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Solution phase synthesis of lead-free perovskite and perovskite-inspired materials

Rainie Dean Nelson
Iowa State University

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Solution phase synthesis of lead-free perovskite and perovskite-inspired materials

by

Rainie D. Nelson

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

DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Program of Study Committee:
Matthew G. Panthani, Major Professor
Eric Cochran
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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2019
DEDICATION

This work is dedicated to my Grandma Livingood. I wish you were here to see me fulfill this dream of ours. I know you would be so proud.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENT</td>
<td>v</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>vi</td>
</tr>
<tr>
<td>CHAPTER 1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 General Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.2 References</td>
<td>5</td>
</tr>
<tr>
<td>CHAPTER 2. LITERATURE REVIEW</td>
<td>8</td>
</tr>
<tr>
<td>2.1 Background and Introductory Material</td>
<td>8</td>
</tr>
<tr>
<td>2.1.1 General Introduction to the Instability of and Efforts to Stabilize Lead Halide Perovskites</td>
<td>8</td>
</tr>
<tr>
<td>2.1.2 Beneficial Properties of Perovskites and Description of Band Gap in Semiconductor Materials</td>
<td>12</td>
</tr>
<tr>
<td>2.1.2.1 Discussion of the existence of band gap</td>
<td>12</td>
</tr>
<tr>
<td>2.1.2.2 Defect tolerance and other good properties of lead halide perovskites</td>
<td>17</td>
</tr>
<tr>
<td>2.1.3 Perovskite Nanocrystals of Cesium Lead Halide</td>
<td>18</td>
</tr>
<tr>
<td>2.1.4 General Synthetic and Characterization Techniques for Colloidal Nanocrystals</td>
<td>20</td>
</tr>
<tr>
<td>2.2 Properties of Bismuth and Incorporation in Bismuth Based Perovskites</td>
<td>24</td>
</tr>
<tr>
<td>2.2.1 Overview of Bismuth</td>
<td>24</td>
</tr>
<tr>
<td>2.2.2 Development of Bismuth Optoelectronics Research</td>
<td>26</td>
</tr>
<tr>
<td>2.3 Reduced Dimension Materials and 2D Perovskites</td>
<td>27</td>
</tr>
<tr>
<td>2.3.1 2D Materials in General</td>
<td>27</td>
</tr>
<tr>
<td>2.3.2 Phenethylammonium and Butylammonium Layered Halide Perovskites</td>
<td>29</td>
</tr>
<tr>
<td>2.4 References</td>
<td>31</td>
</tr>
<tr>
<td>CHAPTER 3. THE EFFECTS OF SOLVENT COORDINATION STRENGTH ON THE MORPHOLOGY OF SOLUTION-PROCESSED BiI$_3$ THIN FILMS</td>
<td>46</td>
</tr>
<tr>
<td>3.1 Abstract</td>
<td>46</td>
</tr>
<tr>
<td>3.2 Introduction</td>
<td>47</td>
</tr>
<tr>
<td>3.3 Experimental Section</td>
<td>49</td>
</tr>
<tr>
<td>3.4 Results and Discussion</td>
<td>52</td>
</tr>
<tr>
<td>3.5 Conclusion</td>
<td>69</td>
</tr>
<tr>
<td>3.6 Acknowledgements</td>
<td>69</td>
</tr>
<tr>
<td>3.7 References</td>
<td>69</td>
</tr>
<tr>
<td>CHAPTER 4. SYNTHESIS AND OPTICAL PROPERTIES OF ORDERED-VACANCY PEROVSKITE CESIUM BISMUTH HALIDE NANOCRYSTALS</td>
<td>75</td>
</tr>
<tr>
<td>4.1 Abstract</td>
<td>75</td>
</tr>
<tr>
<td>4.2 Introduction</td>
<td>76</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4.3 Experimental Methods</td>
<td>77</td>
</tr>
<tr>
<td>4.3.1. Experimental Details</td>
<td>77</td>
</tr>
<tr>
<td>4.3.2 Characterization:</td>
<td>80</td>
</tr>
<tr>
<td>4.4 Results and Discussion</td>
<td>80</td>
</tr>
<tr>
<td>4.5 Summary and Conclusions</td>
<td>89</td>
</tr>
<tr>
<td>4.6 Acknowledgments</td>
<td>90</td>
</tr>
<tr>
<td>4.7 References</td>
<td>90</td>
</tr>
<tr>
<td>CHAPTER 5. LAYERED DOUBLE PEROVSKITES AND THEIR OPTICAL AND STRUCTURAL</td>
<td>97</td>
</tr>
<tr>
<td>CHANGES UPON HEATING OR EXFOLIATION</td>
<td></td>
</tr>
<tr>
<td>5.1 Abstract</td>
<td>97</td>
</tr>
<tr>
<td>5.2 Introduction</td>
<td>98</td>
</tr>
<tr>
<td>5.3 Experimental Methods</td>
<td>100</td>
</tr>
<tr>
<td>5.3.1 Materials</td>
<td>100</td>
</tr>
<tr>
<td>5.3.2 Methods</td>
<td>100</td>
</tr>
<tr>
<td>5.3.3 Characterization Methods</td>
<td>101</td>
</tr>
<tr>
<td>5.4 Results and Discussion</td>
<td>101</td>
</tr>
<tr>
<td>5.4.1 Thermochromic Behavior of $n = 1 \text{PEA}_2\text{AgBiBr}_6$</td>
<td>105</td>
</tr>
<tr>
<td>5.4.2 Exfoliation Based Synthesis of Nanocrystals from Layered</td>
<td>113</td>
</tr>
<tr>
<td>Perovskites</td>
<td></td>
</tr>
<tr>
<td>5.5 Conclusions</td>
<td>117</td>
</tr>
<tr>
<td>5.6 Acknowledgments</td>
<td>118</td>
</tr>
<tr>
<td>5.7 References</td>
<td>118</td>
</tr>
<tr>
<td>CHAPTER 6. BISMUTH BASED SEED NANOPARTICLES FROM</td>
<td>123</td>
</tr>
<tr>
<td>HALOBISMUTHATE PRECURSORS</td>
<td></td>
</tr>
<tr>
<td>6.1 Abstract</td>
<td>123</td>
</tr>
<tr>
<td>6.2 Introduction</td>
<td>123</td>
</tr>
<tr>
<td>6.3 Experimental Methods</td>
<td>124</td>
</tr>
<tr>
<td>6.3.1 Experimental Details</td>
<td>124</td>
</tr>
<tr>
<td>6.3.2 Characterization:</td>
<td>125</td>
</tr>
<tr>
<td>6.4 Results and Discussion</td>
<td>125</td>
</tr>
<tr>
<td>6.5 References</td>
<td>135</td>
</tr>
<tr>
<td>CHAPTER 7. GENERAL CONCLUSION</td>
<td>137</td>
</tr>
</tbody>
</table>
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Thank you Mark and Ginger, for always cheering me on. And Ben, my fiancé, thank you for your love, kindness, and support. Words will never be enough to express my gratitude.
This dissertation is a broad overview of research in the field of lead-free perovskite inspired materials. While lead halide perovskites have promising properties, we sought to investigate non-toxic alternatives – typically ones containing bismuth halides. We looked into the flexibility of this element to be produced on different length scales, fabricating films from bulk material, synthesizing nanocrystals, and growing crystals of 2D layered double perovskites. We discovered that due to complexation with a solvent, bismuth iodide films can be morphology controlled through use of solvent additives. During our synthesis of Cs$_3$Bi$_2$X$_9$ nanocrystals, we found that BiX$_3$ precursors possessed photoluminescence and that treatment of these seeds was crucial to the end product of the reaction. We investigate layered double perovskites containing bismuth and found that these materials have a structural transition and a thermochromic behavior. Further, we determine that these double perovskites can be processed into nanocrystals through sonication. Finally, we investigated the aforementioned Bi seeds to determine methods of controlling the morphology and processability of the seeds, finding that changing an alkylammonium ligand helps direct some amount of self-assembly. We conclude that bismuth based materials have many interesting properties that encourage future investigation into bismuth halides.
CHAPTER 1. INTRODUCTION

1.1 General Introduction

Semiconductor materials are ubiquitous in industrialized society, being used in a wide variety of applications, such as photovoltaics (PVs), temperature sensors, light emitting diodes (LEDs), integrated circuits, lasers, photodetectors, and field effect transistors (FETs). From providing renewable electricity to lighting our homes to running our phones, these semiconductors feature prominently in our daily life. The growth in global population and the increasing demands of functionality and performance of electronic materials necessitates a correlated improvement in what our semiconductor materials can provide. In pursuit of this goal, new materials can be synthesized to tailor to demands. Many of these semiconductor materials will need to function as optoelectronic materials, which combine electronics with light emission, absorption, detection, or control. PVs, for example, will absorb light and then produce a current which will provide electricity. The use of PVs to provide electricity, and perhaps renewable energy that can be used as fuel as well, is a prime example of the need to develop better semiconductor materials for our optoelectronics.

Nowadays the majority of our energy is derived from effectively non-renewable resources like natural gas and petroleum. There are many issues with this status quo. The burning of fossil fuels is associated with potential pollution to the environment through oil spills, which have featured prominently in some past years (BP oil spill). Fossil fuel consumption also releases so called greenhouse gases which accelerate climate change. This has negative effects on flora and fauna in the environment, which cannot adapt to rapid environmental changes, as well as human habitation and infrastructure. A rise in temperatures is associated with things like severe weather (like the increasing intensity of
hurricanes) and flooding, all things that, if they occur too rapidly, could cause major issues. The purchase and dependence on fossil fuels also has national and social consequences, in that countries which heavily rely on imported fossil fuels can occasionally be at the whim of oil markets and the economies of another country. And finally, while not drastically urgent, fossil fuel consumption is also tied to a finite resource – fossil fuels will eventually run out. While we may discover pathways to renew these fossil fuels somehow, there is an easier solution.

The sun illuminates the Earth with far more power than we could possibly use. With a relatively conservative estimate, every day 85 TW of sunlight make it to the surface of the Earth, with solar electricity having a technical potential of 7500 TW. The total global annual usage of energy was approximately 160,000TWh or about 19TW. The energy available from the sun each day exceeds the annual demand for energy. Even with limitations in device efficiency, PV devices covering a modest land area could easily satisfy global energy demand now and in the future as energy demand increases. If PV device efficiencies can be increased and production/maintenance costs decrease then PV becomes the most viable source of renewable energy. Figure 1.1 shows the photovoltaic power potential around the globe. While some areas have more potential output than others, all parts of the globe have some access to PV, which isn’t true for some other types of renewable energy.

PVs can be utilized in remote areas, and some PV materials could be patterned onto flexible substrates to enable niche applications (like solar clothing or backpacks). While there are inherent issues with any technology, solar power harnessed by PV devices offers a great promise in not only the ability to provide renewable energy, but in the ability to provide a great deal more energy than we currently consume.
Traditional materials used for PV include the quintessential material, crystalline silicon, and some newer thin film technologies like cadmium telluride, copper zinc tin sulfide (CZTS) and copper indium gallium sulfide/selenide (CIGS). However, these current technologies do not provide the cost profile and material abundance for large-scale deployment of PV technology.

One relatively new material that offers initial promise in many types of optoelectronic applications, and especially in PV application, is the lead halide perovskite. Perovskites, named for Lev Perovski, are compounds with the formula $ABX_3$, where $A$ is a cation, $B$ is a metal cation, and $X$ is an anion. Perovskites have been researched for quite some time, with the quintessential perovskite being calcium titanate ($\text{CaTiO}_3$). The material was first discovered in the 1800s, and the structure first elucidated by Goldschmidt in 1926, where he detailed the tolerance factors that various materials would have towards forming the
perovskite structure. The structure for calcium titanate was then published in 1943 and barium titanate shortly after in 1945 with a transition from tetragonal to cubic at 200°C. Cesium lead halides were also identified in the late 1950s to have perovskite-like structures at some elevated temperatures. In 1978, the synthesis and cubic structure of the methylammonium lead halides was determined.

In general, investigation of halide perovskites prior to the 2000s focused more on structural elucidation than optoelectronic properties. Some early work done by Mitzi looked at melt-processing of phenethylammonium tin halides for FETs. However, the explosive growth in research surrounding lead halide perovskites for optoelectronic applications did not begin in earnest until after 2009.

In 2009, Kojima et al used a methylammonium lead iodide perovskite in dye-sensitized solar cells with 3.8% power conversion efficiency (PCE). Since that time, lead halide perovskites have been developed and used as the active layer in photovoltaics with >24% PCE, an impressive PCE for a new material to obtain in less than a decade. The highest performing perovskite PVs typically contain a mixture of cations (commonly formamidinium and methylammonium) and a mixture of anions (bromide and iodide). Overall, research on perovskites has advanced to include a multitude of applications, including LEDs, lasers, photodetectors, γ-ray detection, and X-ray imaging.

These halide perovskite materials are able to achieve such promising performance due to some intrinsic electronic properties that will be further discussed in Chapter 2, alongside a detailed presentation of the major drawbacks to the lead halide perovskites – their toxicity and instability. Chapter 2 provides additional background on perovskite and bismuth materials, a brief overview of literature relevant to this document, and discusses some
general knowledge which aids in motivation and understanding of topics in this document. While the promising perovskite materials have many positive characteristics, this document focuses on the investigation of bismuth based materials with the objective of addressing the aforementioned drawbacks of lead halide perovskites. Chapter 3 details the investigation of the use of solvent additives in a bismuth iodide film precursor solution, using adduct chemistry to control morphology in a bismuth iodide film. Chapter 4 moves from improvement of morphology of a bulk bismuth iodide material to a study on synthesis and growth of cesium bismuth halide NCs. Chapter 5 investigates properties of layered double perovskites. Chapter 6 discusses some work on understanding the bismuth seeds present in the synthesis of cesium bismuth halides (this work will be first alluded to in some of the findings in Chapter 3). Chapter 7 will provide a summary and outlook based on the contents of the document.

1.2 References


CHAPTER 2. LITERATURE REVIEW

Perovskite materials, as discussed briefly in Chapter 1, have shown initial promise for optoelectronic devices. This chapter will further develop the issue of instability, which was alluded to previously. In addition, bulk and nanocrystal perovskites will be discussed in detail. General properties important to semiconductors and nanocrystals will be covered to provide enhanced context for the work contained in future chapters. Next, bismuth based materials will be introduced and an argument will be made for their potential for optoelectronics as perovskite-like materials. Finally, this chapter will conclude with the discussion of interesting properties of 2D materials and a background on 2D perovskite materials. This overview of topics will provide the contextual and theoretical background for the various works presented in Chapters 3 through 6.

2.1 Background and Introductory Material

2.1.1 General Introduction to the Instability of and Efforts to Stabilize Lead Halide Perovskites

The high efficiency perovskite material discussed in Chapter 1 usually has the following characteristics: the A site cation is methylammonium (MA) or formamidinium (FA), the B site metal is lead, and the X site anion is a halide, typically iodide, bromide, or chloride. This material, a bulk perovskite structured crystal, can adopt a cubic crystal structure where BX$_6$ octahedra are corner sharing, and the A site cation is located in the center of the cuboctahedral voids. However, this hybrid organic-inorganic lead halide structure is not stable and exposure to regular operating conditions (moisture, air, light, heat) will degrade the material.$^{1-9}$ Studies have shown that degradation is at least partly due to
reaction with $\text{H}_2\text{O}$ and subsequent decomposition of $\text{MAPbI}_3$. One-step in this process is a hydrated intermediate of $\text{PbI}_6^{4-}$ isolated octahedra. In situ grazing incidence neutron scattering experiments have also shown mechanisms of water based degradation on hybrid perovskite films, where high humidity will form metastable hydrate phases and result in domain swelling. This alters the faceting of the crystals, results in incorporation of additional water, and more greatly affects smaller crystals, meaning that film morphology is an important factor.

This reveals the main problem with lead halide perovskites – they are not stable. This downside is compounded by the fact that these perovskites contain lead, which is a toxic material and can be released from the perovskite structure as the unstable material degrades. As a result, much research has focused on addressing the issue of stability or toxicity. This is done with various approaches, many of which include varying the cations (either A site or metal site), anions, or overall structure of the material. Some groups use blends of A site cations, like a mixture of FA and MA. The organic cation can also be replaced by an inorganic element, like cesium, which affords enhanced thermal stability. Cesium lead halides have been successfully integrated into optoelectronic applications, with the current record photovoltaic efficiency of 15.7% at the time this document was prepared. However, the cesium lead halide must be heated to high temperatures in order to access the efficient cubic perovskite structure. Once in the cubic black phase, cesium lead halides will degrade to a yellow non-perovskite phase in ambient environment. In terms of replacing the metal B-site cation, common research efforts focus on replacing the lead with elements like Sn or Ge. Unfortunately, the Sn and Ge perovskites readily undergo oxidation to the 4+ state, rendering the materials unsuitable for optoelectronic application. In some cases,
researchers also will attempt to alloy Pb and Sn to reduce toxicity and potentially inhibit oxidation of Sn.\textsuperscript{25-27} Finally, anion substitution in part or in full can also be done to enhance performance and stability,\textsuperscript{28} though there are some amorphous impurities and spinodal decomposition in mixed-halide perovskites.\textsuperscript{29}

Another method to substitute for the B site metal cation is to synthesize perovskite-like (or vacancy-ordered perovskite) materials.\textsuperscript{30-38} This is true for the case of bismuth, where the structure deviates to $A_3B_2X_9$, sharing some similarities to the perovskite motif of connected octahedra. Instead of corner sharing octahedra, the vacancy type structure in this case has pairs of $BiX_6$ octahedra which are face sharing, forming dimer-like $Bi_2X_9^{3-}$ groupings. The $A_3B_2X_9$ structural configuration of antimony based perovskite-like material differs somewhat, in that $Cs_3Sb_2X_9$ can form 0D dimer forms or a 2D layered structure of octahedra.\textsuperscript{39} Methylammonium antimony halides have also been synthesized\textsuperscript{40, 41} with some preliminary 0.5% PCE demonstrating photovoltaic potential.\textsuperscript{42} $Cs_3Sb_2I_9$ has obtained up to 1.5% PCE,\textsuperscript{43} and a $Rb_3Sb_2I_9$ device also recently achieved a device performance of 0.76% PCE.\textsuperscript{44}

Some groups also do heterovalent substitution of the 2+ lead cation with a 1+ and 3+ element (i.e. $Ag^+$ and $Bi^{3+}$).\textsuperscript{45-51} This forms a so-called double perovskite, where the Ag and Bi $BX_6$ octahedra are commonly shown to alternate in the cubic perovskite pattern. These double perovskites will commonly have structural distortions, like octahedral tilting based on the properties of the metal cations.\textsuperscript{52} Phase transitions of elpasolites, ordered double perovskites of $A_2BB’X_6$, have also been studied with the transitions being somewhat dependent on the A site cation such that monatomic A site cations have displacive mechanisms and larger cations have order-disorder type mechanisms for their transitions.\textsuperscript{53}
Both experimental and theoretical works have been done to characterize the properties of double perovskites. A subset of double perovskites also includes vacancy ordered double perovskites, with structure $A_2BX_6$.\footnote{54}

Finally, the perovskites can also be synthesized with reduced dimensionality to improve stability against moisture. Groups have synthesized single layers of metal halide perovskites in the Riddlesden-Popper and Dion-Jacobson phases,\footnote{55-57} which will be discussed later in further detail in Section 2.3 of this chapter.

Combinations of these individual stabilization methods are also used for example the B site cation or the X site anion may be varied in cesium lead halides or in blended FA and MA lead halides to enhance stability of that material.\footnote{10}

Additionally, nanoplates or nanoparticles of the metal halides have also been synthesized. One particularly interesting example of this is the synthesis of cesium lead halide nanoparticles by the Protesescu group.\footnote{58} Due to surface effects,\footnote{59} at a modest temperature this synthesis is able to produce cesium lead halide nanocrystals in the cubic phase, which is typically only possible at much higher temperatures. There are still some issues with long term stability in the as-synthesized material,\footnote{60} but groups have performed post-synthetic washing and variation of ligands to improve stability\footnote{61-63}, as will be further discussed in Section 2.1.3.

The main limitation on the tuning of the basic perovskite is based on whether the chosen cations and anions will form a perovskite structure. While perovskite-like structures have also proven useful (as in the aforementioned $A_3B_2X_9$), the Goldschmidt tolerance factor gives an indication of whether a combination of elements will form the cubic perovskite structure.\footnote{64} This tolerance factor is a function of the ionic radii for the various component,
where a tolerance factor between 0.8 and 1.0 is commonly accepted to form the 3D perovskite structure with the A site cations in the cuboctahedral voids. This tolerance factor can, in some cases, be used to predict the formation of new perovskite compounds.\textsuperscript{65} However, it is acknowledged that the tolerance factor is not quite suitable for iodide perovskites,\textsuperscript{66} and revised tolerance factor calculations have been proposed which base the cationic radii on the specific anion present.\textsuperscript{67}

\textbf{2.1.2 Beneficial Properties of Perovskites and Description of Band Gap in Semiconductor Materials}

In order to thoroughly discuss some of the beneficial properties of perovskites, it is first helpful to discuss semiconductor materials in general and how they function within optoelectronics.

\textbf{2.1.2.1 Discussion of the existence of band gap}

Different types of practical applications require different classes of materials. Metals, semiconductors and insulators are three general classes of materials that can be somewhat arbitrarily separated based on a fundamental characteristic – their band gap. Metals have no band gap between their valence band and conduction band, semiconductors have a small band gap, and insulators have a large band gap as schematically demonstrated in Figure 2.1. Broadly speaking, a band gap is a gap in energy states which are not accessible to an electron. These states separate a valence band (comprised of valence electrons) and conduction band (empty states that can be accessed upon excitation of electrons) in a material. The inaccessibility of the gap energy states to electrons is representative of states which are not valid solutions of the Schrödinger wave equation.
Semiconductor materials are useful for optoelectronic applications because this energy gap can be used to produce light or current. As mentioned, the conduction band above the band gap can be populated via the excitation of electrons. This excitation can occur through the input of energy in the form of electricity, heat or light. In one example of an optoelectronic device, a photovoltaic cell, light from the sun strikes the surface of a photovoltaic cell. Photons impart their energy \( (E = h\nu) \) to an electron in the valence band. If the energy of that photon is larger than or equal to the energy separation of the band gap, the electron can be promoted to an excited state within the conduction band. The empty state now left in the valence band is referred to as a hole, and the excited electron and remaining hole form pair called an exciton. In a photovoltaic cell, these charges are separated to a
cathode and anode and then recombine in a controlled pathway that enables extraction of current from the device. If there is no band gap, there will be no recombination of charges and no current can be extracted. If the band gap is too small, a large portion of the solar spectrum will not be absorbed because the charges will excite above the band gap but then often relax thermally to the conduction band edge. On the other hand, if the separation is too large, only very high energy photons will properly excite electrons across the band gap, which would lead to inefficient photovoltaics. This is because a large portion of the solar spectrum is at lower energy, as seen in Figure 2.2.

![Solar spectrum intensity at various wavelengths. Reproduced from reference.](image)

There are a few different metrics to establish what kind of material would make a good photovoltaic. Based on device physics and limitations, no photovoltaic device can be 100% efficient. The Shockley-Queisser limit describes the maximum efficiency of a single p-n junction PV by considering efficiency losses that occur within a PV as a result of band gap
limitation (cannot absorb photons with energy lower than the band gap), blackbody radiation (baseline emission) and recombination of electron-hole pairs before transport to the electrodes.\textsuperscript{69} This limit commonly describes the ideal band gap of a semiconductor material for photovoltaics to be around 1.3 or 1.4eV. However, simply having this band gap does not ensure the semiconductor will make an efficient device. There is also a difference between indirect and direct band gaps (Figure 2.3). In the case of an indirect band gap, the valence band maximum (the highest occupied molecular orbital – HOMO) and the conduction band minimum (the lowest unoccupied molecular orbital – LUMO) do not occur at the same so-called k point. This is a value in momentum space.

Figure 2.3 Illustration demonstrating (a) direct and (b) indirect band gap transitions, reproduced from reference.\textsuperscript{70}

For excitation across an indirect band gap the energy to excite across the band gap must be paired with momentum, imparted in the form of a phonon. Because the incident
photon and phonon must collide simultaneously with an electron, this becomes like a three-body collision, representing an event with decreased probability. Silicon, for example, has an indirect band gap and requires a much thicker layer of material to enhance the absorption of light when fabricating a photovoltaic. This increases production cost and decreases flexibility of potential substrates, which further limits possible applications. On the other hand, a direct band gap has the HOMO and LUMO occurring at the same value of momentum, meaning that a photon alone can excite directly across the band gap, making for a potentially more efficient device.

The direct band gap versus indirect band gap property of a semiconductor does not tell the entire story, however. Another more recently developed metric to examine possible photovoltaic efficiency is the spectroscopic limited maximum efficiency (SLME). In this case, the authors acknowledge that materials which have an indirect band gap and a direct band gap close in energy may effectively function as direct band gap semiconductors. They also take into consideration the shape of the absorption spectra and the non radiative recombination mechanisms that may be material specific.

Furthermore, materials which have a band gap outside of the so-called ideal band gap may still find useful application in tandem solar cells. For these materials, there is more than one active layer which absorbs incoming photons. In this case, wider band gap semiconductors can also be useful for photovoltaics.

Clearly the value of the band gap alone does not tell the entire story of a semiconductor. Another important thing to consider, and an area where perovskites seem to shine, is the tolerance or sensitivity of a material to defects within the material.
2.1.2.2 Defect tolerance and other good properties of lead halide perovskites

Lead halide perovskites, and other materials, are predicted to be defect tolerance due to characteristics of their bonding orbitals. Pb and Bi materials are predicted to have antibonding valence orbitals, such that defects like dangling bonds that would normally induce deep gap defect states will instead result in shallow defect states near the band edge.\(^\text{73}\) When defect states exist deep within the band gap they limit the potential of a PV device because the radiative recombination will likely first proceed through relaxation into the defect state (or initial excitation into the defect state), which limits the total energy that can be extracted through the relaxation step. The antibonding characteristic of the valence band is relatively unique, and may explain some of the rapid progress achieved in device efficiency of perovskites. Shockley-Read-Hall recombination is a decay pathway mediated by defects – lead halide perovskites also have small Shockley-Read-Hall recombination.\(^\text{74}\)

However, perovskites also have other characteristics that promote good optoelectronic performance. Solution processed lead halide perovskites demonstrate balanced charge carrier diffusion lengths around 100 nm.\(^\text{75}\) Chloride doping boosts that length above 1 µm.\(^\text{76}\) Lead halide perovskite single crystals have shown charge carrier diffusion lengths above 10 µm in methylammonium lead bromide.\(^\text{77}\) Charge carrier diffusion lengths are relevant for performance because they are representative of the ability of the exciton to move through the physical crystal. If the exciton recombines before reaching the electrodes it will not produce current and the PV device will not function. Almost at the same time, Dong et al. reported that under 1 sun illumination methylammonium lead iodide single crystals had charge carrier diffusion lengths over 175 µm, though that number decreased to around 3 mm under weaker light.\(^\text{78}\) The mechanism for the long charge carrier diffusion lengths was
investigated, demonstrating that a majority of types of recombination rates were low, though the less common Auger recombination rates were somewhat high.\textsuperscript{79}

The lead halide perovskite has been found to have a high absorption coefficient and small Urbach tail, indicating fewer mid-gap energy states that would reduce potential in PV devices.\textsuperscript{80} Tin perovskites have shown high mobilities, which could be appropriate for thin-film transistor applications.\textsuperscript{81} These materials also have interesting excitonic behavior and evidence that very thin materials can work as good absorbers.\textsuperscript{82} The material also has good charge carrier mobilities.\textsuperscript{79, 83, 84}

2.1.3 Perovskite Nanocrystals of Cesium Lead Halide

As mentioned before in Section 2.1.1, one method to stabilize cesium lead halide in the perovskite phase is to synthesize it in nanocrystal form. This section will introduce the seminal work in the synthesis of cesium lead halide nanocrystals and provide a brief introduction to works on halide perovskite nanocrystals. In order to synthesize cesium lead halide nanocrystals, Protesescu et al\textsuperscript{58} used a hot injection synthesis method, where they first dissolved PbX\textsubscript{2} in a mixture of octadecene, oleylamine, and oleic acid at elevated temperature. They then proceeded to inject a previously made and pre-heated cesium oleate material as a source of cesium. The majority of the growth of the nanocrystals was observed in the first few seconds of the reaction. The absorbance and photoluminescence was not found to be size tunable, a common characteristic of semiconducting quantum dots. This would most likely be due to a very small Bohr exciton radius, such that the size of the nanocrystals cannot be made smaller than this radius (a necessary condition for quantum confinement and associated band gap shift to occur). Instead, Protesescu et al\textsuperscript{58} found that the properties of the CsPbX\textsubscript{3} nanocrystals could be tuned by varying the identity of the halide
anion. This can be achieved through initial incorporation of the various halides (i.e. PbI$_2$, PbBr$_2$, and/or PbCl$_2$) or through post-synthesis anion exchange.$^{85}$ Udayabhaskararao$^{60}$ et al investigated the growth mechanism of these colloidal cesium lead halide nanocrystals, finding that the nanocrystal synthesis occurred first through the formation of Pb$^0$ seeds which reacted with the injected Cs-oleate to form CsPbX$_3$ nanocrystals. As a result of this, aging of the reaction precursor had an impact on the morphology of the resultant nanocrystals.

Another interesting finding from the Protesescu paper was that the nanocrystals were synthesized in a cubic structure.$^{58}$ However, bulk CsPbI$_3$ at lower temperature forms an orthorhombic non-perovskite yellow phase with poor optoelectronic properties. The temperature of the synthesis of the CsPbI$_3$ was below the typical phase transition temperature from this orthorhombic phase to a cubic phase with good optoelectronic characteristics. The formation of the cubic structure at temperatures lower than the transition temperature was attributed to surface effects, where surface functionalization can reduce surface energy and change the phase equilibria.$^{59}$ However, some reports question the true phase of the CsPbI$_3$ perovskite at room temperature.$^{86}$ Twinning present in the single nanocrystals can complicate characterization of the crystal structure through destructive interference of signals that would normally correspond to the orthorhombic lattice.$^{87}$

If some of these nanocrystals are indeed cubic upon synthesis, not all of the as-synthesized “cubic” CsPbX$_3$ nanocrystals are stable - over time the nanocrystals will degrade back into the yellow non-perovskite phase. Researchers have used various approaches to enhance the stability of the lead containing materials, some of which are similar to efforts pursued in order to stabilize bulk cesium lead halides. For nanocrystals, however, there are a few unique steps that can be taken to enhance stability. Swarnkar et al. remove excess
unreacted precursor with methyl acetate, and also show some ability to tune the band gap by
changing nanocrystal size with reaction temperature. Oleic acid, while commonly used for
hot-injection syntheses, has also been recognized as a component which may contribute to
instability, with the use of an alkyl phosphinic acid demonstrated stabilization of the cubic
phase in CsPbI$_3$ nanocrystals. Cation halide salt treatments have also been employed for
thin film formation to enhance properties. In addition to these methods, the lead can be
partially substituted or alloyed with another metal (like tin) to enhance air stability.

Cesium lead halides are not the only halide perovskites that have been synthesized in
the form of nanocrystals. Recently, some work has been done on the synthesis of double
perovskite nanocrystals. As mentioned earlier, in this case the lead is commonly replaced
with two heterovalent atoms. For example, a commonly studied double perovskite is
Cs$_2$AgBiBr$_6$, and nanocrystals of this material have been synthesized. Anion-exchange also
allows access to Cs$_2$AgBiI$_6$, which has not yet been synthesized in bulk form to the best of
our knowledge.

Methylammonium lead halide nanocrystals have also been synthesized where
inclusion of antimony (in the form of Cs$_3$Sb$_2$I$_9$) results in surface bound layers that enhance
the PL.

The synthesis of halide perovskite nanocrystals is obviously a topic of interest. The
following section will provide a more detailed description of nanocrystals in general.

2.1.4 General Synthetic and Characterization Techniques for Colloidal Nanocrystals

The hot-injection method is very commonly used for the synthesis of nanoparticles
containing a metal element. However, this is not the only method through which
nanoparticles are synthesized. This section will briefly discuss the synthesis, characterization and relevant theory related to colloidal nanocrystals.

In broad terms there are two general ways to synthesize nanocrystals. Bulk materials can be made and exfoliated or otherwise broken down to form nanomaterials in a top down synthesis, or elemental precursors can be built from the bottom up to synthesize nanocrystals. Bottom up methods can involve solution based methods like hot-injection, heating up, or anti-solvent based precipitation. Top down methods include mechanical or chemical exfoliation, etching, or ball milling.

The nucleation and growth of nanocrystals is important to understand in order to obtain greater control over properties, such as size and surface functionalization. In the event of ubiquitous nucleation and subsequently a slower growth, a larger number of small nanocrystals will be obtained. If growth occurs with relatively little nucleation then larger nanocrystals can be obtained. The parameters of nucleation and growth can be tuned through variation of reaction conditions and reactants.\(^9\)

Ligands, in the case of nanocrystals, have an impact both on the growth of the nanocrystals and on their post-synthetic stabilization. The inclusion of specifically chosen ligands during the synthesis process can control the morphology of nanocrystals. This is typically thought to be a result of preferential attachment of ligand molecules to specific facets of the nanocrystals, with a recent paper arguing that this mechanism is perhaps more likely linked to kinetic control rather than thermodynamic control based on the weaker selectivity needed to kinetically influence shape.\(^2\) Therefore, the nanocrystal growth will occur along a specific direction and result in an alternative shape of crystal. Typical ligands used include oleic acid and oleylamine. These ligands will attach to the surface of the
nanocrystal and provide a post-synthesis effect – the ligands stabilize the nanocrystal in solution. This stabilization effect of ligands is commonly broken into two primary types – steric and electrostatic stabilization. Steric stabilization is commonly seen in organic solvent, and uses long bulky surface ligands to prevent agglomeration and sedimentation of nanocrystals. Electrostatic stabilization utilizes electrostatic repulsion between charged surface moieties in solvents with appreciable dielectric constants. Bare nanocrystals (with no capping surface ligands) will typically agglomerate and then sediment out of solution, with the sedimentation rate depending on particle size, density difference between the particle and the solvent, and the solvent viscosity. Colloidal stability of nanocrystals in solvent is important for processing. Solution-based techniques are often some of the cheaper and more versatile for applications of nanocrystals, such as spin- or spray-coating of films for photovoltaic devices. However, in this case, many of the ligands which are preferred for the synthesis of the nanocrystals (for example long-chain alkylamines) have deleterious impacts on the performance of the devices due to their insulating natures providing a barrier to efficient charge transport. As a result, procedures to achieve exchange of the surface ligands are commonly used. These may be as simple as addition of excess ligand to drive partial or full displacement of the original ligand. Ligand exchange processes could also first involve removal of the original ligand. This enables further tunability of material properties.

Once the nanocrystals have been synthesized, there are several common techniques that are used to characterize the nanocrystals and films made from the nanocrystals. Many of these techniques will be used in future chapters, and so will be briefly discussed here. Diluted samples deposited on conducting grids can be used for Transmission Electron Microscopy
(TEM) measurements. This involves a collimated beam of electrons that strikes the sample, and a camera/detector below the sample that measures the transmission of electrons through the sample. This technique typically gives higher contrast with heavier elements, though TEM can be done on carbon samples with the proper types of grids. TEM provides information about size, shape and polydispersity, and High-Resolution TEM (HRTEM) can also provide atomic level resolution of lattices which can yield information about the d-spacing between planes in the nanocrystal. Another type of electron microscopy commonly used in the nanocrystal field is Scanning Electron Microscopy (SEM). In this case, the electron beam and the detector are both above the sample and the measurement technique scans the surface. The images presented within this document will be of secondary electrons emitted by the samples upon exposure to the electron beam. SEM does not have as high of a resolution as TEM, but does provide depth-of-field and is quite useful for probing grain morphology and film quality. Both types of electron microscopy are often paired with Energy Dispersive X-ray Spectroscopy (EDS), which is used to detect characteristic X-ray ejected from atoms when inner shell electrons are excited to higher states; this provides information about atomic composition. In order to ascertain the actual crystal structure of a material, Powder X-ray Diffraction (PXRD) and Single Crystal XRD (SCXRD) are used. In PXRD, X-rays will scatter off of atoms based on their arrangement within the crystals. Signals collected by the detector represent the d-spacings between various planes in the crystal structure. These can be compared to reference patterns for different types of crystal structures (hexagonal, cubic, etc.) or to potential compositions/structures that are appropriate for the elements included in the synthesis (i.e. if a material is synthesized from precursors containing
Ca, Ti, and O, then it could contain the pure elements, Ca₂O, CaTiO₃, TiO₂, or some other combination where each of these compounds will have a unique XRD pattern).

In terms of solution phase characterization, absorbance and photoluminescence measurements are often used. This is especially useful for semiconducting nanocrystals, where absorbance and photoluminescence can sometimes give information about the size of a nanocrystal. Whenever the size of a nanocrystal is smaller than the Bohr exciton radius, the nanocrystal will experience quantum confinement of the electron and undergo a subsequent blue-shift in the absorbance/PL due to a widening of the band gap. Absorbance and photoluminescence are also used to characterize thin films of nanocrystals. While not utilized within this text, Dynamic Light Scattering and Zeta Potential measurements can also be used in solution to determine hydrodynamic radius and surface charge, respectively.

2.2 Properties of Bismuth and Incorporation in Bismuth Based Perovskites

While lead halide perovskites have many promising features, they will always have an inherent toxicity that may place limitations on their future development. For this reason, bismuth based perovskite and perovskite-like materials are of great interest. The majority of the experimental work discussed in Chapter 1 through Chapter 7 deals with bismuth based materials in various manifestations. This section will discuss the properties of bismuth, the motivation for using bismuth in perovskites or perovskite-like materials, and some initial work demonstrating the potential of bismuth materials for optoelectronic applications.

2.2.1 Overview of Bismuth

Bismuth based materials were historically investigated for x-ray application due to the large x-ray cross section of bismuth. Bismuth is a high-density element with a melting point of 271.4°C. It is a brittle metal that is commonly used when combined with other
elements. Bismuth is a somewhat un-abundant material. The structure of bismuth in ambient conditions is the α-rhombohedral form. Bismuth can be found as bismuth metal or as a compound in ores like bismite (Bi₂O₃), bismutite [(BiO)₂CO₃] and bismuthinite (Bi₂S₃). Commercially, bismuth is often obtained as a byproduct of refining other metal ores (like zinc, copper and lead). Bismuth is a pentavalent post-transition metal with an electron configuration of [Xe] 4f¹⁴5d¹⁰6s²6p³. The most common oxidation state of bismuth is the 3+ oxidation state, though in some cases it can also adopt a 5+ oxidation state. Bismuth has similarities to arsenic and antimony in terms of chemical properties, though is less toxic than these elements.

With a half life of around 19 quintillion years, bismuth-209 is effectively a stable isotope. Interestingly, bismuth has one of the lowest thermal conductivities and also one of the highest Hall coefficients of any metal, where the Hall coefficient has an inverse relationship to charge density. If deposited as a very thin film, bismuth will exhibit semiconducting behavior. Bismuth is also the most naturally diamagnetic of all metals. Finally, bismuth is also unusual in that it expands upon freezing, a property it shares with just Ga and Ge.

In terms of chemistry, when reacted at elevated temperatures with O₂, S or X₂ bismuth will form Bi₂O₃, Bi₂S₃ or BiX₃. When bismuth or bismuth oxide is reacted with acid there is a tendency to form salts of oxoacids like Bi₂(SO₄)₃. Many metals will form bismuthides with interesting structures or physical properties. Partial hydrolysis of BiX₃ will result in the formation of BiOX, and BiOF and BiOI can form by heating BiX₃ in air.
2.2.2 Development of Bismuth Optoelectronics Research

While bismuth is an interesting material in general, recent research has shown the PV application of bismuth. A publication from our group details the use of bismuth iodide in a 1% PCE PV device, achieved through solvent vapor annealing to improve morphology. This work on bismuth is motivated by a couple of different driving forces. There are general chemical similarities to lead that make bismuth promising for implementation into PVs. As discussed earlier, one of the beneficial aspects of the lead halide perovskites is the defect tolerance of lead, arising from the anti-bonding characteristic in the valence band, making the material less susceptible to intrinsic defects. Brandt et al identified bismuth materials as potential materials which could also possess a similar defect tolerance due to the similarities in the valence characteristics. This information, combined with lower toxicity and a demonstrated promise as optoelectronic material has partly driven the blossoming investigation of bismuth halides. In addition, bismuth can also be incorporated into perovskite-like structures when combined with many of the same elements or organic molecules that are used in lead halide perovskites, giving another motivation for study of this material. Methylammonium bismuth halides and cesium bismuth halides have been synthesized and incorporated into photovoltaics with efficiencies of 3.17% and 3.20%, respectively, where the Cs$_3$Bi$_2$I$_9$ PV cells were fabricated using Cs$_3$Bi$_2$I$_9$ nanosheets. In these cases, the structure of the perovskites varies slightly from the standard ABX$_3$ motif to form defect perovskites.

Bismuth is also used in the double perovskite structures like Cs$_2$AgBiBr$_6$, as mentioned in Section 2.1.1. Overall, interest in bismuth based materials for optoelectronics applications has been progressively growing in recent years.
2.3 Reduced Dimension Materials and 2D Perovskites

This final section of the literature review and background will focus on 2D materials and will continue the trend of introducing and understanding the physics of one of the materials that will be discussed in later experimental chapters of this work.

As mentioned previously, reduced dimensionality has been explored as a method to stabilize lead halide perovskites. It also offers another method of tunability for the materials, as it enables the synthesis on different size scales which can lead to novel properties. The nanocrystals described in Section 2.1.3 are one example of a material of reduced dimensionality. Another type of nanomaterial with intriguing properties is the two dimensional nanomaterial. These are often described as nanosheets or nanoplatelets (nanoplates), and have one dimension (height) that is on the nanoscale. These materials have interesting properties that arise as a result of their dimensions. There are also one dimensional nanomaterials, nanowires or nanorods, which have both height and width on the nanoscale. These also have interesting properties, but are outside the scope of this work.

There are many works reviewing unique properties and applications of 1D nanomaterials, including 1D perovskite materials. This section will briefly discuss 2D nanomaterials in general, including a discussion of some of their unique properties, and then will specifically discuss the alkylammonium based 2D halide perovskite materials.

2.3.1 2D Materials in General

One of the most heavily researched 2D materials is graphene, an allotrope of carbon that consists of a honeycombed structure of carbon atoms in a single layer that forms a sheet. This material has fascinating optoelectronic and mechanical properties and is the subject of well-cited reviews. The intense research into graphene has resulted in new or
renewed investigation of several other 2D type nanosheet materials, such as boron nitride and transition metal dichalcogenides. Transition metal dichalcogenides have been studied previously, and many have bandgaps that transition from indirect to direct when 2D layers are formed.\textsuperscript{123}

There has also been a great deal of work done on nanoplates or nanoplatelets, which typically also have fairly small dimensions of length and width.\textsuperscript{124-130} These materials can be synthesized using the same methods as the 0D nanocrystals, with both top-down and bottom-up synthesis methods. With hot-injection, for example, nanoplate structures can often be accessed simply by varying the reaction conditions used to synthesize the 0D material analogues. Most commonly shape control of this type is obtained by varying the reaction temperature. Whether increasing or decreasing the temperature will result in 2D materials depends on the growth mechanism of the nanomaterial.

2D materials are interesting from a fundamental physics standpoint because of the effects of quantum confinement. When one of the dimensions in a material is a few nanometers, the material has the potential to represent a quantum well. The 2D perovskites are also considered multiple-quantum-well structures because of their unique structure. The inorganic semiconductor layers can be considered 2D wells separated by electronic barriers in the form of the bulky insulating organic layers.\textsuperscript{131,132} The excitons inside these layers are confined and display intense PL at room temperature.\textsuperscript{133} Several reasons given for high PL of the 2D perovskites include increased exciton binding energy, strong dielectric and quantum confinements, and shallow defects.\textsuperscript{134}
2.3.2 Phenethylammonium and Butylammonium Layered Halide Perovskites

While the aforementioned 2D materials have very promising properties, with 2D perovskites one has the additional ability to fine tune and modulate the properties of a 2D material by changing the elemental composition and by altering the number of layers. Perovskites have been synthesized in 2D in two different general motifs – they have formed structures of innately layered materials with 2D structures of the inorganic [MX₆]⁴⁺ layered between bulky spacer cations, and they have also been synthesized as 2D nanoplates from various perovskite components.¹²⁷,¹³⁵,¹³⁶

As mentioned previously, the synthesis of perovskites in layered form is meant to enhance their stability. In this case the bulky organic cations that separate the layer provide a hydrophobic barrier to moisture which would otherwise travel to the surface of the perovskite material and react with the components. In general, layered perovskites can be synthesized in different phases. These include the Aurivillius phase, the Dion-Jacobson phase, and the Ruddlesden-Popper phase. The Aurivillius phase has traditionally been found in oxide perovskites, where it consists of layers of ABO₃ separated by Bi₂O₂ ions, such that the overall formula is [Bi₂O₂]²⁺[Aₙ₋₁BₙO₃n+₁]²⁻.¹³⁷ These compounds have mainly been studied as ferroelectrics.¹³⁸ The Dion-Jacobson phase has the ABX₃ layers separated by an alkali metal, such that the formula is M¹⁰⁺Aₙ₋₁BₙX₃n+₁. Finally, the Ruddlesden-Popper phase is a structure where there is some kind of insulating layer that separates one or two layers of the ABX₃ lattice. Indeed, the Ruddlesden-Popper phase is commonly synthesized with lead halide perovskites.⁵⁵,⁵⁶,¹³⁹ Recently, the Dion-Jacobson phase has also been presented.⁵⁷

One of the earlier layered double perovskites, Cs₄CuSb₂Cl₁₂, was layered naturally in a three layer motif without the introduction of bulky alkylammonium cations.¹⁴⁰ For lead
halide perovskites, however, layered requires the introduction of a bulky cation. While a variety of bulky spacer cations have been used, phenethylammonium and n-butylammonium have been two of the popular choices for layering halide perovskites.\textsuperscript{141} Some other types of spacer cations include polyethylenimine and IC\textsubscript{2}H\textsubscript{4}NH\textsubscript{3},\textsuperscript{142,143} as well as some aromatic-O-linker groups, of which a champion PV device of (pyrene-O-propyl-NH\textsubscript{3})\textsubscript{2}PbI\textsubscript{4} had a PCE of 1.38\%.\textsuperscript{144} Layered halide perovskites have been a subject of research interest for quite some time, with reports in the late 1980s investigating optical properties, structure, and exciton binding energy.\textsuperscript{145,146} Mitzi also looked at some layered materials in the late 1990s and early 2000s.\textsuperscript{147-149} As mentioned, these layered halide perovskites can be tuned by varying the number of layers. In this case, a material like phenethylammonium cesium lead iodide can be synthesized.\textsuperscript{56} There is some controversy, however, on the degree to which different numbers of layers can be accessed. While some papers report greater numbers of layers (i.e. n = 5)\textsuperscript{139} there are arguments that n > 3 may not be quite stable thermodynamically,\textsuperscript{150} and that these seemingly larger numbers of layers may just indeed be an average of effects from fewer numbers of layers and bulk cesium lead halides. Recent literature from the Karunadasa group has done some density functional theory (DFT) and concluded that to a certain point, the higher number of layers in a butylammonium cesium silver bismuth bromide layered double perovskite have analogous electronic structures to the bulk cesium silver bismuth bromide, with differences in the band dispersions.\textsuperscript{47}

While these 2D materials are intriguing and offer another phase space of exploration in perovskites, they still have some room for improvement in terms of properties. For example, low electrical conductivity precludes the use of some of these 2D halide perovskites in transistors.\textsuperscript{134} An interesting synthetic approach may be to consider the orientation along
which the planes of layered materials are organized, which may have an impact on transport properties and cationic ligands that could function in these structures (for example controlling whether the sheets have a (100), (110) or (111) orientation).

2.4 References


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CHAPTER 3. THE EFFECTS OF SOLVENT COORDINATION STRENGTH ON THE MORPHOLOGY OF SOLUTION-PROCESSED BiI₃ THIN FILMS

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Roles of authors:
Rainie D. Nelson characterized and analyzed SEM images for all samples, prepared figures, wrote and edited portions of the paper, contributed to experimental planning and formulation of the hypothesis regarding the mechanism of competition between nucleation and growth based on the solvent additive.

Umar H. Hamdeh prepared the bismuth iodide solutions and films, prepared figures, wrote and edited portions of the paper, contributed to experimental planning and hypothesis formulation, collected XRD, and fabricated and tested PV devices.

Bradley J. Ryan discussed experimental plans, prepared figures, and performed FTIR.

Matthew G. Panthani advised, discussed experimental plans.

3.1 Abstract

The remarkable performance of Pb halide perovskites in optoelectronic devices is complicated by concerns over their toxicity, which has motivated a search for Pb free alternatives that have similar performance. Bi halides and halide perovskites have been predicted to be among the most promising Pb free alternatives; however, their performance in devices has fallen short of expectations. One of the major challenges in fabricating efficient devices based on Bi based alternatives has been poor control over the morphology of thin films. Using BiI₃ as a model system, we demonstrate that the film morphology and surface coverage are strongly dependent on the Gutmann donor number of solvents that are used during deposition. We demonstrate that coordinating BiI₃ with strongly complexing solvents in tetrahydrofuran results in conformal films that have been difficult to achieve using conventional deposition techniques.
3.2 Introduction

Pb halide perovskites have demonstrated promising optoelectronic properties and have achieved high laboratory-scale power conversion efficiencies (PCE) of over 23% in solar cells.\textsuperscript{1-4} However, Pb halide perovskites degrade rapidly under ambient operating conditions\textsuperscript{5-10} and are inherently toxic due to the presence of Pb.\textsuperscript{11} This has inspired research in alternative materials with greater stability and lower toxicity, particularly materials which could possess the favorable properties of Pb halide perovskites such as a tunable bandgap,\textsuperscript{12,13} high absorption coefficients,\textsuperscript{14} and large charge carrier diffusion lengths.\textsuperscript{15} Many have attributed the incredible performance of Pb halide perovskites to its “defect-tolerance,” meaning that intrinsic atomic defects that exist within the material tend to have minimal impact on optoelectronic device performance.\textsuperscript{10,16} It has been predicted that many Bi-based compounds would also exhibit defect tolerance,\textsuperscript{16} and this has sparked interest in methylammonium Pb halide (MAPbX\textsubscript{3}) inspired Bi halides that may have similar processability and optoelectronic performance to Pb halide perovskites. These Bi halides are MAPbX\textsubscript{3}-inspired materials owing to their proposed potential similarity in charge-carrier effective masses, orbital character of bands, and static dielectric constants.\textsuperscript{16}

Bi halides (BiX\textsubscript{3}; X = Cl, Br, or I) can be incorporated into crystal structures with either organic or inorganic cations;\textsuperscript{17-25} in these cases the MAPbX\textsubscript{3}-inspired Bi halide compounds, like methylammonium bismuth iodide or cesium bismuth iodide, can adopt a structure that is similar to the Pb halide perovskites.\textsuperscript{17,26} Because of their potential to be incorporated in perovskite-like materials, BiX\textsubscript{3} compounds are of interest as building blocks for the conversion to these MAPbX\textsubscript{3}-inspired hybrid organic-inorganic or all-inorganic Bi halides. While better-known for x-ray detection applications,\textsuperscript{27} there have also been recent reports that have demonstrated the potential of BiX\textsubscript{3} for use in solar cells.\textsuperscript{28-34} However, poor morphology is an
issue that has been thought to limit the PCE of Bi halide and halide perovskite solar cells.\textsuperscript{23} While some improvements in film morphology have been made using vapor processing, the PCE remains low.\textsuperscript{31,34,35}

In order to address the continued limitations due to morphology, some useful similarities between Pb and Bi can be exploited to take advantage of findings within the Pb-based perovskite literature, namely that the morphology of perovskite films can be affected by changes in processing solvent. Both Pb and Bi halides form adducts with a variety of Lewis base solvents;\textsuperscript{36–39} one can exploit this by incorporating prescribed quantities of a given solvent with weaker or stronger complexation strength to tune the crystallization dynamics within thin films. Strongly coordinating ligands compete with I\textsuperscript{−} for coordination sites around Pb\textsuperscript{2+} and Bi\textsuperscript{3+} resulting in the formation of iodoplumbates and iodobismuthates.\textsuperscript{40} By forming a thin film of these Lewis adducts first, the crystallization dynamics of the final metal halide thin film can be tuned through annealing temperatures or the use of anti-solvents. The selection of these complexing solvents has been partially guided by metrics such as vapor pressure,\textsuperscript{41} and criteria for solvent selection can vary between Pb and Bi-based materials, making it necessary to individually study the impact of solvent complexation on Bi halides.\textsuperscript{20,37,42} The use of different solvent complexes has widely investigated for Pb halide perovskites; for example, mixtures of dimethylformamide (DMF) and dimethylsulfoxide (DMSO) have been used to enhance the morphology of α-CsPbI\textsubscript{3} thin films, resulting in a power conversion efficiency of 15.7\%.\textsuperscript{43} This approach was also used with DMSO and 4-tert-butylpyridine in Bi based perovskites to improve morphology of methylammonium bismuth iodide, cesium bismuth iodide, and formamidinium bismuth iodide.\textsuperscript{37} In general, enhancing the morphology of films is of great importance for fabrication of efficient thin film solar cell devices as larger grain sizes will
reduce interfacial barriers that act as recombination sites for charge extraction, and more compact films will lead to increased shunt resistance from decreased pin-hole formation. Since Bi based semiconductors are a relatively unexplored material system, improving the film morphology is the first priority in order to determine the impact of other factors that may be affecting the device performance. Here, we further understanding of how to leverage adduct formation to manipulate grain nucleation and growth in Bi-based systems, and use this understanding to deposit BiI₃ thin films with improved morphology.

3.3 Experimental Section

Materials. BiI₃ solutions were prepared in a glovebox filled with N₂. BiI₃ powder was dissolved to a concentration of 400 mg/mL in anhydrous neat THF, DMF, NMP, or DMSO solvents, or in mixed solvent combinations containing THF with DMF, NMP, DMSO, DMFU, DEA, or GBL (1:1, 1:2, and 1:5 solvent additive:BiI₃). Afterwards the solutions were filtered with a 0.2 µm PTFE filter. The solutions were dark red and optically clear. 200 µL of solution was spin-coated onto a 25 x 25 mm substrate in ambient air conditions at 2000 RPM for 60 seconds. Afterwards, thin films were annealed in air for 20 minutes at 150 °C.

Characterization Methods. X-Ray diffraction (XRD) of thin-films was measured using a Bruker DaVinci D8 Advance diffractometer with a Cu Kα radiation source. Background subtraction of glass was performed using the EVA software. Scanning electron microscope (SEM) images were taken on an FEI Quanta 250 FE-SEM. The accelerating voltage was 15 kV. FT-IR was performed using a Nicolet iS5 with an iD7 ATR accessory.

Chemicals. BiI₃ powder (Beantown Chemical, 99.999% trace metals basis), tetrahydrofuran (THF) (Acros Organics, 99.9% extra pure, anhydrous, stabilised with BHT), dimethylformamide (DMF) (Sigma Aldrich, anhydrous, 99.8%), N-methyl-2-pyrrolidone (NMP) (Sigma Aldrich, anhydrous, 99.5%), dimethylsulfoxide (DMSO) (Sigma Aldrich,
anhydrous, $\geq 99.9\%$), acetone (Sigma Aldrich, $\geq 99.5\%$), isopropanol (Sigma Aldrich, $\geq 99.5\%$), $\gamma$-Butyrolactone (GBL) (Sigma Aldrich ReagentPlus®, $\geq 99\%$), N,N'-dimethylpropyleneurea (DMPU) (Sigma Aldrich, 98%), diethylamine (DEA, Sigma Aldrich 99.5%), Titanium diisopropoxide bis(acetylacetonate (Sigma Aldrich, 75 wt% in isopropanol), Ethanol (Sigma Aldrich, anhydrous, $\leq 0.003\%$ water), 2,2',7,7'-Tetrakis(N,N-di-p-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-MeOTAD) (Lumtec), bis(trifluoromethane)sulfonimide lithium salt (Sigma Aldrich), acetonitrile (Sigma Aldrich, anhydrous, 99.8%), (4-tert-butylpyridine (TBP) (Sigma Aldrich, 96%), chlorobenzene (Sigma Aldrich, anhydrous 99.8%), vanadium oxide ($V_2O_5$) (Sigma, 99.999%) and gold wire (Au) (Kurt J. Lesker, 99.999%) were used as received.

**FTO/Glass preparation.** ITO (Thin Film Devices, Eagle XG, 25 mm x 25 mm x 1.1 mm, 20 ohm/sq), 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) substrates were cleaned by first sonicating in room temperature detergent water (Decon™ Contrex™ AP Labware Detergent) for 20 minutes. The substrates were then thoroughly rinsed with Milli-Q water and subsequently sonicated for an additional 20 minutes each in Milli-Q water, acetone, and isopropanol. The substrates were then thoroughly rinsed once more with Milli-Q water, blown dry with ultra-high purity $N_2$, and treated with $O_2$ plasma for 20 minutes. Solutions were deposited onto films shortly after.

**Sol-gel preparation and deposition of TiO$_2$ layer.** A 0.4 M TiO$_2$ sol-gel was made by combining titanium diisopropoxide bis(acetylacetonate) and anhydrous ethanol. In a typical synthesis, 20 mL of solution is made by combining 3.4 mL of titanium diisopropoxide bis(acetylacetonate) in 16.6 mL of ethanol. All subsequent processing was done in ambient air conditions. The sol-gel is deposited through a 0.2 µm PTFE filter onto the FTO substrate until
the entire substrate is covered entirely and then spin coated at 4500 RPM for 30 seconds to form a thin compact TiO\textsubscript{2} (c-TiO\textsubscript{2}) layer. Next, the substrates are annealed at \(~450\) C (temperature measured with a thermocouple that was placed into the center of the aluminum block) and annealed for at least 30 minutes. Finally, the substrates are removed from the aluminum block and allowed to cool naturally under the convective flow of the fume hood.

After deposition of the c-TiO\textsubscript{2} layer, a mesoporous TiO\textsubscript{2} (m-TiO\textsubscript{2}) layer was deposited. The m-TiO\textsubscript{2} sol-gel was prepared by dissolving 4.5 g of TiO\textsubscript{2} paste in 20 mL of ethanol. The paste was sonicated for 30 – 60 minutes, or until it was completely dissolved in ethanol. 200 µL of the m-TiO\textsubscript{2} sol-gel was deposited onto the c-TiO\textsubscript{2} coated substrate and spin coated at 3000 RPM for 30 seconds. Next, the substrates are annealed at \(~450\) C (temperature measured with a thermocouple that was placed into the center of the aluminum block) and annealed for at least 30 minutes. Finally, the substrates are removed from the aluminum block and allowed to cool naturally under the convective flow of the fume hood. The substrates are stored in an N\textsubscript{2}-filled glovebox until further use.

**Precursor solution preparation and deposition.** A 400 mg/mL BiI\textsubscript{3} solution was prepared in an N\textsubscript{2}-filled glovebox by dissolving BiI\textsubscript{3} powder into anhydrous THF, DMF, NMP, or DMSO. The BiI\textsubscript{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\textsubscript{3} powder in THF, DMF, NMP or DMSO. Afterwards, the solution was filtered with a 0.2 µm PTFE filter. For the solutions with solvent additives, GBL, DMF, NMP, DMSO, DMPU, or DEA was added to the BiI\textsubscript{3} solution dissolved in THF (1:1, 1:2, or 1:5 solvent additive:BiI\textsubscript{3}). A concentration of 100 mg/mL was used for solar cell devices.
BiI₃ solutions were deposited onto glass, FTO, or TiO₂ coated substrates using the same deposition parameters. All processing was done in ambient air conditions. 200 µL of BiI₃ or was deposited onto the selected substrate and spin coated at 2000 RPM for 60 seconds. The films were immediately placed on a 3/8” thick aluminum block on top of a hotplate, with the temperature of the aluminum block set at 150 °C and annealed for 20 minutes. Afterwards, the films were removed from the aluminum block and allowed to cool naturally. The films were stored in N₂-filled glovebox until further use. Different substrates were used depending on the characterization and application of the BiI₃ layer. For UV-Vis and XRD characterization, BiI₃ was deposited on glass substrates. For SEM characterization, BiI₃ was deposited on FTO substrates. Finally, for solar cell application, BiI₃ was deposited onto TiO₂ coated FTO substrates.

**Solar cell device fabrication.** After deposition of the BiI₃ active layer, solar cell devices were completed by depositing the hole transport layer (HTL) and Au metal contact. 20 nm of V₂O₅ was thermally evaporated directly onto the BiI₃ film through a shadow mask at a base pressure of 1x10⁻⁶ mbar. The shadow mask consists of nine circular 8 mm² holes arranged in a square array (3 x 3). To complete the solar cell device, 100 nm of Au was thermally evaporated directly onto the BiI₃ film through a shadow mask at a base pressure of 1x10⁻⁶ mbar.

### 3.4 Results and Discussion

Previous studies related to solution-processed BiI₃ have used tetrahydrofuran (THF) as the processing solvent.³⁰,³¹ In our experience, THF rapidly evaporates during spin-coating, often resulting in difficult-to-avoid macroscopic cracking in the thin films; this effect becomes more pronounced at higher BiI₃ solution concentrations (> 200 mg/mL). High surface tension during spin processing causes the formation of cracks in thin films; cracking in thin films has been generally described.⁴⁹–⁵² The dependence of film morphology on the physical properties
of the solvent have been investigated.\textsuperscript{53,54} The rapid drying of the THF-processed films could arise from two factors: THF has a high vapor pressure, and THF forms a relatively weak complex with BiI\textsubscript{3}.\textsuperscript{35} We hypothesized that the cracking could be reduced through judicious use of a stronger complexing solvent or by using a solvent that has a lower vapor pressure relative to THF. The strength of complexes that are formed between Lewis acids (such as BiX\textsubscript{3}) and Lewis base solvents can be quantified using the Gutmann donor number (DN).\textsuperscript{55,56} Here, we investigate the use of solvents with different DN values and vapor pressures to determine the effect of these properties on BiI\textsubscript{3} thin-film morphology (Figure 3.1).

Initially, we chose to focus on BiI\textsubscript{3} dissolved in neat solvents with varying DN. BiI\textsubscript{3} was dissolved at a concentration of 400 mg/mL in THF, DMF, N-Methyl-2-pyrrolidone (NMP), and DMSO (DN = 20.0, 26.6, 27.3, and 29.8 kcal/mol, respectively) and spin-coated at 2000 RPM for 60 s. Immediately after spin-coating, the films produced from DMF, NMP, and DMSO solutions were red-orange in color, which is indicative of a BiI\textsubscript{3}-solvent complex.\textsuperscript{31,57} BiI\textsubscript{3} thin films, in contrast, are dark brown. Complexed BiI\textsubscript{3} thin films that were spin-coated using NMP or DMSO solvents were stable at room temperature in a glovebox filled with N\textsubscript{2} for several days. However, films that were spin-coated using DMF as a solvent were initially red-orange, but visibly decomposed to BiI\textsubscript{3} after drying in an N\textsubscript{2}-filled glovebox for several hours. The faster decomplexation of the BiI\textsubscript{3}:DMF can be attributed to the lower DN relative to NMP or DMSO. Films that were spin-coated using THF as a solvent immediately decompose to BiI\textsubscript{3}. 
Figure 3.1 Properties of complexing solvents used in this study.\textsuperscript{58,59}

To decompose the solvent complexes and produce BiI\textsubscript{3} thin films, the coated substrates were thermally annealed at 150 °C for 20 minutes. This resulted in a color transition from red-orange to dark brown. While there is no observable difference in morphology when a THF deposited film is not annealed (Figure 3.2), preliminary experiments indicate that annealing conditions may impact the film as shown for DMF deposited films at various temperatures (Figure 3.3). However, for the study of impact of solvent coordination on film morphology we selected 150 °C to ensure more complete decomplexation.

Figure 3.2 SEM images of THF-deposited films left at room temperature and heated for 20 minutes at 150 °C, indicating no major morphological differences between the as-cast film and the annealed film.
Figure 3.3 SEM images of DMF-deposited films left at room temperature and heated 50 and 100 °C, indicating some morphological differences between the as-cast film and the annealed film.

A representative mechanism of the decomplexation and subsequent nucleation and growth into BiI$_3$ films is demonstrated in Figure 3.4; the photographs are representative of the color change progression observed in the films.

Figure 3.4 Representative mechanism of the decomplexation, nucleation, and growth process of the BiI$_3$ film alongside a representative demonstration of the observed color change of films as the decomplexation proceeds. Films imaged are DMSO-deposited BiI$_3$ thin films.

The time scale of the color change is dependent on the solvent complex as strongly coordinating solvents will keep their red-orange color longer than relatively weaker
coordinating solvents. While drying over time, or by gentle heating (~50 °C), the color of the film will transition to the dark brown color of BiI\(_3\). We used UV-Vis absorbance to quantify the changes in absorbance for these films as they transition from the solvent complex phase to BiI\(_3\) (Figure 3.5). The change in absorbance onset from 600 nm to 700 nm indicates the gradual formation of BiI\(_3\).

![Figure 3.5 UV-Vis absorbance of the BiI\(_3\) thin films exhibiting solvent decomplexation over time. The absorbance onset changes from 600 nm, demonstrating the BiI\(_3\) solvent complex phase, to an absorbance onset near 700 nm, demonstrating the BiI\(_3\) phase.](image)

We used FT-IR to investigate the removal of solvents from BiI\(_3\) thin films after thermal annealing at 150 °C for 20 minutes (Figure 3.6). Regardless of the solvent used, we observed features corresponding to the solvent. This suggests that residual solvent remains within the BiI\(_3\) films even after thermal annealing (Figure 3.6). Future experimentation is necessary to determine whether the solvent can be completely removed and whether residual solvent will have a negative impact on performance of devices fabricated from BiI\(_3\) films.
Figure 3.6 FT-IR characterization of BiI₃ thin films with and without thermal annealing and with a chlorobenzene wash and thermal annealing deposited from (a) THF, (b) DMF, (c) NMP, and (d) DMSO.

Figure 3.7 shows scanning electron microscopy (SEM) images that show morphologies of thin films that were spin-coated from neat solutions of BiI₃ in THF, DMF, NMP, and DMSO. The films deposited using these different solvents had markedly different morphologies.
Although there was good surface coverage when using THF (Figure 3.7a), we observed a prevalence of large cracks that would be problematic for solar cell device performance.

![Figure 3.7 SEM images of BiI₃ thin films from solutions of 400 mg/mL of BiI₃ dissolved in (a) THF, (b) DMF, (c) NMP, and (d) DMSO, where DN and vapor pressure in mmHg (Pᵥap) are indicated.](image)

Films that were deposited using a neat solution of DMF resulted in an increase of apparent grain size, but large pinholes were observed in the films (Figure 3.7b). Finally, using NMP or DMSO resulted in large aggregates of BiI₃ crystallites with relatively sparse surface coverage (Figure 3.7c-d). The solvent properties of DN and vapor pressure appeared to play a crucial role in the film morphology for BiI₃ thin films, likely with both parameters impacting the nucleation rate of BiI₃ seeds and the rate at which solvent is removed from the system. We hypothesized that this was a result of the rate of BiI₃ solvent decomplexation. Solvents with low DN and high vapor pressure, such as THF, are amenable to rapid decomplexation after deposition. The short-lived intermediate solvent:BiI₃ complex could result in subsequent rapid nucleation of BiI₃ crystallites leading to the observed morphology in the THF film. Due to the
rapid nucleation of BiI₃ crystallites, we find that BiI₃ films deposited from THF have the smallest apparent grain size. Solvents with high DN and low vapor pressure (i.e., NMP, DMSO) are expected to slow the decomplexation of intermediate phases, which could result in slower nucleation and contribute to the growth processes that result in isolated, but larger aggregates. DMF, which has an intermediate DN and moderate vapor pressure is expected to have a moderate rate of precursor decomplexation which could result in an intermediate rate of nucleation and growth such that the film has improved coverage yet still experiences some of the issues with surface void space.

X-ray diffraction (XRD) was used to probe the effect of solvent choice on the film microstructure (Figure 3.8 and Figure 3.9). For all solutions, we observed a sharp reflection corresponding to the (003) crystallographic plane, as well as smaller diffraction peaks for the (006) and (009) planes, demonstrating a preferred orientation along the c-axis (Figure 3.8 and 3.9). BiI₃ deposited from THF also had intense diffraction peaks along the (2̅13) and (300) crystallographic planes; these peaks decreased in intensity with increasing DN. We hypothesize that the reduction in diffraction intensity for some crystallographic planes and subsequent preferred orientation arises from the differences of the longevity of the intermediate BiI₃-solvent complex. Since the BiI₃-THF complex is weak and decomposes rapidly, it is expected that the diffraction pattern would more closely resemble the powder pattern. However, during the decomplexation of BiI₃-solvent complexes from higher DN solvents, the complex persists for a longer period which we believe causes preferred orientation of grains within thin films. High DN solvent additives may interact strongly with certain crystal facets, stabilizing them, and allowing for preferential growth. Further investigation is necessary to elucidate the nucleation mechanism when using high DN solvent additives for BiI₃. Scherrer
analysis of the XRD patterns (Figure 3.10 and 3.11) indicate that there are no numerical trends in the crystal grain size with the DN of the solutions, and average grain sizes range between 40 – 150 nm.

Figure 3.8 XRD of BiI₃ thin films deposited from neat ligand (THF, DMF, NMP, DMSO) and solvent additive:BiI₃ (1:1, 1:2, and 1:5) dissolved in THF on glass substrates. Triangles indicate peaks used in Scherrer analysis.
Figure 3.9 XRD of BiI$_3$ thin films deposited from neat ligand (THF, DMF, NMP, DMSO) and solvent additive:BiI$_3$ (1:1, and 1:2) dissolved in THF on ITO substrates. Triangles indicate peaks used in Scherrer analysis.
Figure 3.10 Scherrer analysis of BiI₃ films deposited from neat ligand (THF, DMF, NMP, DMSO) and solvent additive:BiI₃ (1:1, 1:2, and 1:5) dissolved in THF on glass substrates.

Figure 3.11 Scherrer analysis of BiI₃ films deposited from neat ligand (THF, DMF, NMP, DMSO) and solvent additive:BiI₃ (1:1, 1:2, and 1:5) dissolved in THF on ITO substrates.
Solvent mixtures or additives are often used to improve film morphology or facilitate processing of Pb-based halide perovskites; these improvements result from control of the crystallization rate of the Pb halide perovskites. The results cannot be directly applied to Bi-based materials given the faster crystallization and often lower solubility of BiI₃ compared to Pb precursors. With our insight of the complexing behavior of BiI₃ we sought to elucidate how a similar approach could be used to control the film morphology of BiI₃. Since the THF-processed film produced consistent surface coverage it was chosen as the base solvent for further experimentation. We expected that adding solvents with greater DNs than THF could provide control over the crystallization process within the film. Previous reports indicate that retarding crystallization in halide perovskite thin films results in improved the film morphology, so we utilized solvents with higher DNs to complex with BiI₃.

We added the following solvents to THF: γ-butyrolactone (GBL), DMF, NMP, DMSO, N,N’-Dimethylpropyleneurea (DMPU), and diethylamine (DEA) (DN = 18.0, 26.6, 27.3, 29.8, 34.0, and 50 kcal/mol, respectively). The solvents were added in equimolar amounts to BiI₃ in a solution of BiI₃ dissolved in THF (400 mg/mL); these samples in THF will be referred to as solvent additive:BiI₃ where the solvent is GBL, DMF, NMP, DMSO, DMPU, or DEA. Because the various solvents may require more than one molar equivalent to fully complex with the BiI₃ molecule, equimolar amounts of solvent additive:BiI₃ were selected as a consistent comparative starting point, whereas complete complexation of BiI₃ with the solvent is represented by BiI₃ in neat solvent. These solutions of 1:1 solvent additive:BiI₃ in THF were spin-coated onto FTO coated substrates. We observed some general trends regarding the impact of the DN. SEM of these films, shown in Figure 3.12, revealed that as the DN increases, the size of the crystal grain aggregates also increases. For solvent additives with very high DN
(DMPU, DEA), we noticed that the solvent complex was more persistent, likely indicating very slow precursor decomplexation. Even though DEA has a relatively low boiling point (56 °C) the film of DEA:BiI₃ did not decompose after heating to 100 °C, indicating the complex was persistent at temperatures much greater than the boiling point of the solvent additive.

Figure 3.12 SEM of films processed from BiI₃ in THF with different solvent additives of (a) GBL, (b) DMF, (c) NMP, (d) DMSO, (e) DMPU, and (f) DEA.
We differentiated the importance of solvent coordination strength and vapor pressure by using DEA and GBL solvent additives. DEA has a high vapor pressure and donor number, while GBL has a relatively low donor number and vapor pressure. DEA has a much greater impact on the film morphology compared to GBL. Whereas previous studies have used vapor pressure as a metric to select solvents for processing, the results shown here reveal that DN is, in some cases, the more important parameter to select appropriate solvents for the fabrication of metal halide and metal halide perovskite thin films.

As observed in Figure 3.12, the use of an equimolar ratio of solvent additive:BiI$_3$ did not appear to yield the necessary combination of grain size and film morphology that would be beneficial for optoelectronic devices. We chose to explore molar ratios lower than 1:1 for solvent additive:BiI$_3$ in order to more finely tune crystallization and growth behavior, as we anticipated that increasing the amount of solvent additive would eventually result in poor morphology films that resembled those made from neat solvent (Figure 3.7c,d). We also narrowed the focus to solvents which disassociated easily from BiI$_3$, but not so rapidly that macroscopic cracking occurs (as was observed using THF). For this reason, we focused on intermediate-DN solvent additives: DMF, NMP, and DMSO. The films were processed with solvent additive:BiI$_3$ molar ratios of 1:1, 1:2, and 1:5, and diluted in THF.

SEM images of the films deposited using different solvent additive:BiI$_3$ ratios are shown in Figure 3.13. For solvents with higher DN (NMP and DMSO), the 1:1 solvent additive:BiI$_3$ films had large domains on the order of micrometers (Figure 3.13d and 3.13g), but also had poor surface coverage. When the amount of solvent additive was decreased (moving from left to the right in Figure 3.13) the BiI$_3$ domain size decreased and the substrate coverage improved, resulting in films without void space (Figure 3.13h). Further decreasing
the relative amount of the high-DN solvent additive resulted in pinholes (Figure 3.13c,f,i). This trend was apparent with DMF as well; however, at a 1:5 ratio macroscopic cracks were observed, indicating the effect of the solvent additive was diminished at lower molar ratios. The molar ratio of solvent additive:BiI₃ was found to influence the crystallographic orientation of the thin films. When the solvent additive:BiI₃ ratio is decreased the crystal structure of the films more closely resembles the THF-deposited film (Figure 3.8 and 3.9), which as previously discussed more closely resembles the BiI₃ powder pattern. We hypothesize that this is a result of the interplay between the solvent additive and the THF solvent; decreasing the amount of solvent additive allowed for faster nucleation of the BiI₃ phase. Increasing the amount of solvent additive causes preferentially alignment within the crystal structure. By varying the solvent DN and solvent additive:BiI₃ ratio we have demonstrated a methodology to engineer the thin film morphology and crystallographic orientation of BiI₃ thin films during spin-coating.

**Figure 3.13** Various ratios of solvents in THF; (a-c) DMF, (d-f) NMP or (g-i) DMSO. The ratios of solvent:BiI₃ were (a,d,g) 1:1, (b,e,h) 1:2 or (c,f,i) 1:5. Thin-films were processed in ambient air conditions (50% – 60% relative humidity).
Solar cells were made to quantify the improvements of film morphology with device performance. We observed an improvement in $J_{SC}$ for devices fabricated in both ambient air conditions and an N$_2$-filled glovebox with the use of higher donor number solvents. Solvent:BiI$_3$ ratio of 1:2 for DMF and 1:5 for NMP and DMSO resulted in the best performing devices (Figure 3.14). Solar cells fabricated in an N$_2$-filled glovebox produced greater short circuit current ($J_{SC}$) but exhibited lower open circuit voltage ($V_{OC}$) compared to films prepared...
in ambient air. We presume the increase in $J_{SC}$ is related to a decrease in the number of pinholes in BiI$_3$ thin-films when processing in an N$_2$-filled glovebox (Figure 3.15). In a previous report, we measured an oxidation layer on the surface of the BiI$_3$ film which may beneficially impact the $V_{OC}$. The $V_{OC}$ of BiI$_3$ is predicted to be 1.1 eV, but may be limited by intrinsic defects that may exist within the film.

![Figure 3.15](image)

**Figure 3.15** SEM of films processed from BiI$_3$ in THF with 1:2 solvent additives:BiI$_3$. In ambient air (RH 50-60%) (a) No SA, (b) DMF, (c) DMSO, (d) NMP. In N$_2$-filled glovebox (e) No SA, (f) DMF, (g) DMSO, (h) NMP.
3.5 Conclusion

By utilizing strongly coordinating solvents, we demonstrated the ability to manipulate the film morphology of solution-processed BiI$_3$ thin films. Controlling the relative molar ratios of solvent additive:BiI$_3$ dissolved in THF using additive solvents with a higher DN than THF (such as DMF, NMP, and DMSO) enabled us to tune the surface coverage, the aggregate size, and the preferred orientation of the BiI$_3$ thin-film. Many additional important factors, including heating rate, substrate composition or texture, and convective heat transfer impact nucleation and growth in film systems and represent areas for future studies. Based on our current result regarding the impact of solvent coordination, we believe DN can be used as a guide to control the crystallization and optimize the film morphology of solution processed Bi halides and Bi halide MAPbX$_3$-inspired thin films.

3.6 Acknowledgements

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3.7 References


CHAPTER 4. SYNTHESIS AND OPTICAL PROPERTIES OF ORDERED-VACANCY PEROVSKITE CESIUM BISMUTH HALIDE NANOCRYSTALS

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Roles:
Rainie D. Nelson performed all of the synthesis and washing of nanoparticles, collected TEM, HRTEM, absorbance, and XRD (except the XRD of the aged cesium bismuth iodide material), performed all experimental planning, and wrote the article

Kalyan Santra conducted the photoluminescence measurements and assisted with interpretation of data

Yujie Wang collected initial photoluminescence measurements demonstrating the reaction product did indeed have PL, note that these particular measurements were used to determine next protocol and were not incorporated as graphical figures in the text.

Atefe Hadi collected the XRD of the aged cesium bismuth iodide material, which was provided by R. Nelson

Jacob W. Petrich, advisor of K. Santra, advised and assisted in data interpretation

Matthew G. Panthani, advised and assisted with experimental planning and discussion and with editing of the manuscript in progress

All authors read and edited the final manuscript.

4.1 Abstract

Perovskite-phase cesium bismuth halide (Cs$_3$Bi$_2$X$_9$; X = Cl, Br, I) nanocrystals were synthesized using a hot-injection approach. These nanocrystals adopted ordered-vacancy perovskite crystal structures and demonstrated composition-tunable optical properties. Growth occurred by initial formation of Bi$^9$ seeds, and morphology was controlled by precursor and seed concentration. The Cs$_3$Bi$_2$I$_9$ nanocrystals demonstrated excellent stability under ambient conditions for several
months. Contrary to previous reports, we find that photoluminescence originates from the precursor material as opposed to the Cs₃Bi₂X₉ nanocrystals.

4.2 Introduction

Halide perovskite compounds have generated interest as semiconductors with widely tunable properties that are compatible with inexpensive processing methods. The unique properties of halide perovskites show great potential for use in optoelectronic applications like photovoltaics (PVs). Halide perovskite materials typically have the general structure ABX₃, with A as a cation (CH₃NH₃⁺, HC(NH₂)₂⁺, Cs⁺), B as a metal (Pb, Sn), and X as an anion (Cl⁻, Br⁻, I⁻). From ∼3.8% efficiency in 2009,¹ the performance of methylammonium lead iodide (MAPbI)–based solar cells has increased rapidly to power conversion efficiencies (PCE) of over 22% in 2017.²⁹ MAPbI has several properties that contribute to this high performance in PVs—a direct bandgap of ∼1.5 eV, long charge carrier diffusion lengths, high defect-tolerance, and small exciton binding energies.¹₀⁻¹₆ However, stability and toxicity remain an issue for MAPbI and related halide perovskite semiconductors.¹⁷, ¹₈ It is well-known that exposure to moderate humidity, temperatures, or insolation can degrade MAPbI.¹⁹⁻²³ Attempts to improve stability of halide perovskite PVs have typically involved partial or full substitution of the A-site cation and X-site anion.²⁻²⁴⁻³⁰ Using colloidal halide perovskite nanocrystals (NCs) can also enhance stability.³¹ Swarnkar et al. processed halide perovskite NCs into thin films with enhanced stability.³² Perovskite CsPbI₃ NCs adopt the black cubic perovskite phase (α-CsPbI₃), which is thermodynamically unstable at room temperature in the bulk.³³ The enhanced stability of the α-phase has been attributed to surface stabilization by the cationic
ligands,\textsuperscript{34} though the NCs can eventually revert back to the yellow non-perovskite $\delta$-phase\textsuperscript{35} which has poor optoelectronic properties.

In addition to addressing stability, there have been efforts to develop Pb-free halide perovskites. Alternatives to Pb include other 6s$^2$ elements such as antimony and bismuth. Recently, bismuth halides and oxyhalides\textsuperscript{36, 37} have demonstrated promise as PV materials, aided by the soft polarizability and defect tolerance of bismuth.\textsuperscript{38} Initial PV devices with BiI$_3$ as the active layer possessed a PCE of 1%\textsuperscript{37}. Bismuth has also been incorporated into defect perovskites with formula A$_3$B$_2$X$_9$. Cs$_3$Bi$_2$I$_9$ films in hexagonal phase were incorporated into $\sim$1% efficient solar cells\textsuperscript{39}. NCs of bismuth based halides have been synthesized via room-temperature reaction\textsuperscript{40, 41} and hot-injection.\textsuperscript{42} Work has also been done on synthesizing antimony halide NCs,\textsuperscript{43} showing promising photoluminescence quantum yield.\textsuperscript{44} In general, there is much promise for lead free halide NCs,\textsuperscript{45} motivating research into growth mechanisms to further enhance efforts to optimize these materials.

### 4.3 Experimental Methods

Given the feasibility of synthesizing cesium bismuth halide NCs, we investigated the hot-injection synthesis of Cs$_3$Bi$_2$X$_9$ NCs, where X includes Cl, Br, and I, in order to elucidate the growth mechanism. To synthesize Cs$_3$Bi$_2$X$_9$ NCs, we initially adapted the method for synthesizing CsPbI$_3$ NCs developed Protesescu \textit{et al.}\textsuperscript{33} with modifications to the precursor stoichiometry. In a typical reaction, heated Cs-oleate was injected into a heated mixture of bismuth halide salt, octadecene (ODE), oleic acid (OA), and oleylamine (OLA). To quench reactions, room-temperature toluene was injected directly into the crude reaction mixture while stirring. To avoid degradation, the NCs were precipitated by simply centrifuging the NCs.

#### 4.3.1 Experimental Details

**Materials:** Oleic acid (OA) (90%), oleylamine (OLA) (70%), 1-octadecene (ODE) (90%), bismuth(III) iodide (99.999%), bismuth(III) chloride (98%), trioctylphosphine (TOP) (90%),
anhydrous toluene (99.8%), and cesium carbonate (99.9%) were purchased from Sigma Aldrich. Bismuth(III) bromide (98%) was purchased from Acros Organics. OA, OLA, and ODE were degassed at 120°C for one hour prior to use in reactions. All other chemicals were used as received.

**Cs-oleate:** Cs-oleate was synthesized by loading 0.02035 g of Cs$_2$CO$_3$ per mL ODE into an appropriately sized flask to contain the desired volume of ODE. Then 0.0625 mL of OA per mL of ODE are added to the flask. The mixture was subsequently dried under vacuum at 120°C for one hour, then heated in a N$_2$ atmosphere at 150°C for two hours to completely dissolve the Cs$_2$CO$_3$, forming a clear, dull yellow solution.

**Cs$_3$Bi$_2$X$_9$ nanoparticles:** For the synthesis of the halide nanoparticles, BiX$_3$ precursor salts (see Table 1 below for amounts for each halide or halide ratio) were measured into a 4mL vial. An aluminum reaction block was placed on a hot plate inside a glovebox, and the temperature was set so that a 4mL vial of ODE with a thermocouple inserted read 120°C (or the appropriate reaction temperature). 1.5mL of ODE was added to the bismuth salt and the vial was placed in the reaction block while being stirred at 950 rpm. After 15 minutes, 150µL of OA and 150µL of OLA were added to the vial. The table below lists the observed status of the vial after OA and OLA were added. Cs-oleate precipitates out of ODE at room temperature, so Cs-oleate was preheated to 100°C prior to injection. 180µL of Cs-oleate was injected into the reaction vial after the BiX$_3$ precursor salt had dissolved; the color at this point is indicated in the table. The reaction was allowed to proceed, in most cases, for 30 seconds. The vial was then removed from the reaction block, and 1mL of anhydrous room temperature toluene was injected into the vial to quench the reaction. A toluene quench was avoided for temperatures above 180°C due to rapid boiling of toluene and loss of material.
Table 1. Nanocrystal synthesis parameters and observations

<table>
<thead>
<tr>
<th>Sample (Cs₃Bi₂X₉)</th>
<th>Mass BiI₃</th>
<th>Mass BiCl₃</th>
<th>Mass BiBr₃</th>
<th>Color/Opacity/After Injection</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = I</td>
<td>7 mg</td>
<td>-</td>
<td>-</td>
<td>Orange/clear/red with orange tint</td>
</tr>
<tr>
<td>X = Cl</td>
<td>-</td>
<td>4.3 mg</td>
<td>-</td>
<td>White/slightly cloudy/same</td>
</tr>
<tr>
<td>X = Br</td>
<td>-</td>
<td>-</td>
<td>6.3 mg</td>
<td>White/very slightly cloudy/clear</td>
</tr>
<tr>
<td>X = 3:1 I:Br</td>
<td>24.9 mg</td>
<td>-</td>
<td>6.4 mg</td>
<td>Yellow-orange/slightly cloudy/red</td>
</tr>
<tr>
<td>X = 1:1 I:Br</td>
<td>15.9 mg</td>
<td>-</td>
<td>12.7 mg</td>
<td>Yellow-orange/clear/yellow</td>
</tr>
<tr>
<td>X = 3:1 Cl:Br</td>
<td>-</td>
<td>12.8 mg</td>
<td>6.3 mg</td>
<td>Colorless/cloudy/same</td>
</tr>
<tr>
<td>X = 1:1 Cl:Br</td>
<td>-</td>
<td>9.1 mg</td>
<td>12.7 mg</td>
<td>Colorless/cloudy/same</td>
</tr>
<tr>
<td>X = 1:3 Cl:Br</td>
<td>-</td>
<td>4.3 mg</td>
<td>19.0 mg</td>
<td>Colorless/mostly clear/same</td>
</tr>
</tbody>
</table>

**Nanocrystal purification and stability:** Anti-solvent was not used for purification, as the use of anti-solvent rapidly degraded the NCs, precipitating a differently colored powder as compared to the powder characterized as Cs₃Bi₂X₉ NCs. The quenched crude reaction mixture was transferred to a centrifuge tube and centrifuged at 12,045 rcf for 15 minutes. If precipitate was not observed, the samples were centrifuged for an additional 10 minutes. The precipitate was then dispersed in fresh anhydrous toluene and stored in a glass vial. For the Cs₃Bi₂X₉, a large proportion of the material precipitated out over time, although the supernatant remained colored. This precipitate could be dispersed temporarily through sonication. Given the size of these nanoparticles, this low colloidal stability is not unexpected. While the nanocrystals were stable in ambient conditions (see Figure 4.8) against ambient moisture, direct injection of distilled water into the nanoparticle mixture resulted in degradation of the sample and loss of the characteristic absorbance peak.
4.3.2 Characterization:

**Powder X-ray diffraction** (XRD) patterns were collected with a Siemens D-500 powder diffractometer with Cu Kα1 radiation. XRD patterns for the sample after 100 days were collected with a Rigaku Ultima IV powder diffractometer with Cu Kα1 radiation.

**Transmission electron microscopy** (TEM) images were recorded using a FEI Tecnai G2-F20 instrument operated at 200 kV.

**UV-Vis absorption spectra** were collected using a Perkin-Elmer Lambda 750 instrument operating in transmission mode.

**Photoluminescence spectra** (Figure 4.11) of BiX₃ and Cs₃Bi₂X₉ in solution were obtained on a Fluoromax-4 spectrometer (Horiba Scientific) using a quartz cuvette of 3-mm pathlength. The excitation wavelengths are 340 nm, 370 nm, and 450 nm for samples containing chloride, bromide, and iodide, respectively. The excitation bandpass and emission bandpass were each 8 nm and the integration time was 0.3 s for the samples containing chloride and bromide. For sample containing iodide, the excitation and emission bandpasses were both 10 nm and the integration time was 1 s. All spectra were corrected for lamp spectral intensity and detector response.

### 4.4 Results and Discussion

Bulk Cs₃Bi₂X₉ is known to adopt an ordered-vacancy perovskite structure⁴⁶ (Figure 4.1b). The cubic ABX₃ perovskite (Figure 4.1a) has corner-sharing octahedra of PbX₆, with the A-site cations in the cuboctahedral voids. The A₃Bi₂X₉ structure, in contrast, has pairs of face-sharing BiX₆ octahedra which form Bi₂X₉³⁻ dimer-like units. These double octahedron are surrounded by the A-site cations.
Figure 4.1 Illustrations depicting the crystal structures of (a) the conventional, ABX$_3$ cubic perovskite (α-CsPbI$_3$-type) and (b) the ordered-vacancy perovskite structure adopted by Cs$_3$Bi$_2$X$_9$. Both are viewed down the c-axis. Designed using VESTA.$^{47}$

X-ray diffraction (XRD) of Cs$_3$Bi$_2$I$_9$ NCs powders confirmed that the NCs synthesized here had this structure (Figure 4.2a). The prominence of the (006) reflection compared to the (203), (204), and (205) reflections suggests that the nanocrystals grow anisotropically, with preferential growth along the c-axis. Transmission electron microscopy (TEM) shows that Cs$_3$Bi$_2$I$_9$ NCs are faceted and polydisperse (39.5 ± 9.3 nm diameter) with regards to crystallite size (Figure 4.2b).

Fig. 4.2 (a) XRD patterns, (b) TEM and (c) HRTEM images of Cs$_3$Bi$_2$I$_9$. Pattern for bulk Cs$_3$Bi$_2$I$_9$ is included for reference.
High-resolution TEM (HRTEM) confirms that the Cs₃Bi₂I₉ NCs are single crystals with an ordered defect perovskite structure (Figure 4.2c). In many TEM images of Cs₃Bi₂X₉ NCs, we observed the presence of small (<3 nm) particles; the lattice of these particles could not be resolved. We found that these small particles are formed in the BiI₃/OA/OLA reaction precursor (Figure 4.3a) before injecting Cs-oleate. This implies that these particles could be Bi⁰ seeds that form during the dissolution of BiI₃. This is consistent with previous reports,⁴⁸ where Pb⁰ seeds were found to form after the dissolution of PbI₂ in a mixture of ODE, OA, and OLA. We hypothesize that these Bi⁰ seeds then react with injected Cs-oleate, with some control of growth afforded by variation in reactant concentration and additional ligands.

**Figure 4.3** TEM of (a) unreacted BiI₃ precursor, (b) reaction at 120 °C for 30 seconds, (c) four times the Bi concentration of b, and (d) eight times the Bi concentration of b.
The Cs$_3$Bi$_2$I$_9$ NC morphology was found to be sensitive to the ratio and concentration of Bi and Cs precursors used during synthesis. When using a near stoichiometric concentration of BiI$_3$ and Cs-oleate ~40 nm quasi-spherical NCs were formed (Figure 4.3b). In this case, the reaction occurs under conditions of slight excess of Cs-oleate, possibly indicating that excess oleic acid ligands or Cs-oleate will facilitate the growth of spherical NCs over the more faceted NCs. This type of effect has been observed before – previous reports have demonstrated that the morphology of metal and metal chalcogenide NCs can be tuned by adjusting the concentration of alkali metal oleate precursor used during synthesis.$^{49, 50}$ We found that reducing the amount of BiI$_3$ precursor results in a lower concentration of Bi$^{0}$ nuclei, which could impact the growth and resulting size of the NCs, consistent with a previous report that found precursor concentration for Cs$_3$Bi$_2$X$_9$ had an impact on resulting NC size.$^{41}$ Using four times excess of BiI$_3$ resulted in more faceted particles with higher polydispersity and the ubiquitous appearance of Bi$^{0}$ metal seeds. In contrast, when an eight times excess of BiI$_3$ was used, no additional change in the Cs$_3$Bi$_2$I$_9$ NC morphology was observed (Figure 4.3d). However, there was a larger concentration of small seed-like particles, supporting the proposed mechanism of formation of Bi$^{0}$ seeds.

These results imply that the growth of the Cs$_3$Bi$_2$X$_9$ NCs is initiated by the number of Bi$^{0}$ nuclei; we hypothesize further control over size and morphology could be obtained by controlling the number of these nuclei in solution. In support of this hypothesis, we found that aging the BiI$_3$/ODE/OA/OLA precursor prior to the injection of Cs-oleate promotes the formation of anisotropic long rectangular NCs (Figure 4.4).
The morphology of the Cs$_3$Bi$_2$I$_9$ NCs can be further tuned by introducing different capping ligands during synthesis. For example, we found that including trioctylphosphine (TOP) into the precursor mixture resulted in a higher concentration of rectangular NCs (Figure 4.5). This could indicate that TOP attaches to specific facets of the Cs$_3$Bi$_2$I$_9$ NCs during nucleation and growth.

Similar anisotropic growth was reported for CsPbI$_3$ NCs that were synthesized in a reaction mixture containing polar molecules.$^{48}$ Udayabhaskararao et al.$^{48}$ deduced that the polar
environment in the CsPbI$_3$ NC reaction mixture facilitated amine protonation, with ammonium species acting to passivate surfaces$^{51}$ and preferentially bind to replace the Cs$^+$ ions. It is possible that a similar mechanism could explain our observed morphology when adding TOP, which is moderately polar. However, given that aging the TOP-free precursor also results in the appearance of long rectangular nanostructures (Figure 4.4) and considering that TOP is a reducing agent, adding TOP to the reaction mixture may accelerate the formation of Bi$^0$ seeds, simulating what would occur in an “aged” precursor.

We found that changing the reaction temperature had little effect on the size or shape of the Cs$_3$Bi$_2$I$_9$ NCs (Figure 4.6). Increasing reaction time resulted in a relatively small increase in particle size. Based on our studies of reaction time, it appears that the NC size and shape are rapidly defined within the first few seconds of reaction (Figure 4.7).

![Figure 4.6](image.png)

**Figure 4.6** UV-Vis Absorption spectra for temperature series experiment with Cs$_3$Bi$_2$I$_9$, with reaction time of 30 seconds
Figure 4.7 TEM showing growth of Cs$_3$Bi$_2$I$_9$ nanoparticles over time, demonstrating minor changes after initial reaction product at low times.

The Cs$_3$Bi$_2$I$_9$ NCs demonstrate remarkable stability under ambient storage conditions for long periods of time. The characteristic absorbance peak at 489 nm remains unchanged for at least 100 days when stored in a vial outside the glovebox after exposure to ambient conditions and the XRD pattern matches to the Cs$_3$Bi$_2$I$_9$ reference (Figure 4.8). In contrast CsPbI$_3$ NCs have been reported to degrade in a few days once exposed to air. This stability makes Cs$_3$Bi$_2$I$_9$ NCs promising for incorporation into highly stable optoelectronic devices.
Figure 4.8 (a) UV-Vis absorbance spectra and (b) XRD data demonstrating stability of nanoparticles over a period of 100 days (Cs$_3$Bi$_2$I$_9$ reference at bottom, PDF#01-089-1846) *indicates a background peak observed in the XRD pattern taken from an empty sample holder.

The synthesis method could be extended to other halides (TEM shown in Figure 4.9) by using different BiX$_3$ salts. Cs$_3$Bi$_2$Br$_9$NCs exhibited a similar morphology to Cs$_3$Bi$_2$I$_9$, but the Cs$_3$Bi$_2$Cl$_9$ NCs formed rectangular nanoplatelets. It was observed that the Cs$_3$Bi$_2$I$_9$ had the fewest number of Bi$^0$ seeds at concentrations equivalent to the other halides – this may be due to solubility differences between the BiX$_3$ salts. The BiI$_3$ was the most readily soluble. By varying composition, the absorbance maximum of the Cs$_3$Bi$_2$X$_9$ NCs (where X indicates either single- or mixtures of halides) could be tuned between 331 (X = Cl) and 489 nm (X = I) as seen in Figure 4.10a.
Figure 4.9 TEM of (a) $\text{Cs}_3\text{Bi}_2\text{Br}_9$ and (b) $\text{Cs}_3\text{Bi}_2\text{Cl}_9$

Figure 4.10 (a) Absorbance of cesium bismuth halides and blends of halides and TEM of (b) 1:1 Br:I, and (c) 1:1 Br:Cl blends

We noticed that mixed halide NCs ($X = \text{Br, I or Br, Cl}$) had broader absorption peaks compared to single-halide NCs. This implies that the mixed-halide NCs may be a mixture of single-halide NCs rather than mixed-halide alloy NCs; however, in TEM only a single morphology is
observed (Figure 4.10b and c). This behaviour is markedly different than CsPbX$_3$ NCs, which are known to readily exchange halides even with other halide-containing NCs in colloidal dispersions.$^{52, 53}$ The apparent inability to synthesize mixed-halide Cs$_3$Bi$_2$X$_9$ NCs could be explained by differences in mobility of anions in the defect perovskite structure, differences in B–X bond energies, or differences in precursor decomposition kinetics.

The measurement and investigation of PL properties and improvement of PL quantum yield is the subject of ongoing research, with the expectation that the predicted excellent defect-tolerance of Cs$_3$Bi$_2$X$_9$$^{54}$ should result in easily detectable PL with decent PL quantum yield. However, initial results have shown that PL observed in the reaction products is also found in the reaction precursor prior to injection of Cs-oleate (Figure 4.11). While similar trends in PL have been reported in other manuscripts$^{40-42}$ the true origin of this PL is unclear, given the difficulty in separating the precursor material from the resulting nanoparticles via centrifugation and the lack of analysis of the precursors in the aforementioned literature.

![Figure 4.11 Absorbance (solid) and photoluminescence (dashed) spectra for Cs$_3$Bi$_2$X$_9$ NCs of X = (a) Cl; (b) Br; (c) I.](image)

4.5 Summary and Conclusions

In conclusion, we report the synthesis of Cs$_3$Bi$_2$X$_9$ NCs with an ordered-vacancy halide perovskite composition, identified factors that influence size and morphology, and characterized
their composition-tunable optical properties. The growth mechanism was found to have similarities to that of CsPbI$_3$ NCs, where growth is initiated by Bi$^0$ metal seeds that subsequently react with injected Cs-oleate. The widely-tunable absorbance and air stability of these Cs$_3$Bi$_2$X$_9$ NCs shows an important step toward stable and efficient Pb-free perovskite optoelectronic devices.

4.6 Acknowledgments

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Conflicts of interest
There are no conflicts to declare.

4.7 References


https://www.nrel.gov/pv/assets/images/efficiency-chart.png (September 2017),


52. Akkerman, Q. A.; D’Innocenzo, V.; Accornero, S.; Scarpellini, A.; Petrozza, A.; Prato, M.; Manna, L., Tuning the Optical Properties of Cesium Lead Halide


5.1 Abstract

Lead halide perovskites have remarkable properties that make them compelling next generation optoelectronic materials. However, stability and toxicity issues are a major roadblock to successful development of applications based on lead halide perovskites. Many routes exist to modify these perovskites; we describe here the combined approach of layering with bulky organic cations and heterovalent substitution of lead to form double perovskites. We demonstrate air and moisture stability, structural transition, and thermochromism of a phenethylammonium silver bismuth bromide perovskite. We describe the structural transition
as relaxation of octahedral tilt and an order-disorder transition of the organic cation and we describe the thermochromism as the result of bismuth-bromide bond length fluctuation. We show that cesium can be incorporated to potentially tune the number of layers. Furthermore, to demonstrate versatility and potential of the materials we sonicate the bismuth containing crystals to form nanocrystals with various morphology.

**5.2 Introduction**

The recent advancements in the synthetic strategies for producing electronic-quality lead halide perovskites coupled with their highly-efficient properties demonstrates great promise for the implementation of this material system in optoelectronics. Used in dye-sensitized solar cells by Kojima et al in 2009, alkyl ammonium lead halides have rapidly risen to efficiencies of 24%. However, two major issues remain at the forefront of research on these promising materials. The first issue is the toxicity of lead; to address this, efforts have been made to replace lead with various metal cations such as tin. The tin-based perovskites are hindered due to the facile oxidation of Sn$^{2+}$ to Sn$^{4+}$, which results in poor performance in optoelectronics. Another method to alleviate toxicity is to replace lead with heterovalent elements (i.e. Bi$^{3+}$ and Ag$^{1+}$), to form double perovskites. These materials have a wide range of bandgaps, and some have been experimentally synthesized directly or through cation exchange methods in both bulk and nanocrystal form.

The other primary issue with the lead perovskites is their lack of stability. Methylammonium lead iodide, the best performing material in terms of photovoltaics, has poor stability under standard operating conditions. This material will degrade due to moisture, heat, and insolation. The thermal stability of the perovskite can be improved by cation substitution of the methylammonium with inorganic cations like cesium. To enhance
stability against moisture, sheets of perovskite octahedra can be sterically isolated into layers by bulky hydrophobic organic ligands, forming the Ruddlesden-Popper phase.\textsuperscript{19-21} In this case, addition of bulky organic layers inhibits the mobility of water molecules and prevents moisture from reaching the lead halide crystal surface and triggering the degradation process. Some of the aforementioned double perovskite and layered materials have relatively wide band gaps. However, the ease of fabrication of these materials would make them good options for multijunction PVs with silicon or CIGS, where multiple active layers are included within the device to enhance efficiency.\textsuperscript{22}

The layered perovskite materials exhibit a number of interesting properties, which could be useful in a variety of applications. Previous reports in literature have identified piezochromism observed in 3D perovskite materials\textsuperscript{23} and thermochromism in diimidazolium halobismuthates,\textsuperscript{24} and one report uses the color change and phase transition from non-perovskite phase to perovskite phase for cesium lead iodide/bromide thermochromic PV windows.\textsuperscript{25} Thermochromic behavior has been described in Cs\textsubscript{2}AgBiBr\textsubscript{6} double perovskites,\textsuperscript{26} though to the best of our knowledge has not been demonstrated in 2D double perovskite materials. In addition, while the structural transition of 2D phenethylammonium layered halide perovskites has been known for a while,\textsuperscript{27} this structural transition has not been fully elucidated. Some work on an imidazolium halogenobismuthate(III) with similar structural features of layered cations between halogenometallate anion structure has potentially attributed this type of structural transition to cationic substructure reconfiguration.\textsuperscript{28}

In this study, we synthesized crystals of PEA\textsubscript{2}AgBiBr\textsubscript{6} as a first step in producing layered double perovskites. We found that these materials undergo a structural transition around 140°C and a macroscopically observable color change from yellow to orange in the
same temperature range. We investigated the nature of this structural transition through X-ray diffraction and DSC/TGA measurements, as well as through the synthesis of structurally similar crystals (namely PEA$_2$AgSbBr$_6$ and OA$_2$AgBiBr$_6$). We demonstrate the incorporation of cesium into the PEA$_2$AgBiBr$_6$ system. We then used a solution exfoliation method to synthesize nanocrystals from a selection of PEA$_2$AgBiBr$_6$ and phenethylammonium cesium silver bismuth bromide crystals.

5.3 Experimental Methods

5.3.1 Materials

Phenethylammonium bromide, phenethylamine, phenethylammonium iodide, cesium bromide, silver bromide, bismuth bromide, hydrobromic acid, hydriodic acid, antimony bromide, octylammonium bromide, toluene, dimethylformamide, chlorobenzene, oleylamine, oleic acid and diethyl ether were used as received.

5.3.2 Methods

**Synthesis of crystals:** Single-crystals of Cs$_2$AgBiBr$_6$ and PEA$_2$AgBiBr$_6$ and other samples were synthesized through an acid-based method. In a typical procedure, stoichiometric amounts of AgBr and BiBr$_3$ were measured into a vial inside a nitrogen filled glovebox. Then, depending on the sample, some combination of CsBr and/or PEABr were also loaded into those vials inside the glovebox. The samples were removed from the glovebox. HBr was pipetted at a given volume into these vials, which were then placed into an aluminum reaction block on a hot plate at 170°C. The samples were boiled for 1 – 2 hours until all powders were fully dissolved, and then the samples were cooled at a ramp rate between 5°C/hr and 10°C/hr to produce small single crystals. These crystals were then separated by vacuum filtration. The samples were dried for at least 20 minutes on the vacuum filter before being washed three
times with diethyl ether. The crystals were stored in air with no visible degradation over at least several months.

5.3.3 Characterization Methods

**Single-Crystal X-ray Diffraction:** Single-crystal x-ray diffraction data was acquired using a Bruker-AXS APEX II. The x-ray structures were determined in the Molecular Structures Lab in the Iowa State University Chemistry Department using PLATON crystallographic software.

**Scanning Electron Microscopy:** Scanning electron microscopy was performed with a FEI Teneo operating at 2 kV and 0.2nA.

5.4 Results and Discussion

Crystals of various double and layered double perovskite halides were synthesized through an acid-based solution synthesis. In accordance with literature, Cs₂AgBiBr₆ adopted a cubic structure (Figure 5.1a) with the cesium cation located in the center of the cuboctahedral voids formed by BiX₆ and AgX₆ octahedra. This synthesis method was also used to synthesize a variety of layered perovskite materials. Of primary interest for this report is the PEA₂AgBiBr₆ crystal. When considering the layered material, Cs₂AgBiBr₆ bulk crystals can be referred to as an infinite number of connected layers of Ag and Bi octahedra, whereas the PEA₂AgBiBr₆ are representative of single layers (n = 1) of Ag and Bi octahedra. Single-crystal X-ray diffraction (SCXRD) was taken at -100 °C of crystals of Cs₂AgBiBr₆ and PEA₂AgBiBr₆ to confirm their structure. When compared to Cs₂AgBiBr₆, the structure of the n = 1 layered PEA₂AgBiBr₆ varies slightly to accommodate the bulky organic cation, with the corner sharing octahedra tilted as compared to the Ag and Bi octahedra in Cs₂AgBiBr₆. The crystal structure of the PEA₂AgBiBr₆ is in the centrosymmetric triclinic P-1 space group, with lattice constants of a = 11.4788 Å, b = 11.5596 Å, and c = 17.2436 Å. Within this structure, the layers of
alternating Bi and Ag octahedra are surrounded by bulky PEA cations (Figure 5.1b), promoting the formation of a 2D crystal.

Figure 5.1 Crystal structure designed with VESTA\textsuperscript{29} from single-crystal XRD of (a) Cs\textsubscript{2}AgBiBr\textsubscript{6} along a-axis and (b) n = 1 layered PEA\textsubscript{2}AgBiBr\textsubscript{6} along a*-axis

Figure 5.2 (a,b) SEM micrographs, (c) photograph and (d) optical microscope image of PEA\textsubscript{2}AgBiBr\textsubscript{6} crystals.
These layers collectively assemble at the microscale in stacks as displayed in Figure 5.2a and 5.2b, resulting in macroscopic yellow crystals with some transparency as shown in the photographs in Figure 5.2c and 5.2d. Also evident in the SEM micrographs is the charging occurring in this material. The size of the crystals is on the order of a few millimeters.

Preliminary optical measurements indicate that synthesis of numbers of layers greater than one should be possible, allowing tuning of optoelectronic properties and a narrowing of the band gap. Connor et al. have demonstrated the synthesis of $n = 2$ layers for butylammonium cesium silver bismuth bromide ($\text{BA}_2\text{CsAgBiBr}_7$). The reproducible synthesis of the higher layers ($n \geq 3$) may be complicated by the large solubility differences between the various precursors. The perovskite materials have been shown to crystallize by inverse temperature crystallization, where the temperature is elevated to induce supersaturation. This could potentially be a result of dissolution of metal halide complexes at elevated temperature that leads to supersaturation as well. Additionally, the alkylammonium cations can align at the air-water interface and template the growth of the crystal with the air-water interface itself contributing to an increase in nucleation probability. In these mechanisms, if some of the complexes do not dissociate or if the alkylammonium cations preferentially grow at the surface as opposed to the cesium cations, the preferred growth could be in favor of lower numbers of layers such that the final crystals contain less cesium than intended.

Figure 5.3a shows powder absorbance of material crystallized with both PEA and Cs cations incorporated, potentially corresponding to a larger number of layers. Figure 5.3b shows the corresponding samples as synthesized in HBr. In light of the previous discussion, it is notable that these crystals likely contained less phenethylammonium than originally intended. This earlier synthesis method involved mixing phenethylamine with hydrobromic acid and
then injecting that material into a mixture of AgBr, BiBr₃, CsBr and HBr. However, the PEA/HBr mixture was only soluble at elevated temperature and would partially freeze upon injection transfer. These crystals were polycrystalline and not appropriate for single-crystal XRD. Single-crystal synthesis of these materials with intermediate layers is an area of ongoing research, as mentioned previously it may require highly precise concentration and temperature profiles to obtain phase pure intermediate layers. As the number of layers is decreased, a blue shift in absorbance with respect to the bulk material is expected due to effects of quantum confinement. Given the red-coloring of the bulk (or n = ∞) Cs₂AgBiBr₆, we expect the quantum confined material to have a more orange or yellow coloring. This trend is indeed observed, as demonstrated in Figure 5.3.

![Figure 5.3](image)

**Figure 5.3** (a) Powder absorbance and (b) optical photographs of PEA-Cs-Ag-Bi-Br with varying numbers of layers

Some verification of incorporation of both PEA cation and Cs cation has been obtained. Figure 5.4 demonstrates SEM and EDS of a sample of yellow-orange crystals alongside FTIR from the same sample. The crystals had ratios of Cs, Ag, and Bi which were targeted for n = 3 layers (PEA₂Cs₂Ag₁.₅Bi₁.₅Br₁₀) but where the amount of PEA was decreased because the injected PEA/HBr precursor froze during injection. The EDS shows that cesium has been
incorporated, and the FTIR demonstrates the presence of organic species. Again, these crystals were obtained in a non-reproducible manner due to freezing of a precursor, and as such we have been unable to obtain single-crystals of the material. This does support the argument, however, that very precise amounts of precursors will be necessary to successfully obtain the desired crystals. A high throughput synthesis technique would be beneficial in experimentally determining appropriate precursor ratios.

![Image](example.com/image.png)

**Figure 5.4** (a) SEM and EDS demonstrating incorporation of Cs, Ag, Bi, and Br and (b) FTIR demonstrating presence of PEA for yellow-orange powder synthesized to be PEA$_2$Cs$_2$Ag$_{1.5}$Bi$_{1.5}$Br$_{10}$ with reduced PEA. (c) also shows the NIST reference spectra for a phenethylamine containing compound.  

### 5.4.1 Thermochromic Behavior of n = 1 PEA$_2$AgBiBr$_6$

In order to assess the stability of the layered compound we conducted studies in which we exposed the material to both water and heat. The material does not dissolve in water, and can be submerged in water and experience no visible change once that water has been dried away. When this material is heated above ~150°C it visibly changes color from yellow to red-
orange as shown in Figure 5.5. As heat is continuously applied, this orange color goes to a red-orange. Then the crystal will melt, followed by a transition in color again to yellow. When the heat source is removed, the color changes to red-orange, and then the melt solidifies, and the color goes back to yellow. This process can be repeated multiple times. Reflectance data from the crystals at different temperatures is shown in Figure 5.6. Samples were mounted on a hot plate rotated at a 90° angle. This data shows a gradual red-shift in the absorbance as the temperature increases.

**Figure 5.5** Orange color observed in PEA$_2$AgBiBr$_6$ crystals upon exposure to UV-light or heating

![Image](image)

**Figure 5.6** Reflectance data of PEA$_2$AgBiBr$_6$ crystals divided by reflectance of mirror standard at various temperatures

![Graph](graph)
We investigated the nature of this color change through combined Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). As shown in Figure 5.7, the material first undergoes an endothermic structural transition that is not associated with any mass loss. This is similar to previous reports on phenethylammonium lead and tin halides.\textsuperscript{27, 35-36} At around 240°C, the material begins to melt and then decompose, with an associated mass loss observable in the TGA likely corresponding to loss of PEA. The additional mass loss that begins around 350°C could be associated with BiI\textsubscript{3} or AgI species. If the degradation temperature is avoided, the material is stable through multiple cycles (Figure 5.8) whereupon the structural transition occurs at the same temperature, although there is hysteresis in forward and reverse directions (heating and cooling, respectively). This indicates that this material is stable against both moisture and heat within reasonable operating ranges for semiconducting (or window) devices.

\textbf{Figure 5.7} DSC/TGA of n = 1 single layered PEA\textsubscript{2}AgBiBr\textsubscript{6}
The structural transition indicated in DSC is not a significant re-structuring of the crystal structure of the PEA$_2$AgBiBr$_6$. We hypothesize that the structural transition is associated with a relaxation of the tilt of the Ag and Bi octahedra in conjunction with an order-disorder type transition of the alkylammonium cation. While some perovskite materials have shown the potential to change color in the presence of ammonia, there is also acknowledgement that octahedral tilting of perovskite materials results in an increase in the band gap, associated with a blue shift in absorbance. The tilting distortions have an impact on the optoelectronic properties due to the nature of the conduction band and valence band edges, where the electronic states of the ions in the BX$_6$ octahedra typically dominate these band edges. Investigation of this structural transition and the related changes in optoelectronic and thermal properties could elucidate how the structural arrangements of the crystals impact these properties.
Figure 5.9 Powder X-ray diffraction at various temperatures of $n = 1$ single layered PEA$_2$AgBiBr$_6$ (Background subtracted using WinPLOTR)
Using VESTA software, the octahedral tilt in the PEA₂AgBiBr₆ structure was manually relaxed as compared to the collected SCXRD data. An XRD pattern was simulated from this modified structure and compared to the tilted version (Figure 5.10). The relaxation of tilt is associated with a shift to lower 2θ in the data. As hypothesized, this may account for some of the observed shift in the data when temperature is increased.

To investigate the end structure of the transition we performed single-crystal XRD at elevated temperature. However, this characterization method cannot be used because at temperatures of 150°C the material no longer possesses a single crystal structure that can be resolved. This may be a result of the disordered organic species convoluting the SCXRD resolution process, as even at 25°C we were unable to perform SCXRD of the sample. Instead, we sought to perform a variety of crystal syntheses to narrow down the likely mechanism of
color change. We targeted the cation sites, namely the organic cation and the 3+ cation. We synthesized octylammonium (OA) silver bismuth bromide and PEA silver antimony bromide. XRD for these materials is shown in Figure 5.11, and indicate structural similarity to the PEA$_2$AgBiBr$_6$, with some shift in peaks for the OA sample as would be expected from inclusion of a smaller alkylammonium cation and contraction of the lattice. The difference in the peak separation between the Sb and Bi containing samples appears to be quite small, consistent with the similar size of Sb and Bi and the very similar crystal structure of PEA$_2$AgSbBr$_6$ (Figure 5.12).

![Figure 5.11 Powder X-ray diffraction of OA-Ag-Bi-Br, PEA-Ag-Sb-Br compared to PEA-Ag-Bi-Br](image)

DSC/TGA was taken of these materials (Figure 5.13) to investigate whether they possessed a structural transition, and visual observations were made regarding changes in color. The OA n = 1 material changed color from yellow to orange upon heating but did not show a structural transition prior to melting and decomposition. While the electronic properties
of the organic cations are already recognized to have importance in the PV performance of layered perovskites\textsuperscript{46} these results suggest that the selection of the cations will also play a role in the structural features and stability of the perovskite beyond simply determining whether the perovskite structure is formed per Goldschmidt tolerance factor. The impact of the metal cation may also be significant, as the PEA\textsubscript{2}AgSbBr\textsubscript{6} crystals did not demonstrate color change upon heating, but did have a structural transition.

**Figure 5.12** Crystal structure of PEA\textsubscript{2}AgSbBr\textsubscript{6} designed with VESTA\textsuperscript{29} from single-crystal XRD, silver polyhedral indicate Ag, orange polyhedral indicate Sb, and the organic cations are shown extended outward from the polyhedral. Hydrogen omitted for clarity

**Figure 5.13** DSC/TGA for samples of (a) PEA-Ag-Sb-Br and (b) OA-Ag-Bi-Br
The combination of the DSC/TGA, PXRD and visual observations suggest that the color change observed is not directly a result of the structural transition. Instead, it is likely due to fluctuations in the bond lengths of the bromobismuthate bonds. The first argument for this mechanism is that the thermochromic behavior of halobismuthates has been documented even in materials which do not undergo structural transitions, which we also observed in the octylammonium silver bismuth bromide. Secondly, in the PEA-Ag-Sb-Br material there was a structural transition feature but no color change. This implies the color change depends on the presence of bismuth and is independent of the structural transition.

5.4.2 Exfoliation Based Synthesis of Nanocrystals from Layered Perovskites

In 2D type materials, such as graphite/graphene systems, exfoliation is a common process to obtain few or single layers of the layered material. To this end, we attempted to perform a liquid phase exfoliation of the layered double perovskite crystals. Yellow crystals of PEA-Cs-Ag-Bi-Br and PEA$_2$AgBiBr$_6$ were exfoliated in oleylamine through sonication in the presence of oleic acid and toluene.

A sample synthesized to correspond to $n = 4$ (PEA$_2$Cs$_3$Ag$_2$Bi$_2$Br$_{13}$) was exfoliated and the resulting sample was centrifuged. It was redispersed in toluene and a TEM grid was prepared. Figure 5.14 displays the TEM collected from this sample, as well as EDS of the sample. The sample contains a variety of nanostructures, including rods and spheres, and HRTEM demonstrates the single-crystal nature of some of these particles. The d-spacing shown in Figure 5.14 does not correspond to an expected d-spacing for Cs$_2$AgBiBr$_6$, though more analysis is needed to identify the overall composition and structure of these nanocrystals. These crystals obtained differ from the results observed in samples where the individual precursor salts are combined and sonicated in chlorobenzene (Figure 5.15). In this case, the
lattice spacing observed is 3.2 Å, which could represent the (222) plane of Cs$_2$AgBiBr$_6$. These results demonstrate a potential to control shape and composition of cesium containing nanocrystalline materials.

Figure 5.14 TEM, HRTEM, and EDS of an exfoliated sample of PEA-CS-Ag-Bi-Br

Figure 5.15 TEM and HRTEM of PEABr, CsBr, BiBr$_3$ and AgBr sonicated in CB
However, cesium was not required for nanocrystals to form as a result of the exfoliation procedure. Samples containing n = 1 PEA$_2$AgBiBr$_6$ were also exfoliated in a similar process, with nanocrystals being formed as shown in Figure 5.16. The case where oleic acid was excluded from the exfoliation process seemed to form nanocrystals more readily. Interestingly, in neither of these cases are large nanosheets observed.

![Figure 5.16 PEAl-AgBiBr$_6$ exfoliated in toluene and oleylamine with or without oleic acid.](image)

It is possible that the energy from the sonication process is a crucial part of the formation of the rod and spherical nanocrystals. When the synthesis process was repeated without actually sonicking the mixture, and instead just manually shaking the materials, the formation of possible sheets was observed by TEM in Figure 5.17. In this case, cesium was included in the sample, indicating cesium is not likely the primary cause for the nanocrystal formation.

![Figure 5.17 TEM of a sample of PEA-Cs-Ag-Bi-Br mixed with toluene, oleylamine and oleic acid and manually shaken.](image)
Given the nature of BiI3 to form adducts with toluene, it is possible that some type of adduct was formed in this exfoliation process, facilitated by the energy from the sonication process, which resulted in preferential formation of spherical and rod-like structures. Heidary et al. indicated that chlorobenzene would be a preferred solvent to attempt exfoliation of bismuth iodide. As such, we investigated the hypothesis that a solvent which coordinates weakly to bismuth iodide (chlorobenzene) will form a larger nanocrystal than a solvent which coordinates strongly to bismuth iodide (dimethylformamide). There seems to be some indication from preliminary experiments that solvent choice can alter the morphology of nanocrystals synthesized through this exfoliation method, as seen for sonicated PEA₂AgBiBr₆ crystals in Figure 5.18. The use of chlorobenzene in the sonication process resulted in the formation of some stacking plate-like nanocrystals. These were not the only particles formed in the process, although changing the relative concentrations of oleylamine, oleic acid and chlorobenzene may enable the selective synthesis of these plate-like nanocrystals.

![Figure 5.18 PEA₂AgBiBr₆ nanocrystals sonicated with oleylamine, oleic acid and chlorobenzene or dimethylformamide](image-url)
Nanocrystals were also present in samples sonicated in chlorobenzene, with oleic acid and oleylamine excluded (Figure 5.19). In this case, the sample appeared to exhibit blue-green photoluminescence. Finally, we demonstrated that this method can be expanded to Pb based layered perovskites as well through sonication of a PEA₂PbI₄ sample (Figure 5.20).

**Figure 5.19** PEA₂AgBiBr₆ nanocrystals sonicated with chlorobenzene

**Figure 5.20** PEA₂PbI₄ nanocrystals sonicated with toluene and oleylamine

5.5 Conclusions

In summary, layered double perovskites with different compositions have been synthesized. Some of these have been characterized with XRD, SCXRD, and/or SEM. The
single layer (n=1) phenethylammonium silver bismuth bromide demonstrates an interesting thermochromic property. This property appears to be related to bond length fluctuations, although the material does also possess a structural transition. Furthermore, this material and the phenethylammonium cesium silver bismuth bromide type materials form multiple nanocrystal shapes when exfoliated in oleylamine and various solvents. These initial results show promise in synthesis of perovskite inspired nanocrystals with various morphologies and properties, as well as draw attention to the role of cation and metal centers in determining structure and structural transitions within layered double perovskite materials.

5.6 Acknowledgments

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5.7 References


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CHAPTER 6. BISMUTH BASED SEED NANOPARTICLES FROM HALOBI SMUTHATE PRECURSORS

Publishing Status: This chapter presents a draft of a paper
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Roles:
Rainie D. Nelson conducted all the synthesis experiments, characterized TEM and HRTEM, absorbance, collected HAADF-STEM and EDS of the Bi/Sb seeds, and did the experimental planning
Kalyan Santra collected PL data
James McBride collected the HAADF-STEM images and EDS of the Bi seeds
Yujie Wang collected preliminary PL data
Jacob Petrich advised
Matthew G. Panthani advised

6.1 Abstract

Bismuth nanoparticles were synthesized through a heat-up method in various solvents. Wavelength tunable photoluminescence was achieved through varying the halide in the BiX$_3$ precursor. Some degree of self-assembly was demonstrated through choice of solvent and ligand system. Energy dispersive spectroscopy was used to determine the composition of the particles produced from BiI$_3$; these particles were composed of bismuth.

6.2 Introduction

Metallic nanoparticles have a wide variety of unique properties and interesting applications, including in biomedicine and biotechnology, imaging, and magnetics.$^{1-3}$ Bismuth is a metal which has historically been investigated for x-ray application as a result of its high
absorption of x-rays. When the dimensionality of bismuth is reduced, it begins to exhibit semiconducting behavior. Bismuth nanoparticles have been used as catalysts in reduction reactions, additives in tribological experiments, and have potential to be used in medical applications as well. Solution-phase syntheses of bismuth nanoparticles provides a promising route to tune the morphology and functionalization of the nanoparticles and could facilitate their use as precursors for various bismuth containing products, similarly to the way in which Scheele et al. used bismuth nanoparticles as a precursor to Bi₂Te₃, though previous attempts to grow Bi₂Te₃ nanowires from Bi seeds had been unsuccessful. In a previous publication we demonstrated that BiX₃ based precursor nanoparticles obtained prior to a Cs₃Bi₂X₉ nanocrystal synthesis demonstrated wavelength tunable photoluminescence (PL). Transmission electron microscopy (TEM) demonstrated the presence of small nanoparticles and the growth and maturation of these seeds (through aging or reduction by addition of trioctylphosphine) had a large impact on the morphology of product nanocrystals. With many potential applications, there is need for a better understanding of the properties of bismuth nanoparticles in their own right and as precursors to other materials. Here, we investigate the chemical composition and structure of these nanoparticles and investigate methods to control their self-assembly and photoluminescence.

6.3 Experimental Methods

6.3.1 Experimental Details

Materials: Bismuth iodide, bismuth chloride, bismuth bromide, antimony iodide, acetone, and anhydrous toluene were used as received. 1-Octadecene (ODE), 1-dodecene, oleic acid (OA), oleylamine (OLA), undecanoic acid, and octylamine were degassed prior to use.
Methods: BiX₃ was measured into vials inside a nitrogen filled glovebox. To these vials, various combinations of solvents and ligands were added, for example octadecene (ODE), oleic acid (OA), and oleylamine (OLA). The reaction vial was heated in an aluminum reaction block for a given time (20 minutes) at a specified temperature (120°C), after which it was removed from the reaction vessel. All reaction steps were performed inside a nitrogen filled glovebox. To prepare samples for TEM, aliquots of the product were diluted into solutions of toluene.

6.3.2 Characterization:

Transmission electron microscopy (TEM) images were recorded using a FEI Tecnai G2-F20 instrument operated at 200 kV. HAADF-STEM was collected on Tecnai Osiris equipped with a SuperX quad EDS detector system and a FEI Titan Themis Cubed equipped with SuperX quad EDS detector.

UV-Vis absorption spectra were collected using a Perkin-Elmer Lambda 750 instrument operating in transmission mode.

Photoluminescence (PL) spectra of BiX₃ in solution were obtained on a Fluoromax-4 spectrometer (Horiba Scientific) using a quartz cuvette. The excitation wavelengths in Figure 6.1 are 340 nm, 370 nm, and 450 nm for samples containing chloride, bromide, and iodide, respectively. The excitation wavelength in Figure 6.7 is 400 nm.

6.4 Results and Discussion

The PL for the various bismuth halide seeds is shown in Figure 6.1, along with absorbance. These seeds are prepared by heating bismuth halides in a mixture of octadecene,
oleic acid, and oleylamine. There are small local peaks in absorbance for BiI$_3$ based seeds at around 480 nm and 530 nm, as well as two features in PL at around 500 nm and 540 nm. Both the BiCl$_3$ and BiBr$_3$ based seeds have PL peaks at around 462 nm and 425 nm, and BiCl$_3$ based seeds have an additional peak at 400 nm.

![Image of absorbance and PL spectra for BiI$_3$, BiBr$_3$, and BiCl$_3$.](image)

**Figure 6.1** Bismuth halide precursor seed PL (dashed) and absorbance (solid) for, from top to bottom, BiI$_3$, BiBr$_3$ and BiCl$_3$.

In our initial synthesis protocol, these nanomaterials were small and suspended in a non-volatile solvent (octadecene). They also appeared to be soluble in many of the common anti-solvents used to crash out nanocrystals (i.e. methanol, ethanol). The particles would not precipitate under centrifugation at 4°C at relatively low rcf (around 25,000) or at room temperature at about 80,000 rcf. Thus far, TEM of the particles was enabled by excessive dilution of the reaction mixture post-reaction. This allowed for some removal of the organic
solvent and ligands. Figure 6.2 displays TEM from each of the three types of bismuth halide precursor seeds (BiCl₃, BiBr₃ and BiI₃), demonstrating the formation of seed particles for all halides.

**Figure 6.2** TEM of BiCl₃, BiBr₃ and BiI₃ precursor seeds dissolved in a mixture of octadecene, oleylamine and oleic acid.

We obtained HRTEM through an acetone wash treatment of the TEM sample grid (Figure 6.3). The lattice spacing observed could be consistent with a high pressure Bi phase (PDF#01-070-2629), with the 2.81Å spacing corresponding to the (111) diffraction plane, the 2.75Å spacing to the (-111) plane and the 2.25Å to either the (020) or the (002) plane.

**Figure 6.3** Acetone washed Bi seed reaction, with various d-spacings and angles displayed.
HAADF STEM and EDS of the acetone washed TEM grid demonstrates that Bi is localized in areas containing the particles, while iodide is distributed throughout the grid (Figure 6.4). This could be indicative of bismuth metal nanoparticles.

![Figure 6.4 HAADF-STEM and EDS of Bi seeds with acetone wash. Scale bar is 60 nm for all images.](image)

However, while these small seeds are relatively uniform the inability to separate them out in solution may inhibit their usefulness in applications or as precursor to the synthesis of other nanoparticles. We thus varied our synthetic methods to improve the processability of these materials and control their morphology. When OA was excluded from the reaction mixture, gray powder settled out after the reaction proceeded. Figure 6.5 displays TEM of this sample, which seems to suggest that at least some of the material observed in the reaction
product consisted of bismuth seed nanocrystals. The average lattice spacing was taken in HRTEM, suggesting that the small particle of around 4 nm has lattice spacing of 2.84 Å. This could correspond to BiOI, where the reference pattern PDF#00-010-0445 has a d-spacing at 2.82 Å representing the (110) plane. The incorporation of oxygen is unexpected given that the reactions are conducted in a nitrogen filled glovebox with oxygen levels near 0 ppm, however the samples are exposed to air during the transit to the imaging facility. The synthesis of BiOI could also be of interest for PVs, as it has a band gap between 1.6 and 2.0 eV and has been used for PV efforts.\textsuperscript{12-16} On the other hand, this could also be the (111) plane from the high pressure Bi phase mentioned previously.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image}
\caption{TEM of bismuth iodide in octadecene and oleylamine heated to 120°C for one hour}
\end{figure}

The use of different reaction systems resulted in different morphology observed in TEM. We replaced oleylamine with a shorter chain alkyl amine, octylamine, and observed that the bismuth seeds tended to self-assemble into ordered stacks. (Figure 6.6). The spacing between the assembled layers does not seem to depend on whether undecanoic acid or oleic acid was included in the synthesis, as both have spacings of around 2.7 or 2.8 nm. Absorbance and PL for the various reaction systems are shown in Figure 6.7a and b, respectively.
The dodecene, undecanoic, octylamine sample could potentially have the highest PL because of contributions from scattering, or the enhancement could stem from the presence of aggregates or structured morphology. The absorbance shows a non-zero tail at high wavelength, likely indicating scattering from larger particles or aggregates. Given the chain-like aggregates observed in TEM of this material (Figure 6.6), it is possible that the small particles are also forming aggregates in solution. While this could be a factor of excess undecanoic acid, given the relatively high freezing point of that material, the sample with dodecene, undecanoic acid, and oleylamine does not show PL, which suggests that the effect is not entirely due to undecanoic acid.
Figure 6.7 (a) absorbance and (b) PL measurements of various BiI$_3$ reaction systems, heated for 20 minutes at 120°C.

We combined different halide salts (BiI$_3$ and BiCl$_3$, BiBr$_3$ and BiI$_3$, or BiBr$_3$ and BiCl$_3$) in one reaction to evaluate the effect of multiple halide components, though no immediate differences are observed through TEM of the samples (Figure 6.8), indicating that continuous tuning of PL between the various BiX$_3$ seeds may be possible through varying the halide ratio. As there is also general interest in the process of blending Bi and Sb cations, as this may enable tuning of the band gap or provide enhancements to stability, we performed a 1:1 BiI$_3$:SbI$_3$ reaction in octadecene, oleic acid, and oleylamine, demonstrating the formation of seed materials with co-localized Bi and Sb (Figure 6.9). More investigation into this material will need to be done in order to determine the precise composition and the structure of the nanoparticles formed from the precursor containing both Bi and Sb, but these preliminary results show promise in the synthesis of Bi and Sb alloys.
**Figure 6.8** TEM of BiI\textsubscript{3} and SbI\textsubscript{3} blend, as well as blends of each of the halides for BiX\textsubscript{3} (all reactions in octadecene, oleic acid, and oleylamine)
Figure 6.9 TEM of BiI$_3$ and SbI$_3$ blend, as well as blends of each of the halides for BiX$_3$ (all reactions in octadecene, oleic acid, and oleylamine)

In addition to the BiI$_3$ and SbI$_3$ blend, we also performed a similar synthesis with SbI$_3$. The presence of PL is inconclusive given that the peak observed in the sample is at the same value as a peak observed in the oleylamine (Figure 6.10). The solubility of the bismuth halide precursor in the reaction mixture is much better than the solubility of the antimony halide precursor, so it is possible that further investigation of the SbI$_3$ (or SbX$_3$) reaction system could result in wavelength tunable PL for that material system. However, that is beyond the scope of the current work.
Figure 6.10 PL spectra for SbI$_3$ in octadecene, oleic acid, and oleylamine, compared to the spectra of oleic acid and oleylamine.

Overall, we demonstrated the facile synthesis of bismuth nanoparticles with wavelength tunable PL through sourcing the Bi from different BiX$_3$ precursors. The use of alkyl amines with different chain lengths in the reaction mixture was shown to impact the self-assembly of the nanoparticles. Finally, we synthesize seeds from halide mixtures, BiI$_3$/SbI$_3$, or SbI$_3$ as preliminary experiments to explore the versatility of this method. These initial experiments indicate the potential for this reaction system as precursors to the synthesis of Bi containing nanocrystals, like Bi$_2$Te$_3$, or the synthesis of self-assemblies of bismuth nanoparticles with various morphologies.
6.5 References


CHAPTER 7. GENERAL CONCLUSION

This document discussed investigation into the structure and properties of various bismuth based materials. The main goal of studying these bismuth based materials was to gain a better understanding of methods that can be used to control their properties. We anticipate that bismuth based materials could potentially function as either a replacement for unstable lead-based perovskites or could develop into an interesting field themselves. We began the discussion in Chapter 3 with bulk bismuth iodide. We investigated a solvent additive based approach to controlling the morphology of spin-processed thin films. Selection of a solvent additive with higher donor number can result in larger grain size. We tuned the ratio of solvent additive to bismuth to obtain a balance between grain size and film coverage, producing films with morphological improvements over those processed in pure solvent. This work has the potential to provide a template for specified growth of bismuth iodide thin films, which could prove useful for their standalone application or for their conversion to perovskite-like materials like methylammonium bismuth iodide and cesium bismuth iodide.

Next, in Chapter 4 we discussed the synthesis and characterization of ordered vacancy cesium bismuth halide nanocrystals. We used HRTEM and XRD to confirm the presence of single-crystal Cs$_3$Bi$_2$I$_9$ nanocrystals. We also determined that aging time, reactant concentration, and presence of reducing agents in the reaction precursor were major factors that influenced size and morphology of the nanocrystals. By changing the composition of the halide, we were able to tune the absorbance. We also identified the growth mechanism to be initiated by growth of bismuth seeds followed by reaction with injected Cs-oleate. The Cs$_3$Bi$_2$I$_9$ nanocrystals were shown to be air-stable over long periods of time. Interestingly, however, we found that PL was observed in the as-synthesized precursor seeds with no
injection of Cs-oleate. As a result of this interesting finding regarding the precursor seeds, we initiated an investigation into the seeds, which is described in Chapter 6.

Continuing with the motif of the exploration of bismuth based perovskites, in Chapter 5 we investigated layered bismuth halide double perovskites. We synthesized a variety of crystals structures, though the focus was primarily on $\text{PEA}_2\text{AgBiBr}_6$ and $\text{PEA-Cs-Ag-Bi-Br}$. We found that $\text{PEA}_2\text{AgBiBr}_6$ adopts a similar crystal structure to $\text{Cs}_2\text{AgBiBr}_6$, with tilting distortions of the $\text{BiBr}_6$ octahedra. This material undergoes a structural transition which we hypothesize is related to relaxations of the octahedral tilting. Heating the material resulted in a color change from yellow to orange, which we attribute to fluctuations in the Bi-Br bond lengths. We also determined that we can incorporate cesium into the structure. We then performed a solution based exfoliation on the layered double perovskite crystals, finding that in doing so we obtain nanocrystals of various morphologies.

As mentioned previously, Chapter 6 detail an investigation into the $\text{BiX}_3$ precursor seeds. We determined that these bismuth based seeds have photoluminescence which can be tuned through selection of halide in the precursor. We also developed a method to encourage self-assembly of the seeds through choice of solvent and ligand.

Overall, this document demonstrates a broad effort to unravel the potential of bismuth based materials by studying various dimensionalities and structural motifs. Overall, we have worked with bismuth on three different length scales. In each of these cases the material exhibits unique properties that can allow for control of the products synthesized from bismuth halide materials. This provides a tunable system that can be targeted towards different applications, from use as a thermochromic detector to inclusion in optoelectronics to use as seed particles with different morphologies for various end-product nanocrystals.