solar cell at approximately 1–2 suns and a 1 M Ω oscilloscope input impedance to simulate open-circuit conditions. The charge carrier lifetime and collection time were calculated by fitting a monoexponential decay function to the transient photovoltage and photocurrent, respectively.

2.4.2. 4 Electrochemical impedance spectroscopy and Mott-Schottky measurements

Electrochemical impedance spectroscopy (EIS) and Mott-Schottky measurements were performed using Ametek VERSASTAT3-200 Potentiostat with frequency analysis module (FDA). An AC signal with perturbation oscillation amplitude 20 mV in the frequency range of 0.1–1 MHz was applied. AC perturbation voltage of 20 mV at a fixed frequency of 20 kHz was applied for the Mott-Schottky measurements. Mott-Schottky plots show the relationship between 1/(C^2) and applied bias from 0 to 1.2 V.

2.4.2. 5 Mobility measurement

Charge extraction quality can be investigated using photoinduced charge carrier extraction with linearly increasing voltage (Photo CELIV) measurement [72-75] in figure 2.15. Charges are generated by a nanosecond pulse laser, which was then collected by the linearly increasing voltage.
Carrier mobility can be calculated using the following equation:[76]

\[ \mu = \frac{2d^2}{3At_{\text{max}}^2} \]

Where \( t_{\text{max}} \) is when the voltage rose to maximum voltage (Figure S25a), A is the slope of the ramp voltage (Figure S25b) applied to collect charge, and d is the thickness of the active layer. The slope of the ramp voltage and the film thickness are constant for all the films. \( t_{\text{max}} \) is the only factor that determines mobility. The lower \( t_{\text{max}} \) of the Rb-incorporated and SG treated samples indicates higher mobility than CsFAMA film. Higher mobility indicates the reason behind the improvement of the \( J_{sc} \) due to efficient charge extraction [77].

2.4.2. 6 \( V_{oc} \) vs. light intensity

Most of the photogenerated charge carriers will be recombined at open-circuit conditions. In this condition, the recombination mechanism can be studied using the following formula [78].
\[ V_{oc} \propto n \frac{kT}{q} \ln(I) \]

Where \( k \) is the Boltzmann constant, \( T \) is the temperature, and \( q \) is the electron charge.

SRH mechanism indicates that electron and hole recombination is dominated by recombination centers and traps known as monomolecular recombination.

When the slope value is greater than the unity of \( \frac{kT}{q} \), SRH recombination is dominant [79]. Lower the value or close to unity means a reduction in monomolecular SRH recombination [80], and bimolecular recombination is dominant [81].

2.4.2. 7 \( J_{sc} \) vs. light intensity

Charge carrier collection and transport mechanism can also be studied from analysis of \( J_{sc} \) vs. incident light intensity. It also provides valuable information about the charge recombination kinetics. The dependence of \( J_{sc} \) vs. light intensity is related by the equation below [82].

\[ J_{sc} \propto I^\alpha \]

\( I \) indicate the light intensity, and \( \alpha \) is derived from the slope of the curve. The value of \( \alpha \) equals unity means devices with no space charge effects [83]. The value of \( \alpha \) close to unity indicates reduced recombination and potential barrier [84, 85]. Significant deviation of the \( \alpha \) value from unity attributes to bimolecular recombination [86] and significantly affects charge collection [87]

2.4.2. 8 SCLC measurement

The devices' trap density is quantitatively calculated using the space charge limited current (SCLC) measurement [88]. The J-V characteristics curve fitted with the Mott-Gurney law for the electron-only devices is shown in figure 5f. Three distinct regions of the curves can be defined by the \( J \propto V^n \) relation where the linear region with
n=1 indicates the ohmic region and n=2 is the SCLC region, also known as the child region. In between these two regions, traps are continuously filled with increasing the bias voltage known as the trap-filled limit (TFL) region, and the current increases abruptly with the bias voltage. The kink point known as the trap-filled-limit-voltage \( (V_{TFL}) \) can be used to calculate the trap density \( (N_t) \) using the following equation [89].

\[
V_{TFL} = \frac{eN_tL^2}{2\varepsilon\varepsilon_o}
\]

where L is the thickness of the perovskite films, \( \varepsilon_o \) the permittivity of the vacuum and \( \varepsilon \) is the dielectric constant of the perovskite [90, 91].
3.1 Introduction

High-quality wide-bandgap perovskite solar cells are challenging to fabricate because of the inferior electronic quality and crystallinity. Smaller grain size, high surface recombination, etc. are the primary reasons for the lower performance. Higher bromide concentration in wide-bandgap perovskite causes charge-carrier traps/defects that can increase recombination rates reducing overall performance and causes significant current density-voltage hysteresis. The formation of excessive lead halides is also a significant issue which reduces the absorption and causes inefficient charge collection from perovskite to the transport layer. Large-bandgap perovskites also suffer significantly from halide segregation. Light-induced halide segregation causes the segregation of iodide and bromide-rich regions, which reduces the open-circuit voltage and limits the benefit of using wide-bandgap perovskite as the top cell in tandem devices. In this project, we have developed a novel wide-bandgap perovskite composition where we introduced rubidium (Rb) to see the performance of the quadruple-cation wide-bandgap perovskite. We also performed secondary growth (SG) treatment using guanidinium iodide (GAI). The synergistic effect of Rb incorporation and SG improved the quality of the perovskite film and converted the excessive lead halides to perovskite, which resulted in improved performance and stability of the wide-bandgap perovskite solar cells.

3.2 Perovskite layer deposition process

Perovskite layers were processed by spin-coating. First, the wettability of the PTAA coated substrate was increased by spin-coating 40 µL of DMF. Immediately after that, 60 µL of perovskite precursor solution was dropped and spin-coated immediately.
The spin-coating was done in two steps. 15 seconds before the end of the second step, 200 µL of ethyl acetate (EA) was dropped. Antisolvent EA was used to wash away excess DMF: DMSO and to start the crystallization process. After spin-coating, the spin-coated film was delayed for 10 minutes and then annealed at 100 °C for 25 minutes (Figure 3.1a).

Secondary growth (SG) was done after cooling down the perovskite layer. For SG, 150 µL of GAI solution (1 mg per mL anhydrous IPA) was dropped and spin-coated for 25 sec. The film was then annealed at 100 °C for 5 minutes (Figure 3.1b).

Figure 3. 1 (a) Schematic presentation of the processing of CsFAMA and RbCsFAMA perovskite layers; (b) performing SG atop RbCsFAMA perovskite.

3.3 **Optimization of process conditions**

Optimization of the process conditions is essential to achieve higher efficiency in perovskite solar cells [92]. Some of the significant optimization processes are briefly described below:
3.3. 1 Composition

Composition plays an important role in wide-bandgap perovskite. We have tried different mol% of Rb in the CsFAMA structure and found that the morphology of the perovskite films was changed with different mol%. It is also observed that the crystallinity and the absorption is also affected by different amounts of Rb due to the change of morphology. We found 5 mol% of Rb is the optimized condition for the higher performance of the device. Higher than this amount results in an additional non-perovskite phase.

We also observed that the amount of GAI during the SG treatment also affects the morphology and the properties of the perovskite. 1mgmL⁻¹ GAI in IPA is suitable to convert the excess lead halides to perovskite. Higher than this amount result in smaller grains with additional phases.

3.3. 2 Molarity of the perovskite precursor solution

Molarity plays a vital role in the morphology of the perovskite thin film. Molarity affects the surface roughness and film thickness of the film, which affect the performance of the PSCs [93]. We have tried different molarities of the perovskite films (0.9, 1.0, 1.11, 1.2 M) and found 1.1 M is the optimized condition to achieve higher performance of the solar cells (Figure 3.2).
3.3. 3 Delayed annealing

Typically, we annealed the perovskite films immediately after spin-coating. We observed that it results in higher surface roughness of the perovskite films due to faster nucleation and crystallization. On the other hand, a delay before the annealing of the perovskite film can result in a smoother film. We found that a delay of 10 min can reduce the RMS surface roughness from 24.90 nm to 13.59 nm (Figure 3.3). Corresponding SEM images are also shown in figure 3.4. It is observed that the grain sizes are not affected that much by delayed annealing. But the presence of excess lead halides is impacted by the delayed annealing. Lower roughness ensures better contact of the ETL atop the perovskite layer, ensuring better charge collection ability from perovskite to the charge transport layer.
Figure 3. Change in the morphology and surface roughness of the perovskite thin films due to delayed annealing. Scale bar: 1 µm

Figure 3. 4 (a-b) Lower and (c-d) higher magnified SEM images of (a and c) immediate and (b and d) delayed annealed perovskite films. Scale bar: 1 µm

3.3. 4 Anti-solvent

Anti-solvent crystallization is one of the most efficient and commonly adopted methods to form a perovskite layer. Anti-solvent plays an essential role in the
crystallization and morphology of the perovskite. Anti-solvent started the crystallization process by forming the seeding layer. Polarity and solubility of the materials have a significant role in the formation of the seeding layer. We observed that different antisolvents have a major impact on the perovskite layers' crystallinity, as presented in figure 3.5. Due to the change in crystallinity, absorption is also affected [94]. We found ethyl acetate produced the highest crystallinity and better absorption of the perovskite. It is to be noted that EA is a greener solvent than chlorobenzene and toluene.

Figure 3.5 Change in crystallinity and absorbance of wide-bandgap perovskite with other anti-solvent dripping.

3.3.5 Annealing temperature

Annealing temperature affects the nucleation and crystallization of the perovskite films. Lower annealing temperature resulted in more seeds which reduced the average grain sizes of the perovskite. On the other hand, higher annealing temperature can degrade the perovskites, which is realized from the excess lead halides on the surface.
Optimized annealing temperature can produce bigger grains without degradation. We have tried a series of annealing temperatures to process perovskites and observed that 100 ⁰C annealing temperature could produce our desired morphology of the perovskite, as shown in figure 3.6.

![Image](image_url)

Figure 3.6 Change in the morphology of the perovskite films at the different annealing temperatures.

### 3.3.6 Glove box temperature

We observed that a fixed glove box (GB) temperature is essential to achieve consistent morphology of the perovskite film. Our analysis showed that GB temperature affects the crystallization of the perovskite and morphology. Grain size gradually increases with the GB temperature up to a specific value. After that, perovskite grain size remains the same with more excess lead halides on the surface. From our findings, 27.5 ⁰C is the optimized GB temperature to process the perovskite layer (Figure 3.7).
3.3.7 Thickness

Thickness plays a crucial role in achieving an efficient solar cell. Higher thickness can absorb a large amount of light and generate more free charge carriers. Higher thickness also ensures the generation of charge carriers far from the surface, which contains more defects. But if the thickness is too large, the photogenerated charge will be too far from the interface, which will increase the chance of recombination. So, an optimized thickness can balance these two and generate more charges with less recombination. We optimized the thickness by controlling the spin coating rate of the perovskite precursor solution. We tried several spinning speeds of the second step and found that 6000 rpm gave us the optimized thickness of ~550 nm, as shown in figure 3.8.

Figure 3. 7 Effect of different glove box temperatures on the perovskite film morphology.
3.3. Other process conditions

We optimized several other process conditions: the annealing time, antisolvent amount, dripping time and the dripping rate, perovskite precursor solvent temperature, etc. We observed 25 minute annealing time at 100 °C is the optimized time. We choose EA as the antisolvent and 200 µL of antisolvent is the optimized condition. We also observed that faster dripping of the antisolvent is better for the perovskite morphology. We also observed that perovskite precursor solution temperature at 70 °C is appropriate for the higher performance of the solar cells.

3.4 Electrical, optical and physical properties of perovskite films

We first perform the study of the effect of Rb incorporation on the morphology of the CsFAMA perovskite films. It is confirmed from the SEM images that adding a small
amount of Rb (5 mol%) exhibited a significantly larger perovskite grain size (Figure 3.9c) compared to reference CsFAMA perovskite thin films (Figure 3.9a). The average grain size measured from the SEM images (Figure 3.10a) increased from 449 ± 144 nm to 1062 ± 309 nm after incorporating Rb (Figure 3.10b), which is due to the influence of Rb on crystallization kinetics and nucleation of perovskite. But Rb fails to remove the excess PbX$_2$ entirely from the surface of the perovskite film (Figure 3.10a), which can reduce the performance of the devices [95].

![Figure 3. 9 Top-view and cross-sectional SEM images of (a and b) CsFAMA, (c and d) RbCsFAMA and (e and f) RbCsFAMA-SG perovskite layers with corresponding cross-sectional SEM images; Scale bars, 500 nm.](image)

A higher concentration of Rb (>5 mol%) also showed larger grain size (Figure 3.11a) and higher absorbance (Figure 3.11d), but new diffraction peaks were observed below 10° (Figure 3.11b and c), which indicates that excess Rb suppressed the formation of the perovskite. We also observed that the perovskite peak ~14° shifted to higher value after adding Rb, which indicates the incorporation of Rb in to perovskite crystal lattice.
Figure 3. 10 (a) SEM images, and (b) Grain size distribution of (Cs0.05FA0.79MA0.16)1-xRbxPb(10.6Br0.4)3 with x=0, 5, 10%. Average grain size is 449 ± 144 nm, 1062 ± 309 nm and 954 ± 200 nm containing 0, 5, 10% Rb in perovskite thin films, respectively.

To remove excess PbX2 from the perovskite film, we studied SG treatment application using guanidinium iodide (GAI). In this step, GAI (1 mg/mL) dissolved in IPA (150 μL) is dropped and spin-coated atop RbCsFAMA perovskite films. We performed the thermal annealing to diffuse GAI into the perovskite layer. The top-view (Figure 3.9e) and cross-sectional (Figure 3.9f) SEM images after SG treatment (FAMACsRb-SG) exhibited that PbX2 precipitates were converted to perovskite, confirming a compositionally more uniform perovskite film.
FWHM confirms higher crystallinity of the Rb incorporated FAMACsRb perovskite thin films (Figure 3.12a and b) after Rb incorporation, which is supported by the superior absorbance (Figure 3.13a). FWHM was calculated for the perovskite peak ~14°. PbX₂/perovskite ratios were calculated with the PbX₂ and perovskite peaks around 12.8 and ~14°. Though the PbX₂/perovskite ratio (Figure 3.12b) calculated from the XRD (Figure 3.12a) reduced after adding Rb. Both the CsFAMA and RbCsFAMA films contained unreacted PbX₂, confirmed from the surface and cross-sectional (Figure 3.9) SEM images (marked by a yellow color circle). SG treatment confirms the removal of access PbX₂ (Figure 3.9e, f), as demonstrated by the lower PbX₂ to PSK area ratio (Figure 3.12b) and higher absorption (Figure 3.13a).
UV-vis absorbance (inset of Figure 3.13: Tauc plot) and PL emission (Figure 3.13b) indicated that the combination of Rb and SG do not noticeably affect the bandgap of the CsFAMA perovskite films.

A higher amount of GAI (>1 mg/mL) suppressed the formation of tetragonal perovskite and introduced new diffraction peaks (Figure 3.14a) which attributed to the photoinactive hexagonal δ-FAPbI₃ (11.5°) and PbX₂ phase (~12.8°) resulted in reduced
absorption (Figure 3.14b) of the perovskite films. SEM images also confirm small grains around the grain boundaries (Figure 3.14c). The results indicate that excess GAI leads to poor morphology with new phases [96].

![Figure 3.14](image)

Figure 3. 14 (a) XRD; (b) UV-vis absorption spectra; and (c) SEM images of RbCsFAMA-SG perovskite layers after secondary growth (SG) with different amount of GAI (0, 1 and 2 mg) per mL IPA.

To study the passivation in perovskite thin films, we have conducted the Kelvin probe force microscopy (KPFM) measurement (Figure 3.15). It is established that perovskite films' charge transport properties are dominated significantly by grain boundary (GB) defects and traps [97-100]. Traps can gather the mobile carriers and become charged, which acts as a potential energy barrier, blocking charge carriers' migration [101]. Besides, this charge accumulation can create a shunting path, which can reduce the performance of the device. Contact potential difference (CPD) from kelvin
probe force microscopy (KPFM) can help understand the passivation of grain GBs. GBs with negative $\Delta$CPD ($CPD_{GB} - CPD_{Grain}$) represent hole barrier/positively charged trap states indicating halide vacancies. Electrons are trapped by these positively charged defects causing the junction shunting [102]. This negative $\Delta$CPD strongly affects the solar cells performance and reduces the $V_{oc}$ and FF. On the other hand, positive $\Delta$CPD ($CPD_{GB} - CPD_{Grain}$) represent an electron barrier, which has less impact on the performance.

Figure 3. 15 Atomic force microscopy topography and contact potential difference (CPD) of (a and b) CsFAMA, (c and d) RbCsFAMA (e and f) RbCsFAMA-SG perovskite thin films. (g-i) Average of 10 line (black line) profiles extracted from the CPD images of
films and the shaded areas represent the error bars. CPD is normalized to the value at the initial position of the grain interior. Scale bars in the AFM images are 500 nm.

Figure 3.15 displays the KPFM measurement of the perovskite films. GBs are recognized from the topography images (Figure 3.15a-c) of the perovskite films, and the CPD variation was measured from the line profiles at the GBs (Figure 3.15d-f). We observed that Rb incorporation and SG technique modified the surface potential, and the differences of surface potential between grains and GBs are reduced, respectively, which suggests the reduction of GB defect states after adding Rb and found lowest after performing SG. It is also observed the ΔCPD is negative, which indicates positive defects. We concluded that halide vacancies at the grain boundaries are dominant and responsible for charge shunting which affects the FF and Voc the devices. Reduced ΔCPD indicates the passivation of the defects after Rb incorporation and SG technique.

Interestingly surface potential nonuniformities at the grains are observed in FAMACs films (SD = ±14 mV) calculated from Figure 3.15g, which reduces to ±8 mV after the treatment. This confirms the better compositional uniformity of the perovskite grain interiors (GIs) after SG treatment as excess PbX₂ on the surface converted to the perovskite phase. More compositional uniformity at GIs and reduced defects at the GBs indicate efficient charge extraction at perovskite (PSK)/electron transport layer (ETL) interface, thus enhancing the devices' performance [103, 104].

At the GBs, trap states are formed due to defects and incomplete atomic bonding disorder [105]. These traps accumulate the carrier charges that reduce the availability of free carriers for conduction. Trap carriers create charge at the grain boundary, which acts as the potential energy barrier. Depending on the barrier, GBs can either block the motion
of carriers among crystallites or create the shunting path. GB model from SP images were used to compute the charge carrier concentration. In this model, a GB corresponds to a surface with surface charges. Therefore, the net doping density ($P_{net}$) of perovskite can be calculated from the barrier height of band bending and the space charge region (SCR) width. The doping density ($P_{net}$) and filled trap states density ($P_{GB,trap}$) can be calculated using equations (1) and (2), respectively [106].

$$P_{net} = \frac{2\varepsilon_o\varepsilon_r \Delta \phi_{GB}}{e^2 W_{GB}^2} \quad (1)$$

$$P_{GB,trap} = \frac{1}{e} \sqrt{8\varepsilon_o\varepsilon_r P_{net} \Delta \phi_{GB}} \quad (2)$$

where $\varepsilon_o$ and $\varepsilon_r$ are the permittivity of free space and dielectric constant of perovskite (absorbing materials), respectively. $\Delta \phi_{GB}$ and $W_{GB}$ are the widths of the space charge region, and the barrier height of band bending.

Figures 3.16a and b show the topography and corresponding CPD of perovskite films, respectively. Figures 3.16c-d are the corresponding CPD distributions of the perovskite films at area 1 and area 2 of CsFAMA, RbCsFAMA, and RbCsFAMA-SG perovskite films, respectively. The defect density and the filled trap states at the GBs of the perovskite films are calculated using equations 1 and 2. Table 3.1 shows the values of $\Delta \phi_{GB}$ and $P_{net}$, and $P_{GB,trap}$ at area 1 and area 2 in the topography.
Figure 3. 16 (a) Topography, (b) CPD, and the CPD distribution of (c) area 1 and (d) area 2 with the Gaussian fitted curve. Scale bar in the AFM images are 500 nm.

The average grain boundary potential barrier of CsFAMA perovskite decreased from 79.87 and 114.04 meV to 66.07 and 55.11 meV after incorporating Rb. The barrier was reduced further to 23.17 and 16.63 meV for perovskite films, which indicates the lowest filled trap states and defect density. These suggest the most efficient charge transport within the grains in RbCsFAMA-SG perovskite films for the highest device performance.
Table 3. Filled trap states and density of defects of perovskite films

<table>
<thead>
<tr>
<th>Area</th>
<th>Grain potential (mV)</th>
<th>GB potential (mV)</th>
<th>GB potential barrier, $\Delta \varphi_{GB}$ (meV)</th>
<th>Defect Density, $P_{net}$ (cm$^{-3}$)</th>
<th>filled trap states Density, $P_{GB, trap}$ (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsFAMA</td>
<td>1</td>
<td>323.41</td>
<td>243.54</td>
<td>79.87</td>
<td>$8.12 \times 10^{16}$</td>
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<tr>
<td></td>
<td>2</td>
<td>347.01</td>
<td>233.12</td>
<td>114.04</td>
<td>$7.28 \times 10^{16}$</td>
</tr>
<tr>
<td>RbCsFAMA</td>
<td>1</td>
<td>364.59</td>
<td>298.52</td>
<td>66.07</td>
<td>$2.11 \times 10^{16}$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>353.54</td>
<td>298.43</td>
<td>55.11</td>
<td>$2.54 \times 10^{16}$</td>
</tr>
<tr>
<td>RbCsFAMA-SG</td>
<td>1</td>
<td>345.82</td>
<td>322.65</td>
<td>23.17</td>
<td>$2.68 \times 10^{15}$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>343.33</td>
<td>326.7</td>
<td>16.63</td>
<td>$5.95 \times 10^{15}$</td>
</tr>
</tbody>
</table>

It is established that GBs and GIs having localized defects serve as the recombination centers which results in inefficient charge transport and separation. Passivation of these defects can improve the charge-carrier properties [107]. After passivation, the improvement of charge-carrier dynamics was analyzed by nanoscale mapping of randomly selected 100 nm by 100 nm area (red square areas in topography images of figure 3.17) at GBs. Local TPC and TPV decays were measured by AFM contact mode, where 1 M$\Omega$ and 50 $\Omega$ and 1 M$\Omega$ were used for the TPC and TPV, respectively. The charge carrier lifetime and transport time were derived from the TPV and TPC measurement following the mono-exponential decay function.

$$Y(t) = Y_0 e^{-\frac{t}{\tau}}$$

where $\tau_r$ (charge carrier recombination lifetime) or $\tau_t$ (transport time) is represented by the time constant $\tau$. We also calculated the diffusion length ($L_D$) from $\tau_t$ and $\tau_r$ using the following equation:

$$L_D = 0.65 \times L \times \sqrt{\frac{\tau_r}{\tau_t}}$$
where L represents the thickness of the perovskite layer.

Figure 3.17 Nanoscale resolved mapping of the charge carrier dynamics marked by the red square 100 nm × 100 nm, where the charge carrier recombination lifetime ($\tau_r$) of (a) CsFAMA (b) RbCsFAMA (c) RbCsFAMA-SG, respectively, (d) profile line of $\tau_r$; charge carrier transport time ($\tau_t$) of the corresponding films, (h) profile line of $\tau_t$; carrier diffusion length ($L_D$) of (i) CsFAMA (j) RbCsFAMA (k) RbCsFAMA-SG and (l) profile line of $L_D$. Scale bar in the images are 20 nm.

Figure 3.17a-c displays the nanoscale charge-carrier recombination lifetime ($\tau_r$) of the perovskite thin films. RbCsFAMA-SG had the highest $\tau_r$ of 9.68 µs compared to 8.94 µs and 7.72 µs for RbCsFAMA and CsFAMA, respectively (Figure 3.17d). On the other hand, charge-carrier transport time ($\tau_t$) of the perovskite films showed the reverse trend.
RbCsFAMA-SG showed the lowest charge transport time of 3.94 µs) at GBs compared to 5.45 µs and 4.66 µs for CsFAMA and RbCsFAMA, respectively (Figure 3.17h). Nanoscale charge-carrier diffusion lengths ($L_D$) calculated from local $\tau_r$ and $\tau_t$ showed improvement in FAMACsRb-SG film. The differences in $L_D$ between the GIs and GBs were much lower in RbCsFAMA-SG film than in the other two films (Figure 3.17l).

The distribution of $\tau_r$, $\tau_t$, and $L_D$ at the GB regions are presented in the pie chart (Figure 3.18) which clearly shows the improvement of charge carrier dynamics after defect passivation.

Figure 3.18 Pie chart distribution of recombination lifetime (a), transport time (b) and diffusion length (c) at GBs for CsFAMA, RbCsFAMA and RbCsFAMA-SG perovskite thin films, respectively.

Figure 3.18a shows the pie chart of the charge carrier recombination lifetime ($\tau_r$) at the GBs of perovskite films. Figure 3.18a shows that ~63% of $\tau_r$ is <8 µs for the CsFAMA sample, 47% for RbCsFAMA and only ~13% for the RbCsFAMA-SG sample. Passivation of the perovskite films improved the lifetime of the perovskite films.
Figures 3.18b represent the pie chart of $\tau_t$. In CsFAMA perovskite GBs, ~39% of $\tau_t$ shows longer charge transport time (>5 µs), which is only ~17% and ~16% for RbCsFAMA and RbCsFAMA -SG, respectively. This indicates a more efficient charge transport capability at GBs of the Rb incorporated, and SG treated perovskite films.

Finally, in the GBs of RbCsFAMA-SG perovskite (Figure 3.18c), only ~19% of $L_D$ is <0.45 µm, which is ~55% and ~64% for RbCsFAMA and CsFAMA, respectively. On the contrary, ~48% of $L_D$ is >0.55 µm, which is much higher than ~4% and ~2% of $L_D$ for the samples, respectively.

We fabricated the p-i-n structured wide-bandgap solar cells using the CsFAMA, RbCsFAMA, and RbCsFAMA-SG perovskite films. We observed that the glove box (GBox) internal temperature and the delayed annealing affect the device performance. These process conditions were optimized accordingly to achieve the highest performance.
Figure 3. 19 SEM images of (a and c) immediate annealing and (b and d) delayed annealed perovskite films at different magnification. Scale bar in the images are 1 µm.

We have adopted the perovskite precursor's spin-coating technique to deposit the films and the antisolvent dripping to extract the solvents followed by thermal annealing. We have observed that the delayed annealing process influences the morphology, especially surface roughness, unreacted PbX₂, and grain size. We first investigated the film morphology by the annealing process. We investigated the effect of delayed annealing using the RbCsFAMA perovskite films and used two different processes: annealing immediately and waiting for 10 min followed by annealing, which we termed delayed annealing after spin-coating of the perovskite precursor solution. We found that both conditions resulted in almost similar grain size (Figure 3.19), but more PbX₂ residues on the film's surface was observed for the immediate annealed film (Figure 3.19). The immediate annealed films showed higher Rms roughness of 24.90 nm compared to 13.59 nm of delayed annealing. But it is established that excessive PbX₂ and higher surface roughness limit PSCs performance [95, 108]. Delayed annealing reduced the surface roughness and excess PbX₂, which motivated us to adopt this procedure to fabricate all of our devices.
Figure 3. 20 Delayed annealed perovskite films at different Process temperatures (GBox temperature during spin-coating) (a) 24.5 °C (b) 25.5 °C (c) 26.5 °C (d) 27.5 °C (e) 28.5 °C. Scale bar in the images are 1 µm.

3.5 Performance study of solar cells

Adopting the delayed annealing process, we now optimized the process temperature inside the GBox during spin-coating. We observed that the grain size is enormously regulated by the process temperature which noticeably affected the performance. We did the SEM of the perovskite films at a series of process temperatures (Figure 3.20) and found that there was a transition point (~26 °C) before which the grain size remained smaller. After that temperature, all the perovskite films showed almost similar (comparatively bigger) grain sizes. We made a series of devices at different process temperatures shown in Figures 3.21 to 3.25, and the optimum temperature was reached at 27.5 °C. Above this temperature, more PbX₂ precipitated at the perovskite surface.
Figure 3. J-V curves of PSCs at process temperature of 24.5 °C.

<table>
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<tr>
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<th>J_{sc}</th>
<th>V_{oc}</th>
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<td>1.04</td>
<td>0.62</td>
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<td>(R) 16.92</td>
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<td>(R) 16.47</td>
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<tr>
<td>RbCsFAMA-SG</td>
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<td>0.73</td>
<td>13.86</td>
</tr>
<tr>
<td></td>
<td>(R) 17.40</td>
<td>1.10</td>
<td>0.73</td>
<td>14.06</td>
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Figure 3. J-V curves of PSCs at process temperature of 25.5 °C.

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<tr>
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<td>1.07</td>
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<tr>
<td></td>
<td>(R) 17.17</td>
<td>1.09</td>
<td>0.69</td>
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<tr>
<td>RbCsFAMA</td>
<td>(F) 16.64</td>
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<td>13.16</td>
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<td>(R) 16.63</td>
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<td>RbCsFAMA-SG</td>
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<td>(R) 18.22</td>
<td>1.12</td>
<td>0.74</td>
<td>15.07</td>
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Figure 3. 22 J-V curves of PSCs at process temperatures of 25.5 °C.

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<tr>
<td>CsFAMA</td>
<td>(F)</td>
<td>16.72</td>
<td>1.13</td>
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<td></td>
<td>(R)</td>
<td>16.62</td>
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<td>1.15</td>
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<td>(R)</td>
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<td></td>
<td>(R)</td>
<td>18.23</td>
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Figure 3. 23 J-V curves of PSCs at process temperatures of 26.5 °C.

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<td>CsFAMA</td>
<td>(F)</td>
<td>17.18</td>
<td>1.13</td>
<td>0.722</td>
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</table>
After optimizing the process conditions, we adopted the delayed annealing and the GBox temperature 27.5 °C to fabricate our solar cell devices. Figure 3.26 shows the J-V curve of the PSCs at variable Rb mol%. We observed that 5 mol% Rb in perovskite precursor showed the highest efficiency. Table 3.2 shows all the photovoltaic parameters

<table>
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<tr>
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<th>J_sc</th>
<th>V_oc</th>
<th>FF</th>
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<td>(R)</td>
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<td>1.14</td>
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<td>RbCsFAMA-SG</td>
<td>(F)</td>
<td>18.64</td>
<td>1.16</td>
<td>0.75</td>
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<tr>
<td></td>
<td>(R)</td>
<td>18.85</td>
<td>1.16</td>
<td>0.75</td>
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</table>

Figure 3. 24 J-V curves of PSCs at process temperatures of 27.5 °C.

Figure 3. 25 J-V curves of PSCs at process temperatures of 28.5 °C.
of the champion cells. Higher Rb concentration reduced the performance, which is due to the suppression of perovskite with excess Rb (Figure 3.11).

Figure 3. 26 J-V curves of the champion cells of RbCsFAMA perovskite with different mol % of Rb.

Table 3. 2 Photovoltaic parameters of RbCsFAMA PSCs processed with different mol% of Rb.

<table>
<thead>
<tr>
<th></th>
<th>J_{sc} (mAcm^{-2})</th>
<th>V_{oc} (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Hysteresis Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Rb</td>
<td>(F) 17.18</td>
<td>1.13</td>
<td>0.72</td>
<td>14.01</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>(R) 17.12</td>
<td>1.14</td>
<td>0.72</td>
<td>14.11</td>
<td></td>
</tr>
<tr>
<td>5% Rb</td>
<td>(F) 17.91</td>
<td>1.16</td>
<td>0.75</td>
<td>15.68</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>(R) 17.98</td>
<td>1.16</td>
<td>0.75</td>
<td>15.59</td>
<td></td>
</tr>
<tr>
<td>10% Rb</td>
<td>(F) 17.06</td>
<td>1.14</td>
<td>0.77</td>
<td>14.90</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>(R) 17.00</td>
<td>1.14</td>
<td>0.78</td>
<td>15.17</td>
<td></td>
</tr>
</tbody>
</table>
To validate the superior performance of 5 mol% Rb, we made several devices at the same batch and confirmed that how Rb mol% affected the photovoltaic parameters, shown by the statistical deviation of the parameters of the RbCsFAMA solar cells in figure 3.27.

![Figure 3.27 Statistical deviation of the parameters of RbCsFAMA perovskite devices at different mol% of Rb.](image)

We also fabricated solar cells using SG technique with different amounts of guanidinium iodide in isopropyl alcohol (IPA) to see the device performances (Figure 3.28). We observed that 1 mg mL\(^{-1}\) GAI showed the highest performance (Table 3.3) as
higher concentration resulted in poor morphology with photoinactive hexagonal δ-FAPbI$_3$ and unreacted PbX$_2$ phases (Figure 3.14).

![Image of J-V curves](image)

Figure 3. 28 J-V curves of the SG treated champion cells of RbCsFAMA-SG perovskites with different GAI amounts.

We also prepared several devices at the same batch to validate the SG treated samples' superior performance at 1 mg mL$^{-1}$ GAI. The statistical derivations at different GAI amounts are seen in figure 3.29. We observed that a higher amount of GAI (>1 mg mL$^{-1}$) resulted in lower performance of the devices. We also observed a vast deviation in performance of the devices with a higher GAI amount. So, we adopted the 5 mol% Rb incorporation and 1 mg mL$^{-1}$ GAI SG treatment to make all our future devices.

Table 3. 3 Photovoltaic parameters of the PSCs processed with different amounts of GAI in SG technique.
<table>
<thead>
<tr>
<th>Secondary Growth (GAI amount per mL)</th>
<th>( J_{sc} ) (mA cm(^{-2}))</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Hysteresis Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mg/mL</td>
<td>(F) 17.91</td>
<td>1.16</td>
<td>0.75</td>
<td>15.68</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>(R) 17.98</td>
<td>1.16</td>
<td>0.75</td>
<td>15.59</td>
<td></td>
</tr>
<tr>
<td>1 mg/mL</td>
<td>(F) 18.61</td>
<td>1.17</td>
<td>0.79</td>
<td>17.16</td>
<td>0.0006</td>
</tr>
<tr>
<td></td>
<td>(R) 18.70</td>
<td>1.17</td>
<td>0.78</td>
<td>17.17</td>
<td></td>
</tr>
<tr>
<td>2 mg/mL</td>
<td>(F) 16.45</td>
<td>1.09</td>
<td>0.76</td>
<td>13.67</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>(R) 16.24</td>
<td>1.11</td>
<td>0.77</td>
<td>13.93</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3. 29 Statistical deviation of the SG treated RbCsFAMA–SG perovskite devices at different GAI amount.
After adopting the optimized process conditions, the photovoltaic performance of Rb incorporated and SG treated films were evaluated by measuring the J-V values of the pin structured PSCs. Figure 3.30 showed the J-V curves of both forward and reverse scans under AM 1.5G illumination. All the devices showed negligible hysteresis behavior (Table 3.4) due to the absence of negative defects (Cation vacancies) at perovskite/ETL interfaces, confirmed by the CPD measurements (Figure 3.15) [109]. The CsFAMA device exhibited a short circuit current density ($J_{sc}$) of 17.18 mA cm$^{-2}$, fill factor (FF) of 72.2%, and the open-circuit voltage ($V_{oc}$) of 1.13V, yielding a PCE of 14.01%. By contrast, the photovoltaic parameters for RbCsFAMA were determined with a $J_{sc}$ of 17.99 mA cm$^{-2}$, FF of 75.5%, a $V_{oc}$ of 1.16 V, and a PCE of 15.75%. Finally, the champion RbCsFAMA-SG device delivered a PCE of 17.71% with a $V_{oc}$ of 1.19, $J_{sc}$ of 18.53 mA cm$^{-2}$; and FF of 80.3%. The integrated $J_{sc}$ values calculated from the external quantum efficiency (EQE) spectra (Figure 3.30b) were in close agreement with the values obtained from the J-V curves. Figure 3.30c shows the statistical data of 30 individual devices. Rb-incorporated and SG treated films showed higher repeatability than CsFAMA devices. The average values with standard deviation (SD) are shown in table 3.4.
Figure 3. 30 (a) J-V curves of the champion devices of CsFAMA, RbCsFAMA and RbCsFAMA-SG perovskite solar cells; (b) EQE of the corresponding solar cell devices; (c) Statistical deviation of the parameters of perovskite devices.

Table 3. 4 Photovoltaic parameters of the champion devices of CsFAMA, RbCsFAMA, and RbCsFAMA-SG perovskite solar cells.

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mAcm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Average±SD Hysteresis Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsFAMA</td>
<td>(F) 17.18</td>
<td>1.13</td>
<td>0.722</td>
<td>14.01</td>
<td>13.36±0.56 0.011</td>
</tr>
<tr>
<td></td>
<td>(R) 17.19</td>
<td>1.14</td>
<td>0.723</td>
<td>14.11</td>
<td></td>
</tr>
<tr>
<td>RbCsFAMA</td>
<td>(F) 17.99</td>
<td>1.16</td>
<td>0.755</td>
<td>15.75</td>
<td>15.24±0.26 0.01</td>
</tr>
<tr>
<td></td>
<td>(R) 17.98</td>
<td>1.16</td>
<td>0.748</td>
<td>15.59</td>
<td></td>
</tr>
</tbody>
</table>
We also did the stability study test under illumination for 3600 sec (Figure 3.31a). We observed that the power gradually decreases with time for CsFAMA devices. But, in the case of RbCsFAMA and RbCsFAMA-SG devices, no change of power is observed. We assume that halide segregation is the reason behind the lower power output with time under continuous illumination. Bromide-rich wide-bandgap perovskite shows halide segregation under continuous illumination, which resulted in I-rich and Br-rich regions. I-rich areas are the smaller-bandgap region which lowers the exciton energy [110]. This may drive the halide segregation process under illumination [111-113]. This I-rich region acts as the trap states and reduces the open-circuit voltage [60, 114]. CsFAMA showed a similar trend at continuous illumination. The open-circuit voltage gradually decreased with time (Figure 3.31b), whereas RbCsFAMA showed a small change. RbCsFAMA-SG showed almost no change under continuous illumination. This indicates the defect passivation of the Rb-incorporated and SG-treated film [115, 116].

<table>
<thead>
<tr>
<th>Device</th>
<th>(F)</th>
<th>1.19</th>
<th>0.793</th>
<th>17.57</th>
<th>16.90±0.32</th>
<th>0.008</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbCsFAMA-SG</td>
<td>18.62</td>
<td>1.19</td>
<td>0.793</td>
<td>17.57</td>
<td>16.90±0.32</td>
<td>0.008</td>
</tr>
<tr>
<td>(R)</td>
<td>18.53</td>
<td>1.19</td>
<td>0.803</td>
<td>17.71</td>
<td>16.90±0.32</td>
<td>0.008</td>
</tr>
</tbody>
</table>

![Graph (a)](image-a.png)  
![Graph (b)](image-b.png)
Figure 3. 31 (a) Stabilized power output at maximum power point under continuous illumination; (b) Open circuit voltage change measured under continuous illumination.

We have also studied the devices' stability test in ambient and inert conditions (Figure 3.32). In inert condition, the stability of the devices is done inside the glove box. On the other hand, the ambient condition was 24±1 °C with 30±5 % humidity. In both cases, SG-treated films showed the highest stability. It indicates that the devices' stability is greatly influenced by the defect passivation of the perovskite layer after incorporating Rb and performing the SG technique.

Figure 3. 32 Photovoltaic parameters of all devices at inert (marked by solid lines) and ambient conditions (marked by dash lines). The inert condition means inside the glove
box, and the ambient condition is 24±1 °C with 30±5 % humidity. The photovoltaic parameters have been divided by the initial data and have been normalized.

3.6 Solar cell device characterization

Photoluminescence was performed for the corresponding perovskite thin films on the glass substrate (Figure 3.33a) to get the insight of defect passivation. It was observed that the PL intensities were relatively higher with Rb and increased more after SG denoting that recombination in the perovskite layer was suppressed. This indicates the reduction of surface non-radiative recombination defects [78] due to surface passivation [117]. Thin PCBM layers were also deposited atop the perovskite films and excited from the ETL sides. More evident PL quenching was observed for the RbCsFAMA/PCBM film which is further improved after SG (Figure 3.33b) in RbCsFAMA-SG/PCBM film. This indicates lower recombination at the interface and higher charge extraction ability of the film after the treatment.

Figure 3.33 (a) Photoluminescence (Steady-state) of the perovskite films on the glass; (b) Photoluminescence spectra of CsFAMA, RbCsFAMA, and RbCsFAMA-SG perovskite thin films with a thin PCBM electron transport layer.
The superior characteristics of the RbCsFAMA film with the further increased performance following SG treatment were also confirmed by Nyquist plots performed in the dark at 0.3 V bias [118]. Figure 3.34 shows the larger charge recombination resistance of treated devices. Reduction of traps and unreacted PbX$_2$ at the surface reduced charge recombination and improved the contact and charge collection efficiency at the ETL interface [119-121].

![Nyquist plots of solar cell devices under the dark condition at 0.3 V bias; Equivalent circuit used for data fitting.](image)

Besides, the collaboration of the Rb addition and SG treatment showed smaller root-mean-square (rms) roughness than that of CsFAMA films (Figure 3.35), which can also contribute to effective charge collection and transport [64, 122].
Figure 3. 35 Root-mean-square (RMS) roughness of the perovskite thin films. Area of the images is 2 µm × 2 µm.

The dark current measurement (Figure 3.36) of the corresponding devices also demonstrated the suppressed charge carrier recombination after introducing Rb and SG. A less steep slope indicates a higher $J_0$ value (Table 3.5) of CsFAMA PSCs suggested a high leakage current which was expected due to higher defect densities at the GBs [123]. A more steeper slope was observed in RbCsFAMA with the Rb addition. Later, passivation of the defects was significantly suppressed after SG treatment using GAI, which resulted in the highest steeper slope of the dark J-V curve. Additionally, both series and shunt resistances (Table 3.5) of the corresponding devices support the above trend. The series resistance decreased, and the shunt resistance increased with Rb and performing SG treatment. SG treated films showed the lowest series resistance due to the conversion of excess lead halides to perovskite, whereas higher shunt resistance means the reduction of defects and trap sites in the perovskite film.
Figure 3. Dark J-V measurement of the SCs using CsFAMA, RbCsFAMA, and RbCsFAMA-SG perovskite layers.

Table 3. Photovoltaic parameters, $R_s$, $R_{sh}$, and $J_0$ under dark conditions.

<table>
<thead>
<tr>
<th></th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (Ω)</th>
<th>$J_0$ (Acm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsFAMA</td>
<td>4.23</td>
<td>3.4 × 10$^3$</td>
<td>6.3 × 10$^{-9}$</td>
</tr>
<tr>
<td>RbCsFAMA</td>
<td>4.0</td>
<td>13.1 × 10$^3$</td>
<td>3.03 × 10$^{-16}$</td>
</tr>
<tr>
<td>RbCsFAMA</td>
<td>2.85</td>
<td>181.9 × 10$^3$</td>
<td>7.5 × 10$^{-17}$</td>
</tr>
</tbody>
</table>

Further investigation of the charge carrier recombination was done by the current-voltage measurement at different light intensities, as shown in figure 3.37. We acquired the Voc and Jsc values in different light intensity from the J-V curves, which is used to study the defect passivation of the perovskite layer after Rb incorporation and SG treatment.
Figure 3. 37 J-V characteristic curves of CsFAMA, RbCsFAMA, and RbCsFAMA-SG perovskite solar cells at different light intensities.

Most of the photogenerated charge carriers will be recombined at open-circuit conditions. In this condition, the recombination mechanism can be studied using the following formula [78].

\[ V_{oc} \propto n \frac{kT}{q} \ln(I) \]

where \( k \) is the Boltzmann constant, \( T \) indicates the temperature, and \( q \) is the electron charge.
SRH mechanism indicates that electron and hole recombination is dominated by recombination centers and traps known as monomolecular recombination. When the slope value is greater than the unity of $\frac{kT}{q}$, SRH recombination is dominant [79]. Lower the value or close to unity means a reduction in monomolecular SRH recombination [80], and bimolecular recombination is dominant [81]. Figure 3.38 shows that the slope decreased from 1.37 kT/q (FAMACs) to 1.20 kT/q and then to 1.13 kT/q after incorporating Rb and SG, respectively. This indicated the effective reduction of the trap-assisted recombination [124].

![Figure 3.38 V_{oc} versus light intensity of CsFAMA, RbCsFAMA and RbCsFAMA-SG perovskite solar cells at different light intensities.](image)

Charge carrier collection and transport mechanism can also be studied from analysis of $J_{sc}$ vs. incident light intensity. It also provides valuable information about the charge recombination kinetics. The dependence of $J_{sc}$ vs. light intensity is related by the equation below [82].

$$J_{sc} \propto I^\alpha$$
where $I$ indicates the light intensity, and $\alpha$ is derived from the slope. The value of $\alpha$ equals unity means devices with no space charge effects [83]. Value of $\alpha$ close to unity indicates reduced recombination and potential barrier [84, 85]. Significant deviation of the value of $\alpha$ from unity attributes to bimolecular recombination [86] and significantly affects charge collection [87]. In figure 3.39, the exponential factor $\alpha$ derived from the relation $J_{sc} \propto I^\alpha$ increased from 0.875 (CsFAMA) to 0.889 (RbCsFAMA). RbCsFAMA-SG based devices showed the highest value of 0.90 compared to RbCsFAMA and CsFAMA, revealing negligible space charge limit and efficient charge collection and transport [84].

![Figure 3.39](image-url)

**Figure 3.39** $J_{sc}$ versus light intensity of CsFAMA, RbCsFAMA and RbCsFAMA-SG perovskite solar cells at different light intensities.

To support the above two characterizations, we performed transient photovoltage (TPV) and photocurrent (TPC) decay at open-circuit and close circuit conditions, respectively (Figure 3.40). These measurements were done by exposing the solar cells with a nanosecond laser pulse. No background light was used for photocurrent,
and charges are extracted in short-circuit (50 Ω) conditions. On the other hand, 1 sun was used for photovoltage measurement using open-circuit (1 M Ω) condition. In TPC measurement, all charges are collected in an external circuit, and the decay curve was fitted using a mono-exponential equation to calculate the charge transport time. In the case of TPV, the decay curve was fitted to calculate the charge carrier lifetime.

Figure 3.40 (a) Photocurrent decay measured by transient photocurrent (TPC) at short circuit condition to calculate the charge transport time; (b) Photovoltage decay under illumination by transient photovoltage (TPV) at open circuit condition to calculate the charge carrier lifetime.

We observed that the charge transport time gradually decreases and lifetime increases after Rb-incorporation and SG treatment Table 3.6. The transport time and the lifetime of CsFAMA devices were 685 and 790 ns, respectively. The shortest transport time of 502 ns was observed in the case of RbCsFAMA-SG devices. RbCsFAMA-SG also delivered the longest charge carrier lifetime of 1249 ns.

Table 3.6 Charge carrier transport and lifetime calculated from the TPC and TPV measurements.
<table>
<thead>
<tr>
<th></th>
<th>Charge transport time (ns)</th>
<th>Charge carrier lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsFAMA</td>
<td>685</td>
<td>790</td>
</tr>
<tr>
<td>RbCsFAMA</td>
<td>633</td>
<td>937</td>
</tr>
<tr>
<td>RbCsFAMA-SG</td>
<td>502</td>
<td>1249</td>
</tr>
</tbody>
</table>

Furthermore, Mott-Schottky characterization showed higher built-in potential ($V_{bi}$) of 1.01 V and 1.05 V for RbCsFAMA and RbCsFAMA-SG, respectively compared to 0.93 V for CsFAMA PSCs (Figure 3.41). This measurement is a hint of the location of the Fermi level [125]. The x-intercept of the linear region of the Mott-Schottky plot is the value equal to the flat-band potential. From figure 3.41, we realized that CsFAMA solar cells have a value of 0.92 V which increased to 1.01 V and 1.05 V for RbCsFAMA and RbCsFAMA-SG solar cells, respectively. Higher $V_{oc}$ is understandable from higher $V_{bi}$, and an indication of improved charge carrier extraction.

![Mott-Schottky curves of the CsFAMA, RbCsFAMA and RbCsFAMA-SG perovskite solar cells.](image)

Figure 3. 41 Mott-Schottky curves of the CsFAMA, RbCsFAMA and RbCsFAMA-SG perovskite solar cells.
Improved charge extraction realized from the Mott-Schottky measurement is further supported by the mobility measurement. To calculate the mobility of the solar cells, we performed the photoinduced charge carrier extraction with linearly increasing voltage (Photo CELIV) measurement [72] as depicted in figure 3.42. It is observed from the figure that it took the shortest time to get the peak current from the RbCsFAMA-SG solar cells (Figure 3.42). It indicates the highest charge mobility in RbCsFAMA-SG. The lowest charge mobility is observed in CsFAMA wide-bandgap perovskite solar cells. This indicates the lower defects and trap states in RbCsFAMA-SG perovskite film. This is because the SG treatment converted the excess lead halides to perovskites and also reduced the positive defects at the grain boundary, which ensures the efficient extraction and flow of the charges from the perovskites to the charge transport layers [126], and is further confirmed by the space charge limited current (SCLC) measurement.

![Mobility measurement using (a) Photo-CELIV curve and (b) applied ramp voltage of CsFAMA, RbCsFAMA and RbCsFAMA-SG perovskite solar cells.](image)

To gain further insights into efficient charge extraction, we quantified the defect density at the interface by employing the space charge limited current (SCLC) model of
an electron-only device. The electron-only device was used to allow the electrons only to flow in one direction. The trap-filled limit voltage ($V_{TFL}$) decreased from 0.39 V to 0.25 V after adding 5 mol% Rb and then to 0.16 V after SG treatment (Figure 3.43). The trap state density ($N_t$), calculated using $V_{TFL}$, shows that Rb had a substantial impact on reducing the traps as trap state density reduces from $5.52 \times 10^{15}$ cm$^{-3}$ to $3.54 \times 10^{15}$ cm$^{-3}$ which was further reduced to $2.26 \times 10^{15}$ cm$^{-3}$ after SG treatment. The reduction of the trap density in SCLC measurement further validates passivation, which is why PSCs performance was increased.

![Graph showing space charge limited current of the electron only devices.]

**Figure 3.43 Space charge limited current of the electron only devices.**

### 3.7 Conclusions

In summary, this work demonstrates an efficient strategy of combining cation management and post-growth technique to passivate GB defects in wide-bandgap PSCs to achieve excellent device performance. By introducing Rb to triple cation perovskite, a novel quadruple-cation 1.78 eV wide-bandgap perovskite layer is formed. In addition, an SG technique using GAI was applied which produces a champion device efficiency of 17.71%. In-depth analysis of GB defects correlating to device performance of the
perovskite films was performed using KPFM and nanoscale charge carrier dynamics mappings to visualize the defect passivation achieved. Our findings indicate that positively charged defects (i.e., halide vacancies) have a large effect on the performance of the wide bandgap PSCs with a severe loss in FF and $V_{oc}$. Such trap-assisted defects can be partially mitigated by cation management and further significantly minimized by SG treatment. Besides, SG using GAI can significantly reduce unreacted PbX$_2$ precipitates from the surface of the film, converting them to the perovskite phase to form a more compositionally uniform and smooth film morphology. We expect that the findings of defects assessments in this work can provide proper guidelines to enable high-efficiency perovskites and realize high-efficiency tandem cells.
4.1 Introduction

In photovoltaic technologies, the remarkable progress of perovskites gives us the hope to fabricate highly efficient and cheaper solar cells. Tandem SCs with an efficient wide-bandgap can increase the efficiency further in a more cost-effective way. Unfortunately, wide-bandgap perovskites have several issues among which the presence of excess lead halides is harmful and responsible for the inferior performance and lower stability. Several factors can affect the presence of excess lead halides (PbX$_2$) on the perovskite, and this excess PbX$_2$ can locate at any position, such as on the surface, grain boundaries and/or at the interface of the perovskite and charge transport layer [127]. Our previous project has observed the adverse effect of excess PbX$_2$ on the perovskite surface [68]. Several groups also reported that excess PbX$_2$ in perovskite films could be detrimental to the performance of the device [95, 128]. It is crucial to realize the origin of excess PbX$_2$ and develop a facile way to remove this unwanted phase from perovskite. In this project, we have developed a technique to regulate the crystallization of the perovskite layer and minimize the formation of excess PbX$_2$ on the surface of the perovskites. This was accomplished by adding poly (methyl methacrylate) (PMMA) in the antisolvent and dripping during spin-coating.

4.2 Perovskite layer deposition process

To control perovskite crystallization without excess PbX$_2$ on the surface, we have added a small amount of PMMA (0.1 mg mL$^{-1}$) in ethyl acetate (EA) anti-solvent. During the spin-coating of the perovskite precursor solution. EA containing PMMA was dripped before the end of the second step followed by thermal annealing.
102

Figure 4.1 Schematic diagram of the PMMA assisted fabrication of the RbCsFAMA wide-bandgap perovskite layer.

4.3 Results and discussion

We first investigated to understand the cause behind the formation of excess lead halides in RbCsFAMA wide-bandgap perovskite. In our structure, we added an excessive amount of lead halides to the perovskite precursor solution as additional lead halides to improve the electrical, optical, and physical properties of perovskites [129-131]. We investigated our perovskite with different annealing temperatures and observed that an additional amount of PbX$_2$ in precursor solution is not the reason behind the excess PbX$_2$ phase on perovskite film. We also observed from the cross-sectional SEM images that the excess PbX$_2$ is only visible on the surface of the perovskite (Figure 3.9). Figure 4.2 shows thermal and microwave-annealed (discussed in chapter 5) perovskite films at different temperatures and power. Our perovskite films showed no excess PbX$_2$ when the layer was processed at lower temperature and power (Figure 5.2). As the temperature or the power was increased, the perovskite films showed excess PbX$_2$ on the surface. As the excess PbX$_2$ is only visible on the surface at higher annealing temperatures, we assume that the presence of this phase is due to the degradation of the perovskite as
methylammonium is a volatile species and can quickly evaporate leaving residual PbX$_2$ [132]. The surface of the perovskite dries fast, and we believe that degradation also starts from the surface, which is confirmed by the excess PbX$_2$ on the surface of the film.

We also observed from figure 4.2 that at lower annealing temperature/microwave power, perovskites are without excess PbX$_2$ which is highly desirable. But the grain sizes are smaller compared to that of the films processed at a higher temperature. To achieve the best performance from the devices, bigger grains without PbX$_2$ is crucial [133].

![Figure 4.2](image)

**Figure 4.2** Effect of process temperature and microwave power on the formation of excess lead halides. Scale bar: 1 µm.

To realize a high-quality perovskite, we need to achieve two goals: slow down the surface crystallization of the perovskite and locking the position of the components to stop volatilization. Our finding suggests that both can be achieved by introducing PMMA on the surface of the perovskite film. We have observed that PbI$_2$ can make an adduct with PMMA, as seen in figure 4.3. Figure 4.3 displays the FTIR transmittance spectra
where the C=O bond in PMMA shows a peak at around ~1730 cm\(^{-1}\). This peak is shifted to lower energy after adding PbI\(_2\). It indicates that PbI\(_2\) makes an adduct with the C=O bond. Due to this bonding, perovskite crystallization slows down in the presence of PMMA \([134]\). Instead of adding PMMA in the perovskite precursor solution, we added PMMA in antisolvent to keep it on the surface of the film.

![FTIR spectra](image)

Figure 4. 3 FTIR transmittance spectra of PMMA: PbI\(_2\) mixture with a molar ratio of 1:1.5.

We used different amounts of PMMA in EA antisolvent to see the effect of PMMA on the morphology of the perovskites (Figure 4.4). We observed that perovskite without PMMA has lots of excess PbX\(_2\) on the surface, noticeable by the white spots. After adding 0.1 mg per mL antisolvent, a significant part of the white spots was removed. When we added 0.2 mg, we achieved our desired perovskite film without any white spots, which indicates PbX\(_2\) free perovskite film. After adding more PMMA, we saw new species (brighter signal) due to the charge accumulation during SEM resulting
from the nonconductive PMMA. To crystallize the perovskite, we used the 100 °C annealing temperature to ensure bigger grains. We achieved our desired big grain perovskite without PbX$_2$ with 0.2 mg PMMA in antisolvent.

Figure 4. 4 SEM images of perovskite films with different amounts of PMMA in EA antisolvent. Scale bar: 1 µm.

To study the charge transport behavior of the perovskite films after adding PMMA, we conducted current sensing atomic force microscope (CS-AFM) measurements. The CS-AFM images of perovskite films with different amounts of PMMA under a bias are shown in figure 4.5. We observed that excess lead halides result in dark spots in CS-AFM image, which indicates the nonconductive behavior of PbX$_2$ and less charge collection compared to the bright spots. After adding 0.1 mg PMMA, the
number of those nonconductive dark spots was reduced which increased the overall average current of the perovskite film. We observed a uniform current distribution of the perovskite film after adding 0.2 mg PMMA which supports the absence of PbX₂ on the surface of the perovskite. We observed a little reduction of the average current, which indicates the uniform distribution of PMMA on the surface as desired. After adding PMMA > 0.2, perovskite also showed uniform current distribution, but the average current reduced drastically which is due to the presence of access PMMA as evident from SEM images (Figure 4.4)

PMMA also passivated the defects at the perovskite grains. Figure 4.5 shows brighter spots at the perovskite grains which indicate charge accumulation at the grain boundaries due to trap states. After adding 0.2 mg PMMA, the grain boundaries showed similar current flow like the grain interior with dark spots in some grain boundary areas, which indicates defect passivation and minimization of trap states [122, 135-138].
Figure 4.5 Current sensing AFM images of perovskite films processed with different PMMA amounts in antisolvent. Scale bar: 500 nm.

We also observed from the topography images that the surface roughness of the perovskite films decreased after adding PMMA. Perovskite film without PMMA showed the highest roughness of 20.5 nm, which gradually decreased with increasing the PMMA amount. It indicates that PMMA laminated the surface and make the surface smoother. We desire to achieve that lamination for position locking of the components and stop the evaporation of methylammonium from the surface. A smooth surface is also beneficial for charge extraction and transport as it facilitates the efficient interface between perovskite and the charge transport layer deposited atop it [139-141].

Figure 4.6 AFM topography images with RMS surface roughness of the perovskite layer with different PMMA amounts in antisolvent. Scale bar: 500 nm.
Figure 4.7 shows the J-V characteristics of the SCs with different amounts of PMMA. Without PMMA, the champion PSC showed an efficiency of 15.97% with J_{sc} of 18.02 mA cm^{-2}, V_{oc} of 1.16, and FF 76.4%. After adding 0.1 mg PMMA, the V_{oc} and FF increased to 1.17 and 78.9%, respectively, with an efficiency of 16.88%. Finally, the PCE of PSC with 0.2 mg PMMA showed the highest efficiency of 18.18%, where the V_{oc} and FF reached 1.20 and 82.4%, respectively. The higher values of V_{oc} and FF indicate better charge extraction and defect passivation of the perovskite films. We observed that the J_{sc} did not change a lot after adding PMMA. Adding PMMA more than 0.2 mg resulted in poor performance of the device due to inefficient charge extraction from perovskite to ETL. The photovoltaic parameters for different amounts of PMMA extracted from the J-V curves are shown in table 4.1.

![Figure 4.7 J-V and EQE of the champion perovskite solar cell devices](image)

Table 4.1 Photovoltaic parameters of the PSCs with different PMMA amounts in antisolvent

<table>
<thead>
<tr>
<th>PMMA 0 mg (F)</th>
<th>J_{sc} (mA cm^{-2})</th>
<th>V_{oc} (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Average±SD Hysteresis Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>18.02</td>
<td>1.16</td>
<td>0.764</td>
<td>15.97</td>
<td>15.51±0.15</td>
</tr>
<tr>
<td>PMMA</td>
<td>(F)</td>
<td>18.29</td>
<td>1.17</td>
<td>0.789</td>
<td>16.88</td>
</tr>
<tr>
<td>---------------</td>
<td>-----</td>
<td>-------</td>
<td>------</td>
<td>-------</td>
<td>---------------------</td>
</tr>
<tr>
<td>PMMA 0.1 mg</td>
<td>(R)</td>
<td>18.13</td>
<td>1.17</td>
<td>0.789</td>
<td>16.73</td>
</tr>
<tr>
<td>PMMA 0.2 mg</td>
<td>(F)</td>
<td>18.37</td>
<td>1.20</td>
<td>0.824</td>
<td>18.18</td>
</tr>
<tr>
<td>PMMA 0.3 mg</td>
<td>(R)</td>
<td>18.53</td>
<td>1.20</td>
<td>0.815</td>
<td>18.12</td>
</tr>
<tr>
<td>PMMA 0.3 mg</td>
<td>(F)</td>
<td>16.52</td>
<td>1.13</td>
<td>0.72</td>
<td>13.43</td>
</tr>
<tr>
<td>PMMA 0.3 mg</td>
<td>(R)</td>
<td>16.48</td>
<td>1.13</td>
<td>0.705</td>
<td>13.13</td>
</tr>
</tbody>
</table>

Figure 4.8 shows the histogram of all the photovoltaic parameters of the PSCs. It is seen from the figures that $V_{oc}$ and FF are mainly affected by the PMMA, and the performances of the devices are highly repeatable. The devices with 0.3 mg PMMA showed inferior performance which is even lower than those without PMMA. It proves that nonconductive species on the surface of the perovskite are detrimental and need to minimize to achieve higher performance. Our crystallization process can halt the formation of nonconductive PbX$_2$ and increase the devices' performance and stability.
Figure 4. 8 Histogram of the all the photovoltaic parameters of the perovskite solar cell devices with different PMMA amounts in antisolvent.

We also have studied the stability of the devices with different amounts of PMMA (Figure 4.9). It is observed that the superior quality of the perovskite films can improve the perovskite devices' stability. PMMA with 0.2 mg showed the highest stability of more than 90% after 500h in ambient conditions. We hypothesized that PMMA laminated the surface of the perovskite and protected it from moisture which is seen from the contact angle measurements of the perovskite films with water (Figure 4.10). But PMMA is not enough to protect the perovskite as PMMA with 0.3 mg shows the lowest stability among all the PSCs. It indicates that PMMA and the quality of the
perovskite films are both critical for stability as degradation starts from the defect sites of the perovskite layer [142, 143].

Figure 4. 9 Stability test of the solar cell devices in inert and ambient conditions.
Figure 4. 10 Contact angle measurement test of the perovskite films with different PMMA amounts in antisolvent.

4.4 Conclusions

We introduced a crystallization method to prepare perovskite films with superior electronic property and morphology and fabricated the PSCs. We observed that up to a certain amount of PMMA (0.2 mg mL⁻¹) improved the performance of the devices by halting the PbX₂. This is done by slower crystallization and locking the perovskite components by laminating the surface of the perovskite film using PMMA. High-quality films with better charge transfer properties and fewer defects improve the performance and stability of the devices.
CHAPTER 5 MICROWAVE-ASSISTED FABRICATION OF EFFICIENT WIDE-BANDGAP PEROVSKITE SOLAR CELLS

5.1 Introduction

Metal halide perovskites are considered the most promising solar energy technology because of their distinct properties, low cost, easy fabrication due to solution-processibility, band tunability, etc. [144-146]. Perovskite film quality plays a vital role in achieving the higher performance of the solar cells [64, 67, 147, 148]. The essential properties are larger grain (with fewer grain boundaries), high crystallinity, uniformity, good coverage of the film, and fewer defects. Several strategies have been proposed to process high-quality perovskite films, such as spin-coating with one or two steps, thermal evaporation, antisolvent, solvent-assisted crystallization, vacuum flashed and chemical vapor-assisted processes, etc. [124, 149-152]. Most of these strategies also require post-thermal annealing to complete the crystallization and further growth of perovskite crystals. The standard procedure to anneal the perovskite films is using the hotplate where the heat is transferred from the surface of the hotplate to the perovskite through the glass substrate. This procedure leads to nonuniform heat distribution, which ultimately ended up with inhomogeneous perovskite films. Several other limitations of this process are the long process time and the degradation of the perovskite film. Degradation happens due to volatile components such as methylammonium and iodine which promotes unwanted miscellaneous perovskite phases. This long thermal annealing process increases the fabrication cost, lowers the stability and the performance of the SCs. Thus, it is necessary to develop a rapid fabrication process to minimize the cost and eliminate the formation of miscellaneous phases in perovskite films.
This project has developed a rapid and cost-effective way to process RbCsFAMA wide-bandgap perovskite using the microwave. We observed that microwave power and process time alter the crystallinity and morphology of the perovskite, and we achieved high-quality perovskite films using 400 W microwave power with a duration of 90 sec which is much shorter than the time required to achieve similar quality perovskites using thermal annealing (~1 hour). The high-quality perovskites achieved in this short time is the uniform distribution of the heat due to the conversion of microwave power at the molecular level within perovskite.

5.2 Perovskite layer deposition process

Figure 5.1 shows the schematic of the thermal and microwave processed (MWP) perovskite. After spin-coating, we need to anneal the perovskite film at 100 °C for 25 minutes which further requires another 30 minutes to cool down before depositing the ETL. In MWP, only 90 sec at 400 W is required to get similar quality perovskite film.

Figure 5. 1 Schematic representation of the thermal and microwaved processed perovskite
5. 3 Results and discussion

We observed that a controlled microwave power level is essential to achieve the desired perovskite films. In the beginning, we conducted our research using a household microwave with a power level of 1000 W. We observed that the perovskite films did not cover the whole area (Figure 5.2). It may occur because of the very rapid crystallization of the perovskite film at this high power.

![SEM images of perovskite films using a household microwave at 1000 W for 2 minutes.](image)

**Power level: 25  Power level: 50  Power level: 100**

Figure 5. 2 SEM images of perovskite films using a household microwave at 1000 W for 2 minutes.

We observed that at low power levels (indicated in the power knob), representing the same 1000 W power but for a less period running in a cycle can produce a pure perovskite phase with a little peak of PbX₂ at ~12.8 ° (Figure 5.3b). The full power level of 1000 W degraded the perovskite as seen by the different phases below ~14 ° in XRD data (Figure 5.3b). It also showed the highest absorption (Figure 5.3a) which is because of the light scattering due to the higher surface roughness as seen from the SEM images (Figure 5.2).
Figure 5. 3 XRD and UV-Vis absorbance spectrum of the perovskite films using a household microwave with a constant power level of 1000 W for 2 minutes.

Having been motivated by the crystallinity and absorption of the MWP perovskite films using household microwave, we conducted our experiments using a lab-based microwave (BP-095) with variable power level ranging from 25 W to 1000W. We purchased the microwave from Microwave Research & Applications, Inc. We prepared perovskite films using a series of different microwave power levels ranging from 50 W to 600 W. We observed that the microwave power level significantly impacted the morphology of the perovskite films. At a low power level, the grain size of the perovskites was smaller. This is because of the higher nucleation rate than the crystal growth kinetic resulting in a more perovskite seed layer which produces a larger number of grains with smaller size. At power level 400 W for 60 sec, a sudden change in grain size was observed. We assume that at this power level, perovskite seeds grow faster than the formation of nuclei, which results in a smaller number of grains with the larger size. Higher than 400 W microwave power degrades the perovskite films confirmed by the white spots due to the nonconductive PbX₂ phase.
Perovskite films formation during this short period is due to the unique properties of microwave heating. Microwave heating can reduce the process duration from hours to minutes and is commonly used in process temperatures > 1000 °C [153-155]. In our case, the polar solvent in our perovskite films (DMF, DMSO and ethyl acetate) absorbs the high-frequency microwave and gets heated. In addition to the heating from the solvents, the ITO substrate absorbs the microwave and delivers uniform heating throughout the substrate. The synergy of these two heating processes results in rapid and uniform heating of the perovskite films [156].

Figure 5. 4 SEM images of perovskite solar cells using different power of lab-based microwave oven. Scale bar: 1 µm.
From figure 5.4, we observed a transition in morphology from 300 to 400 W. Both the microwave power levels were studied to understand the process further. We observed that the bigger grains were achievable with lower power for a longer process time too (Figure 5.5). At 300 W, we get a perovskite grain size similar to 400W, but with a higher process time, as shown in figure 5.6. But the perovskite started degrading during that time, as shown in figure 5.6.

Figure 5. 5 Effect of microwave power and process time on the morphology of wide-bandgap perovskite layer. Scale bar: 1 µm.
Degradation of perovskite with a longer process time at 300 W was also visible from the UV-Vis absorption spectra and XRD data (Figure 5.7). It is seen from the XRD that the (001) PbX\textsubscript{2} peak at ~12.8 ° is more intense with time. Other non-perovskite phases are also visible at higher process time. Degradation of perovskite is also supported by the lower absorption of the perovskite films than that processed with 1 minute. Scale bar: 1 µm.
We also fabricated the solar cells with the perovskite film processed at 300 W with different annealing periods (Figure 5.8), and the photovoltaic parameters are represented in table 5.1. Higher processing time degrades the perovskite film which is reflected in the lower $J_{sc}$ of the solar cells, but the overall performance increases up to 5 min processing time. This is because of the improved fill factor (FF) and the $V_{oc}$, directly related to the defect sites. As the grain size increased, perovskite films produced lower grain boundaries that contain most of the defects [65, 69, 157]. But with the processing time of 7 minutes, perovskite degrades a substantial amount, as seen from the XRD image, which deteriorated the performance of the solar cells.
Figure 5.8 J-V data of the PSCs processed at 300 W with different time.

Table 5.1 Photovoltaic parameters of the champion solar cells processed at 300 W.

<table>
<thead>
<tr>
<th></th>
<th>J_{sc}</th>
<th>V_{oc}</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 W (1 min)</td>
<td>(F) 17.00</td>
<td>1.05</td>
<td>0.63</td>
<td>11.15</td>
</tr>
<tr>
<td></td>
<td>(R) 16.84</td>
<td>1.07</td>
<td>0.63</td>
<td>11.31</td>
</tr>
<tr>
<td>300 W (3 min)</td>
<td>(F) 16.01</td>
<td>1.10</td>
<td>0.65</td>
<td>11.49</td>
</tr>
<tr>
<td></td>
<td>(R) 15.96</td>
<td>1.12</td>
<td>0.67</td>
<td>11.91</td>
</tr>
<tr>
<td>300 W (5 min)</td>
<td>(F) 15.60</td>
<td>1.13</td>
<td>0.73</td>
<td>12.81</td>
</tr>
<tr>
<td></td>
<td>(R) 15.61</td>
<td>1.14</td>
<td>0.74</td>
<td>13.23</td>
</tr>
<tr>
<td>300 W (7 min)</td>
<td>(F) 15.50</td>
<td>1.14</td>
<td>0.56</td>
<td>9.97</td>
</tr>
<tr>
<td></td>
<td>(R) 14.92</td>
<td>1.15</td>
<td>0.57</td>
<td>9.69</td>
</tr>
</tbody>
</table>

Figure 5.9 shows the histogram of all the photovoltaic parameters of the solar cells processed at 300 W at different times. It also supports the gradual decrease of the J_{sc} and higher V_{oc} and FF up to 5 min processing time. This study concluded that 300 W is not a suitable power to achieve higher efficiency in this wide-bandgap structure.
The grain size of the MWP perovskite films increased drastically after applying 400 W power (Figure 5.10). We observed that with time (90 sec) the average grain size increases slightly, indicating the uniform heating of the film in all directions. Uniform heating promotes homogeneous nucleation of the perovskite film providing an enlarged grain size. At 120 sec, MWP perovskite started degrading as visualized by the miscellaneous phase in the perovskite films (Figure 5.10).
We further studied the MWP perovskite films using XRD and UV-vis absorption spectrophotometer in figure 5.11. Perovskite film processed within 60 sec had almost no miscellaneous phase but showed the lowest crystallinity and absorption. It indicates that perovskite is not fully converted at this short time. As the processing time increased to 90 sec, a high perovskite peak intensity was observed (Figure 5.11a) and showed the highest absorbance (Figure 5.11b). Further microwave exposure degraded the perovskite film which was seen by the lower absorption. We also observed different phases of perovskite, as seen in figure 5.11a.
Figure 5. 11 XRD and UV-Vis spectrum of perovskite films processed at 400 W with different times.

We fabricated PSCs with 400 W power with different process times. PSCs processed for 90 sec showed the highest efficiency with improving all the photovoltaic parameters (Table 5.2) among all the devices. Higher $J_{sc}$ is mainly due to the higher absorption and crystallinity of the perovskite [158]. Higher crystallinity indicates lower defects which showed higher FF and $V_{oc}$. On the other hand, PSCs processed with 120 sec showed the lowest FF due to the increased resistance of the miscellaneous phases. Lower $J_{sc}$ indicates the degradation of the perovskite film. We also observed the lowest hysteresis of the 90 sec processed perovskite devices which indicates the reduced trap states in the film.

Figure 5. 12 J-V of the PSCs processed at 400 W with different time
Table 5. 2 Photovoltaic parameters of PSCs processed at 400 W with different process time.

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Hysteresis Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 s</td>
<td>(F) 16.95</td>
<td>1.15</td>
<td>0.738</td>
<td>14.38</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>(R) 16.92</td>
<td>1.14</td>
<td>0.731</td>
<td>14.09</td>
<td></td>
</tr>
<tr>
<td>90 s</td>
<td>(F) 18.08</td>
<td>1.17</td>
<td>0.766</td>
<td>16.20</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>(R) 18.12</td>
<td>1.17</td>
<td>0.766</td>
<td>16.23</td>
<td></td>
</tr>
<tr>
<td>120 s</td>
<td>(F) 17.17</td>
<td>1.16</td>
<td>0.701</td>
<td>13.96</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>(R) 16.96</td>
<td>1.17</td>
<td>0.695</td>
<td>13.79</td>
<td></td>
</tr>
</tbody>
</table>

Finally, we compare the optimized microwave processed devices with the thermal annealing processed perovskite films. Thermally annealed film requires more time (1 hour) to get the highest efficiency of the device which is reduced to 90 sec for the microwave processed film. Both the films showed similar SEM morphology. Microwave processed PSCs showed a little higher efficiency compared to that with thermal annealed devices. So, it is possible to reduce the fabrication cost and time to achieve similar efficiency using the microwave instead of thermal annealing.
Figure 5. Comparison between thermally annealed and microwave processed perovskite solar cells.

5.4 Conclusions

We have developed a rapid and simple crystallization process using the microwave (MWP) to prepare perovskite films. MWP perovskite films can produce the similar performance of the solar cells like the thermally annealed films but in only 90 sec instead of ~1 hour. Both the films showed similarity in morphology. MWP can control the growth and morphology of the perovskites, and an optimized condition results in bigger grain with higher absorption and crystallinity. A champion cell can produce a PCE of 16.23% with negligible hysteresis. Moreover, our rapid crystallization process can reduce the annealing time of perovskite solar cells to seconds. This rapid crystallization process offers the faster large-scale fabrication and commercialization of PSCs.
CHAPTER 6 CONCLUSIONS AND FUTURE WORKS

6.1 Conclusions

To solve the critical issues in wide-bandgap perovskites, we have designed a novel quadruple cations composition and developed several strategies to improve the perovskite layer's electrical, optical, and physical properties. We also performed several characterization techniques to understand the defects and the passivation effect on the charge carrier dynamics of the wide-bandgap structure. Finally, a rapid processing technique using microwave was developed to attain efficient PSCs at lower cost and time.

The main findings of the dissertation are as follows:

- Compositional engineering plays an essential role in altering the morphology and the quality of the wide-bandgap perovskite films. Adding Rb to the ‘A’ site can change the morphology and other properties of the perovskite. Adding Rb up to a certain amount (5 mol%) can increase the grain size of the perovskite. Concentrations higher than this resulted in unwanted miscellaneous phases in perovskite.

- Excess lead halides are detrimental to the performance of the wide-bandgap structure. It is crucial to remove the excess lead halides from the perovskite film. Removal of excess lead halides can improve the interface charge extraction efficiency from the active perovskite layer to the charge transport layer.

- SG technique applied in this dissertation using GAI effectively removed the excess lead halides and converted them to perovskites. Conversion to perovskites increased the light absorption and the charge transfer properties from perovskites to the ETL layer.
- CPD analysis using AFM revealed the type of defects at the grain boundaries in wide-bandgap perovskite. We observed negative CPD at grain boundaries compared to the grain interior. It indicated the presence of positive types of defects at the grain boundaries of the wide-bandgap perovskites.

- GAI at the surface of the perovskite performed the passivation of the positive defects at the grain boundaries. Positive defects represent mainly the halide vacancies, which are minimized by the presence of GAI.

- Defect passivation at the grain boundaries was reflected in the improved charge carrier dynamics of perovskite films. Our lab-developed nanoscale characterization technique was conducted to study these properties. It was observed that SG treated film showed the most extended lifetime and the fastest charge transfer at grain boundaries. It also showed the highest diffusion length of the photogenerated charge.

- Finally, solar cells fabricated from this quadruple cation 1.78 eV wide-bandgap perovskites resulted in 17.71% (Average: 16.90±0.32) efficiency with the improvement of all the photovoltaic parameters compared to 14.17% (Average: 13.36±0.56) of that without Rb and SG treatment.

- In our second project, we studied the reason behind the formation of excess lead halides in wide-bandgap structure and observed that the degradation of the perovskite at the surface due to the volatile methylammonium is responsible for this unwanted phase. To stop the formation of this unwanted excess lead halide phase, we have introduced PMMA on the surface of the perovskite. We utilized the PMMA-PbI₂ adduct to accomplish our goal.
PMMA-PbI$_2$ adduct slowed down the surface crystallization of perovskites and locked the position of the perovskite components. So, the evaporation of the volatile methylammonium was halted, which resulted in excess lead halide free uniform perovskite films.

The absence of excess lead halides on the surface improved the charge transfer quality in perovskite, ensuring efficient charge collection by the ETL layer from perovskites. Moreover, the smoother surface also ensured the efficient contact between the perovskite and ETL.

Finally, this facile technique improved the efficiency to 18.18% (Average: 18.07±0.06) compared to 15.97% (Average: 15.51±0.15) without PMMA with $V_{oc}$ and FF improvement, which indicated the defect passivation and reduction of the series resistance of the structure.

Our final project focused on making a quick and cost-effective way to develop an efficient wide-bandgap structure using the microwave. Our study showed that microwave power played an important role in altering the morphology, and a suitable power level can produce bigger grains. Higher than this power degraded the perovskite whereas lower power was unable to produce desired bigger grains. We found 400 W as the optimized power level.

Our proposed technique reduced the ~ hour thermal annealing time to 90 sec to process efficient wide-bandgap perovskite film. Our microwave-processed devices showed similar performance to the thermally annealed one.
6.2 Future works

Several future works can be done to understand the perovskite structure and achieve superior performance for the commercialization of perovskites which can be the extension of this dissertation. Some of the proposed future works are shown below.

- The bandgap of the wide-bandgap ‘top’ cell depends on the ‘bottom’ cell's bandgap in tandem structure. Our proposed wide-bandgap comprises 40% Br with a bandgap of 1.78 eV. This bandgap is suitable for perovskite-perovskite tandem where the low-bandgap is in between ~1.2 to 1.25 eV. To make a tandem with Si solar cells, a suitable ‘top’ cell with a bandgap of ~1.70 eV is required. This bandgap can be easily achievable by reducing the Br percentage.

- We observed that the SG technique is an excellent strategy to convert the excess lead halides to perovskite. Besides, SG can passivate the grain boundary defects. Our SG technique used guanidinium iodide, but this technique can also be accomplished by other ‘A’ cation salts, such as methylammonium iodide/bromide, formamidinium iodide/bromide, etc. Possibilities of those materials can also be studied.

- Several characterization techniques can be used to study further the crystal structure, composition, and effect of Rb and GAI in perovskite. All these studies can be performed using XPS, TEM, etc. XPS can also be used to study the presence of Rb and GAI in the crystal structure of perovskite.

- We quantified the charge carrier dynamics of the perovskite film using a nanoscale mapping characterization technique developed in our lab. We also performed the TPC and TPV measurement technique to calculate the charge
lifetime and transport time of the whole device. To calculate the charge carrier lifetime of the perovskite film, state of the art TRPL technique can be used.

- Our developed crystallization technique using PMMA can eliminate the excess lead halides from the surface of the film. But due to the non-conductive nature of the PMMA, the $J_{sc}$ of the solar cells were not improved as expected. Other polymers with similar characteristics and higher conductivity can be utilized to solve the issue.

- We optimized the microwave heating technique outside the glove box. It is already evident from several reports that glove boxes are more suitable for preparing perovskite. We assume the better performance of the microwave-processed perovskite inside the glove box.

- Our developed rapid and cost-effective microwave technique showed promising results in our solar cell structure. This annealing technique reduced the processing time of perovskites from ~1 hour to 90 sec in our case. If this technique can be utilized in other layers of the perovskite solar cells, several hours of fabrication work can be accomplished in several minutes.
REFERENCES


