Comparing the Influence of Rubidium and Cesium Dopants on Charge Carrier Dynamics and Microstructure in Hybrid Organic-Inorganic Perovskite Thin Films

by

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Abstract

Hybrid organic-inorganic perovskites (HOIPs) are a class of semiconducting thin films, viable for solar cell applications, that have emerged as serious contenders to traditional silicon-based photovoltaic devices. Research over the past decade has shown that incorporating small amounts of either rubidium or cesium into these thin films further boosts device performance. At the same time, however, rubidium-doping has been observed to solve another device challenge called hysteresis, which is a variation in solar cell efficiency depending on the direction in which voltage is supplied, while cesium-doping is less effective at doing so. This point of difference raises the question as to how each type of perovskite behaves in terms of charge carrier transport—i.e. how the underlying physics of the perovskite may be changed with rubidium- or cesium-addition.

In this thesis, the carrier dynamics of Rb-, Cs-, and RbCs-doped perovskite thin films were elucidated via pump-probe terahertz spectroscopy measurements, with systematic improvements for charge transport being found for all three doping conditions. The carrier mobility—or the extent to which free charges could move in response to an applied electric field—was found to be comparable between Rb-doped and Cs-doped samples. Furthermore, the carrier lifetime—or the extent to which a charge carrier remained in an excited state—was found to be the longest for RbCs hybrid samples. Furthermore, structural comparisons were made using scanning electron microscopy (SEM), which found a slight improvement in grain size for the less heavily doped Rb, Cs, and RbCs samples, as well as x-ray diffraction (XRD), which captured the steady degradation of perovskite into lead iodide over time.
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1. Introduction

1.1 Perovskite Solar Cells:

Hybrid organic-inorganic perovskites (HOIPs) are a promising group of semiconducting thin films for solar cell applications. With clean energy technology becoming increasingly urgent in a more climate-conscious society, HOIPs represent a more cost-effective photovoltaic option compared to conventional silicon-based devices. Not only are HOIPs cheaper and simpler to manufacture than monocrystalline silicon wafers, but perovskite-based solar cells (PSCs) have achieved power conversion efficiencies up to 23.7%, rapidly approaching those of the best silicon cells (26.1%). HOIPs come in a wide variety of compositions (Figure 1.1), which allows for tunable optical and electronic properties—adding to their appeal as a photovoltaic technology as they can be employed in multiple types of solar cell configurations, such as single junction and tandem (multijunction) solar cells.

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[a] Record efficiencies were taken from the 2019 National Renewable Energy Laboratory Best Research-Cell Efficiencies chart, https://www.nrel.gov/pv/assets/pdfs/pv-efficiency-chart.20190103.pdf
Perovskites, as a class of compounds, trace back to the early 19th century when they were discovered by Gustav Rose in the Ural Mountains in 1839. However, only recently have perovskites been employed for photovoltaics—Kojima et al. first used them as a visible light sensitizer for dye-sensitized solar cells in 2009. In general, perovskites obey a cubic crystal structure (Figure 1.2) with molecular formula ABX₃ (based on the mineral CaTiO₃), in which A is a large cation, B is a smaller metal cation, and X is an anion—typically a halide for solar devices. Two of the most common variations for solar energy purposes are methylammonium lead iodide, CH₃NH₃PbI₃ (also referred to as MAPbI₃), and formamidinium lead iodide, CH(NH₂)₂PbI₃ (referred to as FAPbI₃), which have favorable properties, such
as absorption coefficient and charge carrier diffusion length, for solar energy capture.\textsuperscript{7}

![Figure 1.2](image)

**Figure 1.2:** (a) Unit cell for a cubic, organometal halide perovskite. Octahedral coordination around the metal cation, which is typically lead. (b) Common A-site cations used in perovskite solar cells, where MA = methylammonium, FA = formamidinium, Cs = cesium, Rb = rubidium. Figure adapted from Ref. \textsuperscript{4}.

In a complete, single-junction solar cell (Figure 1.3), the perovskite layer acts as the photoactive material and is deposited between a hole transport material and an electron transport material to facilitate charge separation and extraction upon photoexcitation. On the ends of the cell are a metal contact and a conductive substrate which act as electrodes. Many groups in the perovskite field study how these external layers influence perovskite stability and efficiency, such as how they may contribute to cell degradation.\textsuperscript{8–10}
Figure 1.3: Schematic (left) and false colored scanning electron micrograph (right) of a perovskite solar cell. The metal contact is typically gold. HSL is the hole selective layer, ESL is the electron selective layer, and FTO is fluorine-doped tin oxide. The scale bar is 500 nm. Figure adapted from Ref. 4.

As for the perovskite layer itself, there is a strong tie between composition and photophysical properties that requires careful selection of each component. First, the overall bandgap of the perovskite—the energy difference between the valence band and conduction band—must overlap well with the solar energy spectrum so that light absorption will yield large amounts of free charges. For MAPbI₃ and FAPbI₃ the bandgap falls between 1.5-1.6 eV³⁴, which correlates well with the optimized bandgap (1.3 eV) for achieving the Shockley Queisser Efficiency Limit.¹¹ Secondly, another important physical metric is the Goldschmidt tolerance factor, based on atomic radii, which describes what types of A-site cations can incorporate into the perovskite lattice and form a photoactive, black phase (Figure 1.4)—crucial to achieving optimal visible light absorption.¹²,¹³ For a given A-site cation, the ideal tolerance factor for solar cell applications is between 0.8 and 1.0.¹⁴
Figure 1.4: Goldschmidt tolerance factors for various A-site cations. Note that rubidium is slightly outside the range of viable, stand-alone A-site cations. For pure CsPbI₃ and RbPbI₃ compounds, both exhibit a photoinactive, yellow phase before annealing. However, only CsPbI₃ shows a photoactive, black phase after annealing. Figure adapted from Ref. 14.

Perovskite thin films can be manufactured via solution-processed and vapor-assisted pathways (Figure 1.5). For solution-processed films, the general procedure requires mixing appropriate amounts of precursor solutions, spin coating the solutions onto substrates, and annealing each substrate to ensure crystalline perovskite growth. In particular, the “antisolvent” method pioneered by Jeon et al. was adopted by many groups after it was shown to significantly enhance perovskite device performance. For vapor-assisted techniques, the perovskite film can be grown by reacting deposited PbI₂ with organic vapor at low temperature. In any case, the synthesis of highly crystalline thin films with minimal defects plays a crucial role in maximizing device efficiency.
Figure 1.5: (a) Solution-processed method, including antisolvent (toluene) step. Figure adapted from Ref. 15. (b) Vapor-assisted method, where the inorganic film is PbI$_2$ and the organic vapor is CH$_3$NH$_3$I (or MAI). Figure adapted from Ref. 16.

Although PSCs have exhibited unprecedented growth in power conversion efficiencies in recent years, there are still open questions and challenges that must be addressed for them to become a reliable commercial power option. One main issue is hysteresis, or a difference in efficiency depending on how voltage is supplied through the cell (Figure 1.6). In brief, hysteresis creates uncertainty about the true efficiency of the cell, which creates a burden on researchers and manufacturers who rely on a consistent, accurate efficiency benchmark.
Figure 1.6: Current-voltage (J-V) curve for an MAFA-based perovskite solar cell. The device exhibits significant hysteresis in that the forward voltage scan (red curve) does not align exactly with the backward voltage scan (black curve), leading to discrepancies in device characteristics (i.e. fill factor and efficiency). The inset figure displays the efficiency of the device based on an alternative, maximum power point tracking (MPPT) technique. Figure adapted from Ref. 17.

Another significant hurdle is long-term stability, which includes stability from light-, temperature-, and moisture-induced degradation. Some researchers have successfully encapsulated perovskite devices to protect them from ambient humidity—using fluoropolymer coatings—while others have experimented with different compositions (i.e. all inorganic perovskites) that may be more resistant to water and oxygen exposure. In short, observing and characterizing degradation in PSCs will give researchers a comprehensive database toward achieving long-term stability—bringing PSCs closer toward widescale, commercial use.

1.2 Rubidium and Cesium Dopants in PSCs:

In the past few years, research has shown that combining multiple A-site cations and halide anions yields even higher efficiencies than single A-site cation and
halide stoichiometries—i.e. using mixed MA/FA cation and Br/I halide arrangements.\textsuperscript{7,17,20} In particular, doping the A-site with inorganic cations, like cesium and rubidium, further improves photovoltaic performance\textsuperscript{14,21}—albeit the exact reasons how each does so remain unclear. Interestingly, researchers have shown that doping the perovskite layer with rubidium suppresses hysteresis as well—more so than cesium\textsuperscript{17}. However, it is unclear why rubidium eliminates hysteresis most effectively. Consequently, it is important to understand how rubidium and cesium dopants change the fundamental physics and microstructure of perovskite thin films.

1.3 Organization of the Thesis:

In this thesis, using pump-probe terahertz (THz) spectroscopy, rubidium doping was found to enhance the photoconductivity of an MAFA-based perovskite thin film, at least up to 5\% Rb (Chapter 2). This increase in photoconductivity was correlated with an increase in the charge carrier mobility of the sample—or the extent to which free charges could move in response to an applied electric field. This improvement in carrier mobility with Rb-addition became an initial hypothesis of why Rb-doped samples were able to reduce hysteresis so effectively. As a result, similar terahertz photoconductivity tests were performed on a cesium series and a rubidium-cesium hybrid series to deduce whether these samples exhibited correspondingly lower carrier mobilities than rubidium-doped samples (Chapter 3). The mobilities under all three doping conditions were found to be comparable. At the same time, the RbCs samples demonstrated the best carrier lifetimes—or the extent to which a charge carrier remained in an excited state—despite a small decline in mobility over time.
In addition to charge carrier dynamics, the microstructure of each type of thin film was investigated via scanning electron microscopy (SEM) and x-ray diffraction (XRD) (Chapter 4). SEM imaging revealed the presence of two types of grains: perovskite grains and more inorganic-rich grains (called crystallites). Visible dark spots on each sample—from prolonged dry air exposure during terahertz measurements—were magnified under SEM, which revealed that crystallites, but not perovskite grains, were immune to oxygen degradation. Additionally, perovskite grain sizes were found to be comparable across all samples, with the exception being 5% Rb which was composed of unusually large, micrometer-scale grains (as compared to nanometer-scale grains). These observations coincided with the XRD findings, which revealed a significantly large PbI$_2$ peak relative to a standard perovskite peak—suggesting that degradation of perovskite into lead iodide likely took place.
2. Terahertz Photoconductivity Measurements on Rubidium-Doped Perovskite Thin Films

2.1 Introduction:

The main goal from the terahertz measurements was to characterize how adding rubidium changed the photoconductivity of the thin films, if at all. In general, non-contact photoconductivity measurements can be used to study the perovskite light absorber alone without the need for full solar cell fabrication. As the conductivity of the perovskite can be probed via optical methods, material properties can be immediately be probed without having to optimize a device structure along with ETL and HTL materials.

From THz spectroscopy measurements, charge carrier mobility is analyzed. Carrier mobility is a quantity representing how easily free charge carriers (i.e. electron and holes) can move in response to an applied electric field. The mobility value is influenced by the electronic band structure as well as grain sizes and defects within the material. In this study, Rb doping (ranging from 0 to 5%) of an MAFA based perovskite thin film was the condition for altering carrier mobility.

For this experiment, the extent of Rb doping needed to be chosen thoughtfully to be most efficient with the number of samples that could be made. The 0.1% Rb condition was used to test whether improvements in carrier dynamics were apparent even for minimal amounts of Rb addition. The 5% Rb condition was selected as a doping maximum based on corresponding observations by Saliba et al., in which using 5% Rb (for RbₓMAFA devices) yielded the highest efficiencies and 10% Rb led to a slight decline in device performance. Above 5% doping, it was argued that a
Rb-rich, non-perovskite phase segregated out and, as a result, device efficiencies dropped. Finally, the 1% Rb condition was chosen as a reasonable middle condition based on the significant amount of data available for Rb$_1$MAFA devices.

2.2 Experimental Methods:

**General Considerations.** Perovskite thin film synthesis was conducted by members of the MIT Photovoltaic Lab and film characterization was performed at Wesleyan University. All solvents were purchased from Sigma-Aldrich and used without further purification. The organic cation iodide salts were purchased from Dyesol; the lead compounds from TCI and the rubidium iodide from abcr GmbH.$^{17}$

**Thin Film Preparation.$^{17}$** A crystalline quartz substrate was cut into approximately 1” x 1” pieces. The substrates were bathed in ethanol inside a sonicator and further cleaned by UV-ozone for 15 minutes. The perovskite precursor solutions were prepared in a nitrogen-filled glove box. In total, seven samples were made: three single-cation films—MAPbI$_3$, FAPbI$_3$, and MAPbBr$_3$—and four mixed cation films—based on the formula Rb$_x$(MA$_{0.17}$FA$_{0.83}$)$_{(100-x)}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ (which are referred to by the cation portion of the perovskite). The MAFA control solution contained FAI (1 M), PbI$_2$ (1.1 M), MABr (0.2 M) and PbBr$_2$ (0.22 M) in anhydrous DMF:DMSO 4:1 (v:v). For the Rb series, a 1.5 M stock solution of RbI in DMSO was added to MAFA solution in the following volume ratios: 0.1:99.9, 1:99, and 5:95, which are referred to as Rb$_{0.1}$, Rb$_1$, and Rb$_5$, respectively. Each solution was then spin coated in a two-step program (10 s at 1000 rpm and 20 s at 6000 rpm) onto a cleaned quartz substrate. During the latter step, approximately 200 μL of chlorobenzene was
dropped onto each thin film using a glass pipet. The samples were then annealed on a hotplate at 150°C for about 1 hour.

**Packaging and Storage of Perovskite Thin Films.** After annealing, samples were placed in individual cells within a sample holder and labeled using markings on a transparent cover. The holder was vacuum sealed and placed in a Ziploc bag filled with desiccants to remove any residual moisture. After being removed from the glove box and shipped to Wesleyan, the thin films were transferred to a glass desiccator jar to prevent unwanted exposure to humidity.

**Transient Terahertz Photoconductivity Measurements.** Each sample was placed in a sample holder in which a roughly 2-mm wide hole was exposed to laser light and ambient conditions. Before unblocking the laser, the measurement chamber was purged of moisture by filling it with dry air for several minutes. The humidity of the chamber was monitored by a hygrometer and experiments were carried out in a 0% relative humidity environment.

A 400-nm femtosecond laser pulse (called the pump) was directed to illuminate the sample moments before a terahertz probe pulse arrived (Figure 2.1). The repetition rate of the pump pulses was 1 kHz, and the average fluence (energy density) of the pump pulses was calibrated to three different conditions: 7, 23, and 45 \(\mu J/cm^2\) (based on conditions set forth by other terahertz spectroscopy experiments\(^{23,24}\)). The THz probe pulse was a broad band pulse with the peak frequency at 1.2 THz and pulse duration around 1 ps. The time interval between the pump and probe pulses was varied by changing the path length of the pump light (i.e. by moving two mirrors on a delay stage). When passing through the photoexcited
sample, the THz probe signal was attenuated by a certain amount ($\Delta T$), which was proportional to the number of free charge carriers generated by the pump and the carrier mobility of the given sample (Figure 2.2). This attenuation in THz transmission was normalized and mapped as a function of pump-probe interval time, which represented the photoconductivity of the sample over time.

**Figure 2.1**: Schematic of a generic pump-probe terahertz spectroscopy experiment

**Figure 2.2**: Attenuation of the terahertz pulse after passing through a photoexcited sample$^{25}$
2.3 Results and Discussion:

2.3.1 Terahertz Photoconductivity and Carrier Mobility. Figure 2.3 shows the attenuation of THz signal as a function of pump-probe delay time for different samples. The origin of the time axis ($t=0$) corresponds to when the optical pump and THz probe arrive at the same time, leading to the largest photoconductivity. To the left, $\Delta T$ is zero because the sample is not photoexcited when the probe pulse arrives. As time progresses (i.e. to the right of $t=0$), charge carriers relax back down to the ground state because the probe pulse arrives a certain time after the pump pulse. Therefore, the material becomes less photoconductive, so $\Delta T$ decays back toward zero. From this analysis, increasing Rb concentration had a positive effect on the photoconductivity—or as more Rb was added, more terahertz signal was able to be absorbed by the perovskite after photoexcitation (Figure 2.3).

Figure 2.3: $\frac{\Delta T}{T_0}$ vs. time for samples in rubidium series, where $T_0$ was the maximum terahertz signal through the sample (i.e. without any attenuation). The fluence of the pump light was 45 $\mu$J/cm$^2$. The greater the attenuation of the terahertz signal (i.e. the more negative $\frac{\Delta T}{T_0}$ was), the greater the photoconductivity of the sample.
Terahertz attenuation data \( \frac{\Delta T}{T_0} \) was converted into photoconductivity values \( \Delta \sigma \) via Equation 2.1, in which \( n_{SiO_2} = 2.1 \) was the index of refraction of the quartz substrate, \( Z_0 = 377 \, \Omega \) was the impedance of free space, and \( d = 50 \, nm \) was the depth of the excited carriers (taken to be the absorption depth of the perovskite, \( \frac{1}{\alpha} \)).

\[
\Delta \sigma = \left( \frac{1+n_{SiO_2}}{Z_0d} \right) \left| \frac{\Delta T}{T_0} \right| \tag{2.1}
\]

Photoconductivity could be then related to carrier mobility \( \mu \) by Eq. 2.2, in which \( e \) was elementary charge and \( \Delta n \) was excited carrier density.

\[
\Delta \sigma = e \cdot \Delta n \cdot \mu \tag{2.2}
\]

Since it was assumed that increasing Rb concentration did not alter the absorption coefficient of the perovskite significantly (i.e. that each sample would absorb the same amount of pump light), all samples were assumed to have the same excited carrier density \( \Delta n \) of \( 2 \times 10^{19} \) carriers \( \cdot \) cm\(^{-3} \) at the highest fluence. As a result, with \( e \) and \( \Delta n \) being nearly equivalent across the Rb series, the observed increase in photoconductivity was rationalized as an increase in carrier mobility (Table 2.1).

| Rb\(_x\)MAFA | \( \left| \frac{\Delta T}{T_0} \right|_{max} \) | \( \Delta \sigma \) (1/\( \Omega \)/cm) | \( \mu = \frac{\Delta \sigma}{e \Delta n} \) (cm\(^2\)/V/s) |
|-------------|-----------------|-----------------|-----------------|
| Rb\(_0\)     | 2.3\%           | 38 \pm 4        | 12 \pm 1        |
| Rb\(_{0.1}\) | 2.2\%           | 36 \pm 4        | 11 \pm 1        |
| Rb\(_1\)     | 2.5\%           | 41 \pm 4        | 13 \pm 1        |
| Rb\(_5\)     | 3.0\%           | 49 \pm 4        | 15 \pm 1        |

While the differences in carrier mobility between Rb\(_0\) and Rb\(_{0.1}\) were more likely negligible, the carrier mobility of Rb\(_1\) improved by about 8\% compared to Rb\(_0\).
For Rb₅, the carrier mobility increased even further to about 25% higher than Rb₀.

This increase in mobility could have been the result of increasingly larger grain size—since having a larger grain could lower the likelihood of a charge carrier encountering a defect as it oscillates during the applied electric field.¹⁷ Additionally, this increase in photoconductivity could have arisen from a greater suppression of the photoinactive δ-FAPbI₃ phase (i.e. yellow phase), due to Rb replacing FA and contributing toward the photoactive RbMAFA perovskite phase instead.¹⁴,¹⁷,²² Furthermore, if there were some photoinactive RbPbI₃ present, it did not seem to hinder the photoconductivity of the thin film, at least up to doping with 5% Rb. Overall, the increases in photoconductivity and carrier mobility from Rb₀MAFA to Rb₅MAFA could be rationalized as increased suppression of the detrimental yellow phase, the neutral effect of RbPbI₃, and/or slight growth in perovskite grain size.

**2.3.2 Fluence Dependence and Carrier Lifetime.** In addition to mapping photoconductivity at a pump fluence of 45 μJ/cm², the photoconductivity for each sample was measured at fluences of 7 μJ/cm² and 23 μJ/cm² (Figure 2.4). Ideally, if the pump fluence is doubled, neglecting nonlinear factors, there should be twice as many charge carriers excited, meaning the photoconductivity should be expected to double as well. Sublinear relations, however, are often observed because of increased carrier scattering rate when the density of excited carriers is increased.²⁵ In addition, varying the fluence could reveal potential differences in carrier lifetime between samples, as samples may not necessarily exhibit the same decay in photoconductivity under the same conditions. For instance, not only could Rb₀ and Rb₅ differ in terms of maxima for \( \frac{\Delta T}{T_0} \), but they could also exhibit different slopes for \( \frac{\Delta T}{T_0} \) over time.
Figure 2.4: $\frac{\Delta T}{T_0}$ vs. time for Rb$_5$ at various fluences. The changing maxima for $\frac{\Delta T}{T_0}$ correspond to a different density of excited carriers per fluence. The different initial decay rates (i.e. the different slopes for photoconductivity) imply a fluence dependence on carrier lifetime and recombination in the sample.\(^\text{23}\)

Increasing the pump fluence indeed had a two-fold effect: it generated more free carriers (i.e. which led to a greater drop in $\frac{\Delta T}{T_0}$), but it also steepened the initial decay rate of these carriers—implying that as the number of carriers increased, there was a faster type of recombination occurring.\(^\text{23}\) The latter observation could be understood as higher order recombination mechanisms (i.e. bimolecular and Auger recombination) taking place in addition to monomolecular, trap-assisted recombination, which would occur on a longer time-scale.\(^\text{23}\)

While only Rb$_5$ was featured in Figure 2.4, each of the seven samples exhibited a large fluence dependence on photoconductivity. However, the exact relationship between $|\frac{\Delta T}{T_0}|_{max}$ and fluence was not the same between the single-cation, MAFA, and Rb$_x$MAFA thin films (Figure 2.5). Between FAPbI$_3$, MAFA, and
Rb₃MAFA, only Rb₅MAFA was able to maintain a roughly linear relationship between terahertz absorption and fluence, while the other two types of samples tapered off in photoconductivity (relative to their performance at lower fluences). In brief, adding Rb (at least up to 5%) allowed the Rb₃MAFA perovskite to tolerate a higher pump power and operate at a greater photoconductivity than undoped MAFA or single cation samples.

![Graph](image)

**Figure 2.5:** $\frac{\Delta T}{T_0}$ vs. fluence for FA single cation (FAPbI₃), undoped mixed cation (MAFA), and Rb-doped mixed cation (5Rb) thin films. The linear relationship between terahertz absorption and fluence (up to 45 μJ/cm²) only holds for the Rb-doped thin film.

Carrier lifetimes were analyzed based on the overall decay in photoconductivity (i.e. how much $\frac{\Delta T}{T_0}$ diminished over the course of a terahertz scan). This was calculated by $\frac{\Delta T_{t=1600 \text{ ps}} - \Delta T_{t=0 \text{ ps}}}{\Delta T_{t=0 \text{ ps}}}$. Using this method, the lifetimes at the lowest fluence (7 μJ/cm²) were found to be comparable across the Rb series (data not shown). However, as fluence increased, the extent of decay did not increase equivalently for all samples. For Rb₁, the overall decay at the highest fluence (45
μJ/cm²) was less than that of MAFA, Rb₀.₁, and Rb₅ (Figure 2.6)—i.e. the less-doped Rb₁ sample exhibited slightly better carrier lifetime than Rb₅.

**Figure 2.6**: Percent decay in photoconductivity over the course of a terahertz scan at high fluence (45 μJ/cm²). The data was taken from the mean photoconductivity curve after ten scans. The smaller the decay in \( \frac{\Delta T}{T_0} \) over time, the better the carrier lifetime.

Since the photoconductivity decay within the first 1600 ps (Figures 2.4 and 2.6) was not an exponential decay and the magnitude of the decay was small, carrier lifetime cannot be deduced exactly from THz photoconductivity decay alone. If the samples had been analyzed by time-resolved photoluminescence, the carrier lifetimes could have been quantified explicitly, or at least compared more precisely. Knowing the exact lifetimes (\( \tau \)), along with carrier mobilities (\( \mu \)), would have allowed for the comparison of diffusion lengths (\( L_D \)) across the Rb series (Eq. 2.3).²³

\[
L_D \propto \sqrt{\mu \tau}
\]  

(2.3)
2.3.3 Possible Rationale for Hysteresis Suppression. In sum, from terahertz measurements, the carrier mobility of the Rb$_x$MAFA perovskite improved with Rb addition. Additionally, the carrier lifetimes for Rb-doped samples (i.e. Rb$_1$ and Rb$_5$) were either longer or comparable to that of the MAFA control sample. Using these two results in tandem, a rationale for why rubidium could suppress hysteresis in PSC devices so effectively could be because Rb-doped thin films exhibit less sensitivity to changes in an electric field, which would arise from switching the voltage directions during a solar simulation test. Having both longer-lived and more mobile free carriers, Rb-doped perovskites are equipped to transport charges fast enough to avoid electric-field screening from halide and ion migration toward grain boundaries.

2.3.4 Issues with Long-Term Stability of Samples. A follow-up round of terahertz measurements was conducted roughly one month after initial measurements to investigate how the photoconductivity curves of the Rb series may have changed over time. Comparing the photoconductivity curves of MAFA and Rb$_5$MAFA from the very beginning of the experiment with those from the follow-up scans, a similar decline in THz attenuation was observed for both samples (Figure 2.7). Such a drop in performance suggested that some form of degradation in the mixed cation samples had taken place—i.e. through moisture- or oxygen-induced degradation. Sample degradation will be further explored in Chapter 4.
Figure 2.7: $\frac{\Delta T}{T_0}$ over time for MAFA and Rb$_5$MAFA at high fluence, taken roughly one month apart. Each film exhibited less photoconductivity during the follow-up test (referred to as ‘end’ condition), which was a sign that both perovskites may have degraded considerably between the first and last terahertz experiments.

2.4 Conclusion:

In this chapter, Rb-doped MAFA perovskite thin films (with concentration ranging from 0 to 5% Rb) were tested for terahertz carrier mobility and lifetime. The chapter also detailed the optical-pump, terahertz-probe experimental method and data analysis methods. Rubidium doping was found to enhance the photoconductivity of an MAFA-based perovskite thin film, and this increase in photoconductivity was correlated with an increase in the charge carrier mobility of the sample. The mid-doping condition (i.e. Rb$_1$MAFA) led to the best carrier lifetimes as well. An improvement in carrier mobility with Rb-addition became an initial rationale as to why Rb-doped devices exhibited less hysteresis.
3. Carrier Dynamics Comparison Between Rubidium- and Cesium-Doped Thin Films

3.1 Introduction:

The first PSC to exhibit a power conversion efficiency above 20% was not reported until 2015 (using an MAFA mixed cation thin film). Since then, doping the MAFA perovskite with Group I elements (i.e. Cs and Rb or even K) has further improved device performance and stability. In particular, Rb-doped perovskite layers (i.e. Rb$_x$MAFA) has been known to reduce device hysteresis quite substantially, with Cs$_x$MAFA also reducing hysteresis but less effectively.

After observing from terahertz measurements that Rb-doped thin films displayed an elevated carrier mobility, which could potentially explain their ability to reduce hysteresis, the next step was to gather carrier mobility data on Cs-doped analogs. If Cs$_x$MAFA samples exhibited enhanced mobility relative to MAFA, but significantly lower mobility compared to Rb$_x$MAFA, then the framework of improved carrier mobility as a means of curbing hysteresis would be strengthened. Additionally, the effect of RbCs dual incorporation (i.e. Rb$_x$Cs$_x$MAFA) on mobility and lifetime could be investigated as well.

3.2 Experimental Methods:

General Considerations. Perovskite thin film synthesis and solar device testing were conducted by members of the MIT Photovoltaic Lab. The solar device efficiencies were measured using a 450 W xenon light source (Oriel). Thin film characterization was performed at Wesleyan University. The same general process
was used to manufacture and characterize the new Rb, Cs, and RbCs series, as reported earlier for the initial Rb series.

**Thin Film Preparation.** The crystalline quartz substrates were cut such that some pieces turned out to be asymmetrical, but still around 1” x 1” in total area. In total, seven samples were made based on the formula 

\[ \text{Rb}_x\text{Cs}_y(\text{MA}_{0.17}\text{FA}_{0.83})_{100-x-y}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3 \]. For the Rb series, a 1.5 M stock solution of RbI in DMSO was added to MAFA solution in 1:99 and 5:95 volume ratios, which are referred to as Rb₁ and Rb₅, respectively. For the Cs series, the same steps were followed to make Cs₁ and Cs₅ except using a solution of CsI in DMSO instead of RbI. For the RbCs series, both RbI and CsI were incorporated to make Rb₁Cs₁ and Rb₂.₅Cs₂.₅. The solutions were spin-coated onto cleaned quartz substrates and annealed according to the same parameters for the initial Rb series.

**Transient Terahertz Photoconductivity Measurements.** The same procedural steps were taken to measure the terahertz signal and attenuation through the Rb, Cs, and RbCs samples. Because the dimensions of the pump pulse changed slightly (i.e. the area of photoexcitation changed), the power of the laser was re-calibrated to ensure the same fluence conditions of 7, 23, and 45 \( \mu \text{J/cm}^2 \). Additionally, a follow-up scan at 7 \( \mu \text{J/cm}^2 \) (after all three fluence tests from low, mid, to high fluence) was added for each sample as a check to ensure that the sample did not change behavior significantly over the course of the experiment.

**Solar Simulation Measurements.** A 1”x1” solar cell was fabricated for each perovskite thin film. For solar device testing, a given device was placed in a custom sample holder, with a black metal mask made to minimize the amount of
scattered light coming off the device. Cables were connected to jacks on the sample holder to supply voltage and current, and a chiller kept the sample holder at a constant temperature (25°C). The lamp, calibrated to AM 1.5G, supplied photoexcitation, and current-voltage data was obtained by applying an external voltage bias and measuring the current response. The voltage scan rate was set to 10 mV s\(^{-1}\) and probed in both directions (i.e. from negative to positive and vice versa).

### 3.3 Results and Discussion:

#### 3.3.1 Comparison of Carrier Mobilities.

Based on the same process of deriving the carrier mobility from maximum terahertz attenuation, the carrier mobilities of the Cs\(_x\)MAFA and Rb\(_x\)Cs\(_x\)MAFA thin films were found to improve relative to the MAFA control (Figure 3.1). Compared to the Rb-doped samples, the Cs-doped samples exhibited nearly equivalent mobilities—rather than being somewhere in between those of MAFA and Rb\(_x\)MAFA. Consequently, the idea of enhanced carrier mobility being linearly related to the reduction of hysteresis, hypothesized from the previous Rb experiment, was likely not a full picture of hysteresis dynamics. At the same time, it was not unusual that the mobilities of Rb\(_x\)MAFA and Cs\(_x\)MAFA, in fact, overlapped because their corresponding devices have been shown to yield similar solar cell efficiencies.\(^{14,21,22}\) Moreover, the observation that Rb-, Cs-, and RbCs-doped samples all produced a higher mobility than undoped MAFA would explain at the molecular level why each of these triple/quadruple cation perovskites typically boosts solar cell performance.\(^{4,14,17,21,22}\)
Figure 3.1: THz carrier mobility at mid- (23 μJ/cm²) and high-fluence (45 μJ/cm²) for all seven samples. Ideally, the carrier mobilities should stay the same between tests since only the density of excited carriers should change with fluence.

Interestingly, the Rb₃CsₓMAFA samples exhibited a drop in mobility between the mid- and high-fluence photoconductivity tests. Furthermore, the low fluence pump-probe scan designed as a follow-up also showed that the terahertz signal was lower than first recorded. It was initially unclear whether this decrease was due to laser misalignment—which could mean either less terahertz signal getting detected or pump light being partially obstructed—or due to the RbCs samples already degrading from prolonged moisture- or oxygen-exposure. If the cause of the drop were degradation-driven, then the onset of such degradation would be much faster for Rb₃CsₓMAFA than for the other doped samples.

3.3.2 Comparison of Carrier Lifetimes. Similar to the trend for the original Rb-doped series, doping MAFA with Rb, Cs or RbCs improved carrier lifetimes (Figure 3.2 and 3.3). Also, similar to the trend shown in Chapter 2.3.2, the lower concentration samples under each doping condition (i.e. Rb₁, Cs₁, Rb₁Cs₁) all
exhibited longer lifetimes than their higher concentration counterparts. In particular, Rb\textsubscript{1}Cs\textsubscript{1} showed the best lifetimes of the entire group (for the mid-fluence test, the sub-zero decay in photoconductivity for Rb\textsubscript{1}Cs\textsubscript{1} could be explained as a fairly small decay that fell below zero within the error range).

It is possible that the lower concentration samples could be introducing enough dopants to minimize defects in the sample but not to an extent such that significant amounts of photoinactive side phases (i.e. RbPbI\textsubscript{3}) are being formed.\textsuperscript{22}

The best carrier lifetimes, based on overall decay in photoconductivity, were found in the RbCs hybrid films. Such an enhanced lifetime, or better retention of excited carriers, would explain why Rb\textsubscript{x}Cs\textsubscript{x}MAFA devices usually are the best performing solar cells, compared to Rb\textsubscript{x}MAFA and Cs\textsubscript{x}MAFA analogs.\textsuperscript{14,17,21,22}

It is possible that when Rb and Cs are both present, Rb takes on a passivation role because Cs gets preferentially incorporated into the lattice due to its more appropriate Goldschmidt tolerance factor (Figure 1.4). Indeed, Correa-Baena \textit{et al.} argue—based on photoelectron spectroscopy data—that Cs aids the integration of Rb into the perovskite, leading to better crystal quality and homogeneity—thereby providing a driving force toward higher device efficiencies.\textsuperscript{29}

While there is conflicting information in the field on whether Rb and Cs each incorporate into the lattice\textsuperscript{14,30}, the THz lifetime data would support the idea that RbCs dual incorporation leads to a potential passivation effect. Additionally, the longer lifetimes could be compensating for a slightly poorer mobility, thus potentially giving RbCs the best carrier diffusion lengths overall—or the best balance for efficient charge transport.\textsuperscript{14}
Figure 3.2: Percent decay in photoconductivity over the course of a terahertz scan at mid fluence (23 μJ/cm²). The data was taken from an average of ten scans. The smaller the decay in $\frac{\Delta T}{T_0}$ over time, the better the carrier lifetime.

Figure 3.3: Percent decay in photoconductivity over the course of a terahertz scan at high fluence (45 μJ/cm²). The data was also taken from an average of ten scans.
3.3.3 Photovoltaic Device Testing. Three separate rounds of device testing were conducted to investigate whether there was any correlation between terahertz carrier mobility, lifetime, and device performance (Figure 3.4). Excluding the anomalous data for Rb\textsubscript{1}MAFA, which was most likely due to issues during device fabrication and a non-pristine perovskite layer, there was a systematic improvement in efficiency under all three doping conditions—similar to the mobility trends. Moreover, looking at the Cs\textsubscript{x}MAFA and Rb\textsubscript{x}Cs\textsubscript{x}MAFA series, the lower concentration devices, on average, exhibited better efficiencies—tracing back to the longer lifetimes for the less doped thin films. As a result, improved performance at the device level can be linked to improved carrier dynamics at the perovskite level.

It is worth noting that although the highest efficiencies for the doped devices did not exceed 18\%, compared to benchmarks reported from literature\textsuperscript{4,14,17,21,22}, it is most likely because device testing was not conducted with encapsulated devices or in a nitrogen atmosphere—i.e. with checks for eliminating ambient air exposure. Consequently, the Rb\textsubscript{x}Cs\textsubscript{x}MAFA devices may not have been the best performing devices in this case because of their susceptibility to degradation, as shown during the terahertz measurements.
Figure 3.4: Boxplot of power conversion efficiencies (PCE) for devices made from each sample. A total of 15 devices were tested in each sample category. The relatively low efficiencies for Rb$_1$ were attributed to issues during thin film fabrication for the device.

3.4 Conclusion:

In this chapter, terahertz photoconductivity measurements and device performance data were used to look for observable differences between Rb- and Cs-doped perovskite thin films. No major difference between the Rb and Cs series was detected via terahertz spectroscopy—i.e. the improvements in carrier dynamics were quite similar. Carrier mobility was found to increase as soon as at least 1% of Rb, Cs, or a combination of RbCs was introduced. Carrier lifetime was slightly better in the samples containing less dopants as well. RbCs samples were found to potentially degrade most quickly, even as the terahertz measurement was on-going. At the same time, the RbCs samples demonstrated the best carrier lifetimes overall.

4.1 Introduction:

Possible sample degradation observed in both Ch. 2.3.4 and Ch. 3.3.1 motivated the need for structural characterization on the samples used in Ch. 3. From these measurements, scanning electron micrographs reveal several different features, and x-ray diffraction scans show that despite being stored in a dry box, the samples likely experienced observable degradation after a few months.

From Ch. 3.3.1, doping the MAFA perovskite with either Rb\textsubscript{x}, Cs\textsubscript{x}, or Rb\textsubscript{x}Cs\textsubscript{x} (up to maximum doping concentrations of Rb\textsubscript{5}, Cs\textsubscript{5}, and Rb\textsubscript{2.5}Cs\textsubscript{2.5}) each improved carrier mobility. Moreover, the Rb\textsubscript{x}Cs\textsubscript{x} samples exhibited the longest carrier lifetimes. However, the carrier mobilities of Rb\textsubscript{1}Cs\textsubscript{1} and Rb\textsubscript{2.5}Cs\textsubscript{2.5} unexpectedly deteriorated during the terahertz experiment, which was confirmed by a follow-up, repeatability scan. It was unclear why the Rb\textsubscript{x}Cs\textsubscript{x} samples exhibited this behavior, as the Rb\textsubscript{x} and Cs\textsubscript{x} samples did not display a similar decline in mobility.

From prior work, any areas of the sample exposed to the measurement chamber environment were observed to turn a darker hue, even for parts that were not hit by pump pulses (Figure 4.1). However, since these dark spots appeared for all samples—and not just for Rb\textsubscript{x}Cs\textsubscript{x}MAFA—this phenomenon alone could not explain why the hybrid samples suffered such noticeable decline in performance. Consequently, each sample was viewed under SEM to see whether there were different responses to ambient dry air exposure at the local morphological level.
Figure 4.1: Formation of dark spots on $\text{Rb}_{2.5}\text{Cs}_{2.5}\text{MAFA}$ after photoconductivity measurements. Only one of the spots was photoexcited with 400 nm light. Similar dark spots formed on all samples. The location of the spots was due to the nature of the sample holder, which had a line of three possible holes to direct light through.

In addition, the samples were analyzed via XRD to look for changes in overall crystal quality. XRD analysis is a very useful tool for examining the integrity of the perovskite thin film, as the ratio between the lead iodide peak ($2\theta = 12.6^\circ$) and the (110)/(002) perovskite peak ($2\theta = 14^\circ$) can be mapped over time to track any changes in structure. Doping MAFA perovskites with Rb and Cs has been shown to suppress the $\text{PbI}_2$ peak in pristine samples.\textsuperscript{17,21,22} Conversely, inducing perovskite degradation through thermal stress has been shown to increase the intensity of the $\text{PbI}_2$ peak over time (relative to the perovskite peak).\textsuperscript{21}

4.2 Experimental Methods:

**General Considerations.** Care was taken to minimize sample exposure to ambient humidity whenever transporting samples outside of the desiccator jar. SEM imaging and energy dispersive x-ray (EDX) elemental analysis were conducted on a Hitachi SU5000 Scanning Electron Microscope. X-ray diffraction measurements were performed using a copper $K\alpha$ source.
Scanning Electron Microscopy. Each sample was placed on a clean sample holding disk and taped down at the edges with carbon tape. After venting the SEM chamber and configuring specimen dimensions for the sample stage, the chamber was opened and the holder was inserted into place. The chamber was subsequently closed, ensuring the sample just fit under the metal guard, and evacuated. The button pad controlled the position, magnification level, brightness, and contrast of the microscope. The electron beam settings were adjusted to 5.0 kV and 9.0 spot intensity to achieve the sharpest images. After locating and focusing on the desired area, images were taken at 25k and 50k magnification.

X-ray Diffraction. Each sample was placed onto a millimeter-thick metal sample holder such that the edge of the sample was flush with a center ridge. The sample was probed within a 2θ range of 9-16° since the lead iodide and (110)/(002) perovskite peak could be found around 12.6° and 14°, respectively.21,22,31

4.3 Results and Discussion:

4.3.1 Scanning Electron Microscopy. From SEM imaging, there were three main findings. First, when magnifying dark spots (Figure 4.1), certain grains appeared “eroded”—i.e. such grains were not fully intact and, in fact, developed pinholes (Table 4.1). In areas protected from ambient conditions, however, such erosion did not appear. This pattern was consistent across all samples. For Rb_xCs_xMAFA, the extent of this erosion appeared to be the greatest—thus offering a structural reason as to how its performance may have been hindered. Second, within the dark spot regions, there were also grains that did not erode (such grains are referred to as crystallites17). These crystallites, however, were difficult to distinguish
from non-crystallites (i.e. perovskite grains) in areas where erosion was not present. Third, when the SEM probe was switched from secondary electrons (SE) to backscattered electrons (BSE), the contrast between crystallites and non-crystallites improved significantly (Table 4.2). Because the BSE detector was more sensitive to heavier substances, the stronger signal coming from the crystallites suggested that they contained a higher proportion of heavier, inorganic content (i.e. Rb/Cs dopants or Pb). An increase in Rb and Pb content was indeed confirmed for the Rb₅MAFA sample after EDX measurements (Table 4.3).
Table 4.1: Magnified images of regions that were either exposed or unexposed to dry air during terahertz measurements. The development of pinholes (for exposed areas) only occurs on perovskite grains. All SEM images were taken with a BSE probe.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unexposed to dry air</th>
<th>Exposed to dry air</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAFA</td>
<td><img src="image" alt="MAFA Unexposed" /> 2.00μm</td>
<td><img src="image" alt="MAFA Exposed" /> 2.00μm</td>
</tr>
<tr>
<td>Rb₅</td>
<td><img src="image" alt="Rb₅ Unexposed" /> 2.00μm</td>
<td><img src="image" alt="Rb₅ Exposed" /> 2.00μm</td>
</tr>
<tr>
<td>Cs₅</td>
<td><img src="image" alt="Cs₅ Unexposed" /> 2.00μm</td>
<td><img src="image" alt="Cs₅ Exposed" /> 2.00μm</td>
</tr>
<tr>
<td>Rb₂.₅ Cs₂.₅</td>
<td><img src="image" alt="Rb₂.₅ Cs₂.₅ Unexposed" /> 2.00μm</td>
<td><img src="image" alt="Rb₂.₅ Cs₂.₅ Exposed" /> 2.00μm</td>
</tr>
</tbody>
</table>
Table 4.2: Magnified images of regions unexposed to dry air, taken with both SE and BSE probes. The crystallites (brighter contrast grains) are much more discernible when scanned with a BSE probe.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SE</th>
<th>BSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAFA</td>
<td><img src="image1" alt="MAFA SE image" /></td>
<td><img src="image2" alt="MAFA BSE image" /></td>
</tr>
<tr>
<td>Rb&lt;sub&gt;5&lt;/sub&gt;</td>
<td><img src="image3" alt="Rb&lt;sub&gt;5&lt;/sub&gt; SE image" /></td>
<td><img src="image4" alt="Rb&lt;sub&gt;5&lt;/sub&gt; BSE image" /></td>
</tr>
<tr>
<td>Cs&lt;sub&gt;5&lt;/sub&gt;</td>
<td><img src="image5" alt="Cs&lt;sub&gt;5&lt;/sub&gt; SE image" /></td>
<td><img src="image6" alt="Cs&lt;sub&gt;5&lt;/sub&gt; BSE image" /></td>
</tr>
<tr>
<td>Rb&lt;sub&gt;2.5&lt;/sub&gt; Cs&lt;sub&gt;2.5&lt;/sub&gt;</td>
<td><img src="image7" alt="Rb&lt;sub&gt;2.5&lt;/sub&gt; Cs&lt;sub&gt;2.5&lt;/sub&gt; SE image" /></td>
<td><img src="image8" alt="Rb&lt;sub&gt;2.5&lt;/sub&gt; Cs&lt;sub&gt;2.5&lt;/sub&gt; BSE image" /></td>
</tr>
</tbody>
</table>
Table 4.3: SEM-EDX elemental analysis of perovskite and crystallite grains in Rb₅MAFA. Grains types with the same number indicate adjacent grains.

<table>
<thead>
<tr>
<th>Grain type</th>
<th>Rb (atomic %)</th>
<th>Pb (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perovskite 1</td>
<td>1.37</td>
<td>8.56</td>
</tr>
<tr>
<td>Perovskite 2</td>
<td>1.62</td>
<td>7.44</td>
</tr>
<tr>
<td>Crystallite 1</td>
<td>2.88</td>
<td>12.20</td>
</tr>
<tr>
<td>Crystallite 2</td>
<td>3.27</td>
<td>9.96</td>
</tr>
</tbody>
</table>

In sum, crystallites were likely present throughout the perovskite film, but were difficult to distinguish from perovskite grains when using secondary electrons as the SEM probe (versus backscattered electrons). When viewing regions of the perovskite that had been exposed to dry air, these crystallites were more easily identifiable because they were immune to erosion. Both these findings are captured in Figure 4.2, which captures the border of a dark spot. If the erosion or degradation of perovskite grains were induced by moisture, the immunity of a crystallite could be traced back to its higher amount of inorganic content, which would be less susceptible to reacting with water. However, since the measurement chamber was purged of humidity during measurements, the erosion was more likely induced by molecular oxygen from dry air, which could degrade the perovskite into lead oxide or lead iodide. In either case, the crystallites could be viewed as excess PbI₂ or dopant-rich side phases that likely formed during thin film synthesis and spread around the sample during spin-coating and annealing.
Figure 4.2: SEM images of Rb$_{2.5}$Cs$_{2.5}$MAFA at the border of a dark spot taken with (a) an SE and (b) a BSE probe. Area 1 highlights the oxygen-induced degradation of perovskite grains. Area 2 denotes how crystallites are immune to such degradation. Area 3 captures how crystallites are more apparent using BSE (particularly in non-eroded areas).
In addition to these degradation-related findings, the grain sizes of each samples were tabulated using ImageJ software (Table 4.4). It was unclear whether the unusually large grain size for the Rb₅MAFA sample was due to complications during thin film fabrication or from a degradation-related reaction.³⁰,³³ Excluding the data for Rb₅, all perovskite grain sizes were within one standard deviation from the average size of the MAFA control. There was still a slight improvement in average grain size for Rb₁, Cs₁, and both hybrid samples, which could contribute toward their enhanced carrier dynamics and device performance.¹⁷ Moreover, taking the product of average crystallite size and the number of crystallites per image, the higher doped samples (i.e. Cs₅ and Rb₂.₅Cs₂.₅) were found to contain a smaller overall crystallite distribution. This observation would further support the identification of crystallites as PbI₂ because lead iodide excess would similarly decrease with increased doping, due to more reactions between PbI₂ and either RbI or CsI.

Table 4.4: Grain size data for all seven samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Avg. perovskite grain size (nm)</th>
<th>Standard deviation for perovskite grains (nm)</th>
<th>Avg. crystallite grain size (nm)</th>
<th>No. of crystallites (per 25k image)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAFA</td>
<td>530</td>
<td>160</td>
<td>260</td>
<td>50</td>
</tr>
<tr>
<td>Rb₁</td>
<td>630</td>
<td>200</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td>Rb₅</td>
<td>1600</td>
<td>500</td>
<td>800</td>
<td>5-15</td>
</tr>
<tr>
<td>Cs₁</td>
<td>620</td>
<td>200</td>
<td>330</td>
<td>40</td>
</tr>
<tr>
<td>Cs₅</td>
<td>520</td>
<td>180</td>
<td>490</td>
<td>15</td>
</tr>
<tr>
<td>Rb₁Cs₁</td>
<td>580</td>
<td>190</td>
<td>290</td>
<td>40</td>
</tr>
<tr>
<td>Rb₂.₅Cs₂.₅</td>
<td>620</td>
<td>210</td>
<td>480</td>
<td>20</td>
</tr>
</tbody>
</table>
4.3.2 X-ray Diffraction. XRD analysis on all seven samples showed a substantially large PbI$_2$ peak, relative to the perovskite peak, for MAFA, Rb$_1$, Cs$_1$, and Rb$_1$Cs$_1$ (Figure 4.3). Additionally, Cs$_5$ and Rb$_{2.5}$Cs$_{2.5}$ exhibited a slight growth in PbI$_2$, while Rb$_5$ maintained a larger perovskite peak.

![XRD analysis](image)

**Figure 4.3**: XRD analysis of each sample several months after terahertz measurements. The data is normalized to the perovskite peak around $14^\circ$. The PbI$_2$ peak is significantly larger than the perovskite peak, indicating substantial perovskite degradation. The samples had been stored in a desiccator jar, aside being taken out for SEM imaging.

The widespread growth of PbI$_2$ verified that the crystal quality of the samples was compromised, and that oxygen-induced degradation (observed via SEM) likely produced PbI$_2$ as a decomposition product. In addition, having less dopants provided less stability against such degradation as there was a higher proportion of undoped MAFA perovskite to react with oxygen. The anomalously low PbI$_2$ peak for Rb$_5$ could be rationalized by an abnormally large grain size, which would imply a smaller initial PbI$_2$ excess and a larger initial perovskite peak. Furthermore, the size of the PbI$_2$ peak correlated roughly with the average distribution of crystallites per 25k SEM image, which would support the identification of crystallites as lead iodide.
In addition to investigating degradation, XRD analysis could provide structural data on whether Rb and Cs each incorporated into the perovskite lattice. As mentioned in Ch. 3.3.2, certain groups argue that Cs should incorporate into the lattice due to its ideal Goldschmidt factor. If true, such incorporation would lead to a lattice contraction (and a shift to wider $2\theta$ angles) in an MAFA perovskite, as Cs would not occupy as large an A-site as the MAFA mixed cation.$^{14,30}$ Similarly, if Rb did incorporate into the lattice, there would be even stronger contractions due to Rb$^+$ having a smaller ionic radius than Cs$^+$. Conversely, some may argue that Rb could cause an expansion of the lattice (and shifts to smaller angles) because it is, in fact, too small to incorporate into the lattice and can actually extract Br$^-$ ions to form a non-perovskite side phase.$^{30}$ In either case, the locations of the perovskite peak in the Rb- and Cs-doped samples, relative to that in the MAFA sample, could tell which type of mechanism was more accurate.

The perovskite peak for each sample was magnified in an attempt to observe possible shifts to wider or smaller $2\theta$ angles compared to MAFA (Figure 4.4). For Rb$_1$, Rb$_5$, Cs$_1$, and Rb$_1$Cs$_1$, there appeared to be slight shifts to smaller angles, while for Cs$_5$ and Rb$_{2.5}$Cs$_{2.5}$ there appeared to be slight shifts to larger angles.
Figure 4.4: Magnified XRD patterns showing the shift of the main perovskite peak between samples. The position of the peak maximum for MAFA is roughly 14.04°. Shifts towards larger diffraction angles indicate potential lattice contraction, while shifts toward smaller angles indicate potential lattice expansion.\[30\]

While there is not a clear divide between how Rb and Cs alter the perovskite lattice, since Cs\(_1\) induced a shift to smaller—rather than larger—angles, it could be argued that higher doping conditions may bring about such a distinction. Cs\(_5\) appears to induce a lattice contraction while Rb\(_5\) looks to induce a lattice expansion. Furthermore, Rb\(_{2.5}\)Cs\(_{2.5}\) induces a slight lattice contraction, lying between the shifts for Cs\(_5\) and Rb\(_5\). Therefore, as hypothesized in Ch. 3.3.2, the addition of both Rb and Cs could lead to a scenario in which Cs is the dopant that incorporates into the lattice but at least facilitates a homogeneous distribution of Rb within the bulk of the thin film.\[29\]
4.4 Conclusion:

In this chapter, sample microstructure and crystal quality were analyzed via SEM and XRD measurements to characterize the extent of sample degradation. From SEM imaging, two main grain types were identified—perovskite grains and more heavily inorganic crystallites (possibly lead iodide). Looking at areas of the sample which were exposed to terahertz testing conditions, perovskite grains were found to be eroded and covered in pinholes—with the density of pinholes being highest for Rb,Cs,MAFA samples. Moreover, XRD analysis showed the development of a large PbI$_2$ peak across samples, which confirmed that perovskite decomposition (most likely via an oxygen-induced pathway) had occurred.

At the same time, these results were gathered a few months after terahertz measurements. As samples were measured via terahertz spectroscopy as soon as they were received and care was taken to remove as many environmental factors as possible, the trends in carrier mobility and lifetime for Rb- and Cs-doped thin films most likely reflected the behavior of pristine samples. Moreover, slightly enhanced grain sizes for certain Rb- and Cs-doped samples would give structural credibility to the observed carrier dynamic improvements for these thin films.
5. Conclusions and Future Work

The enhancements in terahertz carrier mobility and lifetime for Rb-, Cs-, and RbCs-doped MAFA perovskite thin films provide a fundamental physical rationale as to how each type of doping is able to improve PSC device performance. While the extent of mobility and lifetime improvement was nearly equivalent between Rb-doped and Cs-doped analogs, which negated a linear relationship between mobility and device hysteresis, the observation of RbCs-addition leading to significantly longer lifetimes bolstered the idea of a Rb passivation effect taking place when coupled with Cs incorporation into the perovskite lattice. Such a model would provide a structural basis for why RbCs-doped devices most often deliver “champion” solar cell performances within the PSC field.

Additionally, the SEM documentation of perovskite decomposition (in areas exposed to dry air) and the corresponding growth of the XRD PbI₂ peak over time would each support mechanisms of oxygen-induced perovskite degradation. The extent of this degradation could potentially be coupled with the distribution of inorganic-rich crystallites within each sample.

In the future, conducting time-resolved photoluminescence studies on each dopant series could provide clearer carrier lifetime values, which could be combined with terahertz mobility data to derive charge carrier diffusion lengths for each sample. If such diffusion lengths were longest for RbCs-doped thin films, this could strengthen the passivation model detailed earlier. Furthermore, performing a systematic SEM analysis based on the duration of thin film exposure to dry air could elucidate the onset time of perovskite degradation within each type of sample, thereby
testing whether one doping condition is superior in terms of oxygen stability as well as estimating what the general degradation timeline may be.

Overall, hybrid organic-inorganic perovskite semiconductors provide a timely upgrade to current solar cell technologies and adding Rb- and Cs-dopants to the perovskite absorber layer provides a compositional advantage for PSC device performance. Using them in tandem and optimizing the concentration of each dopant in terms of device efficiency and stability will bring the PSC field closer to a breakthrough commercial device.
References


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