CRYSTAL SYNTHESIS AND OPTICAL PROPERTIES OF

CESIUM LEAD HALIDE SOLAR CELLS

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Abstract

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Lead halide perovskites have rapidly emerged as efficient light-harvesters for thin-film photovoltaics. Solar cells made with partially organic perovskites, such as methylammonium lead iodide, have surpassed 20% efficiency; but have been observed to degrade under high temperatures and after long-term light exposure. Additionally, the optical properties of perovskites are dependent on crystal structure, and therefore formation temperature. Fully-inorganic cesium lead halide (CsPbX₃) perovskite is stable at higher temperatures than organic perovskite, allowing for control of the crystal structure through formation temperature, and potentially improving longevity in an active solar cell. This study reports the properties of CsPbX₃ perovskites and photovoltaic cells; specifically CsPbBr₃, CsPbI₃, and mixed halide intermediates. Crystal structures obtained were determined to vary from orthorhombic/tetragonal to cubic. Performance was best for cells containing perovskite in the cubic phase and light harvesting was best for cells with high iodide content, consistent with theory.
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CHAPTER 1:
INTRODUCTION

1.1 State of the Photovoltaic Field

The demand for clean, renewable energy has never been greater as both the population and per capita energy demand grows; and with much of this growth in developing countries, inexpensive and modular infrastructure is ideal. Sunlight is reliably accessible across the vast majority of the world, and is overall the most plentiful source of renewable energy, outputting about 95 petawatts on the surface of the earth [1]. Photovoltaic (PV) devices, such as solar panels, can utilize the photoelectric effect to convert a fraction of those 95 petawatts into usable electricity. To emphasize the potential of solar energy, if only 0.32% of the land area on earth was covered in solar panels operating at 5% efficiency [2], that energy would be sufficient to completely account for current human energy consumption (estimated at 18 terawatts) [3].

Crystalline-silicon (c-Si) solar cells have already reliably surpassed this 5% mark, and are up to 20% efficient and durable enough to generally maintain at least 80% of their maximum power output after 25 years of use and elemental exposure [4].
Due to its status as the oldest and best-tested technology, approximately 90% of solar cells currently in use for energy production are crystalline-silicon-based [5]. Despite their efficiency and stability, the silicon wafers used in c-Si solar cells must contain few impurities, necessitating expensive processing; and be fairly thick, resulting in a heavy and inflexible cell [5]. Additionally, even though these cells are efficient enough to pay for themselves over time, solar cells developed for applications such as powering a space station need to be efficient by weight far more than they need to be inexpensive. Although these are not huge problems for their present applications, these concerns have helped drive research in the field towards less material-intensive systems that are easier to process and distribute.

A two-pronged approach has been taken to develop more versatile photovoltaics, with research being done on improving both the materials used and the device structure. Photovoltaics with lower material requirements, known as thin-film solar cells, have already demonstrated market viability for systems utilizing three compounds. Of the 10% of the market share made up by thin-film cells [6], cadmium telluride (CdTe) makes up 56%, and hydrogenated amorphous silicon (a-Si:H) and copper indium gallium diselenide (CIGS) each make up 22%. [7] These materials all absorb light orders of magnitude more effectively than silicon wafers, reducing requisite film thickness for similar performance to the order of microns.

Even though they all outperform c-Si by weight, the band gap of a-Si:H (1.8 eV) is not an ideal overlap with the solar spectrum, and the module record efficiency is only 12.2% [8]. CdTe and CIGS both have module record efficiencies of 17.5% [8], but have
not been more widely adopted due to the toxicity risks of cadmium and scarcity of tellurium and gallium [9]. To address these issues, many more compounds are being investigated as emerging thin-films, with focuses on ease of production and usage of safer, more earth-abundant metals.

1.2 Development of Thin-Film Solar Cells

On the straightforward material research side, an example of a new system is copper zinc tin diselenide, an earth-abundant analogue to CIGS. Research challenges for this compound involve synthesis and characterization to ensure imitation of or improvement upon the properties of CIGS. However, much of the emerging thin-film field is focused on novel structural development, working from the systemic side to create infrastructures that work well with known compounds with desirable optical properties. Two major technologies being investigated to this end are dye-sensitized solar cells and colloidal quantum dot solar cells. Dye-sensitized solar cells consist of an inorganic anode, a n-type electron-extractor (such as TiO₂) serving as a scaffold for light-absorbing dye molecules (which can be metallic complexes or organic), and a p-type hole conductor which replenishes the electrons with those received from the cathode. In the case of early dye-sensitized cells, the p-type material is typically a liquid electrolyte for efficient electron replenishment in the dye, although solid-state cells utilizing solid hole transfer materials (HTM) exist. [10] Although low-cost and simple to manufacture, a primary flaw that needs to be addressed the inherent long-term instability due to dye degradation under intense light and heat.
Quantum dot solar cells utilize solution-processed semiconductor nanocrystals (quantum dots) as sensitizers, taking advantage of quantum dots’ size-dependent tunability, allowing for efficient absorption of the solar spectrum [11] [12]. Research must be done on QD surface chemistry to improve initial excitation by photons and charge separation once excited; and QD synthesis and size tuning must also account for potential efficiency losses through mid-gap states [13].

Both systems are pertinent to the focus of this paper, perovskite solar cells, which were first derived from dye-sensitized solar cells, are currently the fastest-advancing and one of the highest-efficiency types of photovoltaic cell. [14] Certain compounds that exist in the perovskite crystal structure (ABX\textsubscript{3}), most prolifically methylammonium lead iodide (MAPbI\textsubscript{3}), have close to ideal band gaps and electronic properties for harvesting sunlight. [15]

1.3 Motivation for Inorganic Perovskite

Methylammonium lead halides (MAPbX\textsubscript{3}) were not used in effective photovoltaic cells until 2009, when an efficiency of 3.8% was reported for solid-state dye-sensitized solar cells prepared with MAPbI\textsubscript{3}. Use of MAPbBr\textsubscript{3} resulted in a higher voltage across the cell but less overall efficiency, hinting towards the tunability of the system and optimization process yet to come. In the past, the compounds had been considered unviable due to their instability in common electrolytes, but recent developments in solid-state photovoltaics; Both were prepared by adding a solution of the perovskite precursors (methylammonium halide and lead halide) to a substrate (Fluorine doped
transparent conductive glass (FTO) with compact and mesoporous TiO$_2$ scaffolding), spin-coating, and annealing. [15]

By 2014, this fundamental method was altered and optimized to bring the efficiency beyond 17%, [16] with the current record over 20%. [8] The perovskite crystal size, phase, and homogeneity significantly affects the efficiency of the finished cell, due to a multitude of exciton recombination pathways leading to short-circuiting in a disordered film [17]. A major factor in the uniformity and phase of the final crystal is the perovskite solution, as if the precursors are not fully solubilized, the crystal will not evenly precipitate upon deposition within the TiO$_2$ layer [18], and the crystal phase will be skewed away from cubic if the precursors are not present in stoichiometric ratios.

Another primary challenge with MAPbI$_3$ is the compound’s lack of stability. It dissolves in liquid water [19] and forms hydrates in relatively low ambient humidity [20]. A MAPbI$_3$/spiro-OMeTAD cell kept at 0% relative operated consistently for 3 weeks, but a similarly prepared cell kept at 50% humidity lost almost half of its efficiency in the same time, and a cell kept at 90% humidity lost 90% of its efficiency within 4 days and stopped working after 6 days [21].

Humidity effects can be mitigated with better sealing, but MAPbI$_3$ is inherently unstable under high temperatures. MAPbI$_3$ was found to shift its absorption spectrum and lose about 7% of its ability to absorb photons when illuminated at 50°C [22], with increased absorption about 400-480 nm suggesting recrystallization of PbI$_2$. As this suggests methylammonium may be unstable under irradiation and heat conditions expected of a solar cell, research on alternative cations is warranted.
1.4 Inorganic Perovskite Basics

Using alternative cations for lead halide perovskites (APbX$_3$) allows for major changes in stability, optical, and electronic properties, although keeping lead as the metal bounds ionic radii of the cations (they must fit within the PbX$_6$ octahedra) [23]. Cesium is the only inorganic cation studied that fits well within this size range, and cesium lead halide (CsPbX$_3$) has been shown to have high band gap tunability, favorable semiconducting properties, and is generally stable as a cubic perovskite. [24]

CsPbX$_3$ has only recently been tested in complete solar cells, but the first results were a promising 5.5% efficiency ($V_{OC}$ over 1.2 V, $J_{SC}$ over 6 mA/cm$^2$) for CsPbBr$_3$ with no HTM, prepared using a similar solution process to that of MAPbX$_3$. [25] CsPbBr$_3$ was found to be more temperature stable than MAPbX$_3$, to the point of allowing an annealing temperature of 250°C, far above the maximum stable temperature of methylammonium. The primary limitation of solution-processed CsPbX$_3$ is that CsPbI$_3$, which has a lower band gap than CsPbBr$_3$, cannot form a cubic perovskite at temperatures convenient for standard solution processing, instead forming an orthorhombic perovskite [26] with a high band gap and poor optical properties. [27]

1.5 Thesis Overview and Objective

Based on the promising but inconsistent initial results of CsPbBr$_3$ solar cells, this thesis makes the case for the material as a viable sensitizer based on photovoltaic theory, and discusses the effect of crystal phase and composition to inform synthetic procedures. Synthetic methods for CsPbX$_3$ are attempted and discussed, evaluation
parameters are established, and experiments performed for this thesis are compared to those in literature. Ultimately, the thesis aims to examine CsPbX$_3$ perovskite in various forms and phases to develop a controlled synthesis procedure to produce pure cubic perovskite; and to consider early results for CsPbX$_3$ solar cells and the development of MAPbX$_3$ perovskite solar cells to inform a fabrication procedure that can utilize CsPbX$_3$ as efficiently as MAPbX$_3$ is utilized today.
CHAPTER 2:
THEORY

2.1 Photovoltaic Theory

Development of thin-film photovoltaics is ongoing, and perovskite solar cells in particular emerged recently and have rapidly evolved since, but the physical fundamentals of photovoltaics are well-understood. To evaluate CsPbX₃ perovskites as sensitizers and determine what can be done to improve cell performance, the known, working optimization process for MAPbX₃ should be considered and the material properties affecting solar cell performance need to be understood and parameterized.

2.1.1 Perovskite Solar Cell Structure and Development

As alluded to in the introduction, the basic anatomy of a perovskite solar cell is a conductive anode, a n-type semiconductor (compact and mesoporous TiO₂), the active light-absorbing compound, a p-type semiconductor and a conductive cathode. For the cells examined in this study, the anode is FTO glass, the n-type semiconductor is staggered compact and mesoporous TiO₂, and the light-absorbing compound is CsPbX₃, unless otherwise stated. The p-type semiconductor is variable based on experiment,
and the cathode is generally gold or silver with indium. At first these pieces were essentially just deposited in order, but over the last several years of development of MAPbX₃ photovoltaics, each step of the fabrication has been optimized. This process is briefly outlined, with to inform discussion of and decisions made for analogous CsPbX₃ processes.

An early advancement in perovskite film formation was the switch to a two-step solution processing method, adding first dissolved lead halide and then dissolved methylammonium halide. This removes the need to find a solvent that dissolves both precursors simultaneously, and allows the lead halide to disperse throughout the mesoporous TiO₂, increasing control of the crystallization rate throughout the film. Upon addition of methylammonium halide, the precursors will begin to react and start crystallizing at a rate determined by precursor concentration, allowing for better morphology control before annealing. [28]

With the advent of the two-step method, the rapid reaction between lead halide and methylammonium is more visually apparent, as a yellow PbI₂ film will immediately turn brown upon contact with methylammonium iodide, often before spin-coating can take place. Although careful blade coating (using the surface tension of the solution to quickly sweep the solvent evenly across the film with the pipette tip) or dipping rather than spin-coating can still generate a homogenous film, slowing down the reaction rate ensures more homogenous crystallization. The forming perovskite has a higher affinity for I than Cl, although mixed-halide MAPbI₃₋ₓClₓ can form with high enough Cl:I ratios. By introducing a small amount of MACl, the presence of MACl will slow the reaction, but
eventually all be replaced by I, adding a halide exchange step to the formation and further improving film homogeneity.[28] Alongside solution chemistry effects, lower annealing temperatures were found to result in a more even perovskite film that better interfaces with the mesoporous TiO$_2$ layer. [29]

Beyond the active layer, the substrate and HTM can improve the performance of a solar cell. As this is added on top of the complete active layer, the HTM has a somewhat reduced impact on active layer film quality, but still must be chosen to thoroughly interface with the perovskite without damaging it.

A common HTM for perovskite solar cells is 2,2′,7,7′-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9′-spirobifluorene (spiro-OMeTAD) [30], typically doped with other p-type materials to further hole transport capability. [31] For a HTM to be most effective, its HOMO level must surpass the active layer’s valence band maximum, which is the case for spiro-OMeTAD and MAPbX$_3$, but differs somewhat depending on the halide used in the perovskite. [32] Aside from its HTM properties, capping with spiro-OMeTAD reduces exposure to ambient air and helps keep MAPbX$_3$ in a stable solid state. [30]

2.1.2 Band Gap and Shockley-Queisser Limit

The most straightforward factor limiting solar cell performance is the band gap of the material serving as the light sensitizer. The band gap for a material is defined in general as the energy difference between the bounds of the valence and conduction bands, essentially defining the energy region where no electrons can exist. Electrons at
the top of the valence band can jump to the bottom of the conduction band by absorbing a photon with enough energy to jump the band gap. A well-designed solar cell will contain a n-type semiconductor to carry the excited electron to the anode, and a p-type semiconductor to serve as hole transport and carry electrons from the cathode to fill the “hole” left by the initial excited electron. If this process is effective enough, the continual excitement and resultant flow of electrons from the cathode to the anode will produce current and voltage across the cell.

A solar cell utilizing a single light-sensitive material (single-junction) necessarily has its efficiency capped based on the band gap of that material. The solar spectrum distributes photons through a multitude of energy levels. Photons with energy lower than the band gap cannot productively excite the electrons in the valence band, and photons with energy higher than the band gap waste that extra energy. The maximum efficiency, defined as the ratio of energy flux from the solar cell sensitizers and the energy flux being absorbed from the sun, of a single band gap is referred to as the Shockley-Queisser limit, and peaks at about 34% for a band gap of 1.34 eV.

2.1.3 Interfacial Dynamics

Another source of deviation from ideal energy conversion, albeit not as fundamental as the Shockley-Queisser limit, is the potential for the n-type and p-type materials to allow an electron and hole to recombine within the solar cell and lose the energy as heat. Although it is possible for a single material to segregate into n-doped and p-doped layers, as is the case for the standard crystalline silicon solar cell, thin film
cells, with a substantially lower mass-to-power ratio, benefit from utilizing multiple materials. The differing band gaps and orbital energy levels of the sensitizer and any intermediates between it and the electrodes represent another opportunity for efficiency loss due to recombination. However, a well-designed solar cell will have p-type and n-type materials that can conduct electrons and holes, respectively, more efficiently than the sensitizer could on its own. Therefore, the sensitizer layer needs to be thick enough to absorb light effectively, but not so thick that the efficiency gained from improved electron and hole transport through the n-type and p-type materials is less than the efficiency lost from electron transfer between compounds. The physical and electronic properties of materials can be used to estimate how effective they might be in conjunction with each other, but there is enough complexity in recombination pathways and procedural difficulty in ensuring consistent homogenous interfacing across a cell that this remains a major point of study.

2.1.4 Equivalent Circuit and Series/Shunt Resistance

With the efficiency of converting captured photons to electrons and the probability of electrons reaching the anode known, regardless of the complexity of those processes, a fairly simple circuit is all that remains. Figure 2.1.3 depicts this equivalent circuit, with each process relevant to solar cell performance labeled as a parameter of the circuit.
Figure 2.1.3: Equivalent circuit representation of a solar cell

In Figure 2.1.3, the arrows incoming on the right represent incident sunlight. The operating current is never equal to that of the sunlight, so current $I_D$ diverted through the diode represents mandatory losses due to the Shockley-Queisser limit and transmittance of the sensitizer. Current $I_{SH}$ represents additional losses due to recombination within a material or at interfaces, with shunt resistance $R_{SH}$ inversely proportional to the probability of those losses: if those losses are minimal, $R_{SH}$ is high, if the electrons and holes easily recombine, $R_{SH}$ is low and the cell can short circuit. Finally, series resistance $R_S$ represents more straightforward effects of cell morphology, including the actual resistance of the materials. If $R_S$ is too high, electrons flow too slowly through the cell, giving them more chances to recombine, and if $R_S$ is much lower than $R_{SH}$, those losses are mitigated. Finally, $I$ and $V$ represent the actual current and voltage of the solar cell, the resultant power used to calculate efficiency $\eta$. Aside from being a visualization tool, the equivalent circuit is useful because it relates the directly measurable parameters $I$ and $V$ of a solar cell to the more complex resistances, which
represent separate processes inside the cell. Since the two resistances effect I and V in
different ways, this makes it possible to more effectively determine where losses in a
cell are coming from.

2.1.5 Parameterization and Hysteresis

As current and voltage are both straightforward to measure and multiply to give
you the power of a system, a straightforward potentiometric test is often used to
quantify the performance of a solar cell. An I-V curve can be measured using a solar
simulator with a potentiostat, and simply consists of measuring the open circuit voltage
(V_{OC}) of the operating cell, and using the potentiostat to bias the cell back to 0,
monitoring the current the entire time. The current reading at a bias of 0 V is the short
circuit current (J_{SC}, converting to current density to account for solar cell area). V_{OC} and
J_{SC} are useful parameters because they represent the maximum voltage and current
attainable by the cell. The path the current follows from V_{OC} to 0 V and back can be
used to estimate the exact values for R_{SH} and R_{S}. In an ideal solar cell, as soon as the
voltage goes below V_{OC}, the current would shoot up to near J_{SC}, asymptotically
approaching it as voltage approaches 0 V. This is not generally the case, and instead in a
good cell there will be a fast linear increase in current with decreasing voltage (voltage-
controlled section) close to V_{OC}, that curves to meet a shallow slope from J_{SC} signifying a
slow decrease in current with increase in voltage close to the origin (current-controlled
section). Figure 2.1.4 shows a sample figure demonstrating this behavior.
Figure 2.1.4: CsPbBr$_3$ solar cell I-V curve from Kulbak, et al. 2015 [25]

Poor cells will approach a single linear relationship, which would suggest the cell is acting more like a resistor for the potentiostat than generating its own power from the light. Regardless of the performance, there will be some point on the I-V curve at which the product of current and voltage is maximized, corresponding to maximum power. The ratio of this maximum power to the theoretical maximum, the product of $V_{OC}$ and $J_{SC}$, is the fill factor, a derived parameter from this test which roughly represents the ideality of the cell. The fill factor is named as such as the ratio is literally the percentage of the rectangle bound at ($V_{OC}$, $J_{SC}$) filled by the rectangle bound at the maximum power point. As such, this allows for the solar cell efficiency (maximum power / incident power) to be defined in terms of $V_{OC}$ and $J_{SC}$, as the product of those two parameters and the fill factor returns the maximum power.

If one of either $V_{OC}$ or $J_{SC}$ seems reasonable for the solar cell but the performance is poor due to a low fill factor, the shape of the curve can give away whether high $R_s$ or
low $R_{SH}$ is the problem. In the event the cell is primarily suffering losses due to recombination, a low $R_{SH}$ shifts the I-V curve to have a steeper slope in the low voltage area leading up to $J_{SC}$. When approaching $V_{OC}$, the current may return to being voltage controlled, and the slope of this section may remain steep (and result in a reduced $V_{OC}$ due to $R_{SH}$ speeding the loss of current with increasing bias voltage). Conversely, a high $R_S$ means that the linear response to voltage near $V_{OC}$ is less dramatic, as the potential across the series resistance is more comparable to the effect of the bias voltage. Once out of this region, the slope to $J_{SC}$ may remain shallow (and result in a reduced $J_{SC}$ due to $R_S$ slowing the initial gain of current with decreasing bias voltage). A cell with good $J_{SC}$ but reduced $V_{OC}$ might have high probability (low $R_{SH}$) recombination traps that quench the potential more effectively than electron flow can; and a cell with good $V_{OC}$ but reduced $J_{SC}$ might have stable but slow electron and hole transport that diminishes the voltage-controlled section less proportionally significant compared to the internal resistance (high $R_S$). If a cell seems generally functional and has a good fill factor but poor overall performance, it suggests both $R_S$ and $R_{SH}$ may be undesirable and the cell materials are antagonistic. If a cell has one good parameter and one bad parameter and a poor fill factor, either most of the generated electrons are recombining (low $V_{OC}$) or the sensitizer is being exhausted of electrons faster than the holes can get replenished (low $J_{SC}$).

A final quirk of I-V curves is hysteresis, difference in performance between a forwards (0V to $V_{OC}$) and backwards ($V_{OC}$ to 0V) scan. Some cells will gain or lose current at a different rates in the same region depending on if the voltage was increasing or
decreasing, potentially leading to an altered maximum power point and change in efficiency. This behavior is detailed in Chapter 5.2.2.

2.2 Crystal Structural Theory

With the relation between physical properties of the constituent materials of a solar cell and its performance understood, potential sensitizers can be identified based on the relevant properties. For the case of CsPbX₃ perovskites, the optimal halide stoichiometry and phase can be determined based on previous studies on the material, but to actually utilize that perovskite in a solar cell, it must be stable during device fabrication and performance.

2.2.1 Perovskite Structure and Properties

In the photovoltaic field, the word “perovskite” is nearly synonymous with MAPbI₃ and related systems. However, the namesake of the perovskite structure is CaTiO₃, and the crystal formation can be attained by various constituents. The general unit cell formula for the perovskite structure is defined as AMX₃, with A and M as positively-charged ions in formation with negatively-charged X ions, with A conventionally being a monovalent cation and M being a divalent cationic metal. For the purposes of this study X specifically represents halides, although as evidenced by CaTiO₃ this is not a strict limitation for the structure.

The ideal perovskite crystal structure is body-centered cubic, with A and M ions in the corners and center with X ions filling the octahedral sites. The constituent ions
define the crystal properties, including the band gap which is of clear importance to single-junction photovoltaics. Optimization of MAPbX₃ has shown linear tunability of the band gap between pure MAPbBr₃ (2.29 eV) and MAPbI₃ (1.57 eV) [33]. However, the same study reported a higher rate of recombination inside the perovskite film in pure MAPbI₃, further indicating the complexity of the system and necessity of optimizing halide stoichiometry.

2.2.2 Tolerance Factors and Conformational Stability

General materials studies on MAPbX₃, CsPbX₃, and various other cation-metal-halide perovskites have shown consistent patterns regarding the halide identity, formation temperature, and crystal phase stability. Depending on the ionic radius of the cation and identity of the metal, the ultimate crystal structure and temperature required to form it is highly dependent on the atomic radius of the halide. The relatively large iodine requires much more initial energy to be packed into a cubic structure, and has a tendency to relax into a skewed orthorhombic or tetragonal structure over time.

Equations 2.2.2-1 and 2.2.2-2 [34] account for these steric effects:

\[
t = \frac{(r_A + r_X)}{\sqrt{2(r_M + r_X)}} \quad (2.2.2-1)
\]

\[
\mu = \frac{r_M}{r_X} \quad (2.2.2-2)
\]

In both equations, \(r_A\), \(r_X\), and \(r_M\) are the ionic radius of the cation, halide, and metal, respectively. The closer \(t\) is to 1, the easier it is to form a cubic perovskite structure. If \((r_A + r_X)\), half the diagonal between corners of a face of the cubic unit cell, is
not close to a factor of $\sqrt{2}$ larger than $(r_M + r_X)$, half the length of the cubic unit cell, then at least one of the ions must not be close-packed in a cubic formation. The second tolerance factor, $\mu$, is simply the ratio of $r_M$ and $r_X$, parameterizing how well the octahedral halide ions fit around the central metal ion. If $\mu$ is less than 0.5 or much greater than 0.8, it is less likely that constituents of these sizes will remain in the cubic phase, as the central metal ion is so small compared to the halide ions the octahedral sites can deform inwards without resistance. Even though this factor does not account for $r_A$, it is an effective second check, as in the case of $r_M << r_X$, the $t$ value can return close to 1 if $(r_A + r_X) \approx \sqrt{2} r_X$ or in the case of $r_X << r_M$ if $r_A \approx \sqrt{2} r_M$.

For the compounds studied, $t_{\text{MAPbBr}_3} = 1.05$, $t_{\text{MAPbI}_3} = 1.02$, $t_{\text{CsPbBr}_3} = 0.86$, $t_{\text{CsPbI}_3} = 0.85$, $\mu_{\text{Pb-Cl}} = 0.66$, and $\mu_{\text{Pb-Br}} = 0.61$. MAPbI$_3$’s comfortable fit in the cubic phase is likely a major contributor to its performance, and the higher $\mu$ values of Cl and Br justify the observation that MAPbI$_3$ is more stable when spiked with Cl or initially mixed with MAPbBr$_3$ [35], even a small percentage of smaller halide ions distributed within the octahedral sites will decrease the volume of the octahedral and decrease the chance of asymmetric packing and collapse out of the cubic state during annealing.

2.2.3 Morphology of Mixed-Halide Crystals

Since halides are the most plentiful compounds in the perovskites studied, it is possible for a fully formed crystal to exchange halides with its surroundings to reach equilibrium without substantially affecting the integrity of the system. The simplest example of this is when the initial perovskite is prepared in solution using multiple
precursors. If an equimolar ratio of PbBr$_2$ and PbI$_2$ are mixed into the same concentration of CsBr, the free ions in solution will order themselves randomly and effectively produce “pure” CsPbBr$_2$, with iodines evenly dispersed through the bromine octahedra after deposition, verified by the single absorption peak between the standard iodine and bromine peaks [36]. This exchange can similarly be done after formation, although depending on the permeability of the film, the concentration of the exchanged halide has the potential to form a gradient based on the exposed surfaces.

A more extreme example of the utility of this technique is can be found by looking to semi-organic perovskites. MAPbI$_3$ that was formed through treatment of MAPbCl$_3$ with excess MAI, was pure (negligible Cl detected in final crystal), as the ionic radii of iodine and chlorine are too disparate to form a mixed intermediate. However, the resulting MAPbI$_3$ was found to be structurally different than directly deposited MAPbI$_3$. The unit cell was somewhat reduced in size, and the emission spectrum recorded displayed a corresponding redshift [35].

2.2.4 Formation and Stability of Cubic Structure

Synthesis and analysis of CsPbX$_3$ nanocrystals [24] verifies the impact of the relatively poor tolerance factor for CsPbI$_3$. A week after formation, a dark but clear suspension of cubic colloidal CsPbI$_3$ had entirely crashed out into off-grey, noncolloidal sediment, whereas the slightly improved CsPbBr$_3$ stayed stable for a month, detailed in Chapter 5.1.3. Initial studies of bulk CsPbI$_3$ reported similar degradation from a clear black crystal to opaque yellow within a few minutes of formation [26].
HTM deposition has been shown to protect MAPbI$_3$ from degradation, but the degradation affecting MAPbI$_3$ is associated with an increased response of PbI$_2$, which is not the case for CsPbI$_3$. XRD confirms that CsPbI$_3$ is not degrading in a way that it departs from the perovskite formula, but rather collapsing from the cubic phase to the more relaxed orthorhombic phase, which is also obtained as a result of insufficient heating during the initial formation of CsPbI$_3$ [24].

A more recent study has shown that sufficiently high annealing temperatures after a liquid deposition result in consistent formation of the cubic phase [37], and no immediate decomposition when followed up with HTM. Verifying the other bulk CsPbI$_3$ studies, the perovskite formed at lower annealing temperature was an orthorhombic-phase material with a shifted absorption spectrum resulting in poor performance. As such, it is possible that pure CsPbI$_3$ can be used in the cubic phase as long as the fabrication process uses sufficiently high annealing temperatures; and based on MAPbX$_3$ studies, there may be an optimum value of x for CsPbBr$_x$I$_{3-x}$ that eases stability concerns but maintains the favorable properties the larger halide.
3.1 Perovskite Synthesis

Three separate base procedures were used for synthesis of CsPbX₃, which produced CsPbX₃ in different forms: bulk crystal formed from addition of CsX to a PbX₂ precursor; bulk crystal deposited directly from CsPbX₃ in solution; and nanocrystals synthesized via hot injection. The bulk crystals are all deposited directly onto TiO₂ substrates and can be easily turned into completed solar cells, whereas the nanocrystals are formed in solution with ligands and binders, resulting in a colloidal solution which must be gradually deposited onto a substrate before testing. Although cubic CsPbBr₃ was the most frequently tested compound in this study, procedures were modified to use alternative halide precursors and annealing temperatures, resulting in multiple compositional and structural systems.
3.1.1 TiO$_2$ Substrate Deposition

Fluorine-doped tin oxide glass (Pilkington Glass, TEC-7, 2mm thickness) (FTO) is cut into 5cm by 10cm rectangles, rinsed with deionized water, air-dried, and then etched using scotch tape to mask the long sides before coating the center of the glass with zinc powder (Alfa Aesar, median 6-9 microns), and applying 2M hydrochloric acid (Sigma-Aldrich, ACS reagent, 37%) for at least 4 minutes.

The etched glass is rinsed again with DI water, washed with detergent (VersaClean), and then submerged in ethanol (KOPTEC, 200 proof) and sonicated for 20 minutes. The cleaned glass is rinsed again with DI water, then plasma cleaned (fed by ambient air) for 5 minutes. At this point, the glass is cut into 5cm by 5cm squares and masked with polyimide tape. Inside a N$_2$ glove box, 0.15M titanium diisopropoxide bis(acetylacetonate) (75 wt. % in isopropanol, Aldrich) in 1-butanol is spin-coated onto the glass and annealed at 125°C for 10 minutes to form the compact TiO$_2$ layer, then 100 mg/mL TiO$_2$ paste prepared as described in Im, et al. 2014, [16] is spin-coated and annealed by ramping from room temperature to 550°C, held at 550°C for an hour, and then allowed to slowly cool. After cooling, electrodes are cut into 2.5cm by 5cm rectangles, and masked with polyimide tape along the anode and back. Masked electrodes are submerged in 20mM titanium (IV) chloride (Alfa Aesar, 99.0% min.) and heated to 90°C for 10 minutes before being rinsed with DI water, heated to 500°C for 30 minutes, cut to 2.5cm by 2.5cm squares, and stored for no more than a week before use. Stored films are reheated to 500°C for 30 minutes before use.
3.1.2 Single Step Direct Deposition

Procedure modified from Ripolles, et al. 2016 [37]

The substrates prepared as in 3.2.1 are masked again on their anodes with polyam ide tape, plasma cleaned for 5 minutes, and brought into the N2 glove box for spin coating. A solution of 20% by weight CsPbBr3 in DMSO is prepared by dissolving an equimolar ratio of lead (II) bromide (Alfa Aesar, 98+%) and CsBr (Aldrich, 99.999% trace metals basis) into DMSO and stirring at 80°C for at least 2 hours. The substrate is heated to 80°C before evenly distributing the solution onto the substrate using a pipette tip, then spin-coating. After spin-coating, the substrate is dried at 80°C for 30 minutes before being annealed at 200°C, 250°C, or 300°C.

3.1.3 Two-Step Direct Deposition

Procedure modified from Kulbak, et al. 2015 [25]

The substrates prepared as in 3.2.1 again have their anodes masked with polyimide tape, are plasma cleaned for 5 minutes, and are brought into the N2 glove box for spin coating. 1M PbBr2 in N,N-Dimethylformamide (Sigma-Aldrich, anhydrous, 99.8%) (DMF) is stirred at 75°C for at least 20 minutes before filtering with a 0.2 micrometer syringe filter. The substrate is heated to 75°C, and then spin-coated with the filtered PbBr2 and annealed at 75°C for 30 minutes. At this point, 15 mg/mL CsBr in methanol (Fisher Scientific, Certified ACS) is applied to the film, either by distributing the solution onto the substrate using a pipette tip and spin-coating (“2-step spin-coat”) or by submerging the PbBr2 film in the CsBr for 10 minutes. Either way, after addition of
CsBr, cells are washed with 2-propanol (Sigma-Aldrich anhydrous, 99.5%), dried with \( \text{N}_2 \), and annealed 10 minutes at 250°C.

3.1.4 Colloidal Nanocrystal Synthesis

Procedure modified from Protesescu, et al. 2015 [24]

In a 3-neck flask, 0.188 mmol of PbX\(_2\) is added to 5 mL of ODE. Stir for 1 hour at 120°C under vacuum. Add 1.5 mL of oleic acid and 1.5 mL of oleylamine under \( \text{N}_2 \) flow, and bring to 180°C-190°C. After PbX\(_2\) appears to have completely solubilized and temperature is stable, inject 0.4 mL Cs-oleate (prepared as in [38]) at 100°C. Let sit 1 minute before submerging in ice-water bath to halt reaction. Decant the ODE, oleic acid, and oleylamine as much as possible, solution should be clear with nanocrystals settled at bottom of flask. Add tert-butyl alcohol and centrifuge for at least 20 minutes until all nanocrystals remain settled even with minor agitation. Decant tert-butyl alcohol, and rinse centrifuge tube with toluene, which can be used to store the nanocrystals as a colloidal solution for up to a week.

3.2 Solar Cell Assembly

After the perovskite film is deposited on the substrate, the HTM and/or contacts are added, depending on the desired final cell structure, to complete the cell and allow for potentiostatic testing.
3.2.1 HTM Deposition

Starting with a FTO/TiO$_2$/CsPbX$_3$ film prepared as in Chapter 3.1, ensure the CsPbX$_3$ film is homogenous and completely dry after the deposition and annealing. After sitting at least an hour, the film is scraped off the etched section of the cell with a razor blade and the exposed glass and FTO is carefully washed with a cotton swab damp with 2-propanol.

Mask the anode with polyimide tape, set the substrate on the spin-coater, and directly pipette the HTM solution onto the spinning substrate. Let the spin-coater continue for at least 30 seconds before drying at 60°C-100°C, depending on the HTM. After drying, store the cell in a desiccator until ready to add electrode contacts.

3.2.2 Solid-State Cell

The FTO/TiO$_2$/CsPbX$_3$/HTM cell prepared according to Chapter 3.2.1 is masked with a thin metal stencil that covers the anode and part of the cell. The masked cells enter the thermal evaporator with gold pellets (Kurt J. Lesker Company, 99.999%), which are deposited as a 100nm onto the etched section and perovskite/HTM layer for use as contacts for potentiostat testing. Indium wire (Alfa Aesar Puratronic, 99.998+% metals basis) is soldered onto the edge of the anode and atop the end of the gold contact to improve conductivity and reduce damage from spring clips while testing.

3.2.3 Liquid Junction Half-Cell

As an alternative to using a HTM, FTO/TiO$_2$/CsPbX$_3$ substrates are cut down to 0.8cm or less and have copper wire soldered directly to the anode. This half-cell is
partially submerged in a specially designed cuvette that functions as one of the necks of a 3-neck flask. The flask is filled with an electrolyte solution, and a metal electrode is partially submerged in a separate neck from the half-cell. At this point, the copper wire leading from the anode and the metal electrode can be used to test the cell in an equivalent manner to a full cell prepared in 3.2.2.

3.3 Halide Exchange

As an additional method of control for the perovskite film composition and phase, CsPbX$_3$ crystals will exchange halides to reach equilibrium with room-temperature solutions containing halides in different ratios than the initial synthesis. This can be used to alter the halide ratio of a desired film morphology without having to change the precursor solution or annealing conditions.

3.3.1 Halide Salt Solution

Modified from Nedelcu et al. 2015. [36]

Starting with a FTO/TiO$_2$/CsPbX$_3$ substrate as prepared in 3.1.1 or 3.1.2, submerge the substrate in a solution of up to 1M of PbBr$_2$ and/or PbI$_2$ in acetonitrile and up to 0.1M HBr and/or HI. If attempting to substitute Br with I, a high-concentration solution should be prepared, and with a greater I:Br ratio than the desired crystal composition. Let the substrate soak for at least an hour, with longer times required for Br to I substitution and for less concentrated solutions.
3.3.2 Halide Nanocrystal Solution

Modified from Nedelcu et al. 2015. [36]

A solution of CsPbX$_3$ nanocrystals prepared as in 3.2.3 can also be used as the donor for halide exchange with a bulk film. Although slower than using a solution with a concentrated halide salt or acid, this method reduces the risk of contaminating or dissolving the substrate. Additionally, as an alternative to using a ratio of mixed-halide precursors for 3.1.3, if solutions of CsPbI$_3$ and CsPbBr$_3$ are mixed, the nanocrystals will exchange halides with each other until equilibrium at CsPbBr$_x$I$_{3-x}$ is reached.
CHAPTER 4:

ANALYTICAL TECHNIQUES

4.1 UV/Visible Light Spectrometry

Absorption spectra of the CsPbX$_3$ nanocrystals were taken using a Varian Cary 50 Bio spectrophotometer, which has a limiting resolution of less than 1.5 nm. All absorption data was recorded from 200nm to 800nm, then normalized with the maximum absorbance of the perovskite system at 1 and the minimum value at 0, to isolate the absorption peaks and allow for comparison between solutions of different concentration or films of different thickness. Automatic baseline correction was utilized before recording data, with a cuvette of the pure solvent (toluene) being used as the baseline for the colloidal perovskites and a blank substrate (FTO/TiO$_2$) being used as the baseline for the bulk film perovskites.
4.2 Fluorescence Spectrometry

Emission spectra were taken using a Horiba Fluorolog with wavelength accuracy of 0.5 nm. An excitation wavelength of 420 nm was used in testing the emission of colloidal CsPbX$_3$, with Coumarin 6 used as reference. Emission was recorded from 480nm to 560nm.

4.3 Solar Simulation and Potentiostat Testing

Solar cell performance was quantified in a solar simulator consisting of a Varian Eimac Xe lamp (calibrated to 100 mW/cm$^2$ at testing range with a ThorLabs S302C Power Sensor) for illumination and a PARSTAT 2263 potentiostat for measuring current and biasing voltage. The PARSTAT 2263 can handle a bias of up to 20 V, with a minimum potential step of 2.5μV. Minimum current range is 200 nA, with a resolution of 120 fA, and measurements can be taken at most every 20μs. Initial testing was done by measuring current over a linear voltage ramp from +1.5 V to -0.5 V at a ramp rate of 0.05 V/sec, then tuning the positive voltage to be roughly 10% greater than the open circuit voltage for the cell for additional tests. Additionally, the champion cells were tested with chronoamperometry and voltammetry methods, which monitored unbiased current and voltage responses, respectively, in conditions of alternating light and dark.
4.4 Scanning Electron Microscopy

SEM scans were done using the Notre Dame Integrated Imaging Facility’s (NDIIF) Field Emission Scanning Electron Microscope Magellan 400 (FEI), which has a spatial resolution of 0.6nm at 15kV and 0.9nm at 1kV. CsPbX₃ cells were cut approximately 1.2 cm from either edge, leaving an 0.1 cm region untouched by the glass cutter. The cells were broken apart, and this region was used as the focus for the cross-sectional SEM images.

4.5 X-Ray Diffraction

XRD patterns were taken with a Bruker D8 Advance Davinci Powder x-ray diffractor, using Mo Kα radiation at wavelength 0.71073Å. Partially assembled cells (FTO-only, FTO/TiO₂) were tested to develop a baseline before testing perovskite solar cells with varying film composition and thickness. Cells were cut down to 1.5 cm squares for testing purposes. TiO₂ substrates and CsPbBr₃ films were first given a broad scan from 0-50 2θ, then several CsPbBr₃ films were scanned from 30.2-31.2 2θ to focus on the clearest characteristic cubic peaks.
CHAPTER 5:
DATA ANALYSIS AND RESULTS

5.1 CsPbX$_3$ Crystal Characterization

Properties and stability of CsPbX$_3$ crystals in bulk films and colloidal solutions were determined experimentally as well as pulled from multiple literature sources in an attempt to find consistencies and discerning factors between procedures and phases.

5.1.1 Absorbance and Fluorescence Spectra

The first characterization test performed on the experimental perovskites was typically measurement of the absorption spectrum. Although on its own the absorption spectrum does not clearly define the exact phase or composition of the perovskite, the shape and location of the absorption peak are known to shift with the crystal size and structure [24]. Figure 5.1.1-1 contrasts CsPbBr$_3$ absorbance spectra between different synthesis methods.
Figure 5.1.1-1: Normalized absorbance spectra for CsPbBr$_3$ films or nanocrystals formed with different methods

Although the general shape of the absorption spectra is similar for all compounds, a distinct redshift from the colloidal nanocrystal solution to 2-step spin-coat method to the 1-step deposition ending with the 2-step dipped method is clear. The dipped 2-step CsPbBr$_3$ solar cells were verified to have the thickest perovskite bulk layer, and the colloidal nanocrystals are approximately 10-12 nm in diameter. The spin-coated 2-step cells and the single step cells were not observed to have a thick perovskite capping layer like the dipped 2-step cells. Instead, both methods resulted in deposition of most of the perovskite within the TiO$_2$ scaffolding, restricting the ability to form the homogenous cubic bulk phase.
Figure 5.1.1-2 displays overlaid absorption and emission spectra of colloidal nanocrystal CsPbBr$_3$ of different sizes, verified via TEM imaging [24].

The recorded absorption spectrum for colloidal nanocrystalline CsPbBr$_3$ appears to best match those of the largest CsPbBr$_3$ crystals tested, and the spectra of the three finished cells is consistent with the theoretically predicted band gap for bulk CsPbBr$_3$. 
As such, colloidal CsPbBr$_3$ is likely not the ideal choice for a solar cell, due to its smaller size increasing band gap energy and decreasing its stability in the cubic phase.

Due to the increased band gap energy of nanocrystalline CsPbBr$_3$ and the lack of an n-type interface, the solutions fluoresce under ambient light reemission of absorbed photons. The proportion of this emission, quantum yield (QY), was calculated for CsPbBr$_3$ to additionally characterize the compound. Coumarin 6 was used as a reference species with known QY of 78%, and Equation 5.1.1 was used to calculate the QY of CsPbBr$_3$.

$$QY = \frac{QY_{ref} \cdot \frac{R^2}{R^2_{ref}} \cdot \frac{F_I}{F_{I ref}} \cdot \frac{Abs}{Abs_{ref}}}{Abs_{ref}}$$  \hspace{1cm} (5.1.1)

In equation 5.1.1, $QY_{ref}$ is the quantum yield of the reference species, $R_I$ is the reference index of the solvents, $F_I$ is the fluorescence intensity of the excited species, and Abs is the absorbance of the species at the excitation wavelength. The champion quantum yield obtained for colloidal nanocrystalline CsPbBr$_3$ was 36.6%.

Emission spectra were additionally taken for CsPbBr$_3$ in solution with various ratios with CsPbl$_3$ (which quickly degraded to a nonemissive orthorhombic phase after synthesis) to examine the potential effects of halide exchange. Figure 5.1.1-3 details these results for pure CsPbBr$_3$, 3:1 Br:I, 1:1 Br:I, 1:3 Br:I, and pure CsPbl$_3$. 

35
Figure 5.1.1-3: Emission spectra of various ratios of colloidal nanocrystalline CsPbBr$_3$ – CsPbI$_3$

Emission patterns of CsPbX$_3$ shift based on the ratio of halides [39], suggesting that this transition is the result of halide exchange between the two perovskites in solution. Upon combination of the pure cubic CsPbBr$_3$ and orthorhombic CsPbI$_3$, the emission intensity redshifted from 515 nm to 555 nm with increasing CsPbI$_3$ concentration, corresponding to band gaps of approximately 2.4 eV to 2.2 eV. Despite the very low emission of pure CsPbI$_3$, the mixed halide peaks retain clear peaks as long as some cubic CsPbBr$_3$ remains. The initial addition (3-1 Br-I) results in a substantial reduction in peak area, but further increasing the amount of iodine (1-1 Br-I) causes a substantial redshift while only decreasing the peak area by the amount expected by dilution of the original cubic perovskite, suggesting that a certain amount of iodine can be added to the cubic CsPbBr$_3$ without destabilizing it. Considering the donor CsPbI$_3$
was orthorhombic and started with no emission of its own, the redshift in the mixed solutions is promising for the potential development of CsPbBr$_{3-x}$I$_x$ perovskites which combine the structure and stability of cubic CsPbBr$_3$ with the optical and electronic properties of CsPbI$_3$.

5.1.2 XRD Patterns vs. Halide Composition and Synthesis Temperature

XRD patterns are the most reliable way to determine the exact structure of a crystal. Figure 5.1.2-1 contains six XRD patterns for cubic CsPbX$_3$ and intermediates, showing the effect of halide composition and lattice size on the diffraction.

![Figure 5.1.2-1: Diffraction patterns for cubic nanocrystalline CsPbX$_3$, X = I, Br, Cl, and intermediates (referenced from [24])]
TEM data verifies that all perovskites studied were in the cubic phase, although the amount of noise and extra diffraction peaks increases with the larger halides. The smoothing of the noise in the iodide perovskite with the addition of bromine suggests mixed-halide structure could improve stability and phase selectivity; and the further noise reduction of chlorine over bromine shows potential structural advantage could be achieved by using chlorine perovskite as a starting point for substitution with more optically favorable halides [40]. The shift in 2θ values is corresponds to reduced lattice parameters and a more relaxed structure, which is expected when a smaller halide is used. As suggested by the tolerance factor, CsPbCl\textsubscript{3} is the most stable in cubic phase, and this results in sharp peaks with minimal noise. As the ratio of larger halides increases, the peaks broaden, and a few orthorhombic peaks become visible. In the transition from CsPbBr\textsubscript{3} to CsPbI\textsubscript{3}, additional non-cubic peaks develop, potentially corresponding to a CsPbI\textsubscript{3}-exclusive tetragonal phase [41].

The film quality of the CsPbBr\textsubscript{3} solar cells prepared for this study was variable compared to pure solution-phase synthesized nanocrystals. Figure 5.1.2-2 shows various CsPbBr\textsubscript{3} films focused around two characteristic peaks, as well as the response of blank glass substrates.
Figure 5.1.2-2: CsPbBr$_3$ films prepared via (a) one-step deposition, and (b) two-step deposition. Solid lines: perovskite films, dotted lines: FTO/TiO$_2$ substrates

The overall peak-to-noise ratio for the one-step CsPbBr$_3$ film is substantially lower than that of the two-step method, likely due to the pure perovskite capping layer formed on the latter. The overall shapes of both XRD spectra are similar, although the minor peaks at 30.4 2θ onset earlier and are greater in magnitude compared to the peaks at 30.8 2θ in figure a. Not only does the film in figure b have a cleaner response, but the major diffraction peak is shown to be split between 30.8 2θ and 30.9 2θ. This additional, smaller peak could potentially be the bulk cubic CsPbBr$_3$ capping layer, as opposed to the more orthorhombic CsPbBr$_3$ formed within the TiO$_2$ layer.

Finally, Figure 5.1.3-3 depicts orthorhombic and cubic CsPbI$_3$ bulk films deposited directly onto glass then capped with poly(methylmetacrylate) (PMMA). The CsPbI$_3$ films were prepared using the single-step deposition method, and various annealing temperatures were used after deposition resulting in formation of distinct phases.
Figure 5.1.3-3: Diffraction patterns of FTO/CsPbI3/PMMA annealed at various temperatures (referenced from [37])

The 150°C diffraction pattern has multiple distinct orthorhombic peaks, which are substantially diminished by increasing the annealing temperature to 250°C. Finally, further increasing the annealing temperature to 350°C allows for the formation of the cubic phase, resulting in the sudden appearance of a sharp (110) peak. Films formed under these conditions were additionally tested to test performance vs. crystal phase, the results of which are discussed in Chapter 5.2.1.
5.1.3 Stability in Various Solvents

To assess the stability of the deposited CsPbBr$_3$ and potential electrolytes for a liquid-junction cell structure, spin-coated CsPbBr$_3$ films were submerged in cuvettes filled with various organic solvents (acetonitrile, toluene, ethyl acetate, dichloromethane, chloroform, tetrahydrofuran, and dimethyl sulfoxide) and monitored in the spectrophotometer. Unlike semi-organic lead halide perovskites, CsPbBr$_3$ was found to remain stable in most of the solvents tested, only dissolving in acetonitrile and dimethyl sulfoxide. To contrast, MAPbI$_3$ was tested in the same set of solvents and was only found to be stable in toluene, chloroform, and dichloromethane [42].

The full absorbance spectra was monitored at each data point, and negligible change was observed in toluene, ethyl acetate, dichloromethane, and tetrahydrofuran. Acetonitrile resulted in a gradual reduction of absorption intensity across all wavelengths, consistent with dissolution, and the dimethyl sulfoxide completely wiped the film on contact, with the resultant absorption spectra not distinguishable from the solvent blank. Figure 5.1.3-1 depicts the film stability by plotting relative absorption at 510 nm over 10-12 minutes for all compounds tested (excluding dimethyl sulfoxide, which would be an immediate flatline).
The ethyl acetate spectra’s apparent increase was reproducible across the triplicate scans, and coincided with the reduction of a secondary peak at approximately 490 nm only present in that solvent. Figure 5.1.1-2 additionally shows additional peaks at lower wavelengths, indicating this peak may correspond to an alternate phase perovskite that was gradually incorporated to the bulk phase upon submersion. Tetrahydrofuran appeared to be dissolving the CsPbBr₃ based on proportional absorbance reduction at all wavelengths, albeit at a much slower rate than the acetonitrile. CsPbBr₃ is slightly less stable in chloroform than tetrahydrofuran, but the instability does not appear to be due to dissolution, based on Figure 5.1.3-2.
Figure 5.1.3-2: Absorption spectra of CsPbBr$_3$ film submerged in chloroform

The magnitude of the maximum absorption peak only slightly decreases over the 10 minutes, but there is a distinct blueshift from 515 nm to 505 nm. Based on the potential of halide exchange between chlorine and bromine [43], it is likely the chloroform and CsPbBr$_3$ reached an equilibrium of a partially brominated trihalomethane and CsPbBr$_{3-x}$Cl$_x$. Although chlorination of the perovskite is not ideal for absorbing the solar spectrum, the speed and ease with which this transformation occurred suggests that in a liquid-junction solar cell, the electrolyte solution is another potential way to tune the optical properties of the perovskite.
5.2 CsPbX$_3$ Solar Cell Characterization

With the basics of CsPbX$_3$ crystals understood, experiments were carried out to test the performance of the variable halide ratios and crystal structures, with additional comparison to and analysis of recently published studies on the materials.

5.2.1 Performance and I-V Curves

The first cells tested in this study were pure CsPbBr$_3$ fabricated using the 2-step deposition method. Figure 5.2.1-1 shows I-V curves of the best cells of initial tests.

The spin-coated cell had an HTM (Spiro) added as the thinner film deposited by the spin-coating method resulted in very high rates of short-circuiting. The HTM improved the response stability, but the primarily linear relationship between current and voltage is representative of resistor behavior, not that of an efficient solar cell.
Conversely, the dipped cell showed a change in current with respect to voltage bias that increased at higher bias, implying a lower shunt resistance and less immediate recombination within the perovskite than the spin-coated cells. The dipped cells also displayed an improved $V_{OC}$, although higher series resistance from the thicker perovskite layer resulted in a reduction in $J_{SC}$.

$\text{CsPbBr}_3$ was also tested in liquid-junction half-cells. Figure 5.2.1-2 shows the champion performance of a $\text{CsPbBr}_3$ half-cell in acetonitrile/20 mM ferrocene.

<table>
<thead>
<tr>
<th>Voc</th>
<th>Jsc</th>
<th>FF</th>
<th>efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.575</td>
<td>0.00727</td>
<td>0.668</td>
<td>0.00279</td>
</tr>
</tbody>
</table>

Figure 5.2.1-2: I-V curve and performance parameters of liquid half-cell $\text{CsPbBr}_3$ in acetonitrile/ferrocene

The $\text{CsPbBr}_3$ film tested was formed using the 2-step spin-coat fabrication method, and compared to the solid-state cell, $V_{OC}$ and fill factor substantially improved. The low $J_{SC}$ kept the system inefficient, and given further testing could potentially be improved by using a different anode (FTO with soldered copper wire, necessary to fit
the cell within the apparatus, was found to have notable resistivity when tested on its own) or alternative electrolytes.

As mentioned in section 5.1.2, the varying phase CsPbI$_3$ displayed a strong correlation between presence of cubic peaks in the XRD and performance of the cell. Figure 5.2.1-3 depicts I-V curves of CsPbI$_3$ films formed via one-step deposition at 3 different annealing temperatures, capped with P3HT as a HTM.

![I-V curves of CsPbI$_3$ films formed at 3 different annealing temperatures](image)

**Table 5.2.1-3**: I-V curves in light (solid line) and dark (dashed line) of CsPbI$_3$ formed at 150°C, 250°C, and 350°C; and performance parameters (referenced from [37])

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>150°C</td>
<td>0.60</td>
<td>1.06</td>
<td>0.45</td>
<td>0.29</td>
</tr>
<tr>
<td>250°C</td>
<td>0.62</td>
<td>0.92</td>
<td>0.42</td>
<td>0.24</td>
</tr>
<tr>
<td>350°C</td>
<td>0.58</td>
<td>0.85</td>
<td>0.50</td>
<td>1.96</td>
</tr>
</tbody>
</table>

Although the orthorhombic CsPbI$_3$ (150°C and 250°C) was observed to have a superior $V_{OC}$, the substantial improvement in $J_{SC}$ suggests a significantly reduced series resistance through the cubic phase of CsPbI$_3$, which logically follows from both the symmetry of a cubic cell improving conductivity and the shifted band gap resulting in improved absorption of the solar spectrum.
This experiment was used as a basis for one in this study, altered to using 

CsPbBrI$_2$ rather than CsPbI$_3$, and lower temperatures of 200°C, 250°C, or 300°C. Figure 5.2.1-4 shows I-V curves for the three champion cells prepared under each condition.

Unlike for CsPbI$_3$, the overall improvement between phases was not clear-cut. The cell formed at 250°C was improved over the one formed at 200°C in every parameter, and as cubic CsPbBr$_3$ has been observed to form at ~210°C, its presence in the structure lowers the formation temperature from that of the pure iodide perovskite. Further increasing the temperature to 300°C increases the J$_{SC}$ even more, consistent with the massive J$_{SC}$ improvement at higher temperature observed in Figure 5.2.1-3, but V$_{OC}$ is reduced by enough to offset it, and the fill factor is also at its lowest, suggesting in increased shunt resistance. Although CsPbI$_3$ is stable at higher temperatures, 300°C is
pushing the stability of CsPbBr$_3$, based on the nanocrystalline synthesis data, and it is possible the stability difference between the two halides at this temperature resulted in inhomogenous deposition and more interfaces within the perovskite for exciton recombination. Further studies on the behavior of this material are detailed in Chapter 5.2.4.

5.2.2 Hysteresis and HTM Effects

The performance of CsPbX$_3$ films is not only dependent on the quality of the perovskite, but also the specific HTM chosen for the cell. The interfacial kinetics between the perovskite and HTM can result in asymmetric performance improvement or reduction. Figure 5.2.2-1 shows I-V curves for high-quality CsPbBr$_3$ solar cells consisting of FTO/TiO$_2$/CsPbBr$_3$ are shown alongside I-V curves of identically prepared films with one of three different HTMs.
In most cases hysteresis should be mitigated by increasing integration time during the scan, but in heterogeneous cells, it may not be unreasonable to consider path-dependent equilibrium states. The hysteresis in plot C suggests series resistance is more of a problem when coming from 0V than \( V_{OC} \). If this is the case, starting from no current and gradually reducing the voltage, which means the HTM goes from equilibrium to starting to receive electrons from the cathode which can then replenish holes in the CsPbBr\(_3\). Since the CsPbBr\(_3\) – TiO\(_2\) system leading to the anode is the same across all four cells shown, it makes sense that this process can start up fairly smoothly; although albeit with a shallower slope in the voltage-controlled section. Once voltage drops to
about 0.8, current is close to JSC, suggesting electrons are being shuttled out through
the anode and back in through the cathode as fast as the system will allow, which seems
reasonable as JSC is similar across all systems, and it is never shifted by hysteresis.
However, starting the scan from JSC has the initial state of everything moving as fast as
possible, CsPbBr$_3$ capturing photons which excite its electrons which move to the TiO$_2$
and anode, and HTM 4,4′-bis(N-carbazolyl)-1,1′-biphenyl (CBP) filling holes with
electrons arriving from the cathode at the same rate. However, as the bias increases
and the maximum current slows down, CsPbBr$_3$/TiO$_2$ are still able to shuttle electrons
out as long as the incident is constant. The increased voltage means less electrons are
coming in the cathode than going out the anode, and holes may be able to accumulate
in the CsPbBr$_3$, which improves the chances of some electron-hole pairs recombining,
and decreases the number of valid electrons that can accept photons. This results in the
current dropping, and as the voltage is slightly more than what it was previously, a
feedback loop based on the current “momentum” is created.

From a higher order perspective, CBP results in worse overall performance than
no HTM, despite improving JSC and slightly improving VOC, meaning the fill factor has to
be the culprit. Since the voltage-controlled region is the most affected, it seems
possible the addition of CBP increased series resistance. Since JSC ends up improved
compared to the JSC of no HTM after working through the hysteresis area, the loss in
max power is due to worse performance at that specific voltage, perhaps due to higher
potential making the CBP interface a less favorable region for holes. Finally, hysteresis
in the opposite direction is seen in the cells using poly(bis(4-phenyl)(2,4,6-
trimethylphenyl)amine] (PTAA), which is also the only HTM that improves on the base cell performance. Conversely to the CBP example, the CsPbBr$_3$-PTAA interface may be so favorable at its high potential max power point, relative to the no-HTM CsPbBr$_3$ that directly interfaced with the cathode, that it creates a feed-forward loop; keeping the existing current flowing to the point of pushing the voltage-controlled region even steeper.

5.2.3 Film Morphology

Although the chemical constituents of the cells are analogous in all methods, the specifics of the procedure were found to impact the morphology of the perovskite films, as has been reported for MAPbI$_3$ cells [29]. In particular, the concentration and method of application of the cesium salt solution in the two-step deposition significantly impacts how the final film forms. In specific, concentrations of 30, 50, and 70 mM CsBr were applied to identical PbBr$_2$ films either by dipping or spin-coating. Figure 5.2.3-1 consists of SEM images of 3 representative cells from these experiments at different angles to showcase various morphological features of CsPbBr$_3$ films.
The perovskite layer has permeated the TiO$_2$ substrate in every film, but b has the most homogenous morphology, with both the spin-coated and dipped 70 mM CsBr films having a thick capping layer of pure CsPbBr$_3$. The surface images for all three show microscopic inhomogeneity, but in image e the TiO$_2$ underlayer remains visible and in images d and f the capping layers completely obscure anything underneath.

Figure 5.2.3-2 depicts a two additional further-zoomed SEM images of the surface of the dipped film in figures c and f.
Figure 5.2.3-2: SEM images of: single perovskite crystals deposited on TiO$_2$ substrate (left), perovskite crystal capping layer (right)

The larger crystals present atop the TiO$_2$ film contrast with the smaller crystals permeating the TiO$_2$ layer, and are likely why the absorbance and XRD data differ substantially between the dipped and spin-coated methods. As the difference between the left and the right image shows, the prevalence of these cubes is not completely consistent across the surface of the cell. As CsPbBr$_3$ is forming via incorporation of CsBr into the already-deposited PbBr$_2$ in the two-step methods, any areas of higher concentration or exposure outside the TiO$_2$ layer serve as seeds for additional CsPbBr$_3$ growth. The discrete phase and thickness of this layer is also observable on the macroscopic level: during testing, the gold contacts evaporated onto these films appeared tackier and less reflective than cells fabricated with other methods, due to light scattering from the rougher surface.
5.2.4 Signal Stability and Light Soaking

Figure 5.2.4-1 displays the results of a sample chronoamperometric study on the champion two-step deposition CsPbBr$_3$ cell (dipped) from Chapter 5.2.1.

![Figure 5.2.4-1: Chronoamperometry of CsPbBr$_3$ solar cell – 9 cycles of simulated solar irradiation, alternating on and off every 30 seconds](image)

Although as with many of the cells fabricated for this study, initial cell performance was unstable, after three cycles that appeared to short-circuit after a few seconds of irradiation and current generation, the recorded current began stabilizing and then increasing after repeated cycling. Due to the thickness of the CsPbBr$_3$ layer and high $V_{OC}$ of the material, there is basis to assume this behavior could be in part due to light soaking as the crystal fills its trap states before ultimately retaining the energy to immediately reach maximum current flow with irradiation onset.

Similar behavior was also observed in CsPbBrI$_2$ films prepared using the single-step deposition. Figure 5.2.4-2 depicts the forward and reverse scans of CsPbBrI$_2$ solar cells before and after 5 minutes of continuous light exposure.
Figure 5.2.4-2: I-V curves and performance for CsPbBrI₂ solar cells before and after 5-minute light soak

The CsPbBrI₂ solar cells formed at 300°C were found to notably change their I-V curve response with successive testing, a feature not notable in the films prepared at lower temperatures. The cells started with primarily resistor behavior and substantial hysteresis between the forward and backward voltage sweeps, but after continual irradiation for 5 minutes, a second test showed reduced current density, increased VOC well beyond what was observed for any of the other cells (even the pre-soak scan had improved VOC from the initial scans in Figure 5.2.1-4), and gradual reduction in JSC. This significant shift in behavior affecting cell efficiency makes a compelling case for future study and optimization of the material.
CHAPTER 6:
CONCLUSIONS

Fully inorganic CsPbX₃ perovskite has different challenges than MAPbX₃, but the first few studies published for CsPbBr₃ and CsPbI₃ show performance similar to that of the earliest for MAPbX₃. The difference between current performance and expected maximum efficiency suggests there is still much development to be done on the CsPbX₃ system; and the current halide-mixing, phase-controlling methodologies used to optimize MAPbX₃ performance provide precedent for potential fruitful innovations.

The band gap of CsPbX₃ is highly tunable within a single-halide system via control of lattice size and crystal phase, and the preservation of cubic structure through halide exchange suggests fabrication of CsPbI₃₋ₓBrₓ could be optimized to utilize the favorable optical properties of CsPbI₃ and the relative stability of CsPbBr₃. The low volatility of cesium means hot-injection for nanocrystal synthesis or high-temperature annealing for direct film deposition can be used to form pure CsPbI₃ in the cubic phase; and post-processing with several options of halide donor can be used to further tune the material after initial formation.
CsPbX$_3$’s stability in various organic solvents means it is a viable sensitizer in more liquid-junction systems than organic perovskites, and electrolytes can be chosen to match the properties of the desired CsPbX$_3$ structure and stoichiometry. The stability in various solvents also allows for complex solution-processing during fabrication,

In summation, CsPbX$_3$ solar cells show promise due to their improved stability and high potential for tunability in systems containing other halides. High-iodide CsPbX$_3$ has stability problems at present, but the potential demonstrated for halide exchange in the bulk phase and between nanocrystals suggest that fabrication methods can be developed to utilize the structural stability of the other halides as a basis for cubic perovskite with a lower band gap and higher potential efficiency than current results for pure CsPbI$_3$. In addition, high sensitivity to HTM and light-soaking properties intrinsic to the perovskite itself provide fertile ground for future optimization for versatile devices.
BIBLIOGRAPHY


