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Solution-processed all-inorganic bismuth-triiodide thin-films for photovoltaic application

Umar Hussein Hamdeh
Iowa State University

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Solution-processed all-inorganic bismuth-triiodide thin-films for photovoltaic application

by

Umar Hussein Hamdeh

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Chemical Engineering

Program of Study Committee:
Matthew G. Panthani, Major Professor
Andrew C. Hillier
D. Raj Raman

The student author and the program of study committee are solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa

2017

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DEDICATION

This thesis is dedicated to my family for their love and support. I’d like to thank my parents Hussein and Amal, my siblings Tania, Samir, Yusuf, Ahmad, Tala, Waleed, Deema, and Sami, and my niece and nephew Yasmeen, and Ehab. It’s your unconditional love that gives me the strength and confidence to overcome any challenge.
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experience with me inspires you to become the next generation of scientists and engineers. That will have a greater impact in the scientific community than any paper I will ever publish. Next, I’d like to thank all my friends, the department faculty, and staff at Iowa State University. You made this an enjoyable experience. Finally, I’d like to thank all the scientists before me. This work stands on the shoulders of many, and I am honored to contribute to the total body of work with this thesis.
Rapid improvement in the efficiency of lead halide perovskite solar cells has led to an expansion in the interest of halide perovskite materials for optoelectronic devices. However, concerns with toxicity and material instability pose serious challenges for the future commercialization of lead halide perovskites solar cells. Thus, alternative materials that share similar optoelectronic properties to lead halide perovskites are being explored. One material that has the potential to replace lead halide perovskites is BiI₃, which is nontoxic and shares a similar electronic structure to lead halide perovskites. All-inorganic solution-processable BiI₃ thin-film photovoltaic devices were developed as a proof-of-concept to demonstrate the potential of BiI₃ thin-films for photovoltaic application. Two-electron donor solvents such as tetrahydrofuran and dimethylformamide were found to form adducts with BiI₃, which made BiI₃ highly soluble in these solvents. BiI₃ thin-films were deposited by spin coating. Solvent annealing BiI₃ thin films at relatively low temperatures (≤ 100 °C) resulted in increased grain size and crystallographic reorientation of grains within the films. The BiI₃ films were stable against oxidation for several months and could withstand several hours of annealing in air at temperatures up to 150 °C without degradation. Surface oxidation was found to improve photovoltaic device performance due to the formation of a BiOI layer at the BiI₃ surface which facilitated hole extraction. BiI₃ solar cells achieved highest power conversion efficiencies of 1.0%, demonstrating the potential of BiI₃ as a non-toxic, air-stable metal halide absorber material for photovoltaic applications. This thesis serves to provide a study of the material chemistry of BiI₃, as well as opens avenues for other potential research projects.
such as an extension of this work to other bismuth-based semiconductors, and the continued
development of BiI$_3$ PV devices.
CHAPTER 1. INTRODUCTION

Bearing in mind the recent advancements of developing countries, and the growing concern from the extensive use of fossil fuels on the environment, the need for an abundant clean source of energy is imperative to the sustainability and future growth of humanity. Sunlight is arguably the best source for an indefinite clean energy source, and the production of photovoltaics could facilitate sustainable economic growth. Over 120,000 TW of solar radiation strikes the Earth’s surface continuously, while our global power consumption in 2013 was only 12.3 TW. As it stands today, solar energy only accounts for 0.9% of the total quantity of electricity generated in the U.S. Over the next 25 years, the Energy Information Administration predicts that roughly 50% of the new energy capacity will be renewable energy sources, such as solar and wind. This highlights both the potential of utilizing sunlight as an alternative energy source, and the economic impetus to produce solar energy.

Currently, one of the drawbacks of using conventional or first-generation photovoltaics (PV) is the high cost of solar power. As of 2013, the capital cost for a conventional 620 MW natural gas power plant is $0.92/watt, while for a 150 MW solar power plant is $3.83/watt. Fixed operation and maintenance costs are also greater for solar power plants with a $0.025/watt estimate compared to $0.013/watt estimate for natural gas. Although the EIA reports a 22% decrease in the overnight capital costs of solar power plants since 2010, and projects a further decrease in the price of solar power with advancing technology; the cost currently is too high to compete with natural gas.

Presently, over 90% of the solar market utilizes crystalline silicon. To produce ultra-high-purity silicon wafers necessary for PV application, highly energy intensive processing is

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necessary, which increases the cost of fabrication. The high temperatures used to produce crystalline silicon is inherently inefficient, and these highly energy intensive processing conditions can inhibit the high-throughput fabrication necessary for PV modules to compete on a global scale. More practical processing conditions for high-throughput fabrication of PV devices is to reduce the temperature of processing to preferably room temperature. Emerging PV technologies — that are solution-processable — aim to circumvent the inefficient processing techniques used to fabricate first-generation PVs. The use of solution-processable materials allows for processing techniques such as roll to roll fabrication, spray coating, and ink-jet printing. Current practices for producing crystalline silicon include growing silicon wafers at temperatures up to 1,400 °C and then processing the wafers further with various vapor deposition techniques. Solution-processable materials, and the techniques used to fabricate PV devices using these materials, provide a low-cost alternative to the production of traditional silicon PV devices.

Another drawback of silicon is that it doesn’t absorb sunlight strongly — due to its indirect bandgap — therefore a thick layer is needed. Silicon is also brittle and needs to be supported on a rigid glass substrate, increasing the module cost further. A reduction in the thickness of PV devices will result in less material being used, reducing the cost of fabrication, as well as its impact on the global material reserves. Emerging PV technologies — such as dye-sensitized solar cells and perovskite solar cells — use 1,000 times less material compared to silicon solar cells. Moreover, emerging PV technologies utilize inexpensive materials that can be fabricated on flexible supports reducing the cost even further. Overall, current fabrication processes for crystalline silicon are inherently inefficient and far too expense. They will not be sufficient to meet the future demand for solar cells as a
major renewable energy source. The need for low-cost, high-throughput processing is necessary to meet this future demand. Thin-film, solution-processable PV devices have the potential to meet these requirements.

Over the past decade, solution-processed inorganic and hybrid organic/inorganic semiconductors have emerged as an inexpensive route for high-performance, large-area electronics such as photovoltaics (PVs), display technologies, and sensing. A number of strategies have emerged for solution-processing inorganic materials; among these are sintered nanocrystals, molecular precursors, and solution-processed nanocrystalline thin films. Currently, copper indium gallium selenide (CIGS) and cadmium telluride (CdTe) are the leaders in thin-film PV technologies. These materials have already demonstrated commercial application, but there are still barriers that need to be overcome for their use over traditional crystalline silicon PV devices. Moreover, scalability is an issue with these material types as there is a scarcity of these elements within the Earth’s crust.

Therefore, within the PV research community, there has been a major incentive to develop Earth-abundant materials for thin-film PV application.

Researchers have begun developing Earth-abundant materials, such as copper zinc tin sulfide (CZTS), iron pyrite (FeS2), lead sulfide (PbS), and tin sulfide (SnS). Unfortunately, at the rate in which the global climate is changing, the need for accelerated discovery of new Earth abundant materials is necessary, as well as a screening processing to determine the potential of these newly discovered materials for use in PV devices. This screening process is necessary to circumvent the years of research needed to determine the viability of materials for PV devices. Brandt et al. developed strategies to expedite the development and screening of new PV materials. From his work, a list of potential materials with promising PV
characteristics was developed using important criteria to judge PV materials. The criteria that was developed was based off the unique properties found in the highly researched perovskite material methylammonium lead iodide (MAPbI3).

Since 2009, MAPbI3 and related “hybrid perovskite” materials have been of enormous interest for PVs due to their ease of processing and mild deposition techniques, and have quickly attained a NREL certified power conversion efficiency (PCE) of over 22%. This remarkable rise in PCE over the course of only a few years has been a result of rapid progress in developing precursor chemistries, processing conditions, and device architectures. However, there are still concerns regarding the commercial viability of hybrid perovskite materials, this includes the toxicity of Pb-based compounds and stability under normal operating conditions. When exposed to moist air for several days or temperatures exceeding 85 °C, MAPbI3 can rapidly degrade into PbI2.

To address the concern of toxicity and stability, many research groups have begun to study related materials that are free of heavy metals, such as CH3NH3SnI3, (CH3NH3)3(Bi2I9), Cs3Sb2I9, and Cs3Bi2I9 in hopes of achieving similarly high PCE to Pb-based hybrid perovskites, but using stable and non-toxic materials. Of these alternatives, Bi-based semiconductors could have the greatest potential due to their chemical similarity to Pb — both Pb and Bi compounds have soft polarizability which allows them to easily form Lewis acid-base pairs. They both also have a [Xe]4f145d106s2 electronic configuration, which includes the presence of an “inert” 6s2 electron pair, making it resistant to oxidation. One of the criteria for the success of MAPbI3 PV devices is the “defect tolerance” that arises from this electronic configuration. Therefore, Bi-based semiconductors could have many of the benefits of Pb-based semiconductors, but without the toxicity concerns.
Motivated by the potential of Bi-based semiconductors, this thesis reports on the development of the material chemistry of bismuth triiodide thin-film (BiI₃) photovoltaics. Currently, there have been very few reports on the use of BiI₃ thin-film photovoltaics. Lehner et al.⁴⁶ developed the first BiI₃ PV device, effectively demonstrating the prospect of BiI₃ thin-film PV devices. However, additional studies are necessary to validate its potential as a PV device. Currently, there is a lack of understanding of the material chemistry of BiI₃ and how that relates to its PV device performance. This thesis developed strategies to produce high-quality BiI₃ thin-films, as well as further understood the material chemistry of BiI₃. Moreover, the strategies developed in this thesis can be extended to other Bi-based semiconductors and serve as a first-step in the development of novel Bi-based semiconductor materials. Chapter 2 is a review of the literature that was used to develop BiI₃ thin film photovoltaics. An overview of the physics of PV devices is discussed, as well as the criteria for highly efficient PV devices and the development of high-quality thin-film morphologies. The methodologies and experimental details used in this thesis are presented in Chapter 3. Chapter 4 focuses on the work done with BiI₃ thin-film PVs, and then Chapter 5 is a discussion on the future work that can stem from the work done in this thesis. Finally, Chapter 6 concludes with a summary of the thesis contributions.
Due to the tremendous gain in efficiency seen with MAPbI$_3$ and other Pb-based hybrid perovskite PV devices, it has spurred a flurry of research into these material’s optical, physical, and chemical properties. Through these studies, the research community has determined the reasons behind the success in the performance of Pb-based hybrid perovskite PV devices. Although these materials suffer from instability in ambient air, decompose at elevated temperatures, and contain the toxic element lead; the study of their optoelectronic properties can guide scientists and engineers in discovering new materials for PV application. In this chapter, an overview of the physics and operation of a photovoltaic device will be discussed. Following will be a discussion on the criteria for an efficient photovoltaic device derived from the study of hybrid organic-inorganic Pb-based halide perovskites. Next will be a review of the literature on how to improve the thin-film morphology of the absorber layer, as well as the overall PV device performance. Finally, a review on bismuth-based semiconductors found in the literature — transitioning into a review of BiI$_3$ PV devices.

**Overview of Photovoltaic Device Physics and Operation**

A solar cell is a photovoltaic device used to convert photons, in the form of sunlight, into usable electrical energy/power through the photovoltaic effect. A simplified version of the structure of a solar cell can be seen in Figure 2.1. Photovoltaic devices utilize the photovoltaic effect in which sunlight is converted directly into electricity through the absorption of energy, in the form of photons, by a semiconductor material. If the energy of a photon is greater than the energy of the semiconductor’s bandgap, an electron-hole pair is created. A photovoltaic device works by utilizing properties of two differently doped
interacting semiconductor materials (p-n junction) to; a) create an electron-hole pair, and b) produce the driving force for the separation of the electron-hole pairs to produce a current. There are important characteristics of sunlight that can affect the performance of photovoltaic device, such as; the spectral irradiance of the sun, atmospheric effects, and Earth’s proximity to the sun. Spectral irradiance from the sun onto the surface of the Earth is summarized in Figure 2.2. The amount of sunlight that strikes Earth’s surface varies depending on the location, time of year, and weather. The effects of these conditions can be summarized as the solar resource, and the available solar resource for the U.S. is shown in Figure 2.3. Using the solar irradiance adjusted for AM1.5G (Figure 2.2), we can see that most of the solar irradiance lies in the visible range (390 – 700 nm), and a bandgap that requires absorption of energy below the visible range would absorb all the light in that region. Therefore, for a single junction PV device, the optical bandgap is ~930 nm (1.3 eV).

Figure 2.1. Simplified PV device layout. Electron-hole pairs are created in the absorber layer. Selective contacts facilitate the diffusion of electrons and holes.
Figure 2.2. Spectral irradiance from the sun. Reproduced from reference.47

Figure 2.3. Solar resources available in the United States. Reproduced from reference.48
A semiconductor is a material in which the valence band and conduction band are separated by a gap of energy between available electronic states. At equilibrium, we have a minimization of the free energy of the system, \( F = U - TS \), where \( F \) is the Helmholtz free energy, \( U \) is the internal energy, \( T \) is temperature, and \( S \) is the entropy of the system. The equilibrium state at 0 K results in the valence band being completely full of electrons, and the conduction band being completely empty i.e. the electrons occupy the lowest possible energy states. As the temperature is increased, electrons are excited into the conduction band, leaving behind an empty state in the valence band called a hole. The absence of an electron (hole), behaves as a particle with a positive charge. Although the increase in temperature results in the increase of the internal energy of the system, the increased number of electrons in the conduction band increase the entropy of the system — resulting in a minimization of free energy. Therefore, at elevated temperatures, electrons occupy states in the conduction band in equilibrium. The concentration of these carriers (the number of electrons in the conduction band or the number of holes in valence band) is the intrinsic concentration of the material. The fermi level, \( E_F \), indicates the energy level in which there is a 50% probability of electron occupancy and can be thought of as the total chemical potential for electrons in the system.

For an intrinsic semiconductor (an undoped semiconductor), the fermi level lies in the middle of the bandgap, as the material is doped with impurities, the fermi level can shift up (for excess number of electrons), or shift down the bandgap (for excess number of holes). The fermi level is an important thermodynamic quantity, and is used to understand the electronic structure of a semiconductor. The number of electrons and holes in the conduction
band \( (n_o) \) and valence band \( (p_o) \) can be calculated by multiplying the fermi function \( f(E) \) by the density of states \( N_c \) (for conduction band), and \( N_v \) (for valence band).

\[
f(E) = \frac{1}{1 + e^{(E - E_F)/kT}} \approx e^{-(E-E_F)/kT}
\]

\[
n_o = N_c e^{-(E_c-E_F)/kT}
\]

\[
p_o = N_v e^{-(E_F-E_v)/kT}
\]

For a PV device to perform work it needs to be taken out of its equilibrium state. This is done when a photon, with an energy greater than the bandgap, is absorbed and an electron is excited from the valence band to the conduction band creating excess carriers. This is the case for a direct transition; for an indirect transition, there needs to be a simultaneous absorption of a photon and a phonon to cause a change in the energy and momentum of an electron. (Figure 2.4). A change in momentum is needed because, for an indirect bandgap the conduction band minimum and valence band maximum do not align in the same \( k \)-space. An absorption of a photon alone can excite an electron from the valence band to the conduction band in an indirect bandgap, however it needs to be high enough energy to transition from the valence band to the conduction band at that \( k \) value. This makes indirect bandgap materials less efficient at creating electron-hole pairs because the rate of simultaneous absorption of a photon and phonon is much less than the rate of photon absorption alone or a photon with an energy much greater than the bandgap is needed to excite an electron. The bandgap depends on the electronic structure of the material, and the choice of material for a PV device is heavily reliant on that bandgap. After the photon excites an electron into the conduction band, there is now an excess number of electrons and holes in the conduction and valence bands compared to equilibrium. The electrochemical potential is now increased,
causing the fermi level to split into quasi fermi levels $E_{F,n}$ and $E_{F,p}$ for electrons and holes respectively. The difference between the electrochemical potentials serves as a quantitative measure of the deviation from equilibrium.

For power to be extracted from the PV device, the electrons and holes need to be separated, thus a driving force is necessary. This can be represented in the schematic shown in Figure 2.1a. By placing a hole selective contact and electron selective contact on either side of the semiconductor, electrons and holes will diffuse to the contacts, generating a current. These selective contacts provide an energetic barrier for carriers of the opposite type to overcome, while providing a potential for the carrier type to diffuse into the contact. When these contacts are connected by an external circuit, the electrons and holes will find each other and recombine, conserving charge.

**Figure 2.4.** Direct and indirect electronic transitions in semiconductors: a) direct transition b) indirect transition. Reproduced from reference.49

In practice, PV devices utilize a p-n junction, that is two oppositely doped semiconductors in intimate contact. The same concepts hold as depicted previously, when the
two semiconductors are in intimate contact (thermal equilibrium), the fermi levels equalize between the two semiconductors due to the diffusion of electrons and holes (equilibrium is reached when there is no net current between the p-n junction). When the two semiconductors are brought together the high concentration of electrons in the n-type material will diffuse into the p-type material, and vice versa for holes. However, the diffusion of carriers results in the development of space charge at the interface; i.e. since electrons diffused from the n-type material to the p-type material there is now uncompensated ions at the interface of the n-type material with a positive charge, known as a donor ion (N_d^+), and vice versa for the p-type semiconductor with acceptor ions (N_a^-). These charges create an electric field, and halt the subsequent diffusion of carriers — forming a depletion region of uncompensated ions. At equilibrium, the electric field is great enough such that there is no net current across the p-n junction. This electric field is known as the contact potential (V_o), and exist only within the depletion region, there is no electric field in the neutral regions of the p-type and n-type semiconductors. Because the fermi levels must be constant throughout the device at equilibrium, the conduction and valence bands of the semiconductors must shift to compensate (Figure 2.5). The extent in which the bands shift provides us a measure of the electrochemical potential (qV_o) of the device at equilibrium. This contact potential is necessary to maintain equilibrium by providing an energetic barrier. More importantly, carriers generated within the depletion region, or minority carriers generated within one diffusion length of the junction will be separated by the electric field and collected by the n-type and p-type materials for electrons and holes respectively.
A p-n junction results in the creation of a diode, and a diode that responds to the absorption of photons is called a photodiode. A diode is a semiconductor device with two terminals that only allows current flow in one direction (a negligible amount of current can flow in the opposite direction), and the current is controlled by the voltage load applied at these terminals. This can be visualized as follows, when a bias is applied that opposes the contact potential of the p-n junction (forward bias), the electric field is reduced and this allows for the diffusion of electrons and holes until a new equilibrium is reached, reducing the depletion width of the p-n junction. When a voltage biased is placed in the same direction (reverse bias) of the contact potential, the electric field is increased, further increasing the electrochemical barrier and preventing carrier diffusion, increasing the depletion region.
(Figure 2.6). In the reverse bias, there is a still a thermally generated current, or saturation current, independent of the voltage, i.e. minority carriers that are thermally excited within the depletion region, or have a diffusion length long enough to allow them to diffuse within the neutral region to the rectifying junction, are swept by the electric field. At \( V = 0 \), the thermally generated current (drift current) is equal to the diffusion current resulting in a net current of zero. The current in a diode is as follows:

\[
I = I_S (e^{\frac{qV_D}{kT}} - 1)
\]

Where \( I_S \) is the saturation current (reverse bias current), \( V_D \) is the voltage across the diode, and \( kT/q \) is the thermal voltage. Since the applied voltage causes a shift in the energy bands, and we assume that that fermi level deep within the neutral region of the semiconductors is essentially the equilibrium value, the shifting of the energy bands under bias implies a separation of the fermi levels on either side of the junction. The difference in the quasi fermi levels of the junction results in the \( V_{oc} \) of the device. The \( V_{oc} \) is the maximum voltage difference between the electrons and holes in the semiconductor and is an important parameter for characterization of PV devices because it gives the maximum voltage that the device can produce and is used to calculate the efficiency of PV devices.
For a PV device, or photodiode, a voltage bias is not being applied, instead the device is placed under illumination. If the incident photons are of an energy greater than the bandgap, $E_g$, this will cause an increase in the number of excited minority carriers. If the optically generated carriers are within one diffusion length of the junction, they will contribute to the current ($I_{op}$). The resulting current due to the collection of these optically generated carriers by the junction is

$$I = I_S \left( e^{\frac{qV_D}{kT}} - 1 \right) - I_{op}$$
Due to illumination, we know have excess carriers in the conduction and valence band of our semiconductors, causing an increasing in the electrochemical potential. Once more, the increase in electrochemical potential results in the splitting of the fermi levels at the junction. The extent in which these fermi levels split is the $V_{OC}$ of the device (Figure 2.7). In this case, however, the splitting of the fermi levels was due to the illumination of the p-n junction, and not due to an applied bias. The appearance of a forward voltage across an illuminated junction is known as the photovoltaic effect. Now the device is providing an external load to the circuit, through the absorption of photons, and this external load and be used to perform work.

**Figure 2.7.** Effects of illumination on the open-circuit voltage of a junction. a) at equilibrium, b) under illumination. Reproduced from reference.49

Important parameters that are used to represent the operation of a PV cell are the short-circuit current, $I_{SC}$ (in certain cases the current density, $J_{SC}$, will be used in the place of $I_{SC}$), the open-circuit voltage, $V_{OC}$, and the fill factor, $FF$. When the device is short circuited ($V = 0$), the current is equal to the optically generated current. The short-circuit current gives you information on the maximum current that can be derived from the PV device due to optically generated and collected carriers. Several factors can affect the short-circuit current, this includes; the area of the solar cell (the dependence on this factor can be removed by
using short-circuit current density, which is the short-circuit current divided by the area of the cell), the spectrum and intensity of light (standardized to AM1.5G), and inherent optoelectronic properties of the semiconductor materials (absorption and reflection of the semiconductor material, and the collection probability of minority carriers). When the device is at open-circuit voltage \((I = 0)\), and the voltage \(V = V_{OC}\), the diode equation becomes

\[
V_{OC} = \frac{kT}{q} \ln\left(\frac{I_{op}}{I_s} + 1\right)
\]

As described previously, the \(V_{OC}\) is the amount of forward bias on the solar cell due to the bias of the junction from the light-generated current and gives the maximum possible voltage that the device can provide. Although the \(I_{SC}\) and the \(V_{OC}\) are the maximum current and voltage that can be derived from the PV device, the power derived from the device is zero at those operating points. The maximum power that a PV device can deliver is the product of the voltage and the current \(P_{max} = I_m V_m\). The values of \(I_m\) and \(V_m\) are the values of the I-V curve in which the power, \(P\), is the greatest value. This is illustrated in Figure 2.8. The ratio of the maximum power from the solar cell to the product of the \(I_{SC}\) and \(V_{OC}\) \((I_{mp}V_{mp}/I_{SC}V_{OC})\) is the FF of the PV device and is a figure of merit for PV device design. The efficiency of a PV device is the maximum power derived from the PV device divided by the power inputted into the device from the light source. The power inputted is the power of 1 sun, which is standardized to 100 mW/cm\(^2\) for laboratory analysis.

\[
\eta = \frac{P_{max}}{P_{in}} = \frac{V_{OC}I_{SC}FF}{P_{in}}
\]
The performance of a device can be affected by both series and shunt resistances. Series resistance is caused from the movement of current throughout the device. Resistive losses can occur from the movement of current from the absorber layer to the electrodes. Graphically, this can be seen in the I-V sweep; high series resistance will affect the slope of the IV curve at the open-circuit voltage point. Low shunt resistance causes power losses in the PV device by providing an alternative current path for the optically generated current. Like series resistance, the effect of shunt resistance can be seen graphically in the I-V sweep. Low shunt resistance will affect the slope of the IV curve at the short-circuit point. The effect of series and shunt resistance will be seen in the FF of PV devices.

There are limits to the efficiency of PV devices for a single junction (one p-n junction) devices. The Shockley-Queisser efficiency limit is a theoretical limit of the efficiency of PV devices, based on the bandgap of the active layer. The Shockley-Queisser efficiency limit for common semiconductors used in PV devices is summarized in Figure 2.9.
The ideal bandgap for a single junction PV device is ~1.3 eV, resulting in a theoretical efficiency of 33%. A bandgap between 1.1 eV and 1.6 eV is desirable for PV devices, as a theoretical limit of >30% can still be achieved, greater than any single junction PV device currently available (Figure 2.10). There are strategies to exceed the theoretical limit, these include: a) tandem junction PV devices,\textsuperscript{51} solar concentrators,\textsuperscript{52} and the use of QD materials.\textsuperscript{53}

\textbf{Figure 2.9.} Theoretical limit of efficiencies for common semiconductors used in PV devices. Source: DOE, Lewis Group at Caltech
Criteria for Efficient Solution-Processable Photovoltaic Materials Derived from Hybrid-Halide Perovskites

Hybrid halide perovskites have attracted an enormous volume of research over the past decade, specifically MAPbI₃, which has quickly surpassed all third-generation PVs with a record efficiency of 22% in 2016 due to its exceptional PV properties. These properties include, a direct bandgap of 1.55 eV,⁵⁴ high carrier mobility of 7.5 cm²V⁻¹s⁻¹ for electrons⁵⁵ and 12.5 cm²V⁻¹s⁻¹ to 66 cm²V⁻¹s⁻¹ for holes,⁵⁸ long carrier diffusion lengths,⁵⁶,⁵⁷ and small exciton binding energies of 0.030 eV.⁵⁸ Furthermore, the material is solution-processable allowing for low-cost fabrication, as has been shown to work with a variety of different hole and electron contact materials.⁵⁹-⁶¹ Lastly, the material is defect-tolerant, such that electronic and structural defects do not affect the transport properties.⁶²,⁶³ However, as discussed previously, the material suffers from poor stability, which remains a significant challenge moving forward. Currently, there is no viable solution to the stability issues facing MAPbI₃, which has forced researchers to start searching for different materials with similar properties.
There are several important criteria that need to be considered when choosing the materials to use in a PV device. For the absorber layer, desirable properties include: proper bandgap, high absorption coefficient, high minority carrier mobility, high minority carrier lifetime, defect-tolerance, and energy bands that align well with common electron and hole transport materials.

The bandgap of the absorber layer is the first property that is considered when choosing suitable materials for use in PV devices. The bandgap determines the maximum theoretical power conversion efficiency for the material. Preferably, a bandgap as close to 1.3 eV is desired for the absorber layer, however, bandgap energies in the range of 1.1 eV to 1.6 eV are suitable. Materials with bandgaps in this range will be able to absorb over the entire visible range of the solar emission spectrum. Direct bandgap materials are preferred over indirect bandgap materials because direct bandgap materials have a stronger absorption compared to indirect bandgap materials. Strong absorption is a critical parameter for the absorber layer, and is characterized by a steep absorption edge in the absorption coefficient slightly above the bandgap energy. Absorption coefficient value ranging from $10^4$ to $10^5$ cm$^{-1}$ or higher is preferred. Although direct bandgap materials are required for strong absorption, an indirect bandgap material can attain high absorption coefficients if a direct transition is available with a suitable energy. Bandgaps with energies greater than 1.6 eV are still of interest, however, their application is geared towards use in a tandem solar cell as the top absorber layer as compared to single junction PV devices.

Trap states within the bandgap can occur due to the presence of impurities. Impurities can be either unintentionally added to the material due to lack control during crystal growth, or purposely added to provide free carriers into the semiconductor. The latter is known as
doping the material. A defect state can either be shallow or deep depending on the amount of energy required to ionize the impurity. Deep-level defects are undesirable as it takes energies larger than the thermal energy, kT, to ionize the impurities. Deep-level defect states within the bandgap provide intermediate states for carriers to be trapped, causing recombination and shortening carrier lifetimes. These impurities act as recombination centers for electrons and holes. Shallow defect states, on the other hand, require very little energy, typically around the thermal energy, kT, to ionize. Shallow defect states have minimal effect on the electronic properties of the semiconductor since the defect states exist either within the valence or conduction bands, or within thermal energy, kT, from the band edge.

In the case of MAPbI₃, defect states that arise from vacancies or structural defects appear within a dispersed valence and conduction band, and this is tied to the presence of a filled Pb 6s² orbital, derived from the partial oxidation of Pb²⁺ relative to its Pb⁴⁺ oxidation state. The orbital character of Pb²⁺ has been acknowledged in literature as the reason for the defect-tolerance seen in Pb-based halide perovskites and is used to explain the shallow binding energy of defects in MAPbI₃. Therefore, elements with similar electronic structures to Pb²⁺ have been identified as possibly being defect-tolerant, and this defect-tolerance is now a highly desirable property and researchers have begun seeking other ns² atoms. Bi³⁺ is an atom with the ns² orbital character, and materials such as BiI₃ and other Bi-based perovskite semiconductors have become of recent interest for use in optoelectronic devices. Brandt et al. created a list of suitable material that share a similar electronic structure to MAPbI₃ and are predicted to possess defect-tolerance.
Techniques for Improved Thin-Film Morphology

Common deposition techniques for metal halides and metal halide perovskites include: spin coating, vapor deposition, and dip-coating, with spin coating being the most common laboratory technique used to deposit thin-films. Important physical parameters such as temperature, vapor pressure, solubility, and precursor concentration control the rate of drying and grain growth of thin-films. Control of these parameters are important for the assembly of dense, high-coverage, uniform films. Common solvents used to dissolve metal halides, and metal halide perovskites include tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide. MAPbI₃ perovskite films can be deposited via sequential deposition of the inorganic and organic precursor, or as a one-step deposition techniques in which mixed solvents of precursors are used. For mixed solvents, the precursor ratio plays a major role in the film morphology, and the ratio of PbI₂:MAI affects the absorption and PL spectra of thin-films. Increasing the ratio of PbI₂:MAI past 0.6 results in the disappearance of impurity peaks in the XRD. One of the strengths of hybrid halide perovskites is the variety of deposition techniques available for the material, highlighting the ease of fabrication that is possible with solution-processing. Moreover, understanding the solvent-precursor interactions is critical for producing high quality thin-film optoelectronic devices.

Since hybrid halide perovskites are solution-processable, the properties of the material can be tuned through substitution of atoms by varying the precursors in the solution. Substitution of the organic cation, and halides of Pb-based hybrid perovskites in the precursor solution provides a facile method to improve the optoelectronic properties of the device. Partial substitution of I⁻ with Cl⁻ in the precursor solution for MAPbI₃ has been shown as strategy to increase the diffusion length of the material. Stranks et al. uncovered a
10-fold greater diffusion length when doping MAPbI$_3$ with PbCl$_2$, creating a mixed-halide perovskite PV device. Studying the mixed halide, and cation lead-based perovskite materials has been a recent strategy to improve the thin-film device performance and stability.

Once the thin-film is deposited onto a substrate, the film can be further processed to improve the film-morphology, crystallinity, and phase purity. Typically, the thin-film is annealed at temperatures greater than 100 °C to grow larger and more ordered grains within the thin film. Although optimization of processing conditions, such as temperature, spin speed and time, and deposition rate can lead to improved film quality, there are other strategies beyond optimization of deposition conditions that can lead to improved results. Two strategies that are of importance in this thesis is solvent vapor annealing (SVA), and hot casting.

Since solution-processable materials, such as hybrid halide perovskites, have constituent parts that are highly soluble in various solvents — PbI$_2$ can form molecular complexes with various solvents — these same solvents can be used to process the materials post-deposition. SVA was originally a strategy used for organic photovoltaics, but has recently been adapted for use in hybrid halide perovskites. SVA is a technique used to increase the grain size of the thin-film, by facilitating the transport of particles to grow larger grains. Solvents with high vapor pressure, and intermediate solubility with the thin-film are the ideal solvents to use for SVA and the effect of SVA on the thin film morphology can be seen rapidly. Larger grains are desired because there are less grain boundaries for carriers to overcome, reducing the surface trap states available for recombination. This technique can also improve the crystallinity of thin-films — resulting in improved carrier mobility within
the thin-film. More importantly, SVA can be used a strategy to reduce the need for high
temperature processing. Yu et al. showed mixed solvent vapor annealing of hybrid halide
perovskites could be performed at room temperature, with promising results, circumventing
the need for thermal annealing. Overall, SVA can be used as an effective strategy to
improve the thin-film morphology — improving the transport properties of carriers — in a
facile, low-cost manner.

![Figure 2.11. Schematics of the inter-diffusion approach and solvent-annealing-induced grain size increase. Reproduced from reference.](image)

Hot casting thin-films is another strategy that can be used to improve the thin-film
morphology of hybrid halide perovskites. Substrates, prior to deposition, are preheated to
temperatures ranging from 100 °C to 150 °C. The substrate is placed on the spin coater and
the solution is then immediately deposited onto the substrate and subsequently spin coated.
The solvent vapor quickly evaporates upon contact with the substrate, leaving a thicker film
as compared to processing at room temperature. More importantly, the film morphology of
the thin-film is greatly improved, and the crystal structure is more uniform and ordered. Nie
et al. reported micrometer sized grains when hot casting thin-films for hybrid halide
perovskites (Figure 2.12). Thin-films with large grain sizes benefit from reduced interfacial
area, suppressing charge trapping. Moreover, large grain sizes have greater mobility, and
lower bulk defects. This allows for improved transport properties through the material,
improving the PV device performance. Tsai et al demonstrated this process on layered hybrid halide perovskites and showed improved thin-film morphology and crystallinity.\textsuperscript{79}

**Figure 2.12.** Schematic of hot casting for large-area crystal growth. Reproduced from reference.\textsuperscript{78}

The techniques discussed in this section highlight the amount of research that has been done on hybrid halide perovskites. The knowledge gained from these studies can be used as a starting point to improve the film morphology when processing novel thin-film materials. Materials that are being screened for potential use as PV absorber layers have similar properties to Pb-based hybrid perovskites, and it is likely that these processing techniques can be extended to other metal halides such as BiI\textsubscript{3} and Bi-based perovskite semiconductors.

**Review of Bismuth Triiodide for PV application**

The toxicity and instability of Pb-based hybrid halide perovskites has prompted two avenues of research; a) improve the stability of MAPbI\textsubscript{3} in air to make it a more viable commercial prospect and b) research new materials that have the similar properties to Pb-based hybrid perovskites that can serve to replace MAPbI\textsubscript{3}. A potential alternative to Pb-based hybrid perovskites include all-inorganic metal halides such as BiI\textsubscript{3}. BiI\textsubscript{3} has a rhombohedral crystal structure (space group R\textsuperscript{3}).\textsuperscript{80} The crystal structure is a layered 2D structure built from BiI\textsubscript{6} octahedra with 1/3 of the cation sites being vacant.\textsuperscript{81} Historically,
there has been some discrepancy on the reported values of the optical bandgap. \textsuperscript{82} Recent reports, however, appear to have shown good agreement. Brandt et al. \textsuperscript{81} studied the potential of BiI\textsubscript{3} PVs; here, they measured an indirect bandgap of 1.79 eV for BiI\textsubscript{3} single-crystals. Lehner et al. \textsuperscript{46} also measured an indirect bandgap of \texttilde 1.8 eV in spin coated BiI\textsubscript{3} thin films. The discrepancy between these values and previously reported values could be due to the measurement sensitivity. Podraza et al. \textsuperscript{82} described how different values of the optical bandgap of BiI\textsubscript{3} can be obtained depending on the measurement technique used, and concluded that UV-Vis transmission spectroscopy is the most reliable method for determining the bandgap of BiI\textsubscript{3}.

Previously, BiI\textsubscript{3} has been of interest for x-ray detection applications because of its large nuclear mass, which gives it a large x-ray cross-section. \textsuperscript{83} Very recently, BiI\textsubscript{3} has begun to garner attention as a potential new type of metal halide thin-film PV material. \textsuperscript{46, 81, 84} The bandgap of BiI\textsubscript{3} makes it suitable for use as an absorber layer for a single-junction solar cell or in the top cell for two-terminal tandem devices. The bandgap can be further tuned to \texttilde 2.1 eV by alloying with SbI\textsubscript{3}. \textsuperscript{85} To date, there have been relatively few reports of implementing BiI\textsubscript{3} in PV devices. Boopathi et al. demonstrated BiI\textsubscript{3} as a hole transport layer (HTL) in an organic PV with an active layer blend of 1:1 poly(3-hexylthiophene):phenyl C61-butyric acid methyl ester. \textsuperscript{86} Lehner et al. recently reported BiI\textsubscript{3} PV devices utilizing an organic HTL achieving a 0.35% efficiency. \textsuperscript{46} While these works have demonstrated the potential for BiI\textsubscript{3} in PVs, the materials chemistry and relationships between processing, structure, and device performance are poorly understood. BiI\textsubscript{3} has several properties that make it a compelling material for PVs. For example, it has the potential to achieve high photocurrents with relatively thin films due to its high absorption coefficient (>10\textsuperscript{5} cm\textsuperscript{-1}) in the visible region of
the solar spectrum. The absorption coefficient in the visible region for BiI₃ is greater than Si and GaAs. Currently, little is understood in terms of how to limit electronic defects, improve carrier transport, or reduce recombination in BiI₃. The reported carrier lifetimes of BiI₃ thin films have been very short (190 – 240 ps), which must be improved to achieve high PCE with BiI₃ solar cells.
CHAPTER 3. METHODOLOGY

Equipment Characterization List

Absorbance, transmittance, and reflectance data were collected with a Perkin Elmer Lambda 750 spectrophotometer equipped with a Labsphere 100 mm integrating sphere. Single crystal x-ray diffraction (XRD) was acquired using a Bruker-AXS APEX II and the x-ray structures were determined in the Molecular Structures Lab in the Iowa State University Chemistry Department using PLATON crystallographic software. Scanning electron microscope (SEM) images were taken on an FEI Quanta 250 FE-SEM. The accelerating voltage was 15 kV. Powder XRD and grazing incidence XRD (GIXRD) patterns of thin films were collected using a Bruker DaVinci D8 Advance diffractometer with a Cu Kα radiation source. Cross-sectional SEM images of the devices were taken with an FEI Helios NanoLab DualBeam SEM in the Ames Laboratory Sensitive Instrument Facility.

X-ray photoelectron spectroscopy (XPS) was acquired with a Kratos Amicus/ESCA 3400 instrument. The samples were irradiated with 240 W unmonochromated Mg Kα x-rays, and photoelectrons (emitted at zero degrees from the surface normal) were detected using a DuPont-type energy analyzer. The pass energy was set at 150 eV. Binding energies were calibrated to adventitious carbon at 284.6 eV. A Shirley background was subtracted from the data using CasaXPS.

PCE of PV devices was determined using current-voltage (J-V) characterization under solar simulation (Newport, M-9119X with an AM1.5G filter). The intensity was adjusted to 100 mW/cm² using an NREL certified Hamamatsu mono-Si photodiode (S1787-04). All devices were tested inside a N₂-filled glovebox. For external quantum efficiency (EQE) measurements, a light source (Oriel model 7340 using 100 W Halogen lamp) with a Jobin...
Yvon monochromator (model H-20-IR) was used to illuminate the device. The light source was chopped at 13 Hz and the electrical signal was collected by a lock-in amplifier (Stanford Research Systems, SR830) under short-circuit conditions. A calibrated Si photodiode with a known spectral response spectra was used as a reference. The measurement was taken under N₂ purge.

Steady-state photoluminescence (PL) spectra could not be obtained without artifacts using a conventional spectrofluorometer due to low fluorescence quantum yield. Therefore a homemade transient absorption spectrometer was used (configuration described previously) with some modifications for PL measurements. A Surelite II Nd:YAG laser (Continuum, USA) was used as the excitation source. The excitation wavelength and irradiance were 532 nm and less than 2×10⁵ W/cm², respectively. Thin films were placed in a front-facing orientation. The spectra were collected using a charge-coupled device detector fitted with a spectrograph. All parameters (such as laser intensity and sample orientation) were kept constant for comparison of the relative spectral intensities.

Excited-state lifetime measurements were carried out with a time-correlated single-photon counting (TCSPC) technique. The TCSPC apparatus has been described elsewhere. An excitation wavelength of 600 nm was generated by a supercontinuum laser (Fianium Ltd.) with a 10 nm bandpass filter. The repetition rate of the laser was set to 1 MHz. An irradiance of 1×10⁶ W/cm² was used owing to the low quantum yield. A Becker & Hickl photon counting card (model SPC-630) was used with an MCP-PMT detector. For the system described, the full width at half-maximum of the instrument response (IRF) was 90 ps. The measurements were performed using a front-facing orientation of the films. A 675 nm long-pass filter was placed after the sample to eliminate scattered excitation light. The decay
parameters were calculated by fitting the decay to the sum of three exponentials after deconvolution of IRF from the decay. The extremely fast component of the signal (less than 15 ps) was discarded, as it cannot be distinguished from a small amount of leakage of scattering from the excitation laser regardless of the use of cross-polarizers to eliminate scattering, given the extremely low PL quantum yield of the films.

**Material Synthesis and Crystallization**

**BiI₃ solution preparation.** A 400 mg/mL BiI₃ solution was prepared in an N₂-filled glovebox by dissolving BiI₃ powder (Sigma-Aldrich, 99.999% metals basis) into Tetrahydrofuran (Fisher, contains 250 ppm BHT as inhibitor, ACS reagent ≥99.0%+). Tetrahydrofuran (THF) was previously prepared by adding molecular sieve (1/4 height of 40 mL scintillation vial) to remove any trace water in the solution and then filtered with a 0.45 µm PTFE filter (molecular sieve that is not filtered can cause the formation of pinholes and comets in the films after spin coating). The BiI₃ solution was sonicated for 30 minutes in a scintillation vial, with the lid wrapped tightly with Parafilm M®, in room temperature water in order to completely dissolve BiI₃ powder in THF. Afterwards, the solution was returned into the N₂-filled glovebox and filtered with a 0.2 µm PTFE filter. The BiI₃ solution was diluted to 100 mg/mL through the addition of purified THF and stored under N₂ for further use. For HI experimentation, a 1:1 molar ratio of hydroiodic acid (Sigma-Aldrich, 57% wt. conc. in water) was added to the solution and further sonicated for five minutes. Preliminary results show some temperature dependence on the solubility of BiI₃ in THF. Upon heating a nearly-saturated solution of BiI₃ in THF, the red solution became increasingly darker with increased temperature. Eventually, precipitation of a black powder – presumably BiI₃, but not
confirmed – was observed on the bottom of the vial with continuous heating. The black powder dissolved upon cooling the vial.

THF is not a suitable solvent to use with the hot-cast processing due its low boiling point (66 °C), therefore N,N-dimethylformamide (DMF) was used as an alternative due to its higher boiling point (153 °C). A 0.2 M solution of BiI$_3$ was prepared by dissolving BiI$_3$ powder in anhydrous DMF (Sigma-Aldrich, anhydrous, 99.8%) in an N$_2$-filled glovebox. The BiI$_3$ solution was sonicated for 30 minutes in a scintillation vial, with the lid wrapped tightly with Parafilm M®, in room temperature water in order to completely dissolve BiI$_3$ powder in DMF. The solution was filtered with a 0.2 µm PTFE filter in air before use.

**Crystallization of BiI$_3$–THF, and BiI$_3$–DMF complexes.** To crystalize the BiI$_3$–THF complex, a nearly-saturated solution composed of BiI$_3$ in THF was prepared in a 3.7 mL vial (Vial A). Vial A (without its cap) was placed inside of a 20 mL vial (Vial B). To the 20 mL vial, 5 mL of hexane was added such that the liquid hexane did not mix with the liquid THF. After adding the hexane, a cap was placed on Vial B, and was allowed to rest undisturbed for ~5 days to permit the vapor transport of hexane to the THF-rich phase. The hexane vapor then naturally diffuses into the THF-rich phase and initiates crystallization. The BiI$_3$–DMF complex was crystalized similarly via the slow introduction of liquid toluene to a nearly-saturated solution containing BiI$_3$ in DMF and Cs$_3$Bi$_2$I$_9$ in DMF respectfuely.

**Thin-Film and Photovoltaic Device Fabrication**

**FTO/Glass preparation.** FTO (Hartford Glass, Tec 7, 25 mm x 25 mm x 2.2 mm, 6-8 ohm/sq) and glass substrates (Thin Film Devices, Eagle XG) were cleaned by first sonicating in room temperature detergent water for 10 minutes. The substrates were then thoroughly rinsed with DI water and subsequently sonicated for an additional 10 minutes each in DI
water, acetone (Sigma-Aldrich, \geq 99.5\%), and isopropanol (Sigma-Aldrich, \geq 99.5\%). The FTO substrates were then thoroughly rinsed once more with DI water, blown dry with ultra-high pure N\textsubscript{2}, and UV treated with O\textsubscript{2} plasma for 20 minutes.

**Solution deposition of TiO\textsubscript{2} and m-TiO\textsubscript{2}:** A compact TiO\textsubscript{2} sol-gel solution was made by combining the following: (1) 0.210 mL of HCl (Fisher, 36.9\% in water), (2) 30.4 mL of ethanol (Fisher, 200 proof), and (3) 2.21 mL of titanium(IV) ethoxide (Sigma-Aldrich, technical grade). The sol-gel solution was stirred vigorously for 30 minutes. A compact thin layer of TiO\textsubscript{2} was deposited through a 0.45 \textmu m PTFE filter onto the FTO substrate until the entire substrate is covered spun at 2000 RPM for 35 seconds in a spin coater. FTO contact points were created by cleaning the contact points of the substrates with ethanol after spin coating. The substrate was then placed on a 3/8” thick aluminum block on top of a hotplate, with the temperature set at \sim 500 °C (temperature measured with a thermocouple that is place into the center of the aluminum plate) and annealed for 30 minutes. Substrates were allowed to cool naturally in air and stored in an N\textsubscript{2}-filled glovebox until further use.

Mesoporous titania (m-TiO\textsubscript{2}) was prepared by combining TiO\textsubscript{2} paste (Dyesol, 30NR-D) with ethanol in a 1:4 weight ratio (1g of TiO\textsubscript{2} paste and 5 mL of ethanol). m-TiO\textsubscript{2} can be used in addition to the planar TiO\textsubscript{2} layer to improve the interfacial contact between the active layer and the TiO\textsubscript{2} layer. The m-TiO\textsubscript{2} solution as sonicated for 30 minutes in a scintillation vial, with the lid wrapped tightly with Parafilm M\textsuperscript{®}, in room temperature water in order to completely dissolve the paste in ethanol. Prior to deposition, the TiO\textsubscript{2} coated FTO substrates was sonicated in an isopropanol bath for 20 minutes, and blown dry with ultra-high pure N\textsubscript{2} gas. The substrate was then placed on a 3/8” thick aluminum block on top of a hotplate, with the temperature set at \sim 500 °C. 150 \mu L of m-TiO\textsubscript{2} was deposited onto the compact TiO\textsubscript{2} layer.
and spun at 2000 RPM for 35 seconds in a spin coater. FTO contact points were created by cleaning the contact points of the substrates with ethanol after spin coating. The substrate was then placed on a 3/8” thick aluminum block on top of a hotplate, with the temperature set at ~500 °C and annealed for 30 minutes. Substrates were allowed to cool naturally in air and stored in an N2-filled glovebox until further use.

Solution deposition of BiI₃. BiI₃ was spin coated in both N₂ and ambient air environments using either THF or DMF solutions — depending on the processing condition used (DMF solution was used for hot-cast processing). 200 µL of the BiI₃ solution was pipetted onto either glass or FTO substrates and spun at 2000 RPM for 35 seconds. This resulted with a BiI₃ layer that was approximately 200 nm thick. BiI₃ thin-films were then placed on a 3/8” thick aluminum block preheated to 100 °C and annealed at one of the various conditions. (A) No solvent vapor annealing (no SVA) and 20 minutes of thermal annealing, (B) THF SVA for 10 minutes of solvent vapor annealing in a THF environment (~20 ppm) and 10 minutes of thermal annealing, and (C) DMF SVA for 10 minutes of solvent vapor annealing (~10 ppm) followed by an additional 10 minutes of thermal annealing in ambient air. For BiI₃ thin-films prepared using the hot-cast processing, BiI₃ thin-films were annealed at one of following conditions. (D) 20 minutes of thermal annealing with No SVA, and (E) DMF SVA for 10 minutes of solvent vapor annealing (~10 ppm) followed by an additional 10 minutes of thermal annealing in ambient air.

Solvent vapor annealing and hot-cast processing. SVA was conducted as depicted in Figure 3.1. First the substrate was placed on the aluminum block and heated for 30 seconds. Then on a freshly cleaned glass substrate (see FTO/glass preparation), 20 µL of DMF or 100 µL of THF was deposited on the corner of the glass substrate furthest from the sample. A
A glass petri dish (200 cm³) was placed on top of the sample and the glass substrate to enclose the solvent vapor. The volume of solvent was optimized such that it was the maximum amount of solvent that could be used without dissolving BiI₃ thin-films at 100 °C.

For hot-cast processing substrates were placed on an aluminum block preheated to 150 °C for 10 minutes. The substrate is removed from the aluminum block and quickly placed on the spin coater. The active layer solution was then deposited onto the heated substrate as described previously. It is important to note that the quality of the thin-film was greatly improved by first depositing the active layer solution and then turning on the spin coater vacuum.

**Figure 3.1.** Depiction of solvent vapor annealing. Solvent is placed on the blank glass substrate on the furthest corner from the sample. A glass petri dish is used to contain the solvent vapor.

**Sulfur vapor annealing.** Sulfur vapor annealing was conducted as depicted in Figure 3.2. 200 µL of the BiI₃ solution was pipetted onto either glass or FTO substrates and spun at 2000 RPM for 35 seconds. This resulted with a BiI₃ layer that was approximately 200 nm thick. BiI₃ thin-films were then placed on a 3/8” thick aluminum block preheated to 140 °C. Next, on two freshly cleaned glass substrates (see FTO/glass preparation) 24 mmol of sulfur
powder was distributed evenly. The glass substrates were placed next to the BiI₃ thin-film, and covered with a glass petri dish (200 cm³) to enclose the sulfur vapor and were annealed for 4 hours. For DMF SVA + sulfur vapor annealing, an additional glass substrate is placed underneath the glass petri dish with 20 µL of solvent, the same as what is done with DMF SVA alone.

**Figure 3.2.** Depiction of sulfur vapor annealing. Sulfur powder is placed on the blank glass substrates. A glass petri dish is used to contain the solvent vapor. For the combined processing, DMF solvent is placed on the blank glass substrate on the furthest corner from the sample.

### Thermal evaporation of metal contacts.

V₂O₅ and MoO₃ were studied for their use as HTL. 20 nm of metal oxide (V₂O₅ (Sigma, 99.999%) or MoO₃ (Acros Organics, 99%)) were thermally evaporated directly onto the BiI₃ film through a shadow mask at a base pressure of 1x10⁻⁶ mbar. This is followed by thermal evaporation of Au (Kurt J. Lesker, 99.999%) to produce a 100 nm thick top contact. The pressure increases during thermal evaporation to ~1x10⁻⁵ mbar at most. The shadow mask consists of nine circular 8 mm² holes arranged in a square array (3 x 3). For Cs₃Bi₂I₉ PV devices, 100 nm of Ag (Kurt J. Lesker, 99.999%) was thermally evaporated as the top contact with the same conditions as described previously. We found that device performance was improved by thermally annealing the
device at 100 °C for 10 minutes after evaporating the metal contacts. This additional processing was only done on the record BiI$_3$ device found in Appendix A and was not done on the other PV devices shown in the main text.
CHAPTER 4. SOLUTION-PROCESSED BISMUTH TRIIODIDE THIN-FILMS FOR PHOTOVOLTAIC APPLICATION

Solution Properties of BiI₃ in THF and DMF Solvent

BiX₃ (X = Cl, Br, I) is known to form adducts or coordination complexes with a range of two-electron donor (Lewis base) ligands, offering the opportunity for facile solution-processing by rendering it soluble in a variety of solvents.⁴⁴ We found that BiI₃ is highly soluble in THF and DMF — with solubility in excess of 400 mg/mL — but it is much less soluble in other solvents such as ethanol. Bi-halides have been previously reported to form coordination complexes with THF.⁹² The absorbance spectra of BiI₃ dissolved in THF and DMF (Figure 4.1a) gives evidence to the formation of molecular complexes, which shows distinct peaks that are starkly different from the absorbance of a thin film of BiI₃. Upon combining BiI₃ powder with THF or DMF at a concentration of 100 mg/mL, THF and DMF easily dissolve BiI₃ and form optically transparent, homogenous solutions. Other solvents such as ethanol do not fully dissolve BiI₃ at this concentration. Another solvent that can be used to dissolve BiI₃ at high concentrations is dimethyl sulfoxide (DMSO). For other Bi-based semiconductors a mixture of DMF and DMSO has been used in literature. ⁴³, ⁹³
To further understand the THF and DMF solvent interactions with BiI₃, crystals were precipitated from the THF and DMF solutions. Crystals precipitated from the THF solution were ruby-red in color and analysis of the single-crystal XRD pattern revealed that these crystals consisted of a heptabismuthate anion \([\text{Bi}_7\text{I}_{24}]^{3-}\) with sodium cations acting as the counter-ion, as shown in Figure 4.2a. The structure of \([\text{Bi}_7\text{I}_{24}]^{3-}\) has been previously described by Monakhov et al. as a BiI₆ octahedral moiety in the center of six edge-sharing BiI₆ arranged in a cyclic arrangement.⁹⁴ In the \([\text{Bi}_7\text{I}_{24}]^{3-}\) crystal structure, six Na⁺ ions exist symmetrically between the planes of two heptabismuthate anions, and thus, both \([\text{Bi}_7\text{I}_{24}]^{3-}\) ions share the charge of the six Na⁺ ions. In addition, THF clusters (12 THF solvent molecules) exist within the voids of the structure but are omitted for clarity. The existence of Na⁺ in THF adducts of bismuth halides has been observed previously by Carmalt et al.⁹² We believe that Na originates from drying THF with sodium wire. The certificate of analysis of the BiI₃ powder purchased from Sigma-Aldrich does not indicate sodium as an impurity. Furthermore, a large quantity of ruby-red crystals (which contain sodium) was obtained.
during crystallization. This implies that the Na is more than just a trace impurity, and THF is likely the Na source.

Orange prismatic crystals were isolated by precipitating BiI₃ dissolved in DMF. Based on single-crystal XRD, we found that these crystals are composed of two distinct structures that exhibit salt-like characteristics; that is, the primitive cell is composed of a cationic structure and anionic structure, as illustrated in Figure 4.2b. The first structure is a Bi³⁺ cation solvated by the oxygen atoms of eight DMF molecules, and the second structure is a trinuclear iodobismuthate anion [Bi₃I₁₂]³⁻. The charge of the BiI³⁺ atom is balanced by the charge of the anionic iodobismuthate molecule. All of the precipitated crystals were unstable upon removing them from the liquid environment; upon doing so, they decompose into BiI₃. This decomposition is similar to what Carmalt et al. reported in their study of THF adducts of bismuth trihalides.⁹² To prevent decomposition, we covered the crystals with Paratone® oil during single crystal XRD analysis. The crystal system of the BiI₃ complex isolated from THF is trigonal, while the crystal system obtained from the DMF solution is monoclinic.

![Unit cells of BiI₃ complexes with (a) THF and (b) DMF solvent.](image)

**Figure 4.2.** Unit cells of BiI₃ complexes with (a) THF and (b) DMF solvent.
Solution-Processing of BiI₃ Thin-Films

We used spin coating to deposit thin-films from the BiI₃ solutions in THF. THF was chosen as the solvent because it was used as the solvent in the development of the first BiI₃ thin-film PV device by Lehner et al.⁴⁶ and we first wanted to reproduce their work. Other solvents — such as DMF — can also be used in the processing of BiI₃ thin-films. A 100 mg/mL solution of BiI₃ in THF was spin coated inside a N₂-filled glovebox, resulting in an approximately 200 nm thick film of BiI₃, as measured by atomic force microscopy (AFM). Spin coating with concentrations greater than 100 mg/mL resulted in cracking of the film. This is due to the high vapor pressure of THF solvent; when using higher concentrations, the rapid evaporation of the solvent results in the breaking of the film. The cracks in the thin-film are more visible using higher concentrations as compared to using concentrations < 100 mg/mL, but presumably still exist with lower concentrations. A thickness versus concentration profile can be found in Figure 4.3a. The thickness of the film was measured by applying a thin scratch on the film with a syringe needle. The difference in height between the valley of the scratch and the film is taken as the thickness. Since only one layer of BiI₃ can be deposited (additional deposition of BiI₃ results in the former layer being dissolved), the thickness of BiI₃ can be varied by the concentration of BiI₃ in solution.

Transmittance measurements of a 200 nm thick film resulted in ~90% absorption at 2.0 eV (Figure 4.3b). Using Tauc analysis and assuming an indirect bandgap, the bandgap of BiI₃ was evaluated to be ~1.83 eV (Figure 4.4) which is slightly larger than the value presented by Brandt et al.⁸¹ and Lehner et al.⁴⁶ The absorption coefficient (a) was calculated using Equation 1 from the transmittance (T), reflectance (R), and thin film thickness (d) measurements. We assumed an indirect bandgap and plotted (ahₜ)^0.5 versus hₜ.⁹⁵ The
bandgap was found by finding the intersection of the linear absorption edge with the sub 
bandgap absorption.\textsuperscript{96} We measured the bandgap to be 1.83 eV, however because of 
thickness of the thin film this could be an overestimation.

Equation 1: \[ a = \frac{-\ln \left( \frac{T}{1-R} \right)}{d} \]

\textbf{Figure 4.3}. (a) Thickness of BiI\textsubscript{3} versus concentration of BiI\textsubscript{3} solution. Thickness determined 
by AFM. (b) Percent transmission of ~200 nm thick BiI\textsubscript{3} thin film

\textbf{Figure 4.4}. Absorbance of a ~200 nm thick BiI\textsubscript{3} thin-film. Inset: Tauc plot for BiI\textsubscript{3} thin film.
As-deposited BiI₃ films are stable for several months in a N₂-filled glovebox without any visible degradation. In ambient air and in a well-lit room, BiI₃ thin films degrade within one week, changing from brown to yellow. This color change indicates a transition to bismuth oxide (Bi₂O₃). However, BiI₃ stored in the dark (in ambient air) are stable for at least several months. This suggests that BiI₃ stability is affected more by light rather than air. Further studies are needed to thoroughly assess the photo-thermal and environmental stability of BiI₃.

When spin coating BiI₃ dissolved in THF, the films transitioned from orange to black, indicating a decomposition of the heptabismuthate-THF complex into BiI₃. When spin coating BiI₃ films co-dissolved in THF and hydroiodic acid (HI), or dissolved in DMF, the film remained orange even after spin coating, indicating that these intermediate complexes are more stable (Figure 4.5). Addition of HI to the precursor was initially investigated because Lehner et al. included HI in their BiI₃ device studies. In our study, HI was added in a 1:1 molar ratio with BiI₃, resulting in a change in color of the solution from light orange to dark red-purple. This red-purple color is consistent with the formation of polytetrahydrofuran, which can form in the presence of strong acids. Upon heating at 100 °C or storing at room temperature overnight, the films decomposed into BiI₃.
Solvent Vapor Annealing of BiI₃ Thin-Films in N₂

When THF was used as the spin coating solvent, grain sizes of 113 ± 37 nm were observed in SEM (Figure 4.6a). Some pinholes were also observed within the films, which could arise from the rapid evaporation of THF. It is well understood that rapid solvent evaporation of polymeric thin films can cause the films to become “kinetically constrained” which can lead to small domain sizes or even formation of amorphous films. Similar effects have also been reported for solvent-annealed hybrid organic-inorganic perovskite materials. The surface appears to have crystallites which extrude from the surface randomly with structures that are elongated in a single direction. Analysis of the XRD pattern (Figure 4.7) confirms that there is preferred crystallographic orientation in the [300] direction — the [300] peak has greater relative intensity compared to the reference of BiI₃ powder. Overall, the peak positions of the XRD pattern are in excellent agreement with the BiI₃ powder pattern indicating good phase purity within the thin film.
We explored solvent vapor annealing (SVA) as a method to promote grain growth and improve film quality. Xiao et al. recently demonstrated SVA as a method to improve film quality, increase grain size, and improve carrier diffusion lengths in methylammonium lead iodide perovskite thin-film PVs. Furthermore, SVA has been a widely used strategy for enhancing charge carrier transport and modifying grain morphology in polymeric and
organic semiconductors.\textsuperscript{75, 102, 103} In our study, BiI\textsubscript{3} thin films were exposed to controlled amounts of a solvent vapor at a controlled temperature.

We studied the effects of exposing spin coated BiI\textsubscript{3} thin films to THF and DMF solvent vapor in an inert (N\textsubscript{2}) environment. SVA with THF and with DMF were found to increase the grain size of BiI\textsubscript{3} thin films. By measuring domain sizes of plan-view SEM, we were able to quantify the effect of SVA on the surface. THF SVA led to a wide dispersity in grain sizes from a maximum size of 315 nm to a minimum size of 36 nm (Figure 4.6b). The THF also appeared to be embedded within a matrix, which may consist of fine-grained or amorphous materials. This is corroborated by XRD (Figure 4.7), which showed weaker intensity. The average grain size of THF SVA films was 127 ± 76 nm. On average, this was only slightly larger compared to films without any SVA treatment; however, there was a much broader grain size distribution and a more isotropic morphology for THF SVA thin films. The polydispersity in grain size after THF SVA suggests Ostwald ripening; that is, larger grains grow at the expense of smaller grains. SVA in a DMF environment resulted in a much different morphology and substantially larger grain sizes compared to no SVA and THF SVA. A maximum size of 2.5 \(\mu\)m and a minimum size of 122 nm on the surface were measured (Figure 4.8 and Figure 4.6c). The larger grain size after DMF SVA indicates DMF vapor facilitates the migration of BiI\textsubscript{3} and promotes grain growth. However, there are large gaps (0.08 ± 0.05 \(\mu\)m\textsuperscript{2}) throughout the film, presumably arising from the coalescence of the BiI\textsubscript{3} to form larger grains. The XRD pattern of the BiI\textsubscript{3} thin film after DMF SVA is also in excellent agreement with the XRD pattern of the BiI\textsubscript{3} powder. The peak intensities become similar to those of the BiI\textsubscript{3} powder reference, implying that the BiI\textsubscript{3} grains recrystallize and
become randomly oriented after DMF SVA. In contrast, the films with THF SVA retained preferred orientation in the [300] direction.

Figure 4.8. SEM image of BiI₃ thin films processed with DMF solvent vapor at (a) 5,000x magnification and (b) 15,000x magnification.

The Role of BiOI and Air-Processing in BiI₃ Thin-Film Photovoltaics

To evaluate the BiI₃ thin films for PV application, we fabricated proof-of-concept PV devices with a superstrate configuration (Glass/FTO/TiO₂/BiI₃/V₂O₅/Au), as illustrated in Figure 4.9. The TiO₂ and BiI₃ are processed via solution-based deposition, while V₂O₅ and Au are deposited via high vacuum thermal vapor deposition. We found that thin film PV devices processed in a N₂-filled glovebox had lower open-circuit voltage ($V_{OC}$) compared to devices where the BiI₃ layer was processed in air (Figure 4.10b). We hypothesize that processing the BiI₃ layer in air creates a thin layer of oxidized material, BiOI, at the surface which facilitates hole extraction at the BiI₃/V₂O₅ interface.
XPS confirmed the existence of oxidized Bi on the surface (Figure 4.10a) and depth profiling (Figure 4.11) indicated that the oxidation only existed at the surface. Depth-profiling XPS was used to estimate the maximum possible thickness of the BiOI layer. An upper limit was established by observing the point at which the oxygen signal approaches 0%. The lower limit was taken as the first valid data point of the depth-profiling after the sputtering process had begun (37 nm). Low resolution prevented greater precision in determining the thickness. To convert etch time into a thickness, the BiI₃ film was estimated to be 200 nm thick and the interface between the BiI₃ film and the silicon substrate was assumed to occur at the crossover between the iodine 3d and silicon 2s atomic percent. This occurred at 41.5 seconds, the etch rate was estimated at 4.6 nm/s. From depth-profiling we conclude that the thickness of the BiOI layer is ~37 nm thick.
Figure 4.10 (a) X-ray photoelectron spectroscopy of thin films processed in a N$_2$-filled glovebox and in ambient air. (b) $J$-$V$ characteristics of BiI$_3$ PVs processed in a N$_2$-filled glovebox and in ambient air.

Figure 4.11. Atomic percentage of elements as a function of etch time.
By more aggressively oxidizing the material we are able to show the existence of BiOI with grazing incidence x-ray diffraction measurements (Figure 4.13). We hypothesize that the BiOI surface layer facilitates charge transport between BiI₃ and the HTL V₂O₅. BiOI is a p-type semiconductor with a valence band maximum of ~ -6.8 eV vs. vacuum, making it suitable for hole extraction from many semiconductors.¹⁰⁴ In the absence of Fermi pinning, many transition metal oxide HTLs with deep work functions such as MoO₃ or V₂O₅ should provide sufficient driving force to extract photogenerated holes from BiI₃; i.e., they should form a favorable contact.¹⁰⁵ However, the \( V_{OC} \) for N₂-processed devices is low, (< 75 mV) implying that Fermi level pinning could occur at the BiI₃/metal oxide interface, limiting the \( V_{OC} \). From this evidence, we infer that the BiOI layer improves the interfacial defect density by reducing Fermi level pinning, thus improving the \( V_{OC} \).

Figure 4.12. Grazing incidence x-ray diffraction of oxidized BiI₃ showing the formation of BiOI. Further oxidation of the material results in the film changing into a yellow color indicating the formation of Bi₂O₃.
**Solvent Vapor Annealing of BiI₃ Thin-Films in Air**

Processing in air also led to a different film morphology compared to processing in N₂. Plan-view SEM of BiI₃ thin films processed in air without any SVA (Figure 4.13) shows uniform surface coverage compared to processing in N₂. However, there are multiple pinholes in the film — presumably due to rapid evaporation of the THF solvent during spin coating. Given that processing in air resulted in improved PV device performance, we investigated SVA in ambient air. We found the result of SVA in air to be different compared to SVA in N₂.

![Figure 4.13. Plan-view SEM images BiI₃ thin films processed without SVA a) in N₂ and b) in air](image)

THF SVA in air resulted in drastically different film morphology compared to SVA in N₂ (Figure 4.14). The grain shape is rod-like compared to more rounded features in N₂-processing. Grain sizes on average from air processing are smaller than processing in N₂. DMF SVA in air resulted in uniform coverage (Figure 4.15), which is in contrast to DMF SVA in N₂, which resulted in film dewetting. The grain shape appears similar in both cases, and is more rounded and isotropic compared to films with THF SVA and no SVA treatment.
However, the grains are smaller on average when processed in air, compared to those processed in N₂.

**Figure 4.14.** Plan-view SEM images BiI₃ thin films processed with THF SVA a) in N₂ and b) in air

**Figure 4.15.** Plan-view SEM images BiI₃ thin films processed with DMF SVA a) in N₂ and b) in air

The difference in the morphologies for THF and DMF SVA films processed in air vs. N₂ could arise from a number of factors. For instance, in N₂ the grains may grow rapidly to minimize interfacial area; while in air, the thin surface oxide layer that forms could stabilizes smaller grain sizes. Overall, DMF SVA in air resulted in continuous films with relatively
monodisperse grains that extended from the surface to the substrate, as observed in cross-sectional SEM (Figure 4.16). The difference between THF SVA and no SVA in air is minimal (Figure 4.17). This may be partially due to the processing temperature. The boiling point for THF is 66 °C, so higher temperatures (>100 °C) would result in THF vapor remaining in the vapor phase and not diffusing into the thin film. The BiOI may also prevent THF diffusion, thus resulting in minimal change when exposed to THF solvent vapor. DMF, on the other hand, has a boiling point of 153 °C, so it is assumed that processing at 100 °C is more favorable for DMF solvent vapors to condense and diffuse into the material.

**Figure 4.16.** Cross sectional SEM images with TLD detector of (a) No SVA BiI$_3$ PV device, and (b) DMF SVA BiI$_3$ PV device both processed in air. Note the smaller grains located in the no SVA.

**Figure 4.17.** Plan-view SEM images BiI$_3$ thin films processed in air with a) No SVA b) THF SVA c) DMF SVA
Improved Device Performance of BiI₃ Thin-Film Photovoltaic Devices Through Solvent Vapor Annealing

We fabricated PV devices using BiI₃ thin films that were completely processed in air (spin coated and SVA in air). J-V characteristics of these devices under AM1.5 illumination can be found in Figure 4.18 for different SVA conditions. The short-circuit current ($J_{SC}$) of BiI₃ PVs processed without SVA is strongly dependent on annealing temperature, with an optimal temperature of 165 °C (Figure 4.19a). However, temperatures greater than 165 °C resulted in the visible degradation of the BiI₃ material during processing. In fact, prolonged exposure to temperatures greater than 150 °C (~6 hours) also resulted in degradation.

![Figure 4.18. J–V characteristics under AM1.5 illumination of BiI₃ thin films processed without SVA (black), with THF SVA (blue), and with DMF SVA (green).](image)

We observed a maximum $J_{SC}$ at 100 °C for devices fabricated with DMF SVA (Figure 4.19b). Temperatures less than 100 °C presumably caused excessive solvent to diffuse into the film, causing partial or complete dissolution (which we observed visually...
with SVA temperatures $\geq 80 \, ^\circ\text{C}$). Prolonged exposure to DMF solvent vapor (> 10 minutes) did not significantly change the $J_{SC}$. In a similar study, Xiao et al. demonstrated the effect of prolonged exposure to solvent vapors on perovskite thin films.\textsuperscript{76} In their study, rapid grain growth was observed within the first 20 minutes of solvent vapor annealing with minimal grain growth afterwards. Typically, an increase in grain size accompanies an increase in the current density of the PV device due to a reduction of grain boundaries. Since the $J_{SC}$ does not change significantly after 10 minutes of SVA, we conclude that the crystal grains reach a near maximum size after a short exposure time to DMF solvent vapors.

![Figure 4.19](image.png)

**Figure 4.19.** (a) The effect of varying the processing temperature on the $J_{SC}$ of BiI$_3$ thin films without SVA. (b) The effect of varying the DMF SVA temperature on the $J_{SC}$ of BiI$_3$ PV devices.

We observed that SVA treatment improves PV device performance. DMF SVA had a large improvement in the $J_{SC}$ with a value of $5.0 \pm 0.9$ (mA/cm$^2$) with 34 measured devices — more than a three-fold improvement over both THF SVA ($1.6 \pm 0.4$ mA/cm$^2$) and no SVA ($1.23 \pm 0.2$ mA/cm$^2$) with 23 and 26 devices measured, respectively. The improvement in $J_{SC}$ was accompanied by a decrease in the fill factor (FF) for DMF SVA devices, thus signifying
a decrease of the shunt resistance with increased grain size. Devices without SVA had a FF of 35.5 ± 0.2 while THF and DMF SVA films had FFs of 33.4 ± 3.7 and 29.9 ± 2.4, respectively. A champion device with PCE of just over 1.0% was achieved using DMF SVA and can be found in the Appendix.

We used external quantum efficiency (EQE) to quantify photogenerated charge carrier extraction in the BiI₃ devices (Figure 4.20a). The DMF SVA devices show much higher EQE compared to the THF SVA and without SVA treatment devices. As expected, this follows the trend of $J_{SC}$ values obtained for these treatments. From analyzing the spectral dependence of EQE, it is seen that there is a relatively poor extraction of higher-energy photons. This implies a loss in photogenerated carrier extraction efficiency for higher-energy photons preferentially absorbed near the TiO₂/BiI₃ interface relative to the remainder of the device — arising from a recombination of electron-hole pairs at defect states near this interface. The EQE suggests a need to evaluate more suitable n-type heterojunction partners in order to improve the PCE of BiI₃ PV devices. A possible strategy to overcome the low electron collection at the BiI₃/TiO₂ interface is to use a CdS buffer layer in-between BiI₃ and TiO₂. A CdS buffer layer has been shown to reduce surface recombination for CIGS PVs.¹⁰⁶, ¹⁰⁷
Figure 4.20. (a) External quantum efficiency (EQE) of BiI$_3$ thin films processed without SVA (black), with THF SVA (blue), and with DMF SVA (green). (b) Steady-state photoluminescence (PL) spectra of BiI$_3$ processed without SVA (black), with THF SVA (blue), and with DMF SVA (green). PL spectra are normalized to the film absorbance at the excitation wavelength (532 nm). (c) Photoluminescence lifetime of BiI$_3$ processed in N$_2$ (red), and in air (blue); the instrumental response function (obtained from a substrate without a BiI$_3$ film using filter that only transmits the excitation light) is shown in black.

We measured PL and PL lifetime to gain insight on how different treatments affect the excited state dynamics (Figure 4.20b). PL was normalized to the film absorbance (Figure 4.21c) at excitation wavelength (532 nm) to remove the effect of variation in film thickness and possible change in absorption cross-section due to heterogeneity. SVA did not have a significant effect on the PL intensity or position, nor was there effect on carrier lifetimes (Figure 4.22). Given the improved device performance with DMF SVA, it was initially surprising to us that there is no change in carrier lifetime. However, this agrees with a report by Brandt et al.$^{81}$, who observed no difference in carrier lifetime between spin coated and physical vapor transport deposited BiI$_3$ thin films which are most likely to differ in morphology. Thus, this implies that the improvement in $J_{SC}$ and device efficiency after DMF SVA arises from increased charge carrier mobility, rather than lifetime, within the active layer. The higher mobility is likely due to the fact that the grains extend the thickness of the absorber layer, reducing transport across BiI$_3$ grain boundaries.
Figure 4.21: The effect of processing conditions on device (a) transmittance, (b) reflectance, and (c) absorbance on BiI₃ thin films.
Figure 4.22. (a) The effect of SVA on PL carrier lifetime. IRF is the instrumental response function. (b) Comparison of PL carrier lifetime between in air and N2-processing. N2-processing resulted in monoexponential fittings, while processing in air resulted in biexponential fittings. Carrier lifetimes were calculated using Equation 2 below.

\[
<\tau>_{PL} = a_1 \cdot \tau_1 + a_2 \cdot \tau_2
\]

BiI₃ films processed in ambient air had longer carrier lifetimes compared those processed in N₂ (Figure 4.20c). This could be due to passivation by the BiOI layer formed on the surface, although the exact origin of the longer carrier lifetime is uncertain. Other characterization techniques, such as carrier lifetime microscopy, would be necessary for detailed understanding.₁⁰⁸
Considering the relatively wide-bandgap of BiI₃, the PV devices reported here exhibit much lower $V_{oc}$ values than expected (i.e., large $V_{oc}$ deficit). In order to improve the $V_{oc}$, there is evidence that the device architecture might need to be modified — specifically the electron and hole-extracting interfaces. As mentioned above, EQE indicated poor collection of charge carriers that were generated near the p-n interface, implying that carrier recombination is higher at this interface. Because $V_{oc}$ is proportional to the ratio of dark and light current, the increased recombination is at least one source of the low $V_{oc}$. Although the best BiI₃ PV devices shown here have much higher PCE, those reported by Lehner et al.⁴⁶ had higher $V_{oc}$ (>400 mV) values. In their study, they used a poly-indacenodithiophenediﬂuoro-benzothiadiazole (PIDT-DFBT) HTL, which had higher $V_{oc}$ values compared to using a poly-triarylamine (PTAA) HTL ($V_{oc} = 220$ mV). The authors attributed this to the fact that PIDT-DFBT has a deeper valence band maximum compared to PTAA.⁴⁶ In our study, MoO₃ was initially chosen as the HTL because of its very deep work function ($\phi = -6.7$ eV, vs. vacuum)¹⁰⁹ However, devices with a V₂O₅ ($\phi = -5.6$ eV)¹¹⁰ HTL resulted in higher $V_{oc}$ values compared to MoO₃ (Figure 4.23). This indicates possible chemical incompatibles between BiI₃ and MoO₃. As discussed previously, we hypothesize that Fermi pinning occurs at the BiI₃/HTL interface. Understanding hole extraction will be a critical aspect to improving the PCE of BiI₃ PVs. Band positions of the entire device architecture, including MoO₃ can be found in Figure 4.24.
Figure 4.23. The effect of varying metal oxide hole transport layers for BiI₃ PV devices. BiI₃ was also found to be incompatible with Ag — using Ag as the top contact of PV devices resulted in the diffusion of BiI₃ into the metal contact. Au was used instead because it was chemically compatible with BiI₃.

Figure 4.24. Energy band diagram of the materials used in the study. Band levels of TiO₂, BiI₃, BiOI, V₂O₅, and MoO₃ were all found in the literature.
Alternative Deposition Method for BiI₃ Thin-Film Photovoltaics

Although originally THF was used as the solvent to dissolve BiI₃ and fabricate thin-films, many issues arise from its use. First, THF has a high vapor pressure (0.268 bar) at room temperature. This causes the solvent to evaporate rapidly during spin processing and causes irregularities in the thin-film. Moreover, the drying rate is extremely sensitive to the presence of residual solvents in the spin bowl, and produces inconsistencies between samples. Therefore, we believe that the use of THF as a solvent for the reproducible fabrication of BiI₃ thin-films is not a suitable choice, and an alternative solvent is necessary to move forward with the development of this material as a potential optoelectronic device.

Since BiI₃ is also highly soluble in DMF, its use as a solvent was a logical next choice to investigate for the fabrication of BiI₃ thin-films. Initially, using DMF as the solvent resulted in device performances that were lower compared to using THF. When fabricating thin-film devices, concentrations of 100 mg/mL were used for both solutions. However, since THF evaporates more rapidly compared to DMF (vapor pressure of 0.007 bar) noticeably thicker films were formed using THF compared to DMF, which is a possible explanation for its better performance — a thicker film will result in a greater amount of light absorbed and will result in a larger current derived from the device. One advantage of using DMF solvent though is that it can be used with the hot casting methodology developed by Nie et al.¹¹⁴ for organometallic perovskites (More information on this methodology can be found in Chapter 3). When hot casting, the substrates are preheated to 150 °C and then the solution is deposited onto the substrate and spin coated. This resulted in a noticeably thicker film. Both DMF SVA, and hot casting were performed on BiI₃ thin-films. The current-voltage characteristics are found in Figure 4.25.
The effect of these processing techniques can be clearly seen as hot casting thin-films results in an increase in the $V_{OC}$, and the use of DMF SVA resulted in an increase of the $J_{SC}$. Combining the processes together, similar device performances can be attained compared to using THF solvent (Figure 4.26). Using THF resulted in a higher $V_{OC}$ compared to using DMF, however, the $V_{OC}$ is more dependent on layers around BiI$_3$, and not as dependent on the thin-film morphology as described previously. The use of DMF resulted in a greater FF — representative of better thin-film morphology, specifically an increase in the shunt resistance. More importantly, this new technique is more reproducible, still facile, and if optimized, could lead to greater results compared to the originally methodology. Hot casting cannot be used with THF since the boiling point is 66 °C, well below the preheated substrate temperature. The solvent will quickly evaporate and result in a poorly constructed thin-film.
Therefore, this new methodology, with the use of DMF solvent, is highly recommended as the preferred methodology moving forward for the fabrication of BiI₃ thin-film PV devices.

![Comparison of current-voltage characteristics between the use of THF solvent with DMF SVA, and the use of DMF solvent with hot-cast processing, and DMF SVA.](image)

**Figure 4.26.** Comparison of current-voltage characteristics between the use of THF solvent with DMF SVA, and the use of DMF solvent with hot-cast processing, and DMF SVA.

In conclusion, by gaining a fundamental understanding of the material chemistry of BiI₃ thin-films, we were able to improve the current density of BiI₃ PV devices. This improvement was a result of enhanced understanding between BiI₃ and THF/DMF solvent interactions. By taking advantage of these unique interactions, we were able to manipulate the thin-film post-deposition using SVA to increase the grain size and improve the crystallinity of the thin-film. Furthermore, we discovered the need for a thin oxidized layer on the surface of BiI₃ that helps facilitate hole transport between the BiI₃ and V₂O₅ interface. Lastly, by probing the optoelectronic properties of BiI₃ thin-films, we were able to determine that the improved film morphology gained by SVA in DMF resulted in an increase in the current collection of the PV device. Thus, we were able to report the first all-inorganic BiI₃ thin-film PV device with the highest reported PCE of 1.0%. 

CHAPTER 5. FUTURE WORKS

Extension of BiI₃ Methodology to Bi-based Semiconductor Materials

The low efficiency of BiI₃ poses a challenge for the future development of the material for use in a single junction PV device, or as the top layer of a tandem junction PV device. The material was predicted to be defect-tolerant because of its electronic configuration, however, it suffers from a large $V_{OC}$ deficit. More studies are necessary to understand the optoelectronic properties of BiI₃ devices; however, it may be important to consider other Bi-based semiconductor materials as well. For comparison, the carrier lifetime of MAPbI₃ thin-films have been measured from 100 to 1000 ns, which is much greater than the carrier lifetime of BiI₃ thin-films which was measured at 860 ps. Moreover, due to the long carrier lifetimes, MAPbI₃ crystals have diffusion lengths up to 175 µm. The transport properties of BiI₃ may not be great enough to make it a candidate to replace MAPbI₃. However, the processing conditions and device architecture developed for BiI₃ can be extended to more complex bismuth-based perovskites, and serve as a starting point for the development of highly-efficient PV devices. First, potential bismuth-based halide perovskite compounds must be identified.

The Goldschmidt tolerance factor can be used to assess the geometric stability and distortion of ABX₃ crystal structures, and indirectly predict and screen for new compounds. The tolerance factor (TF) is defined as the ratio of constituent ionic radii of A, B, and X and is represented mathematically as, $TF = (R_A + R_X)/\sqrt{2}(R_B + R_X)$. When the TF = 1, the compound adopts the ideal cubic close-packed structure, and when TF ≠ 1, the compound has geometric strain, and there is distortion in the crystal structure. Overall, the perovskite phase is predicted to form when the TF is between 0.85 and 1.11. Originally,
the Goldschmidt tolerance factor was designed for ABX₃ (X = O, F, S, Se) compounds, and fails to accurately predict the crystal phase of hybrid halide perovskites. The Goldschmidt tolerance factor uses the hard sphere assumption, which needs to be adjusted for organic cations that are not spherical. Moreover, the ion radius of cations predicted by Shannon et al. were based on oxide and fluoride compounds, and are not accurate when applying them towards the heavier halides (Br-, I-). The Goldschmidt tolerance factor can still be used to predict the crystal phase of compounds, but with the use of an effective ionic radii. By using the effective ionic radii in the Goldschmidt tolerance factor, a list of compounds have been predicted as potential Pb-free halide perovskites replacements.

Although numerous compounds have been predicted by substituting Pb²⁺ for less toxic alternatives such as Sn²⁺ and Ge²⁺, there are less compounds predicted for Bi³⁺ and Sb³⁺. Substituting Pb²⁺ with Bi³⁺ and Sb³⁺ is a viable possibility as Bi³⁺ and Sb³⁺ ions are isoelectronic with Pb²⁺. The substitution will lead to vacancies in the crystal structure, as Bi³⁺ and Sb³⁺ will only occupy 2/3 of the octahedral X₆ voids due to their charge. Alternatively, to accommodate for the trivalent ions, monovalent metal ions (such as Cu, Ag, and Au) can be incorporated into the crystal structure resulting in a double perovskite structure A₂B⁺⁺B⁺⁺⁺X₆. In this manner, you can replace the Pb²⁺ ion with a Bi³⁺ or Sb³⁺ ion and a M⁺ (M= Cu, Ag, Au) ion to account for the vacancies that arise when substituting Bi³⁺ or Sb³⁺ alone. The Goldschmidt tolerance factor can be adjusted for multiple ions accordingly, $\text{TF} = \frac{(R_A + R_X)}{\sqrt{2}} \left[ \frac{(R_{B'} + R_{B''})}{2} + R_X \right]$ by simply taking the average of the ionic radii for the metal (B) sites. Performing this screening process, using the screening process developed by Brandt et al., refining the focus to more stable materials such as all-inorganic compounds, and using iodide as the halide (gives the lowest bandgap compared to other
halides) results in three potential materials Cs$_3$Bi$_2$I$_9$, Cs$_2$CuBiI$_6$, and Cs$_2$AgBiI$_6$ as all-inorganic single and double bismuth-halide perovskite analogs to lead-based hybrid halide perovskites.

Cs$_3$Bi$_2$I$_9$ has been studied previously for its use in PV applications.$^{43,93}$ Initial studies have shown that this material has potential as PV device, and shows greater stability compared to MAPbI$_3$. However, one limitation of Cs$_3$Bi$_2$I$_9$ is that it has a large, indirect band gap (2.2 eV), which is far too great for use in a single junction solar cell. The material could be used as a tandem junction solar cell by reducing the bandgap of the material to $\sim$1.9 eV. Experimentally, Vigneshwaran et al. has shown the bandgap of an analogous organic-inorganic hybrid material, MA$_3$Bi$_2$I$_9$, can be reduced by doping with sulfur.$^{126}$ This has the possibility of being extended to Cs$_3$Bi$_2$I$_9$. More recently, Hong et al. performed a theoretical study on bandgap engineering of Cs$_3$Bi$_2$I$_9$ by addition of Ga and In — among other atoms — to the crystal structure.$^{127}$ These studies show the potential of engineering Cs$_3$Bi$_2$I$_9$ to enhance its photovoltaic properties. Although there have been studies focusing on the electronic properties of this material, there have not been studies done on the material chemistry. The relationship between processing, structure, and device performance of Cs$_3$Bi$_2$I$_9$ is still poorly understood. Since Cs$_3$Bi$_2$I$_9$ forms as an isolated Bi$_2$I$_9^-$ ions with face-sharing Bi-I octahedral, the processing techniques developed for BiI$_3$ is expected to carry over to Cs$_3$Bi$_2$I$_9$.

Only recently has bismuth-halides been shown in the double perovskite structure.$^{123-125}$ Cs$_2$AgBiBr$_6$ has a measured indirect bandgap of 1.95 eV, and shows a long room-temperature PL lifetime of 660 ns. The double perovskites are also predicted to have defect tolerance, and are more stable toward heat and moisture compare to MAPbI$_3$. Xiao et al.$^{128}$
studied the defect chemistry of Bi-based double perovskites and showed that the Ag vacancies in the crystal structure are shallow acceptors, while the Bi vacancies and Ag\textsubscript{Bi} anti-site are deep acceptors. By forming the crystal in Br-poor/Bi-rich conditions, the deep defect states can be suppressed, resulting in longer carrier lifetimes. The long carrier lifetime, and defect-tolerance suggest that these materials may be promising semiconductors for use as absorber layers. McClure et al.\textsuperscript{129} through both solid state and solution routes synthesized Cs\textsubscript{2}AgBiBr\textsubscript{6} and Cs\textsubscript{2}AgBiCl\textsubscript{6}. These materials both had indirect bandgaps, and had bandgap energies of 2.19 and 2.77 eV respectfully. Using iodide as the halide could be one strategy to reducing the bandgap of these double perovskite materials. Finally, Volonakis et al.\textsuperscript{124} used first-principle calculations to study the electronic properties of the entire family of bismuth and antimony based double perovskites.

We found that the molecular precursors for Cs\textsubscript{3}Bi\textsubscript{2}I\textsubscript{9}, Cs\textsubscript{2}CuBiI\textsubscript{6}, and Cs\textsubscript{2}AgBiI\textsubscript{6} are highly soluble in DMF solvent, with concentrations more than 1M. However, when dissolving BiI\textsubscript{3} and AgI/CuI in DMF, AgI/CuI does not dissolve into DMF. Only when CsI is added to the solution does AgI/CuI dissolve. This indicates that presence of Cs leads to the disassociation of the AgI/CuI molecule. It is understood that DMF forms a molecular complex with BiI\textsubscript{3}, but how CsI and AgI/CuI incorporate into this structure is unknown. The absorbance spectra of BiI\textsubscript{3}, Cs\textsubscript{3}Bi\textsubscript{2}I\textsubscript{9}, Cs\textsubscript{2}CuBiI\textsubscript{6}, and Cs\textsubscript{2}AgBiI\textsubscript{6} solutions dissolved in DMF were taken to elucidate the presence of cesium and silver in the molecular complexes (Figure 5.1). The solution absorption of these materials were similar, indicating that the BiI\textsubscript{3}-DMF complex that forms in the BiI\textsubscript{3} solution alone, is forming in the Cs\textsubscript{3}Bi\textsubscript{2}I\textsubscript{9} and Cs\textsubscript{2}CuBiI\textsubscript{6}, and Cs\textsubscript{2}AgBiI\textsubscript{6} solutions as well. However, the presence of Ag/Cu and Cs in the molecular complex could not be directly measured and further analysis is necessary.
To determine how Cs and Ag/Cu fit into the molecular complex, crystals were precipitated from these solutions (see Chapter 3 for more details). For the Cs$_3$Bi$_2$I$_9$, Cs$_2$CuBiI$_6$, and Cs$_2$AgBiI$_6$ solutions, bright red crystals were formed. Unfortunately, due to nature in which the crystals inherently grow, we were unable to analyze the structure with single crystal XRD. The crystals were mosaic, making the analysis difficult. Cs$_3$Bi$_2$I$_9$ is a defect perovskite, so it is possible that the vacancies in the crystal structure could entropically favor this growth behavior. Crystals were also synthesized following the procedure by Slavney et al.$^{125}$ These crystals were grown in an HI solution; the solution was heated to near boiling point temperature of HI for several hours and allowed to cool naturally. Again, the crystals were highly mosaic and we were unable to determine the crystal structure with single crystal XRD. Since, Slavney et al. could successfully synthesize Cs$_2$AgBiBr$_6$ double perovskite crystals using this procedure, and this procedure could not be extended to Cs$_2$AgBiI$_6$, we began to have doubts on whether Cs$_2$CuBiI$_6$ and Cs$_2$AgBiI$_6$ could form, and if the Cs$_3$Bi$_2$I$_9$ phase is more thermodynamically favorable.
Overall, the goal is to produce solution-processable thin-films of Cs$_3$Bi$_2$I$_9$, Cs$_2$CuBiI$_6$, and Cs$_2$AgBiI$_6$. To test whether we could produce Cs$_2$CuBiI$_6$ and Cs$_2$AgBiI$_6$, or if the formation of Cs$_3$Bi$_2$I$_9$ is more favorable, thin-films from solutions were made similarly to BiI$_3$ thin-films. The absorbance of these thin films was taken, and again the absorbance peaks between the Cs$_3$Bi$_2$I$_9$ thin-film (derived from the Cs$_3$Bi$_2$I$_9$ solution) and Cs$_2$CuBiI$_6$ and Cs$_2$AgBiI$_6$ thin-film (derived from the Cs$_2$CuBiI$_6$ and Cs$_2$AgBiI$_6$ solution) were similar, giving evidence of the formation of the same material (Figure 5.2). This is further supported by XRD of the thin-films, which show that the same material was produced (Figure 5.3). If Cs$_2$CuBiI$_6$ and Cs$_2$AgBiI$_6$ were produced in place of Cs$_3$Bi$_2$I$_9$, we would expect shifts in the diffraction peaks relative to Cs$_3$Bi$_2$I$_9$, since the materials should have the same crystal
structure, but differing lattice parameters. This gives evidence that the formation of solution-processable \( \text{Cs}_2\text{CuBiI}_6 \) and \( \text{Cs}_2\text{AgBiI}_6 \) thin-films, with the use of DMF as the solvent, is not possible and different strategies are necessary for the synthesis of solution-processable \( \text{Cs}_2\text{CuBiI}_6 \) and \( \text{Cs}_2\text{AgBiI}_6 \) thin-films.

![Figure 5.2](image)

**Figure 5.2.** Thin-film absorbance of the resulting thin-films from \( \text{Cs}_3\text{Bi}_2\text{I}_9 \) solution (black), \( \text{Cs}_2\text{AgBiI}_6 \) solution (blue) \( \text{Cs}_2\text{CuBiI}_6 \) solution (green).

Although we were not successful at our attempt to produce thin-films of \( \text{Cs}_2\text{AgBiI}_6 \), this thesis does serve to further understand the properties of these new Bi-based double perovskite materials. To fabricate thin-films of these materials, different strategies are necessary, and the proposed facile deposition using DMF as the solvent is not possible. However, if we can fabricate thin-films of these materials, extension of the methodologies developed for \( \text{BiI}_3 \) is hypothesized to work, and should simplify the need to optimize the growth of thin films.
Optimization of Device Architecture for BiI₃ Thin-Film Photovoltaics

As discussed previously in Chapter 4, BiI₃ thin-film photovoltaics suffer from a large $V_{OC}$ deficit. As a wide bandgap material, the $V_{OC}$ is expected to much higher than ~300 mV as shown in this thesis. Analysis of the EQE of the thin-films shows a large decrease in the carrier collection near the TiO₂ and BiI₃ interface indicating a large amount of carrier recombination at the p-n junction interface. Moreover, comparison to literature shows that the use of PIDT-DFBT as the hole-transport layer resulted in a higher $V_{OC}$ compared to our device architecture which used VOₓ and MoOₓ as the hole-transport layers. In order to improve the efficiency of BiI₃ PV devices, the device architecture must be optimized with the correct n-type and hole-transport materials.

Mesoporous TiO₂ (m-TiO₂) was first investigated as an addition to planar TiO₂ layer originally used in BiI₃ PV devices. Before investigating other n-type semiconductor materials as a replacement for TiO₂, we wanted to investigate whether the decrease in carrier collection at the p-n junction interface was due to poor interfacial contact between BiI₃ and TiO₂ or
whether it was due to chemical incompatibilities between BiI₃ and TiO₂. We deposited m-TiO₂ on top of the planar TiO₂ layer, and made devices the same way as described previously (see Chapter 3). We observed that BiI₃ thin-films deposited onto m-TiO₂ were lighter in color, most likely due to BiI₃ filling into the pores of the m-TiO₂ and not forming into a planar layer. This hypothesis is supported by the current-voltage characteristics seen in Figure 5.4, as there is no current derived from the BiI₃ PV devices using m-TiO₂. Since BiI₃ fills the pores of the m-TiO₂ and does not form a planar layer, there is no active layer present in the device.

When hot casting thin-films — which results in thicker films — we observe that the thin-films are visibly darker, and appear the same as samples using planar-TiO₂ alone, and a current can be drawn from this device. Preliminary results show that the use of m-TiO₂ does not result in an improvement of the device $V_{OC}$ indicating that there is likely a chemical compatibility between the p-n junction interface. However, the use of m-TiO₂ did result in an increase of the device FF compared to use of planar TiO₂ alone; specifically, an increase in the shunt resistance. Although we can show a slight improvement in the device performance with the use of m-TiO₂, the device $V_{OC}$ was unaffected by the presence of m-TiO₂ — further providing evidence of the chemical incompatibility of BiI₃ with TiO₂.
Figure 5.4. Current-voltage characteristics of devices under illumination fabricated with and without m-TiO$_2$ layer. The $V_{OC}$ of the devices are the same regardless of the presence of m-TiO$_2$.

BiI$_3$ can be paired with other n-type and hole-transport materials that have been used with halide-perovskite active layers. This includes the following n-type materials: a) fullerene, b) PEDOT: PSS, and c) CdS as an intermediate layer between TiO$_2$ and BiI$_3$. Although metal-oxides are expected to work very well as hole transport layers due to their large work functions, they do not pair well with BiI$_3$. This again could be due to chemical incompatibility between BiI$_3$ and metal-oxide materials. Following the same strategy as the selection of n-type materials, hole-transport materials that have worked well with halide-perovskite active layers can be investigated for use with BiI$_3$. This includes: a) Spiro-OMeTAD, and b) PCMB. Moreover, the same HTL used by Lehner et al.$^{46}$ can be extended to this study to see how their device architecture works with our improved film morphology.

**Bandgap Engineering of BiI$_3$ Thin-Film Photovoltaics**

A semiconductor can be doped with other materials, and in doing so, the optoelectronic and physical properties of the materials can be engineered. Tuning the bandgap of a material by doping is an effective strategy to optimize the properties of a
material. For BiI₃, the current bandgap (1.8 eV) makes it suitable for use in a tandem solar cell, however if the material were to be used in a single junction solar cell the bandgap will need to be reduced to > 1.6 eV. It has been shown that sulfur doping of an analogous material, MA₃Bi₂I₉, can be an effective strategy to reduce the bandgap of the material. Since BiI₃ is a constituent part of the MA₃Bi₂I₉ crystal structure, we hypothesize that sulfur doping BiI₃ will have a similar effect as compared to MA₃Bi₂I₉. Moreover, material doping of BiI₃ could be used as a model to predict the effect of doping on more complex bismuth-based halide perovskite materials.

Originally, sulfur doping was investigated as a strategy to produce BiSI in a more a facile manner starting with BiI₃. BiSI is a bismuth-based semiconductor with a bandgap of 1.53 eV and is also predicted to have defect-tolerance. The methodology developed for sulfur doping of BiI₃ can be found in Chapter 3. In short, BiI₃ thin-films are annealed in sulfur vapor similar manner to DMF SVA; sulfur chunks are placed onto a glass slide and heated past its melting point to produce a sulfur vapor. The sulfur vapors are contained in the glass petri dish, and analogous to DMF SVA, the sulfur vapor will diffuse into the thin film, incorporating sulfur into the crystal structure. Thin films are annealed in a sulfur environment for four hours to ensure the diffusion of sulfur into BiI₃.

Optical characterization of sulfur doping can be found in Figure 5.5. Sulfur doping was studied under two conditions, one in which there was no SVA, and the other in which DMF SVA was conducted at the same time as sulfur doping. Sulfur doping alone resulted in a slight shift in the band-tail, increasing the number of states above the bandgap; similar to what is seen with DMF SVA alone. The combination of DMF SVA and sulfur doping resulted in a slight shift of the bandgap into the red and a greater increase in the band-tail
states. DMF SVA results in a DMF vapor-rich environment that diffuses into the thin-film causing the migration of grains, which enhances the growth of the crystal grains. When sulfur is introduced with DMF SVA, we hypothesize that sulfur vapor can diffuse further into the film, resulting in a greater impact on the crystal structure and thin-film morphology. From Figure 5.5, it is evident that the incorporation of sulfur improves the optical properties of the material, increasing the number of states available near the bandgap of the material. However, the extent in which sulfur is being incorporated into the crystal structure is still to be determined.

Figure 5.5. Absorbance spectra of BiI₃ thin-films exposed to various processing conditions.

X-ray diffraction was used to quantify any changes to the crystal structure resulting from sulfur doping of BiI₃ thin-films (Figure 5.6a). From the XRD patterns, the BiI₃ crystal structure is maintained during sulfur annealing, and the presence of sulfur cannot be determined with this characterization method. There is a reduction in the [113], and [300] diffraction peaks which could be a result of lattice strain due to the incorporate of sulfur.
atoms, however further analysis is necessary to determine how sulfur is being incorporated into the crystal structure. Since there is an increase in band-tail states, we hypothesize that sulfur is passivating defect states at the surface of crystal grains. The physical effect of sulfur doping can be seen in Figure 5.6b using SEM images.

Both DMF SVA, and sulfur annealing show a dramatic change to the physical features of the crystals grains in the BiI₃ thin film. DMF SVA resulted in more oriented crystal growth compared to sulfur annealing — confirmed in the XRD pattern. When combining both processes techniques together, crystal grains appear slightly larger and are less uniform across the surface of the film. There is also a dispersity in the grain size, an indication of Ostwald ripening. The non-uniformity on the surface of BiI₃ thin-films because of the combined DMF SVA and sulfur annealing processing will pose a challenge when producing PV devices. A uniform film is necessary to provide proper interfacial contact between the active layer and the hole transport layer.

Adjusting the thickness of the thin film could be strategy to mitigate this effect, as a thicker film would provide more material to facilitate grain migration, and reduce the possibility of the formation of voids in the thin films which would cause shunting in the device. These preliminary results give evidence that sulfur annealing can affect the film morphology, and with addition of DMF SVA can have greater effect on both the electronic and physical properties of BiI₃ thin-films. Further optimization of this methodology could provide a facile strategy of improving the electronic properties and reducing the bandgap of bismuth-based semiconductors thin-films.
Figure 5.6. (a) XRD of BiI₃ thin films processed in various conditions with BiI₃ and BiSI indexes. (b) SEM images of BiI₃ thin films processed in various conditions.
CHAPTER 6. SUMMARY AND CONCLUSIONS

In summary, we demonstrated that BiI$_3$ forms molecular complexes with coordinating solvents such as THF and DMF, enabling solution-based processing of BiI$_3$ thin films. Molecular complexes have been used widely over the past decade in “dimension reduction” approaches,$^{131}$ however, in most cases dimensional reduction requires the use of a relatively corrosive (reducing) solvent to solubilize the inorganic material. In this case, BiI$_3$ readily forms complexes with relatively benign solvents in a similar manner to PbI$_2$ — but unlike PbI$_2$, the bandgap of BiI$_3$ is suitable for use as a PV absorber layer. Overall, processing in air provided multiple benefits to improving the PCE of BiI$_3$ thin film PVs: a BiOI layer forms at the surface that facilitates hole extraction, and this surface layer also presumably prevents film dewetting during solvent vapor annealing in DMF. Annealing in solvent vapor was found to increase grain size and reduce film porosity, especially in the case of DMF vapor. Based on photoluminescence spectroscopy, we can infer that the improved performance is due to improved carrier mobility, since the excited-state lifetime does not increase after SVA. In non-optimized, all-inorganic PV devices, we achieved 1.0% PCE, which is the highest reported efficiency for this material, and the first report of an all-inorganic BiI$_3$ photovoltaic device structure. This demonstrates the potential of BiI$_3$ as a potential non-toxic alternative to hybrid perovskite materials that has improved air-stability.

Future research that can stem from this thesis is the extension of this work to other bismuth-based semiconductors, specifically bismuth-based perovskite-halide semiconductors which may have possess the important characteristics that are desired from research Pb-based halide perovskites. Overcoming the challenge of solution-processing Cs$_2$AgBiI$_6$ double perovskite thin-films is the next step in the development of bismuth-based semiconductors.
This material has potential to replace Pb-halide perovskite PV devices, by overcoming the toxicity and stability issues with MAPbI₃. Using the processing techniques developed for BiI₃ will accelerate the development of this PV device, circumventing the need to optimize techniques to produce high film quality. BiI₃ still has potential as a PV device, however, the large $V_{OC}$ deficit is a major concern moving forward. This problem can be addressed by doping the material to improve the electronic properties, and passivating trap states that may exist within the bandgap. The continued development of the device architecture can increase the electron and hole extraction, and the overall device performance. This thesis provides the groundwork for the continued research of BiI₃ and other bismuth-based semiconductor materials for PV application.
**NOMENCLATURE**

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<td>PV</td>
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<td>HTL</td>
<td>Hole Transport Layer(s)</td>
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<td>External Quantum Efficiency</td>
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<tr>
<td>THF</td>
<td>Tetrohydrofuran</td>
</tr>
<tr>
<td>DMF</td>
<td>N.N-Dimethylformamide</td>
</tr>
<tr>
<td>HI</td>
<td>Hydroiodic Acid</td>
</tr>
<tr>
<td>PCBM</td>
<td>[6,6]-phenyl-C61-butyric acid methyl ester</td>
</tr>
<tr>
<td>PEDOT: PSS</td>
<td>Poly(3,4-ethylenedioxythiophene) poly(styrene-sulfonate)</td>
</tr>
<tr>
<td>PCE</td>
<td>Power Conversion Efficiency</td>
</tr>
<tr>
<td>J$_{SC}$</td>
<td>Short-circuit Current Density</td>
</tr>
<tr>
<td>V$_{OC}$</td>
<td>Open-circuit Voltage</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>PCE</td>
<td>Power Conversion Efficiency</td>
</tr>
<tr>
<td>J-V</td>
<td>Current-Voltage</td>
</tr>
</tbody>
</table>
TF: Tolerance Factor
REFERENCES


5. Administration, U. S. E. I. Updated Capital Cost Estimates for Utility Scale Electricity

   Generating Plants. [https://www.eia.gov/outlooks/capitalcost/pdf/updated_capcost.pdf](https://www.eia.gov/outlooks/capitalcost/pdf/updated_capcost.pdf) (April 18),


   http://www.nrel.gov/gis/images/eere_pv/national_photovoltaic_2012-01.jpg (March 19th),


50. Shockley, W.; Queisser, H. J., Detailed balance limit of efficiency of p-n junction 

51. Vos, A. D., Detailed balance limit of the efficiency of tandem solar cells. *Journal of 

52. Debije, M. G.; Verbunt, P. P. C., Thirty Years of Luminescent Solar Concentrator 

53. Nozik, A. J., Quantum dot solar cells. *Physica E: Low-dimensional Systems and 

54. Baikie, T.; Fang, Y.; Kadro, J. M.; Schreyer, M.; Wei, F.; Mhaisalkar, S. G.; Graetzel, 
    M.; White, T. J., Synthesis and crystal chemistry of the hybrid perovskite (CH3NH3)PbI3 


56. Deng, Y.; Peng, E.; Shao, Y.; Xiao, Z.; Dong, Q.; Huang, J., Scalable fabrication of 
    efficient organolead trihalide perovskite solar cells with doctor-bladed active layers. *Energy 

57. Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; 
    Sum, T. C., Long-Range Balanced Electron- and Hole-Transport Lengths in Organic- 

    Harlang, T.; Chabera, P.; Pullerits, T.; Stepanov, A.; Wolf, J.-P.; Sundström, V., 
    Organometal Halide Perovskite Solar Cell Materials Rationalized: Ultrafast Charge 

    CH3NH3PbI3 Films: A Simple Process Suitable for Large-Scale Production. *Energy 

60. Bhachu, D. S.; Scanlon, D. O.; Saban, E. J.; Bronstein, H.; Parkin, I. P.; Carmalt, C. 
    J.; Palgrave, R. G., Scalable route to CH3NH3PbI3 perovskite thin films by aerosol assisted 


**APPENDIX ADDITIONAL INFORMATION**

**Post deposition annealing.** BiI₃ PV devices were thermally annealed for ten minutes in air at 100°C after device testing to improve device performance. Device data shown in the thesis were not thermally annealed after deposition of metal contacts.

![Graph showing the effect of post deposition annealing](image)

**Figure A.1.** The effect of post deposition annealing. Champion device IV sweep parameters: \( J_{SC} \) (7.0 mA/cm²), \( V_{OC} \) (364 mV), FF (39.2%), and PCE (1.02%). The device was processed with DMF solvent vapors at 100 °C for ten minutes and thermal annealed at 100 °C for ten minutes.

**Effect of sodium iodide on device performance.** Based on the structure of the BiI₃–THF complex shown in Figure 4.2, we know that there is a non-negligible amount of sodium in the THF solution. In an effort to determine the effect of Na⁺ ions on PV devices, sodium iodide (NaI) (Fisher, ≥99.5%) was added to THF in molar amounts of 1%, 0.1%, and 0.001% of NaI to BiI₃. The addition of NaI had no clear effect on the \( J_{SC} \) of PV devices. Since Na already presumably exists in the THF solvent, we also spin coated BiI₃ films dissolved in DMF (which presumably does not contain Na). NaI was added in the same molar amounts as above (THF). The effect of increasing the NaI concentration resulted in decreasing device

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However, the effect of Na has not been thoroughly investigated and additional experiments (such as eliminating Na from THF) will be needed to fully understand the impact of Na on BiI₃ PVs. Finally, the use of DMF and THF solvent cannot be directly compared because the use of DMF resulted in issues with wetting the substrates during spin coating, thus reducing the quality of the film.

**Figure A.2.** The effect on BiI₃ PV \( J_{sc} \) and \( V_{oc} \) as a result of adding NaI to solutions of BiI₃ dissolved in (a) THF and (b) DMF.