The development of lead-less perovskite materials for the photovoltaic application

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**THE DEVELOPMENT OF LEAD-LESS PEROVSKITE
MATERIALS FOR THE PHOTOVOLTAIC APPLICATION**

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**Interdisciplinary Graduate School
Energy Research Institute @ NTU**

2019

THE DEVELOPMENT OF LEAD-LESS PEROVSKITE MATERIALS FOR THE PHOTOVOLTAIC APPLICATION

CHEN YAN

INTERDISCIPLINARY GRADUATE SCHOOL

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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1 Aug 2019

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Lydia Helena Wong

Authorship Attribution Statement

Chapter 4 is published as T. Krishnamoorthy, H. Ding, Y. Chen, W. L. Leong, T. Baikie, Z. Zhang, M. Sherburne, S. Li, M. Asta, N. Mathews, and S. G. Mhaisalkar, Lead-free Germanium Iodide Perovskite Materials for Photovoltaic Applications. *J. Mater. Chem. A*, **3**, 23829-23832 (2015). DOI: 10.1039/C5TA05741H.

The contributions of the co-authors are as follows:

- Prof Asta, Asst Prof Mathews, and Prof Mhaisalkar provided the initial project direction and edited the manuscript drafts.
- Dr T. Krishnamoorthy, Dr H. Ding, and I prepared the manuscript drafts together. These authors contributed equally to this work.
- I performed all the materials synthesis, collected X-ray diffraction patterns and ultraviolet, visible light spectra, carried scanning electron microscopy, and conducted data evaluation, with the guidance of Dr T. Krishnamoorthy.
- Dr H. Ding and Dr Z. Zhang conducted the high-throughput computational screening. This computational study was revised by A/Prof Li.
- Dr W. L. Leong assisted in the collection of the photoelectron spectroscopy in air data.
- Dr T. Baikie conducted the Rietveld analysis of the powder X-ray diffraction data.

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Abstract

Perovskite solar cells with high efficiency and low fabrication cost have been rapidly developed in response to the pressing demand of the world energy. However, the light absorber materials adopted in the state-of-the-art perovskite solar cells contain the toxic element lead that may pose potential hazards to humans and biological systems. Hence, the discovery and development of new lead-free perovskite materials for the future global commercialization of non-toxic, stable, and efficient perovskite solar cells has become the emerging frontier in photovoltaic research field. In this regards, the thesis here proposed three types of lead-free or lead-less perovskite materials by substituting lead with non-toxic metal elements from the same group as lead in the periodic table (germanium and tin). These model materials were studied through a combination of structural, morphological, optical and electrical characterizations to select the appropriate composition for the application as solar harvesting films in photovoltaic device with measurable performance.

In this thesis, according to the predication of computational analysis on the substitute materials for lead-based perovskites in literature, novel germanium(II) and tin(IV) iodide perovskite materials have been successfully synthesized using solution processes and demonstrated desired optical absorption properties for photovoltaic applications. In these two lead-free perovskite systems, various inorganic or small organic cations were utilized in combination with the lead-free metallic cations and iodic anions to selectively tailor the crystal structure, band edge position, and ambient and thermal stabilities of the resulting perovskites. In addition, a lead-less perovskite system with partial tin(II) substitution exemplified the important role of metallic cations in controlling the charge recombination process within perovskite films and at interfaces.

In summary, the major findings presented in this thesis dissertation highlight the significance of compositional engineering of the perovskite materials to the fine-tuning of their optoelectronic properties and the performance of their associated devices. Furthermore, this thesis work paves the way for the rational design of eco-friendly, stable, and efficient perovskite materials for photovoltaic applications in future.

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Abbreviations

CBM	Conduction Band Minimum
DSC	Differential Scanning Calorimetry
DSSC	Dye-sensitized Solar Cell
EDS	Energy Dispersive X-ray Spectroscopy
EQE	External Quantum Efficiency
ETM	Electron Transporting Material
FA	Formamidinium
FE-SEM	Field Emission Scanning Electron Microscopy
FF	Fill Factor
FTIR	Fourier Transform Infrared Spectroscopy
FTO	Fluorine-doped Tin Oxide
HOMO	Highest Occupied Molecular Orbital
HTM	Hole Transporting Material
IPCE	Incident Photon to Current Efficiency
ITO	Indium Tin Oxide
LUMO	Lowest Unoccupied Molecular Orbital
MA	Methylammonium
PCE	Power Conversion Efficiency
PSC	Perovskite-based Solar Cell
TAS	Transient Absorption Spectroscopy
TCO	Transparent Conducting Oxide
TGA	Thermogravimetric Analysis
VBM	Valence Band Maximum
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

Reducing the lead content in state-of-the-art perovskite light-absorber materials is a pressing need for the development of eco-friendly and stable solar cells. Additionally, understanding the compositional effect on the optoelectronic properties of perovskites is essential for the establishment of high performing perovskite design strategies. This chapter highlights the problem statement of this thesis and the hypotheses to be tested, outlines the goals and scope of this thesis, and provides the novel findings and outcomes obtained from this research project.

1.1 Hypothesis/Problem Statement

With the increasing world population, it becomes more challenging for our society to satisfy the world energy demand. As predicted by world energy forecast, the world energy demand will increase to beyond 100 million barrels of oil by 2050.^[1] Currently, the main energy resources are non-regenerative fossil energy sources, which have negative impacts on the environment. For instance, global warming results from carbon dioxide emission by the burning of oil, coal and natural gas. Therefore, intense research is increasingly required to develop alternative energy resources, which are both renewable and sustainable.

Solar energy is the most abundant carbon-free energy source to satisfy the global energy demand with minimum environment contamination. The electrical devices converting solar energy, i.e. sunlight, into electricity are named as solar cells. Over the latest few years, solar cells based on organic/inorganic lead-based halide perovskites have attracted tremendous attention in the photovoltaic community, due to its combination of high efficiency and low cost.^[2-4] Nevertheless, the potential toxicology issue of lead is a huge drawback for the worldwide application of this class of materials. Its direct solution is to substitute lead in the perovskite material with a non-toxic metallic element.^[5-7] While eliminating the toxicity, one also needs to account for stability in addition to high efficiency. As such, a key scientific challenge is to develop nontoxic, stable perovskite materials for application in the photovoltaic devices.

Reducing the lead content in state-of-the-art perovskite materials brings distinctive advantages in photovoltaic research area: aiding a deeper understanding of the relationship between perovskite composition and photovoltaic performance in actual devices; revealing the rational design strategies for new perovskites to tune the structure, optoelectronic properties, and stability. The complete substitution of lead opens up new possibilities in realizing eco-friendly and efficient perovskite solar cells, while the partial substitution of lead shed more light on the fundamental mechanisms of the perovskite solar cells (PSCs) correlated to metal cation. By bridging materials synthesis and application in actual devices, it is expected that the commercialization of low-cost, high-efficient PSCs without toxicity will take place in the future.

Perovskites commonly employed as light absorbers are defined with a chemical formula of AMX_3 where A is a monovalent cation, M is a divalent metal cation, and X is a halide anion. The synthetic versatility of the AMX_3 perovskite material enables flexible designs of material composition. Firstly, it is feasible to completely replace Pb^{2+} in $APbX_3$ perovskites by a divalent metal cation from the same group of Pb, i.e. Ge^{2+} . Examples have been shown that perovskites based on tin ($ASnX_3$), which is located in the same group as Pb and Ge in the periodic table, can be applied in the photovoltaic devices.^[8-10] A computational insight has been provided by Korbel et al. that perovskites based on Pb, Sn, or Ge are highly promising candidates for photovoltaic applications.^[11] Moreover, Asta's group has used high-throughput computational methods to screen for possible inorganic lead-free halide perovskites.^[12] Their work indicates a Ge-based perovskite ($CsGeI_3$) is thermodynamically stable and has a bandgap suitable for photovoltaic applications.

Secondly, it is possible to partially substitute Pb^{2+} in hybrid perovskites by Sn^{2+} without compromising efficiency and stability of devices based on $APb_{1-x}Sn_xX_3$ perovskites. In literature, it has been demonstrated that pure Sn-based perovskites exhibit poor stability under moisture and air, which limits its application in high-efficiency devices.^[13] Since the ionic radii of Pb^{2+} (1.19 Å) and Sn^{2+} (1.1 Å) are close to each other, incorporating some proportion of Sn into Pb-based perovskites shall not disrupt the three-dimensional (3D) metal-halide octahedra cage. Additionally, the metal cation in the $APbX_3$ perovskite forms its lower conduction band.^[14] Hence, varying the Sn proportion in $APb_{1-x}Sn_xX_3$ perovskites could tune bandgap, alter optoelectronic properties, and further influence the photovoltaic performance of devices.

Thirdly, it is plausible for the M-site in AMX_3 perovskites to be occupied by a tetravalent cation, i.e. Sn^{4+} , forming a derived structure like A_2MX_6 . Comparing perovskites based on Sn with different valency, A_2MX_6 perovskites shall have higher air stability than AMX_3 perovskites. Unlike Pb, the highest oxidation state of Sn is tetravalent rather than divalent. As a result, AMX_3 perovskites involving Sn^{2+} can degrade upon the exposure to air because they are oxidized spontaneously to form the tetravalent ions. In contrast, A_2MX_6 perovskites where tin stays in its stable oxidation state (Sn^{4+}) can avoid the degradation in

the ambient environment. Therefore, the air stability can be improved by altering the valency of M-site cation.

Lastly, altering the A-site cation in either AMX_3 or A_2MX_6 perovskites shall tune the structural and optical properties. Comparing Ge based perovskites with different monovalent A-site cation, inorganic Ge based perovskites may exhibit lower bandgap than organic Ge based perovskites. Based on the band structure of cubic $CsGeI_3$ calculated by Asta's group, Ge based perovskites possibly have a direct bandgap, the value of which can be affected by the lattice constant.^[12] Hence, the bandgap of Ge based perovskites can be tuned by changing A-site cation with a different ionic size. Similarly, A-site cation can be exploited to tailor the optical and electrical properties of Sn(IV) based perovskites. In the computational study of Cai et al., it was demonstrated that the bandgap reduces when Cs^+ cation in A_2SnX_6 perovskites is replaced by smaller Rb^+ .^[15] Possibly, inorganic Cs^+ cation can be replaced by slightly larger organic cation (MA^+ or FA^+), which may lead to increased bandgap.

1.2 Objectives and Scope

The objective of this thesis is to develop new low-toxic metal based, stable perovskites as solar harvesting materials in photovoltaic devices.

To fulfil the aforementioned objective, this project involves the study of both material properties and photovoltaic devices based on three types of lead-less perovskite systems, including (i) germanium-based perovskites ($AGeI_3$, where $A = Cs, MA, FA$), (ii) lead-tin(II) binary perovskites [$FAPb_{1-x}Sn_x(I_{0.8}Br_{0.2})_3$, with $0 < x \leq 1.0$], and (iii) tin(IV)-based perovskite derivatives (A_2SnI_6 , where $A = Rb, Cs, MA, FA$). The scope of this thesis is divided as follows:

1. Developing low-toxic metal substituted perovskite materials

- a) Synthesizing inorganic/organic metal halide perovskites based on pure Ge^{2+} , partial / pure Sn^{2+} and pure Sn^{4+}

- b) Evaluation on the chemical composition, phase transition and stability of the synthesized perovskite powders / thin-films
- 2. Understanding the structural-morphological-optical properties of Pb-less perovskite thin film and electrical properties of the corresponding photovoltaic device
 - a) Study on the crystal structure, morphology, absorbance, bandgap, and band alignment with common charge selective materials for Pb-less perovskite film
 - b) Investigation on the electrical properties of Pb-less perovskite based solar cells and the factors limiting their photovoltaic performance
- 3. Investigating charge recombination mechanism in the perovskite and at the interface of perovskite / charge selective contacts for the high-performing Pb-Sn-based perovskite solar cells

1.3 Dissertation Overview

The thesis addresses the development of lead-less perovskite materials applied as the light harvester in solar cells, and is composed of the following 7 chapters.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning the work in the solar cell field based on organic/inorganic metal halide perovskite materials. The current progress in both lead-based and lead-free PSCs is presented from an historical perspective. It demonstrates the architecture and working principles of PSCs, and discusses the advantages and disadvantages of this class of solar cells. The drawback of lead-based PSCs leads to the introduction of the promising low-toxic metal based perovskite materials. This chapter guides the reader to the gaps in knowledge that this research project is addressing.

Chapter 3 discusses the rationale for the choice of particular methodologies employed in this project. It also elaborates the experimental procedures of perovskite material synthesis and PSC fabrication, the principles underlying the selected characterization techniques, and the methods of data analysis.

Chapter 4 presents the study of optoelectronic properties of inorganic/organic lead-free, germanium based perovskites. Besides investigating the effect of the cation substitution in Ge-based perovskites, AGeI_3 (where $A = \text{Cs, MA, FA}$), on the crystal structure and band gap, Ge-based perovskites for the first time were successfully applied as light harvesters in solar cells. In addition, the reasons of poor device performances have been explained.

Chapter 5 demonstrates how compositional engineering strategies can be applied to design a novel perovskite with ideal bandgap and optimized photovoltaic performance. The lead-tin binary perovskite system, A(Pb,Sn)X_3 (where $A = \text{FA}$, $X = \text{I}_{0.8}\text{Br}_{0.2}$), was utilized to study the charge recombination mechanism in perovskites and at interfaces through dynamic absorbance spectroscopy and electrochemical impedance spectroscopy. The results of this chapter elucidate that a small proportion of tin incorporation in lead-based mixed-halide perovskites allows for a stabilized perovskite structure, a tunable band gap, enhanced absorption, and hence its corresponding solar cells yield high efficiencies.

Chapter 6 elaborates the impact of A-site cation on the structural and optical properties and the stability under heat and air of tin (IV)-based iodide perovskites, A_2SnI_6 (where $A = \text{Rb, Cs, MA, FA}$). Although these perovskite derivatives show promising stability and suitable band gap for photovoltaic application, their use as a lead-free perovskite light absorber was obstructed by difficult processability as thin films and misalignment of with commonly used contact materials.

Chapter 7 summarizes the main achievements and draws versatile guidelines for controlling structural, optical, and electronic properties of perovskites by compositional engineering. It demonstrates the extent to which the hypothesis is proven and the objective is met. Based on the outcomes obtained in this thesis, the opportunities and strategies for future work are presented.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Demonstrating for the first time, successful applications of Pb-free Ge-based halide perovskites (CsGeI_3 and MAGeI_3) in photovoltaic devices. These Ge-based compounds are stable up to 150 °C, confirming the prediction of the computational screening.
2. Revealing the essential role of Sn content in controlling the charge recombination process in solar cells based on Pb-less Sn(II)-based Br-containing perovskites $[\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3]$, where $0 \leq x \leq 1$.
3. Discovering new hybrid Pb-free Sn(IV)-based perovskites (MA_2SnI_6 and FA_2SnI_6) that exhibit low dimensional perovskite structure but enhanced air stability and ideal bandgaps ~ 1.3 eV, in comparison with the Sn(II)-based perovskite.
4. Correlating the A-site cation ($A = \text{Cs}, \text{MA}, \text{FA}$) to the optoelectronic properties of the Pb-free Ge or Sn(IV) based perovskites (AGeI_3 or A_2SnI_6).

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Chapter 2

Literature Review

This chapter reviews the compositional engineering strategies of organic/inorganic metal halide perovskites, presenting the evolution from lead-based to lead-free perovskite solar cells. The fundamental concepts of lead-based perovskite solar cells are described, from the perovskite crystal structure to the major drawbacks limiting their application in commercial devices. An introduction of low-toxic metal incorporated perovskite solar cells are provided, with discussions on the challenges of developing new nontoxic, stable perovskites.

2.1 Overview

Solar cells based on organometal halide perovskites have attracted tremendous attentions from a broad scientific community in recent years, driven by their high efficiencies and low cost. The efficiency progress of the best research-cells based on various materials and photovoltaic technologies is summarized in Figure 2.1, where the stunningly rising efficiencies of perovskite based solar cells (PSCs) are highlighted in a red circle.^[1] When first reported in late 2012, solid-state solar cells incorporating methylammonium lead iodide (MAPbI₃) absorbers successfully produced power conversion efficiencies (PCEs) close to 10%.^[2, 3] Since then, their efficiencies have been rapidly improved with intensive efforts of researchers in the photovoltaic field, most recently reaching a certified 23.3%.^[1]

Figure 2.1 Overview of the best research-cell efficiencies of various photovoltaic technologies. (This graph was created and prepared by the National Renewable Energy Laboratory (NREL) for the US Department of Energy.)^[1]

Organometal halide perovskites are identified as highly promising solar harvesting materials in realizing efficient, low-cost photovoltaics, thanks to its solution processability, ideal band gap^[4, 5], high absorption coefficient^[6], high carrier mobility^[7, 8], long carrier lifetime^[9], and long charge diffusion length^[10]. The most widely studied PSCs in recent

years incorporate lead-based perovskite absorber materials. Beyond the aforementioned excellent properties, the potential toxicology issue of lead is a huge drawback for real-world applications of this technology. Hence, the family of hybrid perovskites has been expanded to new members, such as low-toxic metal incorporated perovskites and low-dimensional perovskite derivatives.

The synthetic versatility and structural tolerance of perovskites allows a broad choice of metal cations, opening up new possibilities in developing low-toxic, efficient PSCs. The research in this direction requires compositional engineering strategies to control the structural and optoelectronic properties of perovskites. Meanwhile, it faces the challenges of bridging material design and functional devices fabrication. The following sections will present the research evolution from Pb-based PSCs to low-toxic metal based PSCs, and discuss the role of metallic cation in influencing the photovoltaic performance.

2.2 Organic/inorganic lead-based halide perovskite solar cells

2.2.1 Crystal structure and composition

The term “perovskite” refers to a relatively old family of materials adopting the crystal structure, namely AMX_3 , which was first discovered in calcium titanate ($CaTiO_3$).^[11-13] Such crystal structure is characterized by a three-dimensional octahedra (MX_6) as shown in Figure 2.2. These octahedra are continuously corner-shared and the coordination site left among them are occupied by the component A. In terms of organic/inorganic metal halide perovskites, A represents a monovalent cation, M a divalent metal cation and X an anion from the halide series.

Figure 2.2 Crystal structure of AMX_3 perovskite with the origin centered at (a) the M site and (b) the A site

The A-site cations have shown direct influence on the formation of a close packed perovskite structure but weak contribution to electronic properties.^[14] They work to fulfill the charge neutrality and function as “fillers” between inorganic octahedra layers. The three-dimensional (3D) symmetry can be achieved when the A site is occupied by a small cation, such as cesium (Cs^+), methylammonium ($CH_3NH_3^+$ or MA^+), and formamidinium ($HC(NH_2)_2^+$ or FA^+).^[15] Nevertheless, the incorporation of larger cations can disrupt the 3D octahedra cage.^[16, 17] In terms of lead based halide perovskites, as the name implies, the M metal cation sites are occupied by divalent Pb^{2+} ions, which contribute to the formation of lower conduction band.^[18] On the other hand, the X anion sites are occupied by monovalent halide anions (I^- , Br^- , Cl^-), contributing to the formation of upper valence band.^[18] This anion is not necessarily restricted to a single halide element. Continuous tuning of the bandgap by incorporating two halides (e.g. I^- and Br^-) has been demonstrated in many reports.^[19, 20]

A tolerance factor (TF), developed by Goldschmidt,^[21] are widely used to predict the formation of a stable 3D perovskite structure, described by the following equation:

$$t = \frac{R_A + R_X}{\sqrt{2}(R_M + R_X)}$$

where R_A , R_M , and R_X represent the effective ionic radii of ions A, B, and X, respectively. In general, it is feasible to form perovskites with cubic symmetry when $0.8 < t < 1$. Based on this approach, G. Kieslich et al. calculated TFs for a set of 13 protonated amines, 21 divalent metals, and 8 anionic species (Figure 2.3) and proposed the potential formation of

over 600 new hybrid perovskites.^[22]

Figure 2.3 Overview of the general amines, metal cations, and anions applied in the calculation of TFs. In all, 2352 TFs were calculated, of which 742 (562 organic anion based, 180 halide based) lie in the range $0.8 < t < 1$.^[22]

2.2.2 Device architecture and working mechanism

The extensive interests on PSCs do not only focus on improving device performance but also lie in developing new device architecture. So far, the high PCEs can be obtained in devices based on two general cell structures: mesoscopic structure with perovskite layer capped on the semiconducting oxide nanoparticle (e.g. TiO₂) scaffold and planar structure with perovskite thin-film layer sandwiched between two charge transporting layers, as schematically illustrated in Figure 2.4a-b.^[23,24] It obviously shows that the major difference between these two cell structures lies in the presence of mesoporous scaffold.

Figure 2.4 Schematic illustration of the device architecture of (a) mesoscopic PSC and (b) planar PSC, and the charge generation and transport mechanism in (c) mesoscopic PSC and (d) planar PSC.^[23]

In the PSCs with mesoscopic structure reported by Kim et al., hybrid perovskite acts as a light absorbing material.^[2] The perovskite capped mesoporous TiO₂ layer is sandwiched between an n-type TiO₂ layer for electron transporting and a p-type spiro-OMeTAD layer for hole transporting. As a scaffold, the mesoporous TiO₂ layer provides large surface areas for perovskite loading. Meanwhile, it provides sufficient electron transport paths between perovskite absorber and n-type contact. As illustrated in Figure 2.4c, the photoinduced electrons are injected from perovskite absorbers into the scaffold and n-type contact, while the concomitantly generated holes are extracted by the p-type contact.^[25] Further investigation demonstrates that hybrid perovskites are ambipolar charge conductors and capable of efficiently transporting both electrons and holes.^[9, 10, 26] Therefore, the scaffold, n-type contact, or p-type contact can be removed from the mesoscopic device architecture without greatly scarifying device performances.^[27-29]

In the family of PSCs based on planar structure, there are two categories: conventional structure with n-i-p configuration and inverted structure with p-i-n configuration (where n denotes n-type electron-transporting layer, i represents perovskite absorbing layer, and p denotes p-type hole-transporting layer). As can be seen in Figure 2.5, these two planar structures are differentiated in the sequence of deposition procedure.^[30] Compared to the mesoscopic PSC, the conventional planar PSC does not incorporate a mesoporous metal oxide scaffold. In the PSCs with planar structure built by Liu et al., a thin film of hybrid perovskite is directly deposited onto a compact n-type metal oxide (TiO₂), followed by subsequent coating of a p-type organic polymer (spiro-OMeTAD) and top metal contact.^[28] In terms of PSCs with inverted planar structure, Docampo et al. deposited a hybrid perovskite thin film on top of a hole selective layer (PEDOT:PSS), followed with an electron selective layer (PCBM).^[31] As illustrated in Figure 2.4d, the fundamental operating mechanism in planar PSCs can be described as that perovskites absorb light and generate holes and electrons that are injected into p-type and n-type contacts, respectively.

Figure 2.5 Schematic diagram of planar heterojunction solar cells with (a) conventional “n-i-p” and (b) inverted “p-i-n” configurations.^[30]

Several studies demonstrated that PSCs with mesoscopic architecture delivered high efficiencies, while relatively high efficiencies were also observed in PSCs with planar architecture.^[32-35] Device performance can be influenced not only by the solar cell structure but also by the fabrication process and the material employed in the individual layers.^{[28,}

^{36-38]} Consequently, it is difficult to compare these two architectures based on PCE alone. The removal of mesoporous scaffold extends the flexibility in choice of charge transporting materials as well as deposition methods for perovskites.^[39-42] Additionally, the planar architecture enables the low-temperature processability for flexible devices.^[31, 43, 44] Nevertheless, it requires a careful control of perovskite crystallization process to achieve homogenous and uniform perovskite thin films for high performances.^[45, 46] So far, it is still an open question in the photovoltaic field regarding the most advantageous device architecture for PSCs.

2.2.3 Advantages and disadvantages

Perovskite based photovoltaics present many advantages over conventional silicon based solar cells. PSCs not only allow simple solution-based deposition method^[47] (Figure 2.6a) but also provide both flexibility and transparency^[31, 44]. Taking the most commonly studied perovskite, methylammonium lead iodide (MAPbI_3), as an example, it shows a suitable bandgap (1.55 eV) as solar harvesting material. Its direct bandgap allows energy from the sunlight to be directly transferred from photons to chemical energy. Additionally, its energy band positions align favorably with common charge transporting materials (Figure 2.6b).^[3] Besides strong and broad light absorption, it also exhibits long charge carrier diffusion length and lifetime (Figure 2.6c).^[9, 10] Additionally, its strong optoelectronic properties are not sensitive to the presence of defects due to the antibonding interactions at the valence band maximum.^[48] Taking advantage of these suitable intrinsic properties for photovoltaics mentioned above, the efficiency of PSCs is comparable to that of silicon based solar cells with a much lower production cost.

Figure 2.6 (a) Schematic illustration of film deposition through spin-coating procedures^[47], (b) Schematic energy level diagram of TiO_2 , MAPbI_3 , and spiro-OMeTAD^[3], and (c) charge diffusion length plot versus photoluminescent lifetime quenching ratios for MAPbI_3 perovskite^[9].

Despite the stunning advantages of PSCs, such devices also face a few issues drawing them back from future largescale manufacturing and worldwide commercialization. One key limitation of state-of-the-art PSCs is the use of hazardous element Pb. For instance, in a scenario of solar cell encapsulation rupture, the degradation of perovskites may occur upon water exposure. In this case, Pb^{2+} ions will dissolve into rainwater causing significant environmental impact as well as harming the health of both plants and animals. In addition to the Pb-toxicity issue, PSCs also suffer from the instability against air and moisture. It has been reported that the efficiency of Pb-based PSCs gradually reduced in moist ambient air due to its highly hygroscopic organic component.^[41] Therefore, a key scientific challenge is to eliminate Pb from the perovskite system as well as to improve its air stability.

2.3 Low-toxic metal incorporated perovskites for photovoltaic applications

The reported low-toxic metal incorporated perovskite materials in solar cell devices can be divided into two classes based on the valence of the metal cation substituting for Pb^{2+} ions, as demonstrated in Figure 2.7. One class (the two columns on the left in Figure 2.7) shares the same chemical formula as the organometal halide materials, i.e. AMX_3 (where M denotes single or double divalent cations). By now, Sn-based perovskites have been widely applied as solar harvesters in solar cells.^[49-51] Thanks to the similar ionic radii, Pb^{2+} can be partially substituted by Sn^{2+} , forming $\text{A}(\text{M}_1\text{M}_2)\text{X}_3$ -like binary perovskites.^[52] Additionally,

the computational work also shows the potential of developing Ge-based perovskites for photovoltaic applications.^[53] Except for the elements from the same group as Pb in the periodic table, the family of transition metals allows a wider choice of Pb candidates, e.g. Cu, Co, and Mn.^[54-56] In terms of the other class, Pb^{2+} is substituted by heterovalent metal cations, and the stoichiometric coefficient of A^+ and X^- are adjusted to maintain the charge balance. A_3MX_9 (where M is a trivalent cation) perovskite variant forms when the metal elements from neighboring group of Pb takes place of Pb sites.^[57] Moreover, previous research has shown that Sn-based A_2MX_6 (where the oxidation state of M is +4) perovskite variant can be used as a hole transporting material.^[58] Alternatively, the M site can be occupied by two cations with different valence, i.e. $\text{AM}_1\text{M}_2\text{X}_3$ (where M_1 is monovalent while M_2 is trivalent).^[59] The examples of perovskites from these two classes will be further discussed in details in the following sections.

Figure 2.7 Overview of lead-free perovskite materials, with the oxidation state of the M-site metals highlighted in red.

2.3.1 Lead-free tin-based halide perovskites (ASnX_3)

Remarkably, two groups successfully fabricated completely lead-free tin-based PSCs where a MASnX_3 perovskite was prepared on a mesoporous TiO_2 scaffold, achieving PCE

of 5.73% and 6.4%.^[49, 51] MASnI_3 perovskite possesses a lower bandgap of 1.30 eV compared to the Pb analogue (1.55 eV). In addition, the substitution of iodine with bromine can favorably tune the bandgap energetics of $\text{MASnI}_{3-x}\text{Br}_x$ perovskites.^[51] As shown in Figure 2.8a, the absorption onset exhibited a blueshift from MASnI_3 to MASnBr_3 , indicating that Br incorporation widened the bandgap. Meanwhile, the corresponding device color turned from dark brown for MASnI_3 to transparent yellow for MASnBr_3 . This bandgap tuning behavior can be attributed to the lattice construction which increases metal-halide orbital overlap, thus decreasing the bandgap.^[60] Unfortunately, these Sn-based PSCs suffered from a rapid PCE loss in air as a result of the inherent instability of Sn^{2+} , which poses obstacles to their practical applications.^[61]

Figure 2.8 (a) Tunability of absorbance and color in $\text{MASnI}_{3-x}\text{Br}_x$ perovskites arise from halide substitution;^[51] (b) Photocurrent density-voltage (J–V) characteristics for CsSnI_3 based PSCs with different SnF_2 concentrations;^[62] A statistical analysis of the reported (c) photovoltages and (d) efficiencies of ASnI_3 (A = MA, FA, Cs) based PSCs (updated until 2017)^[63].

Following up on the initial synthesis of MASnI_3 perovskites, Mulmudi et al. successfully replaced MA with Cs to form all-inorganic CsSnI_3 perovskites with a bandgap of 1.30 eV,

as the same as MASnI_3 .^[50] However, CsSnI_3 based PSCs yielded a much lower PCE of 0.0003%, which is primarily attributed to the intrinsic defects present in CsSnI_3 , that is, Sn cation vacancies. As shown in Figure 2.8b, the addition of SnF_2 in the synthesis of CsSnI_3 significantly improved the PCE to 2.02%. It was revealed that SnF_2 additives suppress the oxidation from Sn^{2+} to Sn^{4+} , and thus reduce the concentration of Sn^{2+} vacancies. Since then, the majority of solution-processed Sn-involved perovskites have included SnF_2 in an attempt to counteract the facile oxidation of tin.^[64-67]

A statistical analysis of the photovoltage and efficiency for thus far reported 3D Sn-based PSCs is presented in Figure 2.8c-d, where three types of ASnI_3 are compared based on different A-site cations, being Cs, MA and FA.^[63] Their low average photovoltage of around 0.4 V implies a severe charge recombination which possibly originates from high defect density present in these Sn-based perovskites. In terms of the efficiency, FASnI_3 devices produced higher average PCE (~ 5%) than MASnI_3 and CsSnI_3 devices (~ 2%). The best reported PCE of 8.12% was attained in a $(\text{FA})_{0.75}(\text{MA})_{0.25}\text{SnI}_3$ solar cell, demonstrating the efficiency enhancement by the cation-mixing approach.^[65] Despite the phenomenal properties of Sn-based ASnX_3 perovskites, such as low exciton binding energy^[63], optimal bandgap between 1.2–1.4 eV^[68] and high carrier mobility^[7], several critical challenges have hindered their photovoltaic performance, including poor long-term stability, fast-crystallization induced non-uniform film morphology, short charge diffusion length, and high intrinsic carrier concentration arise from a p-type self-doping^[69].

2.3.2 Lead-tin binary perovskites ($\text{APb}_{1-x}\text{Sn}_x\text{X}_3$)

The first two reports on $\text{MAPb}_{1-x}\text{Sn}_x\text{I}_3$ PSCs were published together in the same year when lead-free MASnX_3 PSCs came out.^[70, 71] Both of them underscored that no phase separation occurred for $\text{MAPb}_{1-x}\text{Sn}_x\text{I}_3$ perovskites regardless of the value of Pb/Sn ratio. These lead and tin alloyed halide perovskites still adopted the classic 3D perovskite structure where the metal site is randomly occupied by either Sn or Pb cation (Figure 2.9a). Moreover, the electrical conductivity of the Pb/Sn alloys was lower than that of the neat Sn analogue by 2 to 3 orders of magnitude (Figure 2.9b). Thus, Pb incorporation into Sn-based perovskites possibly lowers down the intrinsic carrier density to acceptable levels, suppressing charge

carrier recombination. Interestingly, partial Sn substitution in MAPbI₃ perovskite extended the light absorption onset up to 1060 nm (Figure 2.9c). In other words, the optical bandgap was narrowed down to 1.17 eV, which is the lowest value obtained for the whole perovskite family. Notably, an anomalous bandgap behavior has been universally demonstrated in various Pb/Sn binary perovskite systems in which the minimum bandgap occurred at an intermediate composition.^[66, 70, 72, 73] As illustrated in the case of MAPb_xSn_{1-x}I₃ (Figure 2.9b), its bandgap as a function of Pb content showed a bowing trend, instead of an expected linear change. On one hand, a bandgap reduction is resulted from the heavy Pb atom induced spin-orbit coupling in the electronic band structure. On the other hand, a bandgap enlargement is caused by the phase transition towards a more distorted lattice with more Pb²⁺ ions.^[74] Hence, the anomalous bandgap evolution in mixed Pb and Sn perovskites is ascribed to an integral effect of these two competing mechanisms.

Initially, both teams of Kanatzidis and Hayase developed MAPb_{0.5}Sn_{0.5}I₃ solar cells based on mesoscopic device structure using different organic HTMs, and obtained PCEs of 7.27% and 4.18%, respectively, higher than that of the pristine Sn-based PSC.^[70, 71] By adopting the inverted planar device structure as well as doping with chloride ions, PSCs based on MAPb_{0.85}Sn_{0.15}I_{3-y}Cl_y perovskites achieved a higher PCE around 10%.^[75] With the introduction of anti-solvent washing approach, the morphology of perovskite films was effectively controlled, and uniform and compact perovskite films formed. As a result, the PCE was further improved to 14.35% for PSCs with a MAPb_{0.75}Sn_{0.25}I₃ absorber.^[76] Furthermore, a 20% Br incorporation led to an increased bandgap of 1.35 eV and an enhanced PCE of 14.71% for a MAPb_{0.5}Sn_{0.5}(I_{0.8}Br_{0.2})₃ based PSC (Figure 2.9d).^[77] Through a careful control of the perovskite composition, a low bandgap of 1.2 eV has been attained for (FASnI₃)_{0.6}(MAPbI₃)_{0.4} perovskite.^[52] The PCE of the corresponding PSC has been boosted to 17.6% along with a remarkably high photocurrent of 28.5 mA/cm² (Figure 2.9e-f). The record values of photovoltage and photovoltaic efficiency for Pb/Sn binary iodide-based PSCs have been plotted in Figure 2.9g-h, respectively (updated until 2017). Both photovoltage and efficiency reduce systematically as tin content becomes rich, presenting a trade-off between photovoltaic efficiencies and the lead toxicity. Moreover, the reduction of photovoltage with increasing Sn addition implies a growth of charge recombination which possibly correlates to the high defect density in Sn-included

perovskites. Therefore, strategies like interfacial engineering for the enhancement of charge transport at interfaces can be helpful to further improve the efficiency of lead-less tin-based halide PSCs.

Figure 2.9 (a) Crystal structure, (b) optical bandgap and electrical resistivity of MAPb_xSn_{1-x}I₃ perovskites;^[70] (c) Incident photo-to-current efficiency (IPCE) spectra of MAPb_xSn_{1-x}I₃ (x = 0.5, 1) based PSCs;^[71] (d) J-V curves of MAPb_{0.75}Sn_{0.25}I₃ and MAPb_{0.5}Sn_{0.5}(I_{0.8}Br_{0.2})₃ based PSCs;^[77] (e) Cross-sectional SEM image and (f) J-V curves of the best-performing device with a 620 nm (FASnI₃)_{0.6}(MAPbI₃)_{0.4} absorber;^[52] A statistical analysis of (g) photovoltages and (h) efficiencies of PSCs based on APb_{1-x}Sn_xI₃ (where A = MA, FA, Cs or their mixtures, x = 0.2–0.4 for low tin region, x = 0.5 for 50–50 region, and x = 0.6–0.9 for tin-rich region) reported until 2017^[63].

In general, metal substitution dramatically influences the overall optoelectronic properties, since metal cation directly impacts the nature of the band-to-band electronic transition.^[18] Halide substitution has been widely exploited to tune the perovskite bandgap, that is, the bandgap increases as iodine is gradually replaced by bromine.^[78, 79] The A-site cation in the AMX_3 perovskite, as the electronically inactive component, governs the dimensionality of the perovskite structure, and its effect on the bandgap tuning depends on the perovskite materials. Here, the compositional engineering strategy, a careful control on the individual components of the $APb_{1-y}Sn_yX_3$ perovskite, enables the fine tuning of their optoelectronic properties and the optimization of photovoltaic performance for Pb-Sn binary PSCs. Overall, the combination of the reduced toxic lead content, the low bandgaps, the suitable intrinsic carrier concentration, and the high attainable efficiency enables lead-less tin-based perovskites to be promising candidates for photovoltaic applications, especially for the application in tandem configuration as a bottom cell.^[52, 72, 76]

2.3.3 Tin-deficient derived perovskites (A_2SnX_6) with enhanced air-stability

The successful substitution of divalent Pb^{2+} cations by tetravalent tin cations (Sn^{4+}) in the $APbX_3$ perovskite opens up a new horizon for the development of lead-free metal halide perovskites.^[58] This new class of derived perovskites, referred as to A_2MX_6 defect-ordered perovskites, adopts the crystal structure similar to AMX_3 perovskites as illustrated in Figure 2.10.^[80] It can be seen that MI_6 octahedra are discrete in A_2MX_6 structure since half of octahedral Sn atoms in AMX_3 structure are replaced by vacancies (i.e. defects). Alternatively, its formula can be written as $ASn_{0.5}X_3$ where 0.5 indicates the 50% deficient octahedral Sn atoms compared to $ASnX_3$.

Figure 2.10 Crystal structure of (a) $CsSnI_3$ and (b) Cs_2SnI_6 , where the orange octahedra in $CsSnI_3$ structure are replaced by vacancies in Cs_2SnI_6 structure.^[80]

Initially, Cs_2SnI_6 defect perovskites have been employed as a HTM in dye-sensitized solar cells (DSSCs), due to their high conductivity.^[58, 81] DSSC adopts the mesoscopic architecture of PSCs where perovskite absorbers are replaced by dye molecules.^[82] Lee et al. developed DSSCs using Cs_2SnI_6 as HTM and achieved PCE of near 7 %. Except for the top metal contact, the whole device involved Cs_2SnI_6 was fabricated in ambient, indicating these perovskites are highly stable under air and moisture. In addition, solar cells with Cs_2SnI_6 based HTM have shown a long operational stability. As shown in Figure 2.11a, their photovoltaic performance retained almost unchanged over 700 hours, which is better than the reported 500-hour stability of lead based perovskite solar cells.^[2] Thus, air-stable A_2SnI_6 perovskites opens new opportunity for Sn-based perovskites to be reconsidered as a candidate for lead free PSCs.

Later on, Cs_2SnI_6 defect perovskites have been utilized as a light absorbing material in PSCs, regarding their proper band gap and high absorption coefficient. The bandgap of Cs_2SnI_6 is about 1.48 eV which is very close to the bandgap of CsSnI_3 (1.3 eV), MASnI_3 (1.26 eV) and FASnI_3 (1.4 eV).^[68] Qiu et al. fabricated lead-free Cs_2SnI_6 based PSCs in a planar n-i-p device structure and obtained PCE of close to 1% in air.^[83] Nevertheless, these unsealed devices exhibited a severe PCE degradation after 180 hours (Figure 2.11b-c), which could originate from the bias induced material degradation or the instable organic HTM. Through replacing TiO_2 by zinc oxide (ZnO) nanorod arrays as ETM, a slightly lower PCE of 0.857% was achieved.^[84] In addition to the inorganic Cs_2SnI_6 perovskite, Maughan et al. developed hybrid A_2SnI_6 defect perovskites based on the optoelectronically active tropylium ion (C_7H_7^+).^[85] This aromatic organic cation contains a delocalized positive charge and thus is chemically stable as a reactant. $(\text{C}_7\text{H}_7)_2\text{SnI}_6$ exhibits a large absorbance feature, solely due to intramolecular electronic transitions of C_7H_7^+ ions. Thus, the incorporation of the tropylium ion into the inorganic tin-iodide framework enhances the optoelectronic properties.

Figure 2.11 Long-term measurement of the photovoltaic parameters taken at regular intervals as a function of time for (a) Cs₂SnI₆ based DDSCs^[58] (b) & (c) Cs₂SnI₆ based PSCs^[83].

Table 2.1 J–V characteristics of Cs₂SnI₆-incorporated devices with different architectures.

ETM/Absorber/HTM	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	Ref.
TiO ₂ /Z907/Cs ₂ SnI ₆	13.2	0.571	61.3	4.63	[58]
TiO ₂ /N719/Cs ₂ SnI ₆	14.7	0.631	68.1	6.32	[58]
TiO ₂ /multiple dyes/Cs ₂ SnI ₆	16.9	0.623	66.1	6.94	[58]
TiO ₂ /Cs ₂ SnI ₆ /P3HT	5.41	0.51	35.0	0.96	[66]
ZnO/Cs ₂ SnI ₆ /P3HT	3.20	0.52	51.5	0.86	[68]

Developing A₂SnI₆ defect perovskites enables the realization of low-cost, eco-friendly and air-stable PSCs. The photovoltaic parameters of all the Cs₂SnI₆-incorporated solar cells in literature have been summarized in Table 2.1, where Cs₂SnI₆-based PSCs show low PCEs (less than 1%). Future works on introducing other organic cation into A₂SnI₆ structure are expected to help tune optoelectronic properties and improve efficiencies in these solar cells.

2.3.4 Going beyond tin-based perovskite alternatives for lead substitution

Other than Pb and Sn, Ge is another alternative from the group IV metal and its divalent cation (Ge^{2+}) exhibits smaller ionic radii (0.73 Å) than Sn^{2+} (1.1 Å) and Pb^{2+} (1.19 Å). Calculated tolerance factors for CsGeI_3 , MAGeI_3 , and FAGeI_3 are 0.934, 0.965 and 1.062, respectively, indicating the possible formation of their ideal 3D perovskite structures. Stoumpos et al. synthesized a series of Ge-based AGeI_3 perovskites (where A = Cs, MA, FA, etc.) through altering A-site cations and characterized their crystal structure, band gap and nonlinear optical properties.^[86] This work demonstrated the successful formation of 3D perovskite structures for CsGeI_3 , MAGeI_3 , and FAGeI_3 compounds, as indicated by their proper tolerance factors. The theoretical study by Sun et al. indicates that MAGeI_3 is more chemically stable than Sn-analogue but less stable than Pb-analogue, based on the calculated formation energies.^[87] Moreover, MAGeI_3 is predicted to hold better charge transport properties than both MASnI_3 and MAPbI_3 , since its calculated effective mass is the smallest among the three perovskites. D. B. Mitzi compared the optical property of the low-dimensional perovskite series, $(\text{NBT})_2\text{MI}_4$ (NBT = n-buthylammonium), as a function of group IVB element (Ge, Sn, Pb) by photoluminescence (PL) spectroscopy.^[88] A strong red-shift of PL peak (i.e. reduction in bandgap) was observed in the order of $\text{M} = \text{Pb} \rightarrow \text{Sn} \rightarrow \text{Ge}$. At the same time, the peak intensity qualitatively decreased and the peak width increased, which possibly correlates to the greater propensity for oxidation in Sn and Ge based perovskites. This phenomenon further supports that metal substitution can strongly impact the optical property. All of these reports showed a strong motivation for MAGeI_3 perovskite for APbX_3 replacement in PSCs, encouraging further research on exploiting CsGeI_3 , MAGeI_3 , and FAGeI_3 perovskites as light harvesters in real solar cells.

Apart from the perovskites based on group IV metals with AMX_3 or A_2MX_6 structure, bismuth (Bi) based perovskites with A_3MX_9 structure are applicable in photovoltaic devices. Park et al. estimated the optical bandgap value of $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite being around 2.2 eV (Figure 2.12a).^[89] The mesoscopic structured PSCs based on this compound obtained a PCE of 1.09% (Figure 2.12b). Although the efficiency is relatively low, these solar cells without encapsulation show no decay within one month in dark and dry air (humidity below 10%). Furthermore, the excellent air stability of $\text{MA}_3\text{Bi}_2\text{I}_9$ perovskite was

investigated by Hoyer et al. It was observed that its film remained the same visual appearance after exposure to ambient air (humidity around 61%) for 26 days (Figure 2.12c).^[90] Besides Bi, antimony (Sb), as another group V metal element, also demonstrates its applicability as a light absorber in photovoltaics. Saparov et al. successfully incorporated $\text{Cs}_3\text{Sb}_2\text{I}_9$ perovskites with bandgap of 2.05 eV into a planar structured PSC yielding a PCE less than 1%, lower than its Bi analogue (Figure 2.12d-e).^[91] These findings open a new path towards air-stable lead-free PSCs through Bi and Sb-based perovskites and derivatives. Nevertheless, the bandgap of these compounds is generally around 2 eV, contributing to poor photocurrent and thus limiting their role as the principal absorber in photovoltaics.

Figure 2.12 (a) Tauc plots for three kinds of Bi-based perovskites;^[89] (b) J-V curves for PSCs based on A_3BiX_9 compounds;^[89] (c) Stability of MA_3BiI_9 perovskite in air compared to conventional MAPbI_3 ;^[90] (d) Tauc plot for Cs_3SbI_9 perovskite (inset shows the corresponding thin film);^[91] (e) J-V curves for a representative Cs_3SbI_9 based PSC^[90].

In recent years, theoretical investigations using first principles calculation based on density functional theory have explored more and more candidates for Pb replacement in perovskite.^[48, 92, 93] Intensive attentions have been attracted by perovskites based on Ge, Sn, Sb, and Bi ions, which are recognized as defect tolerant compounds. Comparing Sn^{2+} , Ge^{2+} , Bi^{3+} , and Sb^{3+} cations, they all possess an outer ns^2 electrons structure similar to Pb^{2+} ($6s^2$). It has been elucidated that the outer ns^2 electronic configuration of metal cations contributes to shallow defect states at the band edges, leading to a strong optical absorption and an efficient carrier transport in their correlated perovskites.^[12, 94] All in all, these perovskites have a bright future for photovoltaics and more experimental efforts are demanded for accelerating their device performance in the near future.

2.4 Challenges and open questions

Figure 2.13 Efficiency improvements over time for a range of Pb, Sn, Sb, and Bi based solar absorbers (updated until 2016).^[95]

Figure 2.13 summarizes the efficiency record of solar cells using Pb, Sn, Sb, and Bi based materials as solar harvesting materials. In the past few years, the efficiency of these lead-free solar cells has experienced a rapidly increase, largely inspired by the hope of

eliminating toxic element lead. Regarding perovskite materials alone, Pb and Sn based perovskites largely dominate the PSC field thanks to their tunable bandgap, better charge transport properties, and higher film-forming ability for photovoltaic applications. So far, the highest efficiency record of Sn-based PSCs is 9%,^[67] which is still far away from Pb-based PSCs with a certified PCE of 23.3%.^[1] Surprisingly, PSCs based on perovskites combining Pb and Sn achieved 17.6% efficiencies, considered as highly efficient solar cells with reduced toxic content.^[52] Although Ge-based perovskites have been predicted to be a lead-free perovskite light absorber by theoretical study, its application in efficient solar cells is still in its infancy. The application of Sn or Ge-based perovskites is limited by their instability in air, which triggers the development of defect-ordered perovskites with enhanced air stability, such as A_2SnX_6 , A_3BiX_9 and A_3SbX_9 . However, most PSCs incorporating these perovskite derivatives suffered from poor efficiencies lower than 1%.^[57, 83, 91] Hence, the rational design of lead-less perovskites for photovoltaic application would open challenges on playing balance among efficiency, toxicity, and stability. In particular, this thesis study has addressed the following challenges:

- How to develop alternative Pb-free perovskites and incorporate them in PSCs as the light absorbing layer?
- What is the impact of Sn content on the structural, morphological and optoelectronic properties of Pb-Sn binary perovskites? How to control the device performance through compositional engineering?
- Can the Sn-based defect ordered perovskites be applied as light absorbers? How does the A-site cation impact their stability?

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Chapter 3

Experimental Methodology

The objectives of this project require an experimental methodology involving solution-based synthesis, multidisciplinary characterizations on structure, morphology and optoelectronic properties, and photovoltaic application. In this chapter, the rationales for the selection of particular methodologies to address our research objectives are provided. In addition, detailed procedures of synthesizing materials, depositing thin-films and fabricating devices are described. In the end, the working principles underlying the characterization techniques employed are explained and the methods of data analysis are discussed in details.

3.1 Rationale for selection

This project aims to develop rational strategies of experimentally identifying ideal low-toxicity, high-stability perovskite candidates for photovoltaic applications. To fulfill this project objective, firstly a non-toxic metal element (M) is selected to replace lead in the perovskite based on the theoretical studies in the literature. Next, M-based halide perovskites are experimentally synthesized using simple solution-based process. For the study of the compositional effect on the perovskite properties, the ion substitution is applied on the organic / inorganic cation component of the perovskite (Cs^+ , MA^+ , FA^+) or the halide anion component (I^- , Br^-). Following on, the synthesized perovskite materials, in either powder or thin-film form, are characterized on composition, structure, morphology, optical and electrical properties, and stability against air or heat. Lastly, the perovskite thin films are applied in solar cells as the absorber layer, followed by the investigation on their device performance and charge recombination mechanism. Together, the interrelation among composition (depends on the synthesis process), property (measured by the characteristic technique), and application can be understood. A flow chart of the experimental process described above is shown in Figure 3.1.

Figure 3.1 A flow chart to illustrate the experimental process.

At the beginning of this thesis, it has been introduced that the perovskite structure is composed of three components, including the metal cation, the organic / inorganic cation and the halide anion. Each component has both active and passive effects on the tuning of

the crystalline structure, leading to the change of the opto-electronic properties. By tailoring the composition of these three components, the perovskite properties can be controlled to improve the device performance. This method is known as the compositional engineering. A smart combination of these three component is essential to design ideal, environmental-friendly, stable perovskites for photovoltaic applications. In this project, totally three types of perovskites have been investigated, and their compositions are listed as follow.

- I. Germanium-based perovskites, $AGeI_3$ ($A = Cs, MA, FA$)
- II. Lead and tin binary perovskites, $A(Pb,Sn)X_3$ ($A = FA, X = I_{0.8}Br_{0.2}$)
- III. Tin (IV)-based perovskite derivative, A_2SnI_6 ($A = Rb, Cs, MA, FA$)

The following session presents the precursor chemicals purchased, the synthesis procedure of perovskite materials based on Ge^{2+} , Sn^{2+} and Sn^{4+} , and the fabrication process of devices with mesoporous / inverted architecture. In the last session of this chapter, the rationale for the selection of each particular characterization technique used in this project is elaborated, as well as the introduction of the working principle underlying the instrument employed.

3.2 Material synthesis and device fabrication

3.2.1 Chemicals

The following chemicals were purchased from Sigma-Aldrich: tin (II) iodide (SnI_2 , 99.99%), dimethylformamide (DMF, anhydrous 99.8%), dimethyl sulfoxide (DMSO, anhydrous 99.8%), diethyl ether (anhydrous 99.8%), chlorobenzene (anhydrous 99.8%), hydroiodic acid (HI, puriss. p.a. $\geq 67\%$), hypophosphorous acid (H_3PO_2 , 50 wt. % in H_2O), germanium dioxide (GeO_2 , $\geq 99.99\%$), cesium iodide (CsI, 99.999%), tin (IV) iodide (SnI_4 , 99.99%), and rubidium iodide (RbI, 99.999%). The following chemicals were purchased from Dyesol: methylammonium iodide (CH_3NH_3I or MAI), formamidinium iodide ($HC(NH_2)_2I$ or FAI), formamidinium bromide ($HC(NH_2)_2Br$ or FABr), and titanium oxide (TiO_2) paste (30NRD). Lead (II) iodide (PbI_2 , 99.99%) was purchased from Tokyo Chemical Industry (TCI). Poly(3,4-ethylenedioxythiophene) polystyrenesulfonate

(PEDOT:PSS) solution was purchased from Heraeus Limited. Phenyl-C60-butyric acid methyl ester (PC₆₀BM) and bathocuproine (BCP) was purchased from Nano-C. For the substrates used for device fabrication, TEC 7 (6-8 ohm/sq) was purchased from Nippon Sheet Glass. Quartz glass was used for optical measurements in UV-Vis absorption spectroscopy. All the chemicals and substrates listed above were used as received.

3.2.2 Synthesis of Ge-based iodide perovskites

Aqueous HI (1.5 ml) was mixed with deionized water (1 ml) and aqueous H₃PO₂ (1 ml), forming a colorless solution. GeO₂ (104 mg, 1 mmol) was mixed in the solvent mixture and dissolved by heated up to 90 °C using an oil bath. After about 10 min, the solutions turned lemon-like yellow. Three different iodide salts were added in different batch. Upon the addition of solid CsI (260 mg, 1 mmol), a black solid precipitated immediately. Upon the addition of solid CH₃NH₃I (159 mg, 1 mmol), a dark red solid precipitated immediately. Upon the addition of solid HC(NH₂)₂I (172 mg, 1 mmol), an orange solid precipitated immediately. The solutions were cooled down to room temperature without stirring. During cooling, more dark red precipitate and orange precipitate formed while black precipitate remained the same. The solutions went through centrifuge, and the top supernatant solvent was removed. The left crystals were washed with a minimum quantity of dried ethanol. Synthesis was done under inert atmosphere. The final products were dried in vacuum at room temperature for 24 hours, and then immediately transferred into a nitrogen-filled glovebox for thin-film deposition. The precursor solution was prepared by dissolving solid perovskite in DMF at 1M concentration and filtered using 0.2 um filter. The filtered solution was deposited on the TiO₂ substrates by spin coating at 4000 rpm for 30 sec, followed by annealing the samples at 70 °C for 10 min.

3.2.3 Synthesis of Pb-Sn binary mixed-halide perovskites

In this study, the 20% bromide was introduced into the I/Br mixed-halide system via FABr rather than PbBr₂ or SnBr₂. 1 mmol PbI₂ (or SnI₂), 0.4 mmol FAI and 0.6 mmol FABr were dissolved in the mixed solvent of DMF:DMSO (v:v = 4:1) with different volumes, (i.e.

1000 uL, 900 uL, 800 uL, and 700 uL, corresponding to the concentration of 1 M, 1.25 M, 1.43 M, and 1.67 M, respectively). In the precursor of $\text{FASn}(\text{I}_{0.8}\text{Br}_{0.2})_3$, 10 mol% SnF_2 was added as the reductant to suppress the oxidation of Sn^{2+} to Sn^{4+} . The Pb-based and Sn-based precursor solutions of the same concentration were mixed based on the x value to form the compositions required (i.e. $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$, where $x = 0.2, 0.4, 0.6$, and 0.8). The perovskite film was deposited by a single-step spin-coating method with anti-solvent dripping. In brief, the perovskite solution was spin-casted at 5000 rpm for 55 s and diethyl ether was fast dripped onto the spinning substrate. Subsequently, the resulting substrate was annealed at 100 °C for 10 min. When preparing the sample for the UV-Vis absorption scanning, the perovskite film was deposited on Quartz glass. For the other film characterizations, the perovskite film was prepared on glass slice. To minimize the deterioration in air, the perovskite films were coated with a polymer poly(methylmethacrylate) (PMMA) layer by drop-casting.

3.2.4 Synthesis of Sn (IV)-based iodide perovskites

In a typical procedure, 1 mmol SnI_4 were dissolved in the mixed solvent of 10 ml absolute ethanol and 1 ml HI in a 50 ml three-necked flask and kept under a flow of high-purity argon at 60 °C with strong magnetic stirring. When all the orange SnI_4 disappeared, 2 mmol AI ($A = \text{Cs}^+, \text{Rb}^+, \text{MA}^+, \text{FA}^+$) was added into the brown solution. Spontaneously, a black precipitate formed (same color for the four A_2SnI_6 perovskites). Subsequently, the resulting solution was heated up to 100 °C and kept at this temperature for 4 hours. After cooling down to room temperature naturally, the precipitate was isolated via centrifugation at 10000 rpm for 10 min, and the top supernatant solvent was removed. The residual SnI_4 was removed by washing the precipitate with diethyl ether multiple times. In the end, the A_2SnI_6 perovskite was obtained by drying the precipitate in vacuum for overnight. It shall be noted that when synthesizing hybrid perovskites (MA_2SnI_6 or FA_2SnI_6), the addition of 10 mol% excess SnI_4 is necessary for a complete consumption of MAI or FAI.

3.2.5 Device fabrication

In order to protect instable perovskites (i.e. AGeI_3 and $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$) from oxygen and moisture, the fabrication processes involving perovskites were all conducted in a nitrogen-filled glovebox where oxygen (O_2) level is below 0.1 ppm and hydrogen oxide (H_2O) level is less than 5 ppm. The substrate of Fluorine-doped Tin oxide (FTO) coated glass were etched with zinc powder and HCl (2M), resulted in the formation of the desired electrode pattern. All the substrates, including pre-patterned ITO / FTO glass, Quartz and glass slice, were cleaned in Decon soap, deionized water, ethanol and IPA sequentially under ultrasonication. The clean substrate was blew by nitrogen gas, and treated by ozone plasma for 15 min prior to use.

The perovskite solar cells with a mesoporous structure of glass/FTO/ TiO_2 (ETL)/ AGeI_3 or A_2SnI_6 perovskites/Spiro-OMeTAD (HTL)/Au were fabricated through the following steps. Titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-propanol) diluted in ethanol (1:9 v/v) was sprayed on the substrates and sintered for 30 min at 500 °C, forming a blocking layer of TiO_2 (60-70 nm). After cooling to room temperature, the substrates were treated in 40mM TiCl_4 solution for 30 min at 70 °C, followed by the annealing at 500 °C for 30 min. TiO_2 paste diluted in ethanol (2:7 w/w) was spin-coated onto the blocking layer to form a mesoporous TiO_2 layer. The substrates were treated in 20 mM TiCl_4 solution at 70 °C for 30 min and annealed at 500 °C for 30 min prior to transferring into the glovebox. Then the perovskite layer was deposited by the procedures described above. Spiro-OMeTAD was dissolved in chlorobenzene (70 mg/ml) and spin-coated on the substrates, forming a hole transporting layer. Finally, Au electrodes were deposited on these substrates by thermal evaporation.

The inverted planar perovskite solar cells with a structure of glass/ITO/PEDOT:PSS (HTL)/ $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ /PC₆₀BM (ETL)/BCP/Ag were fabricated through the following steps. The as-purchased PEDOT:PSS solution was filtered through a PES membrane (0.45 μm) and spin-casted onto the glass/ITO substrate at 3000 rpm for 60 s. The substrate was then transferred into the glovebox and annealed at 150 °C for 10 min. Subsequently, the perovskite layer was deposited by the procedures described above. Prior

to use, the PCBM solution in chlorobenzene (20 mg/mL) was kept at 70 °C under stirring for overnight. When the perovskite-coated substrate cooled down to the room temperature, the well-dissolved PCBM solution was spin-casted at 2000 rpm for 90 s. Finally, a 8 nm BCP layer and a 70 nm silver layer were evaporated under high vacuum.

3.3 Characterization techniques

3.3.1 Structural and morphological characterization

X-ray diffraction (XRD) is a non-destructive analytical technique and widely used to investigate the atom orientation in the crystalline materials.^[1] In this work, the XRD measurement was performed to understand the crystal structure and evaluate the phase purity of perovskite materials. The XRD patterns (diffractogram) were collected with a Bruker D8 Advance diffractometer (Bragg-Brentano geometry for power samples) equipped with a Cu $K\alpha$ X-ray tube operated at 40 kV and 40 mA, and measured with a step size of 0.02° and a time per step of 1 sec. The Ge-based perovskite powder samples were mounted in a Bruker air-sensitive sample holder. Variable temperature powder XRD patterns were collected on a diffractometer (Cu $K\alpha$ of 40 kV and 40 mA; step size of 0.02°; time per step of 0.5 sec) from room temperature 27 °C to 150 °C. Experimental fitting of the data was carried out from 10-60° 2 θ using *TOPAS V4.1*. The lattice parameters of the AGeI₃ (A = Cs, MA and FA) perovskite were extracted via a Pawley fit and compared with the literature reported values.

The configuration of the XRD working procedure is briefly illustrated in Figure 3.2. When X-rays irradiate on a material, they are scattered by the atoms periodically in a long-rang array in the material (crystal). Depending on the atomic orientation (crystal structure), the X-rays are deflected at specific angle. A detector moves across a range of angles along the goniometer to collect the deflected X-rays. The intensity of X-ray signal detected against the angle of the moving detector yields a unique fingerprint of the atomic arrangement in its crystal structure, known as an XRD pattern or diffractogram. As shown in Figure 3.2, there are two working procedures, Bragg-Brentano geometry^[2] and Grazing incidence^[3], for power and thin-film samples, respectively. In terms of the powder sample, the X-ray

source moves along the goniometer at the same angle as the detector. As for the thin-film sample, when the incident angle is relatively high, the X-ray can penetrate through the film and irradiate on the substrate. As a result, the signals detected at high angles are mainly contributed by the substrate, causing transparency error. Therefore, the X-ray source should be fixed at a low incident angle, which allows a shallow penetration to avoid the substrate. This set-up is referred to as the Grazing incidence configuration.

Figure 3.2 Schematic XRD configuration of Bragg-Brentano geometry^[2] (left panel), and Grazing incidence^[3] (right panel).

Figure 3.3 Pictorial illustration of Bragg's Law^[4] (left panel) and XRD pattern (right panel).

The Bragg's Law describes the diffraction behavior of X-rays corresponding to a crystalline material.^[4] As illustrated in Figure 3.3, the X-ray with a wavelength (λ) close to the interplanar distance (d) in the unit cell can be reflected such that the reflection angle (θ) equals to the incident angle (θ). Meanwhile, the difference in the path length is an integer (n) of the wavelength, as expressed by the equation in the graph (left panel) below. According to this equation, an increase of the lattice spacing leads to a smaller diffraction

angle. As the lattice spacing is affected by the size of the element, when one ion in the material is substituted by another slight larger ion without changing its crystal structure, the XRD peaks will shift toward the left hand side. Hence, XRD analysis is helpful to study the effect of element substitution or doping on the crystal structure.

The analysis of diffractogram can reveal both qualitative and quantitative information, including the crystal structure, the degree of crystallinity, the lattice parameters of the unit cell, and the amount of different phase present in the present sample. In a typical XRD pattern of crystalline material, there are multiple characteristic peaks, corresponding to each crystal plane in the unit cell. The position of these peaks are utilized for qualitative phase analysis and lattice parameter calculation. Additionally, the intensity of these peaks are useful for quantitative phase analysis and the identification of crystal structure and preferred orientation. Moreover, the peak width (or profile) is dependent on the crystalline size strain, and defects. Except for the XRD peaks, the background indicates the amorphous content involved in the material.

Scanning electron microscopy (SEM) is widely used to characterize the microstructure of solid materials in nano-scale using beams of electrons.^[5] In this work, the top-view images of perovskite thin films and cross-sectional images of devices were recorded by a field emission scanning electron microscope (FESEM, JEOL JSM-7600F), at electron accelerating voltage of 5 kV. *Energy-dispersive X-ray (EDX) spectroscopy* was conducted to analyze the chemical composition of the AgI_3 powder samples under an accelerating voltage of 20 kV.

A scanning electron microscope can scan the surface of a material using a focused electron beam, yielding its topographical images.^[6] Typically, it consists of six components, including the electron gun, electromagnet, detector, thick metallic casing, high vacuum pump, and conductive sample holder. Firstly, an electron gun generates a beam of electrons to probe the material surface. For example, a sharply tipped-tungsten filament can emit electrons when a highly powerful electric field is applied close to its tip. Such electron gun is referred to as the field emission gun.^[7] There are other types of electron guns, such as thermionic tungsten, lanthanum hexaboride, field emission, and Schottky emitter.

Secondly, a few electromagnets, acting like the glass lens, converge the electron beam emitting from the electron gun.^[8] When the electrons pass through the electromagnetic coil, a magnetic field is applied to interact with the electrons. By fine tuning the strength of the magnetic field, the electron beam can be bended to precisely focus on the specimen. Thirdly, different types of the detector can collect different signals emitted from different parts of the interaction volume in the material, as pictorially explained in Figure 3.4.^[9] For instance, the secondary electron imaging (SEI) detector collects secondary electrons from the sample surface, yielding topographical information; the backscattered electron (BSE) detector collects high-angle (or back) scattered electrons, revealing the atomic number and phase differences. Additionally, a high vacuum environment is required for the microscope to operate, due to the shallow penetration depth of electrons. Therefore, both rotary pump and diffusion pump are attached to provide an extremely low pressure in the chamber, and also a thick metallic casing is necessary to house the microscope and to protect it from structure disruption. Lastly, a sample holder is required to be conductive. Otherwise, electrons will accumulate at the spot where the specimen is irradiated by the electron beam, causing electron charging.

Figure 3.4 Schematic diagram of the interaction volume in the material irradiated by an electron beam.^[9]

Figure 3.5 Schematic diagram of the interaction between the electron beam and the electron cloud in an element (a) low-angle scattering, (b) high-angle (back) scattering, (c) emission of a secondary electron and characteristic X-ray, and (d) emission of an Auger electron.^[10]

As shown in Figure 3.5, the electron from an electron beam can interact with the electron cloud surrounding the atom in a solid material in different ways, generating different types of signals and providing different information on the material properties.^[10] The electrons ejected from the K-shell of the atom are referred to as secondary electrons, which possess low-energy. The collection of these signals by the SEI detector across a certain area generates a two-dimensional image, representing the topography of the sample surface. In terms of a homogeneous material with a rough surface, different amount of secondary electrons are detected at different regions, due to their different directions facing the detector. The intensity of the signal, depending on the amount of secondary electrons detected, affects the brightness contrast of the SEM images. Therefore, the SEM image can present a three-dimensional appearance of the sample surface.

3.3.2 Compositional characterization

Energy-dispersive X-ray (EDX) spectroscopy is a technique detecting the characteristic X-ray for elemental analysis.^[11, 12] As shown in Figure 3.5c, the interaction between the electron beam and the sample can generate X-ray photons, which possess characteristic energy corresponding to the specific element present in the sample. Such signals are referred to as the characteristic X-ray. They can be collected by the EDX detector and constitute to the peaks in the EDX spectrum. The peak position indicates the species of the elements present in the sample, while the peak area is used to calculate the amount of the corresponding element. The background is mainly contributed by the X-ray photons whose energy level is not related to any existing element.

X-ray photoelectron spectroscopy (XPS) was utilized for the compositional study, since this technique provides quantitative information of stoichiometry and chemical state up to 10 nm of the surface depth.^[13] XPS measurements were carried out using a Theta Probe X-ray photoelectron spectrometer (ESCALab 250i-XL & Thetaprobe A1333) under a base pressure of $< 5 \times 10^{-10}$ mbar and equipped with a monochromatic Al K α (1486.7 eV) X-ray source. In terms of the perovskites with divalent Ge / Sn cations, it was also used to verify the oxidation state at surface. The instable Ge-based samples were directly transferred from glovebox to vacuum sample holder to avoid the degradation induced by air exposure. The restively air-stable Pb-Sn-binary / Sn (IV)-based samples were quickly loaded into the instrument with minimized air exposure.

Figure 3.6 Schematic diagram of the X-ray photoelectron spectrometer working procedure.^[14]

The basic components of a XPS system are displayed in Figure 3.6.^[14] A solid sample is placed in an ultra-high vacuum ($<10^{-8}$ torr) environment. When it is irradiated by a focused beam of X-rays with a particular wavelength or energy (E_{photon}), electrons are excited from their bound states into free electrons, and collected by electron collection lens. These electrons are only emitted from the very top surface of the sample, and the less bound electrons can escape more easily, carrying higher energy (E_{kinetic}). The kinetic energy of the electrons are measured by the energy analyzer, while their counts are measured by the electron detector. During the measurement, a few eV of kinetic energy possibly are absorbed by the detector, which is assigned to an instrumental correction factor ($\emptyset$). XPS spectra are obtained by plotting the counts of electrons and the electron binding energy that was determined using the equation below. By analyzing the peak positions and intensities, the chemical states of the sample and the atomic percentages can be determined.

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \emptyset)$$

Thermogravimetric (TGA) analysis and Differential scanning calorimetry (DSC) characterization were employed to investigate the phase transition, the degradation mechanism and the thermal stability of perovskites.^[15,16] The instrument, TGA Q500 V6.7 (TA Instruments), was used to continuously measure the sample weight over a temperature range from 27 °C to 800 °C at a ramp of 10 °C/min under nitrogen atmosphere. The thermogravimetric data collected was compiled into a plot of weight percentage of initial weight versus temperature, which is known as the TGA curve. Its first derivative was then plotted to determine the temperature of characteristic decomposition. A Q10 V9.9 Build 303 calorimeter (TA Instruments) was used to probe the heat flux from -50 °C to the perovskite decomposition temperature (measured by TGA) at a cooling / heating rate of 10 °C/min under nitrogen atmosphere. In the DSC curve obtained, there are positive and negative peaks, which represent the enthalpy change of exothermic and endothermic reactions, respectively. These enthalpy changes can be attributed to the phase transition of the impurity in the sample.

3.3.3 Optical characterization

UV-VIS-NIR spectrophotometer with an integrating sphere attachment (Shimadzu UV-3600, ISR-3100) was used to record the absorbance (A), transmittance (T) and reflectance (R) spectra of thin film samples in this work. The reflectance standard was a highly refined barium sulfate powder (Wako, pure). This instrument is capable of scanning in the wavelength range of ultraviolet (UV), visible light (VIS), and near infrared (NIR) radiation (i.e. between 190 nm and 3300 nm) at room temperature in air.

A typical spectrophotometer consists of four components, including light source, monochromator, sample compartment, and detector.^[17] The light source involves two lamps, D2 lamp and Halogen lamp, selectively used for the measurement in the UV region (190 to 350 nm) and VIS-IR region (350 to 3300 nm), respectively. The monochromator is applied to select light with a specific wavelength from the dispersed white light generated by the lamp. In the end, the detector collects the light transmitted through the sample or reflected by the sample across a range of wavelength.

Usually the absorbance measurement probes the transmission profile as a function of wavelength, from which the absorbance can be derived according to $A = \log_{10} \frac{1}{T}$, where

T is the ratio between the transmitted light intensity and the incident light intensity, i.e. $\frac{I_t}{I_0}$.

When measuring transmission of thin film samples with rough surface or powdered samples, the light passing through the sample bends due to refraction. As a result, the transmitted beam deviates from the detector surface, causing some inaccuracies. To solve this problem, an integrating sphere shall be attached to the setup. As schematically illustrated in Figure 3.7a, the transmitted beams are repeatedly scattered in the interior of the spherical shell. Its highly reflective sphere wall normalizes the scattered transmitted beams, and all outcome signals are captured by the detector at centre. In addition, the integrating sphere attachment is helpful to measure different types of reflection. The specular reflection refers to that a light beam is reflected symmetrically with respect to the normal line, while the diffuse reflection is known as the reflected beams scattered in different directions on curved surfaces. The measurement of diffuse reflection is shown in

Figure 3.7b. The beam from light source enters the spherical shell through S port with 0° incident angle. As a result, specular reflected beam exists the integrating sphere without being detected, and only diffused reflected beams are collected by the detector. The measurement of total reflection including both diffuse reflection and specular reflection is shown in Figure 3.7c where the incident light comes from R port with a small incident angle. In both measurements, barium sulphate (BaSO_4) white plate is applied for baseline correction which defines 100 $R\%$.

Figure 3.7 Schematic diagram of (a) transmission measurement (b) diffuse reflection measurement and (c) total reflection measurement using an integrating sphere attachment.^[17]

The analysis of the obtained absorbance / transmittance / reflectance spectra can produce the following information:

(i) *Band gap* is interpreted as the difference in energy levels between the conduction band minimum (CBM) and the valence band maximum (VBM).^[18] It can be directly obtained from the absorption spectrum and its value depends on the position of the

absorption onset, at which the absorbance start to increase.

(ii) *Absorption coefficient* (α) influences the penetration distance for the incident light of a particular wavelength in a material, and reveals how readily a material absorbs photons. It can be calculated by the following equations when the thickness of thin film (t) is known.

$$\alpha = 2.303 \frac{A}{t}, \text{ or } \alpha = \frac{1}{t} \ln \frac{(1 - R)^2}{T}$$

(iii) *Tauc plot* is a method that is widely used to determine the band gap energy (E_g). The Tauc relational expression^[19] is given by

$$(h\nu\alpha)^{\frac{1}{n}} = A(h\nu - E_g)$$

where A is a proportional constant and n denotes the electronic transition type of the material. The photo energy ($h\nu$) in eV is related to the incident wavelength (λ) in nm by the equation of $h\nu = 1239.7/\lambda$. As for the direct allowed transition type, the value of the exponent n is $1/2$. A plot of $(h\nu\alpha)^2$ versus $h\nu$ can be established, where a tangent line at the inflection point intersects the horizontal axis, and the value of E_g can be estimated from this point of intersection.

(iv) *Urbach energy* (E_U), which is also referred to as the band tail energy, indicates the energy width of the absorption edge.^[20] It is weakly dependent on the temperature but associated with the crystallization and the disordering of the material. The empirical Urbach rule describes that the absorption coefficient at around the absorption edge is an exponential function of the photon energy at a certain temperature, as expressed in the equation below, where is α_0 a constant.

$$\alpha = \alpha_0 e^{\frac{h\nu}{E_U}}$$

The exponential tail, which is known as Urbach tail, presents in the disordered and low crystalline material due to the localized states dispersed in the band gap. By plotting the logarithm of absorption coefficient ($\ln \alpha$) against photo energy ($h\nu$), E_U can be estimated from the slope of the linear portion at the absorption edge, i.e. $E_U^{-1} = \Delta(\ln \alpha)/\Delta(h\nu)$.

Transient absorption spectroscopy (TAS) measurement was performed to understand the photo-excited charge carrier dynamics. In a transient absorption spectrometer, an oscillator produces a short laser pulse (femtosecond for ultrafast TAS) at a wavelength where the sample exhibits a strong absorption. This beam is then split into two components: one is so-called pump beam which optically excites the sample in ground state; the other is probe beam with a low intensity and will arrive at the excited sample with a delay time (τ) relative to the pump beam, as shown schematically in Figure 3.8.^[21] Herein, a HeliosTM setup (Ultrafast Systems LLC) with chirp-correction was employed to collect TA signals. The probe beam (white light continuum in the range of 400 – 800 nm) was generated from a sapphire crystal (3 mm) using a Coherent LibraTM laser system (150 fs FWHM, 80MHz repetition rate, 800 nm fundamental wavelength). The diameter of spot size is ~ 1 mm. The TA signal is given by the difference in absorption induced by the pump and probe beams (ΔA). The TAS spectrum of ΔA versus wavelength contains information on the dynamic processes occurring in the sample under study, e.g. band-to-band transition, photoinduced transition and simulated emission. Additionally, the TAS spectrum of ΔA versus τ is beneficial to measure how long the charge carrier exists, i.e. carrier lifetime.

Figure 3.8 Schematic depiction of TAS working procedure.^[21]

3.3.4 Valence band maximum measurement

Photoelectron spectroscopy in air (PESA) was conducted by using a Riken Keiki AC-2

PESA spectrometer with a power setting of 800 nW and a power number of 0.33. This instrument combines an open counter as the electron detector with an ultraviolet (UV) source to characterize the sample surface within 20 nm in the air, as shown in Figure 3.9. When the UV energy gradually accumulates at the sample surface, the electron at the highest occupied molecular orbital (HOMO) start to excite and emit at a certain energy level. The yield of photoelectrons versus the excitation energy provided by the UV source constitutes the photoelectron spectrum. As illustrated in Figure 3.9, the work function is estimated by the position of the intersection point between the horizontal baseline and the linear fitting of the inflection. The slope of the fitted line depends on the film thickness. As the film becomes thinner, more photoelectrons can easily escape from the bulk, resulting in higher yield and larger slope.^[22,23]

Figure 3.9 Schematic diagram of the PESA working procedure (left panel) and a typical photoelectron spectrum (right panel).^[22, 23]

3.3.5 Electrical characterization

Hall effect measurement was carried out to estimate the carrier mobility and carrier density of perovskites using a MMR technologies hall measurement system in a four-probe configuration. The thin-film samples with four square electrodes ($1.6 \text{ mm} \times 1.6 \text{ mm}$) of gold in square geometry ($1 \text{ cm} \times 1 \text{ cm}$) were measured in air at room temperature (302 K). A long, thin bar of semiconductor is present in a combination of magnetic field (B) and electric field (E), which are perpendicular to each other.^[24] When an electron inside the

semiconductor moves with a velocity (v) along the E direction, it experiences a Lorentz Force normal to both fields, $-q(E + v \times B)$. As a result, the electron drifts away from the E direction to the sample side. The accumulation of such electrons leads to a potential reduction across the two sides of the sample, known as the Hall voltage (V_H). With the measured V_H and known values of B and current (I), the sheet density can be determined, n_s or $p_s = IB/qV_H$. With the sheet resistivity (R_s) measured by the van der Pauw technique^[25] and the known value of layer thickness (d), the carrier density (bulk) and mobility can be calculated based on the following equations.

$$\text{carrier density, } n = \frac{n_s}{d}, \text{ or } p = \frac{p_s}{d}$$

$$\text{mobility, } \mu = (qn_s R_s)^{-1}, \text{ or } \mu = (qp_s R_s)^{-1}$$

The photovoltaic performance of solar cells were characterized by both photocurrent density-voltage (J-V) curves and incident photon-to-current efficiency (IPCE) spectra. The I-V curves were measured by an Agilent 4155C analyzer under AM 1.5G (100 mW/cm²) intensity illumination generated from an AAA graded solar simulator (San-EI Electric, XEC-301S) with a 450 W Xenon lamp (model 81172, Oriel). A reference cell (Oriel PN91150V) was applied for calibration. The IPCE spectra were measured using a lock-in amplifier (Stanford Research Systems, SRS 810) with a white light channeled from a Newport 300 W Xenon lamp, and passing through a 17 Hz mechanical chopper wheel and a monochromator (Oriel Cornerstone 130). DC mode was applied without bias light.

By applying voltage across the solar cell and measuring the current response of the solar cell, a few primary photovoltaic parameters can be extracted from the photocurrent density-photovoltage (J - V) curve (Figure 3.10), listed as follows.^[27]

(i) *Short circuit current density* (J_{sc}) describes the maximum current density of a solar cell under the zero-resistance loading condition, and its value is determined at $V = 0$.

(ii) *Open circuit voltage* (V_{oc}) describes the maximum voltage supplied by a solar cell, and its value is determined at $J = 0$.

(iii) *Fill factor* (FF) describes how large the maximum power is in respect to the product of the V_{oc} and J_{sc} . Its value is calculated by

$$FF = \frac{P_{max}}{J_{sc} \cdot V_{oc}} = \frac{J_{P_{max}} \cdot V_{P_{max}}}{I_{sc} \cdot V_{oc}}$$

in accordance to the ratio between the maximum rectangular area under the J - V curve and the full rectangle expanded by the V_{oc} and J_{sc} values.

(iv) *Power conversion efficiency (PCE)* describes how much power of the incident light can be converted to the electric power, and its value is calculated by

$$PCE = \frac{P_{max}}{P_{light}} = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_{light}}$$

where P_{light} is the incident power of the sunlight.

Figure 3.10 J - V curve of a typical solar cell in the dark and under illumination.^[28]

The *ideality factor* (n) can be used to identify the dominant type of the recombination mechanism.^[29] In the extreme cases, $n = 1$ represents bimolecular (radiative) recombination, and $n = 2$ indicates Shockley-Read-Hall (SRH, monomolecular, non-radiative) recombination. To estimate the value of ideality factor, the light dependent I - V measurement was carried out, where I - V curves were recorded under different light intensity (controlled by light filter). Then V_{oc} was plotted against the logarithm of light intensity (L) and a linear fit was established. The ideality factor n can be calculated from the slope of the fitted linear line by the equation below, where k_B is the Boltzmann constant, q is the unit charge, and T is the temperature.

$$n = \frac{q}{k_B T} \cdot \frac{\Delta V_{oc}}{\Delta \ln(L)}$$

The external quantum efficiency (EQE) spectrum, which is also known as IPCE spectrum, provides information about how efficiently photons are converted to electrons by the solar cell under study in the wavelength range of interest. As shown in Figure 3.11, a typical EQE measurement setup consists of the following components: light source, chopper wheel to change the light frequency of the on-off pattern, monochromator to select light of a particular wavelength interval, lock-in amplifier to lower the signal-to-noise ratio, light detector, current meter, and a monitor cell of which the EQE at each wavelength is known.^[30] During a test, two identical monochromatic light beams are incident on the test cell and monitor cell individually, and a computer records the current produced by them (I and I_{ref}). Hence, the EQE of the test cell can be determined as $EQE_{ref} \cdot I/I_{ref}$.

Figure 3.11 Schematic setup of a typical EQE measurement system.^[30]

According to the EQE spectrum, the cut-off at long wavelengths corresponds to the electrical bandgap of light absorber, which is supposed to match with its optical bandgap extracted from absorption spectrum. When the EQE measurement is performed under short circuit condition, J_{sc} can be determined from EQE spectrum by integrating across all the relevant wavelength, described as

$$J_{sc} = -q \int_{\lambda_1}^{\lambda_2} \phi_{\lambda}^{1.5AM} EQE(\lambda) d\lambda$$

where $\phi_{\lambda}^{1.5AM}$ is the spectral photon flux. Compared to the J_{sc} determined by J - V measurement, it is independent of the spectral shape of the used light source and the shading mask applied.

The *electrochemical impedance spectroscopy (EIS)* is a powerful technique applied widely to gain a deep insight into the recombination dynamics inside complete solar cells.^[31] It records the linear alternating current ($I(\omega)$) as a function of frequency (ω) in response to a small-amplitude alternating voltage ($V(\omega)$) applied on the solar cell. The impedance ($Z(\omega)$) refers to the frequency domain ratio of the voltage to the current. It can be represented as a complex quantity involving resistance as the real component ($Z'(\omega)$) and reactance as the imaginary component ($Z''(\omega)$), as described in the following equation with j as the imaginary unit.

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = Z'(\omega) + j \cdot Z''(\omega)$$

Figure 3.12 Example of (a) Nyquist plot and (b) the equivalent circuit used for fittings (solid lines). R_s represents the series resistance. The sum of R_1 and R_2 results in the total recombination resistance. C_s and C_g account for the surface accumulation capacitance and the geometrical capacitance, respectively.^[32]

As for data analysis, the EIS spectrum can be drawn as Nyquist plot where $Z'(\omega)$ is plotted against $Z''(\omega)$, and further be fitted to an equivalent circuit comprising the internal resistive and capacitive response elements (Figure 3.12). It is likely to connect these response elements to different charge dynamic mechanisms that might take place at differentiated layer / interface of the solar cell. By the equivalent circuit analysis of solar cells, recombination resistances can be collected to understand the effect of carrier recombination losses on the photovoltaic performance.

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Chapter 4

Developing lead-free perovskites based on germanium as light harvesting materials in solar cells

Germanium (Ge) has been predicted by the computational screening as a promising nontoxic element to replace lead (Pb) in halide perovskite materials as light harvesters. By adopting A-site cation substitution, three lead-free iodide perovskite materials with chemical formulae of $A\text{GeI}_3$ ($A = \text{Cs}$, CH_3NH_3 or $\text{HC}(\text{NH}_2)_2$) have been synthesized successfully. These compounds display bandgaps correlated with the A-site cation size and show thermal stability up to 150 °C. The hybrid perovskite $\text{CH}_3\text{NH}_3\text{GeI}_3$ -based solar cells yield higher efficiencies than the all-inorganic perovskite CsGeI_3 -based devices, but both are limited by rough and discontinuous film morphologies and oxidation-induced instability. The present work demonstrate a rational strategy for developing lead-free perovskite-based light harvesting materials by combining computational screening and experimental efforts.

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4.1 Introduction

Following up on initial synthesis of CsPbX_3 ($X = \text{Cl, Br or I}$) perovskites, Weber et al. successfully replaced inorganic cesium cations (Cs^+) with organic methylammonium cations (CH_3NH_3^+), opening up a new horizon for the development of inorganic-organic metal-halide perovskite materials.^[1] In the past decade, major breakthroughs have come with this series of materials in photovoltaic applications, leading to a rapid increase in the interest on these materials.^[2-4] The efficiency of devices based on inorganic-organic perovskites has leapt from 3.8% to the most recent highest certificated value of 23.3%.^[5-8] This value has surpassed the efficiencies of devices based on amorphous silicon and is almost on par with those using cadmium telluride (CdTe), or copper indium gallium selenide (CIGS).^[9, 10] With such promising device efficiency, low cost of starting materials and simple solution processing, inorganic-organic halide perovskites are an attractive alternative to conventional photovoltaics. However, the Pb-toxicity issue of current perovskite based photovoltaic devices is regarded as a key concern for future large-scale manufacturing and commercialization. Provided that the solar cell encapsulation ruptures, Pb ions may dissolve into rainwater causing significant environmental detriment. In this context, future commercial utilization requires the replacement of Pb in the perovskite structure, while maintaining analogous optical and photovoltaic performance.^[11, 12]

High-throughput computational methods based on density-functional theory (DFT) have been used to screen for candidate inorganic halide perovskites AMX_3 , with desirable bandgaps and chemical stability. A total of 360 AMX_3 chemical compositions were considered, with monovalent A^+ and X^- ions chosen from 3 alkali metals (K, Rb and Cs) and 3 halogen elements (Cl, Br and I), respectively, in combination with 40 candidate divalent M^{2+} cations. The bandgaps predicted from the calculations are illustrated in Appendix Figure A.1, which are expected to underestimate the true values measured experimentally. From the results of the computational screening exercise, considering only the calculated bandgap values, totally 9 candidate compositions have been identified. The thermodynamic stability of these compositions were further evaluated with calculated energies to determine whether the AMX_3 compositions would decompose to simpler binary phases. As a result, only three compounds, namely RbSnBr_3 , CsSnBr_3 and CsGeI_3 , are

predicted to be energetically stable and exhibit bandgaps suitable for light harvesting. In the literature, Sn-based perovskites have been considered to a much greater degree than Ge-based halide perovskites.^[13] Therefore, subsequent experimental efforts shall be devoted to the potential applications of Ge-based halide perovskite compounds for solar cells.

In this work, three Ge-based iodide perovskite compounds (AGeI_3 , $A = \text{Cs, MA, FA}$) have been successfully synthesized. Prior to the incorporation into real devices, the fundamental photovoltaic properties of these compounds were characterized. The obtained results demonstrate that CsGeI_3 and MAGeI_3 are suitable for light harvesting owing to their stable crystal structure, desirable bandgap and strong thermal stability. Nevertheless, all of the three AGeI_3 compounds suffered from poor film morphology and strong propensity for germanium oxidation, contributing to low efficiencies of the corresponding solar cells. With further enhancement on the photovoltaic performance, Ge-based halide perovskite materials are expected to be applied in photovoltaic devices requiring wide bandgap, such as the top cell in tandem configuration.

4.2 Development of germanium-based iodide perovskites

4.2.1 Crystal structure and phase transition

Experimentally, all-inorganic perovskite CsGeI_3 was initially synthesized using a simple solution-processing method where hypophosphorous acid was applied as a strong reducing agent in chemical synthesis. Through the replacement of Cs^+ with methylammonium (MA^+) and formamidinium (FA^+) cations at A-sites, two alternative hybrid perovskites (MAGeI_3 and FAGeI_3) were further fabricated. The powder X-ray diffraction (XRD) patterns of fresh prepared AGeI_3 ($A = \text{Cs, MA, FA}$) crystals are shown in Figure 4.1a. The main peaks in the three different compounds can all be indexed as trigonal cells. These single-phase samples adopt rhombohedral symmetry ($R3m$ space group symmetry) at room temperature (Figure 4.1b), which is in good agreement with the previous reports.^[14,15]

Figure 4.1 Pawley fit of the powder X-ray diffraction patterns of (a) CsGeI₃, (b) MAGeI₃ and (c) FAGEI₃ perovskites; (d) Schematic crystal structure of AGeI₃ (A =Cs, MA, FA) perovskite, where red balls denote A-site cations, green balls denote Ge cations, and blue balls denote I anions.

In order to study their phase transition, variable temperature XRD measurements have been performed. Based on the XRD patterns at various temperatures, both lattice parameters and lattice angle of rhombohedral unit cells at room temperature have been extracted and plotted in Figure 4.2. At room temperature, CsGeI₃ adopting rhombohedral crystal structure ($a = 5.98 \text{ \AA}$ and $\alpha = 88.6^\circ$), is very close to the cubic perovskite structure considered in the calculations ($a = 5.99 \text{ \AA}$ and $\alpha = 90^\circ$). The replacement of Cs with larger MA or FA molecules leads to a rhombohedral angle (α) that is further away from 90° . The increased structural distortions due to cation replacement are also consistent with the prediction based on empirical perovskite tolerance factors which shows a larger deviation from one with larger A-site cation.

Figure 4.2 (a) Lattice parameter and (b) lattice angle of rhombohedral crystal structure for AGeI₃ (A =Cs, MA, FA) perovskites at different temperatures.

Many of the halide perovskites exhibit multiple phase transitions at temperature ranges achievable by a solar cell under external operating conditions. This structural phase transition is expected to influence the electronic band structure of the material and therefore impact the photovoltaic properties. The long-term stability of the device may also have an effect because of the change in volume of the crystal.^[16] Contrastingly, variable temperature XRD measurements in the germanium halides reveal no structural change to a higher symmetry cubic system for any of the Ge samples investigated (Figure 4.2). For each perovskite, an increase in temperature resulted in a corresponding increase in angle α towards 90° . However complete sample decomposition was observed before a 90° angle, and hence a cubic system could not be obtained. Although the perovskite tolerance factor can be a useful guide to predict the stability of the perovskite structure-type, it does not take into account distortions arising from electronic contributions, e.g. the influence of stereochemically active ns^2 lone-pair electrons that generally become more pronounced through the Pb^{2+} , Sn^{2+} and Ge^{2+} series. In this context, detailed structural investigations are still required to elucidate the symmetry properties of these materials, and will form part of our future work.^[17]

Figure 4.3 (a) Thermogram of AGeI_3 ($A = \text{Cs}, \text{MA}, \text{FA}$) perovskites, (b) Differential scanning calorimetry of representative CsGeI_3 perovskite.

Thermal stability of all three Ge-based perovskite compounds have been studied through thermogravimetric analysis (TGA). Their TGA curves collected under nitrogen atmosphere are demonstrated in Figure 4.3a. CsGeI_3 shows higher stability (up to around 350°C) in comparison with the other two hybrid perovskites (up to around 250°C). MAGeI_3 follows

a single step degradation pathway. This single step could account for the sublimation of the perovskite, but when the material was heated in a glass petri dish at around 250 °C (in an inert atmosphere) white fumes were released first, immediately followed by orange fumes. So it is clear that MAGeI_3 decomposes first and the decomposed product goes in to vapour state. Comparatively, FAGeI_3 exhibited less stability and follows a two stage degradation pathway where the first weight loss of 44 % was consistent with the complete transformation to GeI_2 . Differential scanning calorimetric analysis of CsGeI_3 demonstrates its stability in the range of device working temperatures (Figure 4.3b).

4.2.2 Optoelectronic properties depending on the A-site cation

The band gap of each Ge-based perovskite compound has been determined by the Tauc plot shown in Figure 4.4a. With increasing size of the A^+ cation in the structure, the colours of the compounds change from black to red and then orange for Cs^+ , MA^+ and FA^+ based perovskites. The estimated values of band gap derived from Tauc plots is 1.63 eV, 2.0 eV and 2.35 eV for CsGeI_3 , MAGeI_3 and FAGeI_3 , respectively. The experimentally measured bandgap of CsGeI_3 is about 0.4 eV higher than CsSnI_3 , which agrees well with the trends in the calculated PBE bandgaps. The computed band structure of cubic CsGeI_3 , as well as projected density of states, is plotted in Figure 4.4b, where the energy of highest occupied state is set as 0 eV. It can be seen that a direct band gap is located at the R-(0.5, 0.5, 0.5) point of the Brillouin zone. The valence band maximum is primarily Ge-s in character, with some hybridization with I-s states, while the character of the states at the conduction band minimum is dominated by Ge-p states. This suggests that the light absorption would result in an electronic transition that would occur mainly between Ge bonding and antibonding orbitals. This kind of “intra-atomic” band gap structure in general leads to the anomalous band gap behaviour, where increase of the lattice constant will give rise to further energy splitting between these orbitals and corresponding increase in the bandgap of the materials (as noted within these germanium based perovskites). The band gap deformation potential $a_g = dE/d \ln a$ is calculated as 10.05 eV, which is larger than the values reported for Sn-based perovskites.^[18] This suggests the potential for larger bandgap tuning by cation substitution in Ge-based perovskites.

Figure 4.4 (a) Optical absorption spectrum of CsGeI₃, MAGeI₃ and FAGEI₃, in comparison with CsSnI₃, (b) Calculated band structure and projected density of states of CsGeI₃.

Photoemission spectroscopy in air was used to measure the valence band energy level of all these three Ge-based perovskite compounds and the result is shown in Figure 4.5a. The measured values of valence band maximum (VBM) of CsGeI₃, MAGeI₃ and FAGEI₃ perovskites are -5.10, -5.2, and -5.5 eV, respectively. According to the observed optical band gap values, the conduction band minimum (CBM) are calculated, being -3.47, -3.2 and -3.15 eV, respectively, as shown in Figure 4.5b. The replacement of Cs with MA and FA molecules decreases the valence band level and this follows the same trend as in other metal halide systems.^[11,19,20]

Figure 4.5 (a) Photoelectron spectroscopy in air (PESA) of powder samples, (b) Schematic energy level diagram of CsGeI₃, MAGeI₃ and FAGEI₃ perovskites.

4.2.3 Morphological features of perovskite thin-films

SEM images of top view of the three Ge-based perovskite thin films have been taken to investigate their morphology, as shown in Figure 4.6. These films were fabricated with the semi-transparent solutions of perovskites in dimethylformamide (DMF) solvent. Comparing these three films, FAGEI₃ film is the worst where particles aggregated together. Although CsGeI₃ and MAGEI₃ films are better than FAGEI₃ film, none of them completely cover the mesoporous TiO₂ substrate. A number of pin holes can be clearly observed, which can lower the device performance. Other organic solvent, such as dimethyl sulfoxide (DMSO), have been tried to dissolve these Ge-based iodide compounds, and however this did not solve the problem.

Figure 4.6 SEM images showing top view of thin film of (a) CsGeI₃, (b) MAGEI₃, and (c) FAGEI₃ perovskites.

The dissolution of Ge-based perovskites in most organic polar solvents is not satisfactory due to the presence of hygroscopic phosphorous oxoacids as confirmed by FTIR spectrum results. The FTIR spectra of MAGEI₃ has been compared to the spectra of both H₃PO₂ and H₃PO₄. As shown in Figure 4.7a, the three curves overlap at 1000 cm⁻¹ wavenumber. Their presence can be further proved by the XPS narrow scan for P 2p, of which the result is shown in Figure 4.7b. Phosphorous acid (added as a reducing agent) with its OH group is involved in hydrogen bonding with iodide, making it very challenging to extract it.

Figure 4.7 (a) FTIR spectra of MAGeI₃ and phosphoric oxyacid, (b) XPS narrow scans of CsGeI₃ and MAGeI₃ for P 2p.

4.3 Development of solar cells based on germanium iodide perovskites

Figure 4.8 SEM images showing the cross-section view of device.

Both CsGeI₃ and MAGeI₃ compounds have been further applied in mesoscopic structured solar cells, where Ge-based perovskite was processed on a mesoporous TiO₂ scaffold, and compact TiO₂ and spiro-OMeTAD were employed as electron- and hole-selective contacts, respectively. The cross-sectional SEM image of a typical device architecture is presented in Figure 4.8. It can be seen that large voids lie at the interface of perovskite/ spiro-

OMeTAD, indicating a weak contact between these two layers, possibly arise from the high roughness of the perovskite layer. The current density-voltage (J - V) characteristics of AGeI_3 ($A = \text{Cs, MA}$) based photovoltaic devices are shown in Figure 4.9a, and the photovoltaic parameters are summarized in Table 4.

Figure 4.9 (a) J - V curves of photovoltaic devices fabricated with different Ge-based halide perovskites, (b) IPCE spectrum of MAGeI_3 device.

Table 4.1 Photovoltaic performance parameters of perovskite solar cells based on CsGeI_3 and MAGeI_3 materials under simulated full sunlight of $100 \text{ mW}\cdot\text{cm}^{-2}$.

Perovskites	$J_{\text{sc}} (\text{mA}\cdot\text{cm}^{-2})$	$V_{\text{oc}} (\text{mV})$	FF (%)	PCE (%)
CsGeI_3	5.7	74	27	0.11
MAGeI_3	4.0	150	30	0.20

The champion devices exhibit photocurrent density of $5.7 \text{ mA}\cdot\text{cm}^{-2}$ and $4 \text{ mA}\cdot\text{cm}^{-2}$ for CsGeI_3 and MAGeI_3 compounds respectively as shown in Figure 4.9a. These values are encouragingly higher than that derived from the pristine Sn-based perovskite compounds. However, the solar cells suffered from very poor open circuit voltages. The poor photovoltages could be attributed to Ge^{4+} formation by oxidation which is supported by XPS measurements as shown in Figure 4.10. Due to the poor film quality of FAGeI_3 , its corresponding solar cells did not show any photocurrent (Figure 4.6). Due to the instability of CsGeI_3 film in ambient atmosphere, only IPCE measurements of MAGeI_3 device were successfully performed (Figure 4.9b). It can be seen that the device was responsive from about 620 nm and the integrated photocurrent ($3.7 \text{ mA}\cdot\text{cm}^{-2}$) corresponded well with the

J-V characteristics measured short circuit current density ($4 \text{ mA}\cdot\text{cm}^{-2}$). New preparation methods of Ge-based perovskite without phosphoric oxyacid and under a strict control of synthesis atmosphere, precursors may lead to significant improvement of the film quality along with the device performance.

Figure 4.10 XPS narrow scans of CsGeI_3 and MAgGeI_3 for Ge 2p.

4.4 Conclusions

In summary, high-throughput computational screening has suggested that germanium can work as a suitable substitution for lead in AMX_3 halide perovskite materials for solar cell applications. Experimentally CsGeI_3 crystals with stable rhombohedral crystal structures have been synthesized, which do not show phase changes in the range of device working temperatures. Furthermore, MAGeI_3 and FAGeI_3 crystals have been synthesized and compared with CsGeI_3 crystals in terms of their crystal structure, band gap, and thermal stability. The photocurrent values of 5.7 and $4 \text{ mA}\cdot\text{cm}^{-2}$ were displayed by the solar cells based on CsGeI_3 and MAGeI_3 , respectively. The poor photovoltage governed poor device efficiencies could be attributed to their poor film quality and high tendency to oxidation of Ge^{2+} . Overall, the results of the present study demonstrate potential applications for Ge-based halide perovskite compounds in photovoltaic devices, in a good agreement to the prediction from the computational screening.

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Chapter 5

The Function of Tin Substitution in Formamidinium-based Mixed-halide Lead-Tin Binary Perovskite Solar Cells

A series of lead-tin binary perovskites containing 20% bromine ($\text{FAPb}_{1-x}\text{Sn}_x\text{I}_{2.4}\text{Br}_{0.6}$) have been comprehensively investigated to understand the function of Sn substitution. The Pb-Sn binary perovskites have demonstrated enhanced phase purity, surface coverage, and absorption coefficients, significantly surpassing pure Pb or Sn based perovskites. The mixed-Pb-Sn-based PSCs exhibited suppressed charge carrier recombination and lower potential losses as compared to pure Pb or Sn based PSCs. Ultimately, an optimal Sn substitution of $x = 0.4$ with an ideal bandgap close to 1.4 eV have yielded PCEs up to 10.1% in ambient air, demonstrating a potential path towards low-toxicity and high-efficiency PSCs based on Pb-Sn binary mixed-halide perovskites.

5.1 Introduction

In comparison to Ge-based perovskites, Sn-based perovskites possess lower bandgap and higher stability. Over the last few years, Sn-based PSCs have achieved dramatic progresses in the power conversion efficiency (PCE) enhancement. However, its highest value reported to date is still far away from the record of Pb-based PSCs. Lately, the combination of formamidinium tin iodide (FASnI₃) and methylammonium lead iodide (MAPbI₃) has exemplified highly efficient PSCs with a low content of toxic Pb.^[1] Later on, it was revealed that introducing bromine (Br) into Pb-Sn binary iodide perovskites suppressed trap-assisted recombination, contributing to the high photovoltage.^[2] The compositional engineering has been utilized to fine-tune the structural, morphological, and optoelectronic properties of AMX₃ perovskites via tailoring organic / inorganic cations (A⁺), metal cations (M²⁺), and halide anions (X⁻).

Nearly all the recorded highly efficient PSCs based on either Pb or Sn to date are dominated by FA rather than MA at A-sites.^[3-6] Meanwhile, most highly efficient Pb-containing PSCs encompass 10–20% of Br incorporation at X sites.^[2, 7-9] Snaith et al. reported that varying halide ratio between Br and I in formamidinium lead trihalide perovskites enabled broad bandgap tunability and voltage enhancement.^[10] Nevertheless, excess Br incorporation in FAPb(I_{1-x}Br_x)₃ (0.3 < x < 0.6) system caused the formation of yellowing films, indicating Br-induced structural instability. This problem was solved by mixing Cs with FA, which slightly widened the bandgap and weaken the absorption.^[11] Alternatively, Sn incorporation was found to greatly improve the photostability of MAPbI_{3-x}Br_x perovskites.^[12] Therefore, we proposed to partially substitute Pb²⁺ with Sn²⁺ in FAPb(I_{0.8}Br_{0.2})₃ system for improving phase stability, together with the reduction of Pb usage.

In this work, the bromide was introduced into the crystal lattice though FAPbI₃ regarding its higher solubility in comparison with PbBr₂ and SnBr₂. We have systematically investigated the compositional effect of Sn content on the structural, morphological, and optical properties of FAPb_{1-x}Sn_x(I_{0.8}Br_{0.2})₃ perovskites films. Compared to pure Pb or Sn perovskites, Pb-Sn binary perovskites demonstrated single perovskite phase, homogenous

films with higher surface coverage, and smaller bandgap approaching the optimal bandgap (1.1–1.4 eV). Furthermore, we incorporated $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskites into an inverted planar device architecture, and studied the recombination mechanism in the resultant PSCs with the aid of in-depth spectroscopic characterizations. The optimal Sn content in the studied Pb-Sn binary system was found to be $x = 0.4$, where the perovskite exhibited proper band alignment with its charge selective contacts and less recombination in its devices. As such, the highest PCE of 10.1% has been achieved with a negligible hysteresis. Our work paves the way for further development of environmentally benign and highly efficient Pb-less PSCs via compositional engineering.

5.2 Compositional effect of tin content in $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskites

The elemental composition of $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ (where x denotes the Sn content given by the precursors, and $x = 0, 0.2, 0.4, 0.6, 0.8$, and 1.0) was investigated by X-ray photoelectron spectroscopy. The as-deposited perovskite films were sealed in a N_2 atmosphere bag during transportation and immediately loaded into XPS instrument with minimized air exposure. Nevertheless, the XPS peak of Sn 3d core level for all Sn-containing samples exhibited two chemical states (Sn1 and Sn2) as given by Appendix Figure A.2a-e, indicative of air induced oxidation. The chemical state of Sn1 at ~ 486 eV potentially originates from Sn^{2+} while Sn2 at a higher binding energy of ~ 487 eV is likely to be Sn-Br oxide.^[13] The much lower peak of Sn2 compared to Sn1 implies that Sn oxidation was maximally suppressed owing to the fast loading process. It is generally known that the elemental composition reflected by XPS correlates with the material within ~ 10 nm of the surface depth. To further study the elemental composition of the sample at a deeper region (a depth of > 10 nm from the top surface), argon etching was performed on all the samples until the signal of adventitious Carbon is eliminated. A single chemical state for Sn (at ~ 486 eV) was identified for all the etched samples with $x \geq 0.4$, as shown in Appendix Figure A.2f-j. This leads us to believe that Sn exists only in the Sn^{2+} state in the fabricated $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskite and the earlier observation of Sn having two chemical states is limited to the surface due to oxidation during XPS sample transfer. Notably, an additional chemical state at ~ 485 eV was observed in the Sn 3d_{5/2} peak for the

$x = 0.2$ sample, corresponding to Sn^0 . The precipitation of Sn could be ascribed to the unreacted PbI_2 left in the $x = 0.2$ perovskite film, as revealed by its XRD pattern later. The obtained elemental composition of Sn before and after etching are summarized in Figure 5.1. Interestingly, all Pb-Sn binary perovskite samples demonstrated elemental composition difference from top surface (before etching) to the region of > 10 nm depth into the bulk (after etching). Compared to the Sn content expected from the precursor solution (hollow circles in Figure 5.1), the Sn content at a depth > 10 nm from the surface (red spheres) was slightly lower, while the Sn content at the top surface (green spheres) was significantly higher. Especially, the $x = 0.8$ sample possessed nearly 100% Sn at surface. It is likely that Sn atoms tend to accumulate at the surface of the $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ binary perovskites due to their smaller ionic radii, similar to the accumulation of smaller Ge atoms at surface in mixed-Sn-Ge-based binary perovskite ($\text{FA}_{0.75}\text{MA}_{0.25}\text{Sn}_{0.95}\text{Ge}_{0.05}\text{I}_3$) films.^[14] In the current case, it is also feasible that the inhomogeneous distribution of Sn contents along the vertical direction of the sample is a consequence of Br incorporation.

Figure 5.1 Comparison of Sn contents for the $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ ($x = 0.2 - 1.0$) samples before and after etching, obtained by XPS characterization.

5.2.1 Tailoring the crystallographic phase and surface morphology

The $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ ($x = 0, 0.2, 0.4, 0.6, 0.8$, and 1.0) perovskite films were prepared at different annealing temperatures that depend on x value, and the resultant films appeared

in different colours. When preparing the neat Pb-based perovskite ($x = 0$) film, the sample annealed at 100 °C exhibited a bright yellow colour, and turned to reddish brown at a higher annealing temperature of 150 °C. As 20% Pb was substituted by Sn at the M-sites, the sample ($x = 0.2$) exhibited a brown colour subsequent to anti-solvent dripping, and turned to reddish black instantly upon annealing at 100 °C. The phenomena of colour change indicate the formation of perovskite phase. With further replacement of Pb by Sn, the samples ($x = 0.4 - 1.0$) all were annealed at 100 °C and displayed black colours. It was also observed that the $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ films involving Sn contents ($x \geq 0.2$) gradually turned to black at room temperature without post-annealing on a hot plate. Hence, the incorporation of Sn into the Pb-based I/Br mixed-halide perovskite system can significantly reduce the crystallization temperature of perovskite phase.

The crystallographic phase and structure of the Pb-Sn binary perovskite films were characterized by X-ray diffractometric (XRD) measurements, and all the relevant XRD patterns are displayed in Figure 5.2a. In the XRD pattern of the neat Pb sample ($x = 0$), the peak at approximately 11.6° indicated the formation of photoinactive yellow phase FAPbI_3 (marked with a hashtag #), consistent with the observation in other perovskites with mixed I-Br composition.^[8, 11] Except for $x = 0$, all compositions exhibited typical diffraction peaks matching with the previously reported orthorhombic perovskite structure of FASnI_3 .^[15, 16] Upon 20% Sn substitution of Pb ($x = 0.2$), the yellow non-perovskite phase completely disappeared. Instead, an intense peak was observed at 12.7° (marked with an asterisk *) originating from the residual PbI_2 impurities. For the samples with more Sn incorporation, the XRD patterns ($x \geq 0.4$) displayed a single crystalline perovskite phase with random orientation. Irrespective of the Sn content, the typical perovskite peak at ~14° did not show an obvious shift of positions. It is noted that the major diffraction peak (highest-intensity peak) shifted from ~14° to ~25° as x approached 1.0, implying that the crystallite turned its orientation direction from the plane of (100) towards (102) with increasing Sn incorporation. These XRD results demonstrate that the Sn incorporation induced the formation of black perovskite phase and also changed the crystallographic texture of the thin-film based on the FA-based Pb-Sn binary perovskites with 20% Br.

Figure 5.2 (a) XRD patterns and (b) SEM images of FAPb_{1-x}Sn_x(I_{0.8}Br_{0.2})₃ ($x = 0, 0.2, 0.4, 0.6, 0.8$, and 1.0) perovskite films. The scale bar in each image is 1 μm.

The surface morphology of the FAPb_{1-x}Sn_x(I_{0.8}Br_{0.2})₃ perovskite films with different Sn contents was investigated by scanning electron microscopy (SEM). As depicted in Figure 5.2b and Appendix Figure A.3, all compositions exhibited complete surface coverage, densely packed crystalline structure and apparent crystallite domains, except for the pure Sn films ($x = 1.0$). The present voids in the pure Sn film enable direct contacts between charge transporting materials sandwiched the perovskite absorbers, potentially accelerating the charge recombination in pure Sn-based PSCs. Regarding to the grain size, the Pb-Sn binary perovskite films ($0.2 \leq x \leq 0.8$) formed smaller grains than the pure Sn

perovskite film. It is attributed to the retardation of Sn-induced fast crystallization upon the incorporation of Pb, thus improving the morphology of Pb-Sn binary perovskite films.

In addition, it has been found that the anti-solvent treatment is essential to obtain these high-quality perovskite films. As portrayed in the SEM images of $\text{FAPb}_{0.6}\text{Sn}_{0.4}(\text{I}_{0.8}\text{Br}_{0.2})_3$ film fabricated without and with anti-solvent dripping (Figure 5.3a and Appendix Figure A.3c, respectively), there were large clusters of blur crystallite domains and remarkable vacant spaces on the former substrate. Comparing the XRD patterns of the $\text{FAPb}_{0.6}\text{Sn}_{0.4}(\text{I}_{0.8}\text{Br}_{0.2})_3$ film treated with (dash line) and without (solid line) anti-solvent (Figure 5.3b), all characteristic peaks remained the same position while the peak intensity of (100) plane dramatically enhanced. Hence, the anti-solvent treatment unaffected the composition of this type of perovskite film. Instead, it tuned the crystallite orientation towards (100) plane. Both SEM and XRD results demonstrated that removing anti-solvent treatment leads to expanded void area, increased inhomogeneity, reduced crystallinity, and tuned crystallite orientation.

Figure 5.3 (a) SEM image of $\text{FAPb}_{0.6}\text{Sn}_{0.4}(\text{I}_{0.8}\text{Br}_{0.2})_3$ sample prepared without anti-solvent dripping, where the scale bar is 10 μm, and (b) its corresponding XRD pattern.

5.2.2 Tuning optical property and air stability

Tuning of band-gap energy is at the core of solar cell application since it determines the photon harvesting capacity over wavelength. According to the Beer-Lambert law with the

assumption of uniform attenuation, the absorption coefficients (α) were calculated by the expression of $\alpha = (A \cdot \ln 10)/t$, where A is absorbance and t denotes the film thickness. As seen in Figure 5.4a, the Pb-Sn binary perovskites ($x = 0.4 - 0.8$) exhibited higher absorption coefficients than neat Pb or Sn perovskite ($x = 0$ or 1.0) over the entire spectra range of 400 – 1000 nm. Hence, coupling of Pb and Sn enhances the absorption property for FA-based mixed-halide perovskites. In the absorption coefficient curve for $x = 0$, there are multiple absorption crests but no characteristic perovskite absorption onset, further confirming the non-perovskite phase present in the $x = 0$ sample as revealed by its XRD pattern (Figure 5.2a).^[8] As for the Sn-incorporated samples ($x = 0.2 - 1.0$), their absorption coefficient spectra mainly involved two absorption onsets. The first absorption onset in the long wavelength region (800 – 900 nm) is attributed to the direct gap transition from the valence band maximum (VBM) to the conduction band minimum (CBM) and hence is used to identify the optical band gap energy (E_g). However, the origin of the second absorption onset in the short wavelength range (600 – 700 nm) is still unresolved.

Figure 5.4 (a) Absorption coefficient spectra and (b) Tauc plot for $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskites.

In an attempt to ascertain E_g with higher accuracy, the Tauc plots of $(\alpha h\nu)^2$ versus energy ($h\nu$) were established in Figure 5.4b where the E_g values were identified by extrapolating the linear portion at absorption onset. Figure 5.5a summarizes the values of E_g estimated by different methods as a function of Sn content. It also includes the values of E_g extracted from external quantum efficiency (EQE) spectra, which will be discussed in the following section. The abnormally high E_g value for $x = 0$ is associated with its reddish non-perovskite phase. As the x value was progressively tuned from 0.2 to 1.0, the E_g values undergone an anomalous nonlinear evolution, well in line with previous observations reported in most Pb-Sn binary iodide perovskites.^[17-19] Kanatzidis et al. attribute this phenomenon to the competition between the spin-orbit coupling of Pb^{2+} and Sn^{2+} ions and lattice distortions.^[20] It has been reported by McGehee et al. that $FAPb_{1-x}Sn_xI_3$ ($0.2 \leq x \leq 0.8$) perovskites demonstrated E_g values of 1.2 – 1.3 eV.^[18] In comparison, $FAPb_{1-x}Sn_x(I_{0.8}Br_{0.2})_3$ perovskites containing 20% Br possessed relatively high bandgaps of around 1.4 eV, which are close to the ideal bandgap (1.34 eV) predicted by the well-known Shockley-Queisser limits.^[21]

Figure 5.5 (a) Bandgaps extracted from Tauc plots and EQE spectra and (b) the absorbance at 500nm plotted over time for $FAPb_{1-x}Sn_x(I_{0.8}Br_{0.2})_3$ perovskites.

Next, the ambient stability of the studied perovskite thin-films was evaluated via time-resolved UV-Vis absorption measurements. The absorption spectra were acquired over an hour, while the films were exposed to ambient air in dark, as displayed in Appendix Figure A.4. The absorbance of $FASn(I_{0.8}Br_{0.2})_3$ over the entire spectra range decreased gradually within half an hour, while the absorption spectrum of $FAPb(I_{0.8}Br_{0.2})_3$ maintained

the same as its initial shape. Figure 5.5b shows the plots of A/A_0 (the fraction of absorbance remained) over time at 500 nm (where all studied perovskites exhibited a relatively high absorbance). After one-hour exposure to ambient air, 100 %, 100 %, 99 %, 95 %, 92 % and 87 % of A_0 at 500 nm was retained for perovskites with $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0 , respectively. Thus, the improved ambient stability was found in the in Sn-poor perovskites ($x = 0.2$ and 0.4), due to a lower propensity for Sn oxidation. Although the XPS results suggested that all the Sn-involved films were slightly oxidized at top surface upon minimized air exposure, the bulk films for Sn-poor perovskites exhibited no degradation of their optical absorption properties within an hour in air.

Figure 5.6 (a) PESA measurement result of $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskites. (b) Band alignment between perovskites and charge transporting materials applied in the solar cells.

To further understand the influence of Sn incorporation on the optoelectronic properties, the energy level of VBM was estimated by photoemission spectroscopy in air (PESA), as shown in Figure 5.6a.^[22] As Sn content increased from 0 to 1.0, the VBM gradually shifted upwards from -5.49 eV to -4.99 eV relatively to the vacuum level. Furthermore, the CBM levels were estimated by adding E_g on VBM. Combined with the literature values of PEDOT:PSS and PC₆₀BM,^[2,23] the energy band alignments between $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskites and the widely used charge transporting materials are presented in Figure 5.6b. It is noted that as Sn content approached towards 1.0, the gap between the VBM level of perovskite and the lowest unoccupied molecular orbital (LUMO) level of PC₆₀BM straitened. Therefore, charge carrier recombination and a V_{oc} loss are expected to occur in the Sn-rich perovskite incorporated devices.^[24]

5.2.3 Altering device performance of Pb-Sn-based perovskite solar cells

The photovoltaic behaviour of $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskites was systematically assessed by fabricating and characterizing solar cells with a planar p-i-n architecture where PEDOT:PSS and PC_{60}BM were employed as the contacts for extracting holes and electrons, respectively. The achieved photovoltaic parameters as well as their variations at different Sn contents ($x = 0 - 1.0$) are described in Figure 5.7a-d. The photocurrent density versus voltage (J–V) curves of best-performing devices at different Sn compositions are portrayed in Figure 5.8a and their photovoltaic parameters are tabulated in Table 5.1.

Figure 5.7 Photovoltaic parameters of $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ based PSCs: (a) J_{sc} , (b) V_{oc} , V_{oc} loss presented as black hollow circles, (c) FF, and (d) PCE.

In terms of the short-circuit current density (J_{sc}), the neat Pb-based devices ($x = 0$) suffered from extremely low J_{sc} below 2 mA/cm², as shown in Figure 5.7a. It increased nearly 10 times upon the substitution of Pb with 20% Sn ($x = 0.2$). The highest J_{sc} of ~ 20 mA/cm²

was achieved in the devices with $x = 0.6$, which is slightly higher than those with $x = 0.4$. The higher values of J_{sc} for $x = 0.4$ and 0.6 can be attributed to their higher absorption coefficients over the entire spectra range (Figure 5.4a) compared to the rest of the compositions. As x increased beyond 0.6 , J_{sc} continuously dropped to ~ 10 mA/cm². This J_{sc} trend was further validated by external quantum efficiency (EQE) measurements for the best-performing devices listed in Table 5.1. The spectral dependent EQE curves for the devices with different Sn contents are presented in Figure 5.8b. Notably, these EQE curves all demonstrated a wave-like shape, because of the reflection-interference of the incident light in planar solar cells. At 500 nm, the neat Pb-based device shew a crest while the other devices shew a trough, which is correlated with its intense absorptions at 500 nm (Figure 5.4a). As illustrated in Table 5.1, the J_{sc} integrated from EQE spectra showed the same trend as the J_{sc} obtained from J–V characteristics when x was tuned from 0 to 1.

Figure 5.8 (a) J–V characteristics, and (b) EQE spectra for FAPb_{1-x}Sn_x(I_{0.8}Br_{0.2})₃ based PSCs.

Table 5.1 Photovoltaic parameters for best-performing PSCs based on FAPb_{1-x}Sn_x(I_{0.8}Br_{0.2})₃ ($x = 0, 0.2, 0.4, 0.6, 0.8$, and 1.0) perovskites.

Sn content / x value	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)	J_s , from EQE (mA cm ⁻²)	V_{oc} loss (V)
0.0 (Pb)	1.58	0.97	0.43	0.66	2.36	1.17
0.2	14.44	0.70	0.55	5.53	14.59	0.75
0.4	19.68	0.70	0.65	8.94	19.03	0.70
0.6	20.39	0.68	0.60	8.36	20.64	0.72
0.8	15.29	0.41	0.51	3.20	16.29	1.05
1.0 (Sn)	11.34	0.34	0.52	1.99	12.17	1.20

In addition, the EQE data of these direct bandgap perovskites were exploited to evaluate electrical bandgap (E_g) via plotting $[h\nu \times \ln(1 - EQE)]^2$ against $h\nu$, as displayed in Figure 5.9a. The attained E_g values well agree with the E_g values identified from Tauc plots, with a negligible variance (less than 0.05 eV). As seen in Figure 5.5a, both curves of optical and electrical bandgaps versus Sn content manifested a bowing shape with the minimum E_g appearing at $x = 0.6$. Moreover, the EQE spectra provides the information on the energy width of the absorption edge, referred to as Urbach energy (E_u).^[25] Based on the plot of $\ln[-\ln(1 - EQE)]$ against energy, E_u was estimated from the slope of the linear portion near the absorption onset. It can be seen in Figure 5.9b that all Sn-substituted perovskites exhibited much lower E_u than the pure Pb-based perovskites (81.7 meV), suggesting the improved material quality associated to the Sn incorporation. Along with the increasing Sn content from 0.2 to 1.0, the E_u gradually fell from 25.6 meV to 20.2 meV, implying that the band edge disorder reduced with the increasing Sn incorporation.

Figure 5.9 (a) Electrical bandgap and (b) Urbach energy estimated from EQE spectra for $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskites.

The open-circuit voltage (V_{oc}), together with the V_{oc} loss estimated from optical bandgap ($E_g - qV_{oc}$), were plotted in Figure 5.7b. The highest V_{oc} close to 1 V was yielded by pure Pb-based devices ($x = 0$), correlating with its highest bandgap of ~ 2.1 eV. As for the mixed Pb-Sn-based perovskites with bandgaps near 1.4 eV, the devices of $x = 0.2 - 0.6$ exhibited similar V_{oc} approaching 0.7 V, while the devices of $x = 0.8$ provided much lower V_{oc} of around 0.4 V, followed by the devices of $x = 1.0$. As demonstrated in Table 5.1, the lowest V_{oc} loss presented in devices with $x = 0.4$ among all the examined compositions. The slightly higher V_{oc} loss for $x = 1.0$ could be related to the PbI_2 impurities in its perovskite films, inferred from its XRD pattern. According to the PESA results previously discussed, the VBM position of perovskite shifted towards the LUMO level of PC₆₀BM as $x = 0.4 \rightarrow 1.0$, rising the potentiality of charge recombination at interface and thus increasing the V_{oc} loss. Especially, the larger V_{oc} loss over 1 V incurred in the Sn-rich devices of $x = 0.8$ and 1.0, which could arise from their fast degradation in air, as proved by the time-resolved absorption measurements. Additionally, the discontinuous perovskite films with pin-holes in pure Sn-based device could contribute to its highest V_{oc} loss, thereby lowering its V_{oc} .

Next, Figure 5.7c illustrated that the fill factor (FF) exceeded 0.5 in all devices, except for the neat Pb-based devices (~ 0.4). Ultimately, regarding the power conversion efficiency (PCE) involved in Figure 5.7d, the hybrid Pb-Sn-based devices performed much more superiorly than the pure Pb or Sn based devices. As seen from the typical J–V curves in Figure 5.8a and the device parameters in Table 5.1, the most outperforming devices incorporated the $x = 0.4$ perovskites and exhibited a PCE approaching 9 % with the lowest V_{oc} loss. A slightly lower PCE of 8.36 % was provided by the lowest bandgap devices of $x = 0.6$ with the highest J_{sc} reaching ~ 20 mA/cm². Such high efficiencies could be attributed to higher crystallinity, higher absorption coefficients, lower bandgap and lower V_{oc} loss compared to the other samples, together with their high surface coverage of perovskite films.

Overall, the neat Pb-based PSCs suffered from extremely low PCE although they possessed the highest V_{oc} owing to their largest E_g . Their device performance was primarily limited by the low J_{sc} since their non-perovskite phase exhibited poor absorption coefficients. The neat Sn-based PSCs demonstrated second lowest PCE and the lowest V_{oc} . Their high V_{oc}

loss could be a consequence of the mismatch between the absorber CBM and the LUMO level of electron selective material. Additionally, the voids present in their perovskite films allowed direct contacts between PEDOT:PSS and PC₆₀BM, potentially increasing the recombination rate. Among the partially Sn-substituted PSCs, devices of $x = 0.4$ yielded the highest PCE, followed by devices of $x = 0.6$. Their outstanding device performances were owing to continuous film morphology, high absorption coefficients, ideal bandgaps of ~ 1.4 eV, and well band alignment with charge transporting materials. Attempts to explore more details underlying the performance difference have been carried out through the investigation on the charge recombination processes and hysteresis effects, as discussed in the following section.

5.3 Charge recombination analysis of Pb-Sn binary perovskite solar cells

The recombination mechanism governing the device performance of FAPb_{1-x}Sn_x(I_{0.8}Br_{0.2})₃ PSCs with different Sn contents was distinguished by the ideality factor (n), which was extracted using Suns- V_{oc} method or light intensity (L) dependence of V_{oc} . Figure 5.10a displays the plot of the V_{oc} as a function of L on a semi-logarithmic scale for the highly performing devices ($x = 0.4$ and 0.6) and the pristine Sn device ($x = 1.0$). The value of n was calculated from the slope of the fitting line according to the expression of $\frac{\Delta V_{oc}}{\Delta \ln L} = n \frac{k_B T}{q}$, where q is electron charge, k_B is Boltzmann constant, and T is temperature.^[28, 29] In the extreme cases, $n = 1$ represents bimolecular (or radiative) recombination, whereas $n = 2$ signifies Shockley-Read-Hall (SRH, or trap-assisted) recombination.^[26, 27] Trap-assisted SRH type of recombination as a dominant recombination has been frequently revealed in most PSCs.^[2, 25] As given in Table 5.2, the n values of 1.39 and 1.56 were obtained for $x = 0.4$ and 0.6 , respectively. The higher n value signifies that the trap-assisted recombination was more prominent in the device with $x = 0.6$, contributing to its slightly higher V_{oc} loss. As for $x = 1.0$, the device exhibits an $n = 0.91$ at low incident light intensities (up to 32 mW/cm²), indicating a bimolecular recombination as the dominant recombination. However, the higher value of $n = 2.59$ at higher illumination regime (between 32 and 100 mW/cm²) implies that the dominant recombination changed to trap-assisted recombination, resulting in its poor PCEs at AM 1.5 illumination.

Table 5.2 Summary of the information on the ideality factor (n) and the index number (α) extracted from light intensity dependent J – V characteristics.

Sn content	Ideality factor, n	Index number, α
$x = 0.4$	1.39 ± 0.09	0.88 ± 0.01
$x = 0.6$	1.56 ± 0.10	0.87 ± 0.01
$x = 1.0$ (Sn)	$0.91 \pm 0.10, 2.59 \pm 0.24$	0.63 ± 0.05

Following the identification of dominant recombination type at open circuit, the recombination process at short circuit was further investigated through the relationship between J_{sc} and L . As shown in Figure 5.10b, the plot of J_{sc} against L in log scale was fitted to a power law dependence of $J_{sc} \propto L^\alpha$. In p-i-n solar cells, the α value of 1 is interpreted as a linear relationship of J_{sc} with L . Comparing the α values for different Sn contents listed in Table 5.2, the devices with $x = 0.4$ and 0.6 demonstrated higher α values than the device with $x = 1.0$, signifying more effective charge collection and less recombination losses under short-circuit conditions. The α value for $x = 1.0$ that deviates far from unity can be attributed to the bimolecular recombination, space charge defects, and variations in mobility between the two carriers.^[30]

To gain deep insights into the impact of Sn incorporation on the recombination dynamics, electrochemical impedance spectroscopy (EIS) was measured for the $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ ($x = 0.4, 0.6, 1.0$) based PSCs at 0 V applied bias under 0.9 sun illumination at room temperature with the frequency varying from 1 MHz to 10 Hz. As shown in Figure 5.10c, the obtained Nyquist plots feature two distinguishable arcs separated in frequencies. The electrical equivalent circuit used for fitting is portrayed in Figure 5.10d. It consists of an external series resistance (R_s), two internal resistive components (R_{HF} and R_{LF}) and two capacitive elements (C_g and CPE_{LF}). R_{HF} and C_g correlate to the resistance and geometrical capacitance at high frequency range of the applied AC signal, whereas R_{LF} and CPE_{LF} contribute to the impedance response at low frequency range.^[31, 32] Here, constant phase element (CPE) rather than ideal capacitor was applied for more accurate fittings. The summation of R_{HF} and R_{LF} is identical to the total recombination resistance (R_{rec}), ascribed to recombination processes present at interface and perovskite layer. The resultant values of R_s , R_{HF} , R_{LF} and R_{rec} for $x = 0.4, 0.6$, and 1.0 are summarized in Table 5.3. The R_s values

are similar for different x values, indicative of a similar ohmic contribution from contacts and wires. The higher value of R_{rec} for $x = 0.4$ elucidates reduced recombination inside the corresponding solar cell, consistent with its higher V_{oc} . The severe recombination in the device with complete Sn incorporation ($x = 1.0$) could be attributed to the narrow energy gap between the VBM level of $\text{FASn}(\text{I}_{0.8}\text{Br}_{0.2})_3$ and the LUMO level of PC_{60}BM (Figure 5.6b) and its void-containing film morphology.

Figure 5.10 The light intensity dependence of (a) V_{oc} and (b) J_{sc} for $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ based PSCs with $x = 0.4, 0.6, 1.0$. (c) Nyquist plots of $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ ($x = 0.4, 0.6, 1.0$) based PSCs, measured under 0.9 sun illumination without bias. (d) The schematic illustration of the equivalent electrical circuit used for fits (solid lines).

Table 5.3 The resistances (R_s , R_{HF} , R_{LF} and R_{rec}) extracted from the fittings of Nyquist spectra for the $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ based PSCs with different Sn contents ($x = 0.4, 0.6, 1.0$).

Sn content	R_s (Ω)	R_{HF} ($\text{k}\Omega$)	R_{LF} ($\text{k}\Omega$)	R_{rec} ($\text{k}\Omega$)
$x = 0.4$	22.9	1.4	6.2	7.6
$x = 0.6$	25.6	0.9	4.6	5.5
$x = 1.0$ (Sn)	24.2	0.6	0.1	0.7

Figure 5.11 (a) Steady-state TA spectra, and (b) TA dynamics of FAPb_{1-x}Sn_x(I_{0.8}Br_{0.2})₃ ($x = 0.4, 0.6, 1.0$) perovskites.

Apart from the recombination dynamics in devices, the photoexcited charge-carrier dynamics within perovskite films was further investigated via transient absorption (TA) spectroscopy measurements.^[23] Figure 5.11a displays the steady-state TA spectra for the thin-film samples of FAPb_{1-x}Sn_x(I_{0.8}Br_{0.2})₃ with $x = 0.4, 0.6$ and 1.0 . The differential absorption ($-\Delta A$) peak position corresponds to the position of the band-edge photobleaching (PB, ie., $-\Delta A > 0$). For $x = 0.4, 0.6$, and 1.0 samples, the PB peak positions are at 850 nm, 870 nm and 760 nm, which are consistent with their absorption onset at 880 nm, 890 nm and 800 nm, respectively (Figure 5.4a). The TA dynamics in Figure 5.11b were well fitted with two exponential time constants (τ_1 and τ_2) with varied amplitudes of A_1 and A_2 . The average carrier lifetime (τ_{ave}) was determined by the expression of $\tau_{ave} = A_1\tau_1 + A_2\tau_2$. The extracted fitting results were summarized in Table 5.4, which reveal that the slow decay lifetime (τ_2) dominated the overall decay lifetime (i.e. $A_2 > A_1$). Notably, the τ_{ave} value increases from 1.5 ± 0.2 ns to 7.7 ± 0.5 ns as Sn content increased, suggesting

the slower carrier recombination with increasing Sn content. This is likely due to the higher defect densities in the binary perovskites, as inferred from their higher E_u values compared to the pure Sn perovskite (Figure 5.9b). Nevertheless, the studied devices with increasing Sn content manifested reducing V_{oc} and increasing R_{rec} . By correlating the information obtained from TA and EIS with the real device performance, it can be proposed that the recombination occurring at interfaces between perovskite and charge selective contact relatively limits the V_{oc} and overall device performance compared to the recombination present within perovskite layer.

Table 5.4 Fitting parameters of TAS spectra for $FAPb_{1-x}Sn_x(I_{0.8}Br_{0.2})_3$ ($x = 0.4, 0.6$ and 1.0).

Sn content	λ_{probe} (nm)	A1	τ_1 (ps)	A2	τ_2 (ps)	τ_{ave} (ps)
x = 0.4	850	0.46	112 ± 20	0.54	2700 ± 200	1500 ± 200
x = 0.6	870	0.38	18 ± 4	0.62	4300 ± 400	2700 ± 300
x = 1.0 (Sn)	760	0.36	23 ± 2	0.64	12000 ± 600	7700 ± 500

5.4 Optimization of photovoltaic performance via precursor adjustment

In most reported solution-processing of pure Sn-based perovskites, SnF_2 additive has been included in the precursor in an attempt to suppress Sn^{2+} oxidation and thus compensate for Sn^{2+} vacancies.^[33,34] Nevertheless, the effect of Sn addition is not clear yet for the mixed Sn and Pb PSCs. Similar photovoltaic performance has been observed in the devices with or without SnF_2 additive.^[19,35] To explore the impact of SnF_2 additive on the photovoltaic properties, photovoltaic devices were prepared based on the $FAPb_{0.6}Sn_{0.4}(I_{0.8}Br_{0.2})_3$ perovskites with the optimum Sn content ($x = 0.4$). The examined SnF_2 concentrations range between 0 and 20 mol%, and the photovoltaic results are summarized in Table 5.5 and Figure 5.12a-b. When the SnF_2 concentration is below 10 mol%, the PCE is around 6.7%. Compared to the sample without SnF_2 , the addition of 10 mol% SnF_2 enhanced the V_{oc} and FF while reduced the J_{sc} . Although the highest value of the PCE slightly decreases, the variation of the PCE turns diminutive. When the SnF_2 concentration exceeds 10 mol%, the overall photovoltaic performance tends to deteriorate with a widened variation. This inferior trend can be attributed to the precipitation of SnF_2 at higher SnF_2 concentrations.

As can be seen in inset of Figure 5.12b, in the case of 20 mol% SnF_2 , SnF_2 particles lie at the grain boundaries.^[16] Therefore, the addition of SnF_2 did not dramatically enhance the efficiencies of PSCs based on $\text{FAPb}_{0.6}\text{Sn}_{0.4}(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskite, which is in contrast to the situation reported in the PSCs based on pure Sn perovskites.^[34,36] Instead, SnF_2 additives of concentration less than 10 mol% solely helped to reduce the efficiency variation. It is feasible that here SnF_2 additives play the role of a strong reducing agent in chemical synthesis rather than the tin compensator.

Figure 5.12 (a) J–V curves and (b) PCEs of $\text{FAPb}_{0.6}\text{Sn}_{0.4}(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskite solar cells dependent on the SnF_2 concentration. The inset shows the SEM image of a $\text{FAPb}_{0.6}\text{Sn}_{0.4}(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskite film with 20 mol% SnF_2 (the scale bar is 1 μm).

Table 5.5 Photovoltaic parameters for best-performing PSCs based on $\text{FAPb}_{0.6}\text{Sn}_{0.4}(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskite with different concentration of SnF_2 additive.

SnF_2 concentration	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
0 mol%	19.15	0.60	0.59	6.75
5 mol%	16.52	0.64	0.63	6.71
10 mol%	19.06	0.63	0.57	6.84
15 mol%	14.73	0.67	0.60	5.94
20 mol%	14.22	0.66	0.45	4.23

To further optimize the photovoltaic performance of $\text{FAPb}_{0.6}\text{Sn}_{0.4}(\text{I}_{0.8}\text{Br}_{0.2})_3$ based PSCs, the thickness of perovskite layer was tuned by adjusting the concentration of the precursor solution. It has been demonstrated that photocurrent increased rapidly with increasing

thickness of perovskite films due to the absorption enhancement, and then gradually saturated with further increase in absorber thickness because of the solubility limit of perovskite precursor.^[2] Hence, a champion solar cell was successfully fabricated with a thick $\text{FAPb}_{0.6}\text{Sn}_{0.4}(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskite film (~ 500 nm). The cross-sectional SEM image for the champion device is portrayed in the inset of Figure 5.13a. Each individual layer in the solar cell stack (glass / ITO / PEDOT:PSS (HTM)/ perovskite / PC_{60}BM (ETM)/ BCP / Ag) was flat, compact and free of pin-holes. It is noticeable that the grains in the perovskite layer did not entirely align along x direction but randomly stacked in y direction. In this case, the grain boundaries against y direction could function as obstacles to the charge transfer between perovskite layer and ETM/HTM layer, resulting in the voltage lose.

Figure 5.13 (a) J–V curves measured under $100 \text{ mW}/\text{cm}^2$ illumination (solid line) and in the dark (dash line) under forward (solid spheres) and reverse (hollow circles) direction of an optimized inverted solar cell based on $\text{FAPb}_{0.6}\text{Sn}_{0.4}(\text{I}_{0.8}\text{Br}_{0.2})_3$. The insets include a cross-sectional SEM image of the champion device (where the scale bar is 100 nm) and a table of its photovoltaic parameters. (b) Reproducible PECs of 20 prepared $\text{FAPb}_{0.6}\text{Sn}_{0.4}(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskite solar cells.

The J–V curves of the champion solar cell measured in the forward and backward directions were presented in Figure 5.13a, along with its corresponding characteristic device parameters. The J_{sc} of this cell scanned in the forward direction is $21.54 \text{ mA}/\text{cm}^2$; the V_{oc} is 0.71 V, and the FF is 0.66, yielding a PCE of 10.07%. When scanned in the backward direction, the PCE increases to 10.27%, due to an improvement of the J_{sc} to $22.13 \text{ mA}/\text{cm}^2$. The V_{oc} slightly drops to 0.70 V, and the FF still stays at 0.66. Since the difference of PCE received in the opposite scan directions is merely 0.20%, the J–V hysteresis of the

champion cell is negligible. Finally, the reproducibility of $\text{FAPb}_{0.6}\text{Sn}_{0.4}(\text{I}_{0.8}\text{Br}_{0.2})_3$ based PSCs has been demonstrated through the PCE histogram in Figure 5.13b, where the average PCE of total 20 devices is 8.22%.

5.5 Conclusions

In summary, the influence of Sn incorporation has been comprehensively investigated in the FA-based 20% Br-containing Pb-Sn binary perovskite system, $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$). By gradually substituting Pb with Sn into parental $\text{FAPb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskite, it was found that the Sn incorporation stabilized the perovskite phase, reduced crystallization temperature and impressively enhanced absorption coefficients. In comparison to the completely Sn replaced perovskites, i.e. $\text{FASn}(\text{I}_{0.8}\text{Br}_{0.2})_3$, the Pb-Sn binary perovskites possessed continuous film morphology and better band alignment with the applied charge selective contacts. As such, the planar heterojunction PSCs combining Pb and Sn significantly surpassed the pure Pb or Sn-based PSCs in terms of the photovoltaic performance. The optimum $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ PSCs with $x = 0.4$ yielded the highest PCE of 10.1 % in ambient air without any encapsulation as a consequence of enhanced absorption and suppressed charge carrier recombination kinetics. Overall, our work sheds some light for further understanding the role of Sn content in the recombination mechanism in perovskites and PSCs, and developing efficient PSCs using less Pb in future.

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Chapter 6

Developing air-stable lead-free tetravalent-tin-based perovskite derivatives for potential photovoltaic application

The development of inorganic $A_2\text{SnI}_6$ ($A = \text{Cs}, \text{Rb}$) derived-perovskites have been motivated by the computational studies indicating their suitable bandgap and structural stability for potential photovoltaic application. Via A-site substitution with small organic cations ($A = \text{MA}, \text{FA}$), totally four $A_2\text{SnI}_6$ compounds were synthesized and characterized to elaborate their structure deformation, bandgap tuning and stability variation correlated with the A-site cation. Due to the limited processability of continuous-morphology films, only Cs_2SnI_6 and MA_2SnI_6 demonstrated potential applications in photovoltaic devices as light absorbers. The superior thermal and air stability and ideal bandgap ($\sim 1.34 \text{ eV}$) of $A_2\text{SnI}_6$ compounds in present study paves the way for the realization of environmental benign efficient perovskite solar cells.

6.1 Introduction

Currently both tin (Sn) and germanium (Ge) based AMX_3 perovskites suffer from the rapid degradation in air. Since divalent Sn^{2+} and Ge^{2+} are not at their highest oxidation states, compounds involving these cations can be spontaneously oxidized upon exposure to air.^[1] To suppress this high propensity for oxidation, A_2MX_6 perovskite derivatives have been developed, where divalent metal cation (M^{2+}) is replaced by tetravalent metal cation (M^{4+}). In this new class of derived perovskites, lead-free all-inorganic cesium tin iodide perovskites (Cs_2SnI_6) have received dramatic computational and experimental efforts from photovoltaic community.^[2-4] When Cs_2SnI_6 compound was first applied in photovoltaic devices, it functioned as a hole conductor in dye sensitized solar cells (DSSCs), due to its high conductivity.^[5] On account of its superior bandgap (~ 1.3 eV), it was further employed as light absorbing layer in perovskite solar cells (PSCs) and achieved an efficiency close to 1%.^[1, 6] Additionally, the intensive investigation on this material is driven by its outstanding stability under moisture and air, compared to conventional Pb or Sn based AMX_3 perovskites.^[7, 8]

In the AMX_3 perovskite system, the substitution of A-site cation has demonstrated significant effects on the crystal structure deformation and bandgap tuning.^[9, 10] Although all-inorganic Cs_2SnI_6 has been well studied in literature, its organic A-cation based analogue is rarely investigated. To date, only Maughan et al. employed aromatic $C_7H_7^+$ in A_2SnI_6 structure for absorbance enhancement.^[11] Moreover, Xiao et al. elucidated that the Sn cation in Cs_2SnI_6 is at +2 oxidation state similar to $CsSnI_3$ based on the computation methods, and Sn-I bonds is composed of half ionic bonds and covalent bonds, contributing to its chemical air stability.^[12] However, the real oxidation state for Sn cation in A_2SnI_6 compounds remains unidentified, which requires further experimental studies.

According to literature, A_2MX_6 compounds exhibit zero-dimensional (0D) perovskite variant structure, as compared to the 3D AMX_3 perovskite structure. When the divalent M^{2+} cation is replaced by tetravalent M^{4+} cation, half of the metal atoms are missing to maintain the neutron balance. Consequently, the octahedral $[BX_6]^{2-}$ in A_2MX_6 are isolated to each other rather than connect together by corner-sharing in AMX_3 . In addition, Cai et

al. have computationally investigated the chemical trend of bandgap for a series of all-inorganic A_2MX_6 compounds, including Cs_2SnI_6 and Rb_2SnI_6 , using density-functional-theory and hybrid functions.^[3] It has been found that Rb_2SnI_6 exhibited slight larger bandgap than Cs_2SnI_6 , as a result of tetragonal distortion favored by the compound with relatively small A-site cation size such as Rb_2SnI_6 . More details of the structural and optical properties of A_2SnI_6 compounds is discussed as follow.

In this work, a series of lead-free tetravalent-Sn-based halide compounds A_2SnI_6 ($A = Cs, Rb, MA, FA$) were successfully fabricated through a simple solution-processed method. The substitution of A-site cation contributed to the deformation of crystal structure, along with a minor tuning of band gap energy. Furthermore, the A-site cation was found to have a minor influence on the chemical state for Sn cations in A_2SnI_6 . In addition to the structural and optical properties, the thermal and ambient stabilities were investigated in this study. Next, A_2SnI_6 films was further fabricated for the application in photovoltaic devices as light absorbers. Ultimately, the primary photovoltaic behaviors of MA_2SnI_6 based devices underscores new opportunities for the development of efficient lead-free highly-stable PSCs. The present study paves the way for further development of A_2SnI_6 based PSCs.

6.2 Structural, chemical and optical characterizations of A_2SnI_6 compounds

6.2.1 Structure deformation and bandgap tuning via A-cation substitution

Following the solution-processed method described by Lee et al., lead-free perovskite derivatives A_2SnI_6 powders with different A-site cations ($A = Cs, Rb, MA, FA$) have been successfully synthesized in ambient condition.^[5] Note that the yield of organic A-cation incorporated compounds was lower than the neat inorganic A-cation based compounds since some amount of their products were dissolved in ethanol during the washing step. The crystal structure of A_2SnI_6 ($A = Cs, Rb, MA, FA$) compounds were investigated using the powder X-ray diffractometer (XRD) (Figure 6.1). According to literature, the well-studied Cs_2SnI_6 exhibits the cubic K_2PtCl_6 -type ($Fm-3m$) structure with $a = 11.64 \text{ \AA}$ identified by Pawley fit.^[10] The diffraction peaks of the as-synthesized Cs_2SnI_6 powder are consistent with the pattern reported in literature.^[5,7,8] Furthermore, MA_2SnI_6 and FA_2SnI_6

compounds with larger A-site cations adopted cubic crystal structure at room temperature similar to Cs_2SnI_6 . Through the substitution of Cs^+ by MA^+ and FA^+ , the characteristic diffraction peak for Cs_2SnI_6 at ~ 26.5 degrees shifted to the lower 2θ angle region, indicating an extension of crystal lattice. As the ionic radius of the A-site cation in A_2SnI_6 increased from $1.67 \text{ \AA}$ to $1.80 \text{ \AA}$ and to $1.9\text{--}2.2 \text{ \AA}$,^[13] the lattice parameter of A_2SnI_6 increased from $11.63 \text{ \AA}$ to $12.02 \text{ \AA}$ and to $12.34 \text{ \AA}$, respectively. When Cs^+ was substituted by Rb^+ with smaller cation size ($1.52 \text{ \AA}$), the crystal structure converted to tetragonal shape due to the distorted orientation of SnI_6 octahedra. This experimental finding on the crystal structure transformation is consistent with the computational analysis.^[3] Note that this result is different from the report in database where Rb_2SnI_6 exhibits the same cubic structure as Cs_2SnI_6 with a slightly smaller lattice parameter of $a = 11.64 \text{ \AA}$.^[14] On contrary, the Rb_2SnI_6 in the current case adopted the same tetragonal structure as Rb_2TeI_6 ($P4/mnc$) with $a = 8.07 \text{ \AA}$ and $c = 11.78 \text{ \AA}$.^[15] As Rb_2TeI_6 becomes cubic upon heating, Rb_2SnI_6 may also exhibit such phase transition, which will be discussed later in this work.

Figure 6.1 (a) XRD patterns; SEM images of crystals for: (b) Cs_2SnI_6 , (c) Rb_2SnI_6 , (d) MA_2SnI_6 , and (e) FA_2SnI_6 , with the scale bar of 100 μm , 100 μm , 100 nm, and 1 μm , respectively.

According to the calculated band structure and density of states (DOS) demonstrated in literature, both Cs_2SnI_6 and Rb_2SnI_6 are direct bandgap semiconductors at Γ point, with valence band derived from I-p states and conduction band derived from Sn-s and I-p states.^[3] Using Tauc fit of the absorbance data, as shown in Figure 6.2, the bandgap values of A_2SnI_6 ($\text{A} = \text{Cs}, \text{Rb}, \text{MA}, \text{FA}$) compounds were all identified at around 1.34 eV. This bandgap is translated to a Shockley-Queisser efficiency limit of 33% for a single p-n junction solar cell.^[16] It thereby elucidates the potential suitability of these A_2SnI_6 compounds for developing efficient PSCs. Additionally, the minor difference among their bandgaps suggested that A-site cations are electronic inactive in A_2SnI_6 compounds, in a good agreement to the computational prediction. It is worth to note that the bandgap value of the Cs_2SnI_6 has been reported as 1.26 eV, 1.35 eV, and 1.62 eV by other works.^[5, 7, 17] These results were attained from the Cs_2SnI_6 films prepared by different deposition methods, e.g. sequential electron-spraying, sequential vapour deposition and phase transition from unstable CsSnI_3 .

Figure 6.2 Tauc plots of A_2SnI_6 ($\text{A} = \text{Cs}, \text{Rb}, \text{MA}, \text{FA}$) compounds.

6.2.2 Identification of the chemical state of tin

To identify the chemical state of Sn cations in A_2SnI_6 compounds, the X-ray photoelectron spectroscopy (XPS) analysis was performed, and the attained XPS spectra of the Sn $3d_{5/2}$ peak were displayed in Figure 6.3a-d. Marshall et al. have reported that the binding energy of Sn $3d_{5/2}$ from CsSnI_3 , SnI_2 , and SnI_4 is located at approximately 485.97 eV, 486.16 eV, and 487.18 eV, respectively.^[18] It is noted that the values for SnI_2 and CsSnI_3 are slightly

different, although the chemical states of Sn cations are expected to be the same (Sn^{2+}) in these two compounds. This demonstrated that the binding energy of Sn 3d core level could be altered by the A-site cation incorporation. Hence, a reasonable comparison of the binding energy for the Sn cations with different valences is supposed to be established on the compounds with the same A-site cation. Provided that pure Sn^{2+} in SnI_2 and pure Sn^{4+} in SnI_4 , the binding energy of Sn 3d_{5/2} shifts 1.02 eV towards the large energy region when the oxidation state of Sn cations rises by +2.

Figure 6.3 High resolution XPS spectra and peak fitting of the Sn 3d core-level peaks for: (a) Cs_2SnI_6 , (b) Rb_2SnI_6 , (c) MA_2SnI_6 , and (d) FA_2SnI_6 .

Contrary to the XPS results reported by Marshall et al., Xiao et al. argued that the real oxidation state of the Sn ion in Cs_2SnI_6 is +2 similar to CsSnI_3 based on the density functional theory (DFT) calculations.^[12] As shown in Figure 6.3a, the peak of Sn 3d_{5/2} in Cs_2SnI_6 was observed to be at the binding energy of 487.24 eV. Compared with that in CsSnI_3 (485.97 eV), the Sn ion with higher oxidation state exhibits higher binding energy, consistent with the aforementioned increment from SnI_2 to SnI_4 . This phenomenon could

be attributed to the electron configuration of the outmost orbital that is $5s^2$ for Sn^{2+} and $5s^0$ for Sn^{4+} . With more loss of Sn 5s electrons, electrons at Sn 3d core-level bind stronger to the nucleus, hence higher binding energy. Combining the literature observations and our findings, it can be thus concluded that Sn cations in Cs_2SnI_6 possess higher oxidation state than CsSnI_3 even if it may not be ideal +4.

According to the XPS data shown in Figure 6.3a-d, a single chemical state was identified for Sn 3d core level at around 487 eV for all the four A_2SnI_6 compounds. However, their binding energy values of Sn $3d_{5/2}$ were not identical. Instead, the binding energy gradually increased with varying A-site cation in the order of $\text{A} = \text{Cs} \rightarrow \text{Rb} \rightarrow \text{MA} \rightarrow \text{FA}$, showing a difference of 0.46 eV between Cs_2SnI_6 and FA_2SnI_6 . Comparing the A_2SnI_6 with similar crystal structure ($\text{A} = \text{Cs}, \text{MA}, \text{FA}$), the compound with larger A-site cations exhibits higher binding energy, which indicates that the Sn cations have lost more 5s electrons to I cations. Therefore, the size of A-site cation affects the binding energy of Sn cation in A_2MX_6 perovskite derivatives.

6.2.3 Investigation on Phase stability against heat and air

The thermal stability of the four lead-free perovskite variant A_2SnI_6 ($\text{A} = \text{Cs}, \text{Rb}, \text{MA}, \text{FA}$) powders were investigated using thermal-gravimetric analysis (TGA). As indicated in Figure 6.4a, all of the four compounds are stable below 150 °C, and Cs_2SnI_6 remains as cubic structure until 300 °C. In comparison to MAPbI_3 of which the bare spin-coated film rapidly degraded to PbI_2 in air at 150 °C,^[9] A_2SnI_6 compounds are more thermally stable. Additionally, the all-inorganic Cs_2SnI_6 and Rb_2SnI_6 exhibited a two-stage weight loss while the hybrid MA_2SnI_6 and FA_2SnI_6 lost all their weight in one step. After the first stage of decomposition, Cs_2SnI_6 and Rb_2SnI_6 lost ~54% and ~58% of the initial weight, corresponding to the molecular weight fraction of SnI_4 (54.7% and 59.6%, respectively). In the second stage, the retained materials start to decompose at ~600 °C, correlating to the decomposition of CsI and RbI with melting point of 621 °C and 646.8 °C, respectively. Hence, these findings revealed that during the heat treatments of Cs_2SnI_6 and Rb_2SnI_6 , the evaporation of SnI_4 happened first, followed by the melting of CsI and RbI. This thermal

degradation mechanism can be expressed in the chemical reaction of $A_2SnI_6 \xrightarrow{\Delta} 2AI + SnI_4 \uparrow$. In contrast, the decomposition processes of A_2SnI_6 and AI are not distinguishable for MA_2SnI_6 and FA_2SnI_6 . The melting points of MAI and FAI are 270 °C and 242 °C, respectively, which are close to the decomposition temperature of ~200 °C. As a consequence, the volatile MAI / FAI and SnI_4 came out together between of 200 – 300 °C, and MA_2SnI_6 / FA_2SnI_6 decomposed completely.

In literature, the thermal stability of Cs_2SnI_6 has been investigated via TGA and differential scanning calorimetry (DSC) up to 600 °C.^[19] The Cs_2SnI_6 powder was prepared by a modified chemical bath method where SnI_2 was applied as the precursor to form $CsSnI_3$ and acetone functioned as the oxidizer to transform $CsSnI_3$ to Cs_2SnI_6 .^[20] Its TGA curve demonstrated a dramatic weight loss of ~50% at ~170 °C, originating from the decomposition of Cs_2SnI_6 . In its DSC curve, an exothermic peak was observed at ~300 °C, well in line with its TGA result. Therefore, our experimental results further affirmed that Cs_2SnI_6 is thermally stable up to ~300 °C.

Figure 6.4 (a) Thermal gravimetric curves of A_2SnI_6 ($A = Cs, Rb, MA, FA$) compounds; (b) Differential scanning calorimetry of representative A_2SnI_6 compounds.

Next, the phase stability below the degradation temperature was examined by DSC and the results are presented in Figure 6.4b. According to their DSC curves, Cs_2SnI_6 and MA_2SnI_6 are stable in cubic crystal structure between -50 °C and 150 °C. Notably, Rb_2SnI_6 and FA_2SnI_6 demonstrated exothermic crest (heat release) and opposite endothermic trough (heat absorption) at ~50 °C and around 0 °C, respectively, indicative of potential phase

transitions. To further understand the origin of these thermic peaks, XRD analysis at various temperatures were conducted. For Rb_2SnI_6 , its XRD patterns were recorded at room temperature (RT), 70 °C, and 100 °C with a heating rate of 10 °C / min, as shown in Figure 6.5a. Using the same cooling rate, the XRD patterns of FA_2SnI_6 were recorded at 5 °C, room temperature, and −10 °C, as displayed in Figure 6.5b.

Figure 6.5 Temperature dependent XRD patterns for (a) Rb_2SnI_6 , and (d) FA_2SnI_6 (RT denotes room temperature of ~26 °C).

Notably for Rb_2SnI_6 , its XRD pattern at the temperature over 50 °C (70 °C and 100 °C) involved fewer diffraction peaks than that at room temperature, confirming the phase transition indicated by the DSC study. Thereby, the crystal structure of Rb_2SnI_6 transformed from tetragonal to cubic upon heating beyond 50 °C. However, this structure deformation is reversible when the temperature returns to room temperature. At 70 °C (red solid line), the peak at 30.0 and 31.1 degrees (marked with the hashtag + and #, respectively) merged into a single peak at 30.6 degrees (marked with an asterisk *) related to the (004) plane involved in the XRD of Cs_2SnI_6 . Further heating to 100 °C (olive dash line) resulted in the slightly increased peak intensity or the enhanced crystallinity rather than the phase transformation to another crystal structure. In terms of FA_2SnI_6 , at 5 °C (red solid line), the XRD pattern was nearly the same as the XRD pattern at room temperature. However, at −10 °C (olive dash line) an additional peak appeared at 17.6 degrees (marked with an asterisk *). Thus, thermic peaks around 0 °C in the DSC curve of FA_2SnI_6 (Figure 6.4b) is not caused by the structure deformation but the formation of some unidentified impurities.

Figure 6.6 XRD patterns for (a) Rb_2SnI_6 , and (d) FA_2SnI_6 powders which were stored in the ambient condition with relative humidity (RH) of $\sim 60\%$ at room temperature for 30 days. The insets display the optical images of the degraded samples.

In addition to the thermal stability, the air stability of Rb_2SnI_6 and FA_2SnI_6 powders were also investigated by XRD analysis. The as-prepared powder samples of Rb_2SnI_6 and FA_2SnI_6 were stored in ambient air with relative humidity of $\sim 60\%$ at room temperature for 30 days. In Figure 6.6, the XRD patterns of fresh and degraded samples were presented as black and red, respectively, along with the photographs of the degraded powders shown in the insets. In the degraded Rb_2SnI_6 sample, some white powder was observed, indicative of a minor degradation. The XRD pattern reveals some peaks (e.g. around 25, 30, 44 degrees marked with hashtags #, +, &, respectively) split into two peaks, signifying a lowering of crystal symmetry. The minor impurity peak appearing at 21.2 degrees (marked with an asterisk *) might be associated to the white impurity RbI . As for FA_2SnI_6 , the initial dark black powders severely degraded to yellow powders. In its relevant XRD pattern, the three broad diffraction crests (all marked with a hashtag #) along with the intense background possibly suggested that FA_2SnI_6 completely degraded and thus a potential mixture of FAI , SnI_4 , and SnO_2 formed. This lower air stability is attributed to the propensity of FA^+ to form hydrogen bonding with water in air. In literature, the air stability of Cs_2SnI_6 powder has been studied by Jiang et al., which demonstrated that it undergone a minor decomposition and slight CsI impurity formed after exposing to air for one month.^[19] Hence, in comparison to Cs_2SnI_6 , Rb_2SnI_6 is relatively stable in air for one month while FA_2SnI_6 is less stable due to the incorporation of the organic A-site cation.

Table 6.1 Summary of the structural information, optical property and thermal stability for A_2SnI_6 ($A = Cs, Rb, MA, FA$) compounds.

Properties	Rb_2SnI_6	Cs_2SnI_6	MA_2SnI_6	FA_2SnI_6
A-site cation radius ^[13]	1.52 Å	1.67 Å	1.80 Å	1.9-2.2 Å
Crystal structure	Tetragonal	Cubic ($Cs_2SnI_6 < MA_2SnI_6 < FA_2SnI_6$)		
Bandgap	1.38 eV	1.32 eV	1.36 eV	1.38 eV
Decomposition temperature	200 °C	250 °C	200 °C	150 °C

Finally, the aforementioned crystal structure, the estimated bandgap and decomposition temperature, of the lead-free perovskite derivatives A_2SnI_6 ($A = Cs, Rb, MA, FA$) are summarized in Table 6.1. Except for Rb_2SnI_6 , the other three compounds possess similar cubic structure. Moreover, their bandgap values gradually increase with increasing radii of the A-site cation. Nevertheless, their decomposition temperatures decrease in the order of $A = Cs \rightarrow MA \rightarrow FA$. Because of the smaller A-site cation, Rb_2SnI_6 favors a less symmetric structure, and slightly higher bandgap, compared to Cs_2SnI_6 . Based on their bandgap of ~ 1.34 eV and excellent thermal stability beyond 150 °C, the four A_2SnI_6 compounds are possibly suitable for photovoltaic applications.

6.3 Applications of A_2SnI_6 compounds in photovoltaic devices

To apply the lead-free A_2SnI_6 ($A = Cs, Rb, MA, FA$) compounds into photovoltaic devices as the light absorbing materials, their powders were dissolved in DMF solvent and spin-coated on the mesoporous TiO_2 substrate, followed by annealing at 100 °C. The surface morphology of the resultant films obtained by scanning electron microscopy (SEM) are shown in Figure 6.7. None of the A_2SnI_6 films deposited by single-step spin-coating exhibited a complete surface coverage. As shown in Figure 6.7a, large cubic crystals of the Rb_2SnI_6 films could be attributed to the fast precipitation of RbI . On the contrary, Cs_2SnI_6 films contained small grains distributing randomly (Figure 6.7b). As for the hybrid compounds, FA_2SnI_6 films formed islands of grains along with large uncovered areas (Figure 6.7d), and MA_2SnI_6 films exhibited grain clusters with dendritic shapes (Figure

6.7e). All of these poor film morphologies could be a consequence of the inhomogeneous crystallization of A_2SnI_6 . In an attempt to improve the film morphology, a sequential deposition method was adopted, where the spin-coated AI film was dipped into the SnI_4 solution, followed by spinning to remove excess solution and annealing at 100 °C. Consequently, the morphology of Cs_2SnI_6 and MA_2SnI_6 films are improved with increased surface coverage on TiO_2 substrates, as shown in Figure 6.7c and f, respectively. Therefore, the full PV device with the architecture of FTO/ planar TiO_2 / mesoporous TiO_2 / A_2SnI_6 / Spiro/ Au were constructed using optimized Cs_2SnI_6 and MA_2SnI_6 films as photoabsorbers.

Figure 6.7 The top-view SEM images of (a) Rb_2SnI_6 films (b) Cs_2SnI_6 films deposited by single-step spin-coating, (c) Cs_2SnI_6 films deposited by sequential spin-coating, (d) FA_2SnI_6 films, (e) MA_2SnI_6 films deposited by single-step spin-coating, and (f) MA_2SnI_6 films deposited by sequential spin-coating. The scale bar is 1 μm in all the images.

In the fabrication of the Cs_2SnI_6 / MA_2SnI_6 based PSCs, mesoporous scaffold was adopted as the substrate of perovskites for higher loading of absorber materials, in comparison with planar charge transport layer. The photocurrent–voltage (J–V) characteristics of the best-performing solar cells incorporating Cs_2SnI_6 and MA_2SnI_6 compounds are presented in Figure 6.8a and b, along with their photovoltaic parameters listed in the insets. Both devices yielded power conversion efficiencies (PCEs) of $\sim 0.01\%$, and Cs_2SnI_6 incorporated device provided higher open-circuit voltage (V_{oc}) while MA_2SnI_6 incorporated device possessed higher short-circuit current density (J_{sc}). This signifies that the potential loss in Cs_2SnI_6

incorporated device were less than that in MA_2SnI_6 incorporated device. It is noted that the air-stable Cs_2SnI_6 compounds have been utilized as light absorbers in other works. However, none of them achieved PCEs exceeding 1%, and the highest record of PCE to date is 0.96%, together with J_{sc} of 5.4 mA/cm^2 , V_{oc} of 0.51 V and fill factor (FF) of 0.35.^[1, 6, 8] Compared to the highest-PCE device reported in literature, our champion device based on Cs_2SnI_6 compounds demonstrated higher FF. This enhanced FF might be correlated to the reduced resistivity evaluated by the following DC Hall measurements.

Figure 6.8 J–V characteristics for the champion PSCs based on (a) Cs_2SnI_6 and (b) MA_2SnI_6 compounds, measured under illumination and dark. The insets demonstrate the photovoltaic parameters of the corresponding device.

According to the DC Hall data listed in Table 6.2, the polycrystalline pellet of Cs_2SnI_6 possessed a carrier density of $2.8 \times 10^{15} \text{ cm}^{-3}$ and mobility of $72 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. In comparison to Cs_2SnI_6 , MA_2SnI_6 exhibited a similar carrier density and lower mobility. The higher resistivity demonstrated by MA_2SnI_6 contributed to its lower FF of the device based on MA_2SnI_6 as compared to Cs_2SnI_6 . Additionally, the literature values of Cs_2SnI_6 pellet, CsSnI_3 film and MAPbI_3 film are also presented in Table 6.2. The Cs_2SnI_6 prepared in the current case was less resistive than the Cs_2SnI_6 demonstrated in literature, along with higher carrier density and much lower mobility. Compared to the CsSnI_3 perovskite, both carrier density and mobility are suppressed in Cs_2SnI_6 and MA_2SnI_6 , due to the absence of Sn cation vacancies.^[21] These relatively modest electrical transport characteristics in Cs_2SnI_6 and MA_2SnI_6 make them more promising as photovoltaic materials than the unstable CsSnI_3 . Furthermore, the high-performance photovoltaic material MAPbI_3 is

reported to possess significantly lower carrier density and higher mobility than Cs_2SnI_6 , contributing to a long carrier lifetime.^[22]

Table 6.2 Electrical properties of Cs_2SnI_6 and MA_2SnI_6 compounds estimated by the Hall Effect and compared with the literature values of Cs_2SnI_6 pellet, CsSnI_3 film and MAPbI_3 film.

Electrical Properties	Cs_2SnI_6	MA_2SnI_6	Cs_2SnI_6 (ref.) ^[5]	CsSnI_3 (ref.) ^[23]	MAPbI_3 (ref.) ^[10, 24]
Carrier density (cm^{-3})	2.8×10^{15}	2.1×10^{15}	$\sim 1 \times 10^{14}$	$< 1 \times 10^{17}$	$\sim 1 \times 10^9$
Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	72	14	310	585	66 – 140
Resistivity ($\Omega\cdot\text{cm}$)	54	287	100	0.9	-

Next, the valence band edge of A_2SnI_6 ($\text{A} = \text{Cs}, \text{Rb}, \text{MA}, \text{FA}$) compounds was estimated via ultraviolet photoelectron spectroscopy (UPS) and the relevant results are demonstrated in Appendix Figure A.5. The conduction band edge was determined by adding the band gap energy identified by Tauc fit onto the corresponding valence band edge. Together with the literature values of widely-studied charge transporting materials, the band diagram was depicted in Figure 6.9. The valence band maximum (VBM) of A_2SnI_6 are significantly lower than the highest unoccupied molecular orbital (HOMO) level of the hole transporting materials (Spiro and P3HT), implying an inefficient hole extraction. Moreover, their conduction band minimum (CBM) are lower than that of the electron transporting materials (TiO_2 and SnO_2) and meanwhile close to HOMO level of Spiro and P3HT, indicating high potential losses due to the charge carrier recombination at the interface between A_2SnI_6 and Spiro / P3HT. In comparison to the CBM of Cs_2SnI_6 reported in literature (e.g. -4.01 eV and -4.67 eV), our CBM is lower, as the optoelectronic properties are dependent on the synthesis conditions.^[8, 17] The study of band alignment in this work thus underscores the need to find suitable ETL and HTL beyond the conventional ones to expand the search of a Pb-less perovskite based absorber.

Figure 6.9 Band diagram of $A_2\text{SnI}_6$ solar absorbing compounds and widely-studied charge transporting materials.

Overall, the extremely poor photovoltaic performance from Cs_2SnI_6 and MA_2SnI_6 incorporated devices are associated to (1) void-containing film morphology, and (2) mismatch of band alignment between the Cs_2SnI_6 / MA_2SnI_6 compound and the applied charge selective materials, as demonstrated by the aforementioned experimental results. In the future, the photovoltaic behaviors can be improved by optimizing the film morphology and the charge transporting layers. Additional properties such as carrier lifetimes and diffusion lengths should be further investigated to gain deep insights of the recombination dynamics in these pronounced air-stable lead-free materials.

6.4 Conclusions

In conclusion, all the four $A_2\text{SnI}_6$ ($A = \text{Cs}, \text{Rb}, \text{MA}, \text{FA}$) compounds possess ideal bandgap close to 1.34 eV and prominent thermal stability up to 150 °C. Rb_2SnI_6 with a smaller A-site cation favours tetragonal crystal structure and transits to more symmetric cubic structure upon heating over 50 °C. FA_2SnI_6 exhibits cubic structure as Cs_2SnI_6 and MA_2SnI_6 at room temperature, and some impurities possibly formed during cooling below 0 °C. Additionally, it is less stable than the all-inorganic Cs_2SnI_6 and Rb_2SnI_6 compounds in air. Due to the difficulty in controlling the crystallization process, only Cs_2SnI_6 and MA_2SnI_6 films with better film morphology were exploited as light absorber in mesoscopic

solar cells. The poor PCEs of ~0.01% were potentially attributed to the improper band alignment with the applied charge selective contacts.

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Chapter 7

Conclusion and Future Work

This chapter concludes the thesis by drawing general guidelines on the design strategies of non-toxic and stable perovskite materials for photovoltaic applications based on the findings of this thesis work. Additionally, the extent of how the outcomes of this dissertation were reflected in the original hypotheses is addressed. Finally, the opportunities of the three types of perovskite materials developed in this research are discussed for future perspectives.

7.1 Impact and outcomes

The development of new lead-free perovskite solar harvesting materials that are non-toxic and stable to substitute the lead-based perovskites in the state-of-the-art highly-efficient perovskite solar cells has become a challenging frontier in the photovoltaic research field. According to the recent studies, the efficiency of tin-based perovskite solar cells have been improved approaching 10%, making them one of the most potential candidates for environmental-friendly PSCs.^[1, 2] However, some practical concerns are raised regarding the instability of tin-based perovskite materials in air due to the spontaneous oxidation from Sn(II) to Sn(IV) and the acidic by-product formed during the oxidation that may be harmful to living cells.^[3] To resolve these issues regarding toxicity/instability and explore new substitutes for lead-based perovskites, several hypothesis have been proposed:

- (i) It is feasible to completely replace Pb^{2+} in APbX_3 perovskites by a divalent metal cation from the same group of Pb, i.e. Ge^{2+} .
- (ii) It is possible to partially substitute Pb^{2+} in hybrid perovskites by Sn^{2+} without compromising efficiency and stability of devices based on $\text{APb}_{1-x}\text{Sn}_x\text{X}_3$ perovskites.
- (iii) It is plausible for the M-site in AMX_3 perovskites to be occupied by a tetravalent cation, i.e. Sn^{4+} , forming a derived structure like A_2MX_6 .
- (iv) Altering the A-site cation in either AMX_3 or A_2MX_6 perovskites shall tune the structural and optical properties.

In this thesis work, three classes of perovskite materials with different chemical compositions have been developed and their optoelectronic properties and photovoltaic applications have been investigated to prove or disprove these hypothesis. The novel findings of this study are summarized and presented below.

1. *The first successful application of lead-free germanium-based halide perovskites (CsGeI_3 and MAGeI_3) in photovoltaic devices.*

The solar cells employing lead/tin-based perovskites as light harvesters have demonstrated highly-efficient performance. As lead, tin and germanium are all located in the same group of the period table, eco-friendly germanium-based perovskite materials were predicted to

replace lead-based perovskites in PSCs. This study demonstrated for the first time the successful application of both inorganic and organic germanium-based halide perovskites (AGeI_3 , where $A = \text{Cs, MA, or FA}$) in photovoltaic devices. While their device performances are suppressed by their poor film morphology and Ge^{2+} -oxidation induced instability, these germanium-based perovskite materials exhibited high thermal stability, allowing them to work in the high-temperature environment (up to 150°C). Furthermore, this study paves a new way for expanding the bandgap of perovskites by introducing germanium instead of tailoring the halide anion. The recent demonstration of germanium-based mixed-halide PSCs further suggests germanium as a potential alternative for substituting lead.^[4]

2. *The essential role of tin incorporation in tuning optoelectronic properties and controlling charge recombination process in the lead-tin binary perovskites $[\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$, where $0 \leq x \leq 1$].*

The lead-tin binary perovskites possessed, rather uniquely, narrower bandgaps than either pure lead- or pure tin- based perovskites that are close to the ideal bandgap (1.34 eV) predicted by the well-known Shockley-Queisser limits.^[5] In addition, the charge recombination process within the monocrystalline perovskite layers and the mesoscopic perovskite devices were further investigated via transient absorption and electrochemical impedance spectroscopic characterizations respectively. Perovskite layers with higher tin content shows longer carrier lifetime, suggesting slower carrier recombination, which however is in conflict with the findings for perovskite devices. Correlating to the decreasing photovoltage with the increasing tin content, it can be concluded that the severe charge recombination presented at interfaces rather than in perovskite layer governed the device performance. Overall, this work sets a typical example for tuning optoelectronic properties and photovoltaic performance by tailoring the M-site metal cation in AMX_3 perovskites, making binary perovskites an ideal platform to design light-absorber materials with less toxic lead content.

3. *The discovery and development of new hybrid lead-free tin(IV)-based perovskite compounds (MA_2SnI_6 and FA_2SnI_6) with reduced dimensionality, enhanced ambient stability and ideal bandgap.*

In this study, the complete replacement of divalent lead cations by tetravalent tin cations leads to the formation of a series of zero-dimensional perovskite derivatives ($A_2\text{SnI}_6$, where $A = \text{Rb}, \text{Cs}, \text{MA}, \text{or FA}$), due to the lack of tin cations to connect SnI_6 octahedral together. For the first time, the air-stable solution-processed MA_2SnI_6 films were adopted as light absorber in mesoporous lead-free perovskite solar cells. Although their associated devices show poor performance, these lead-free $A_2\text{SnI}_6$ compounds possess ideal bandgaps close to 1.34 eV and pronounced ambient and thermal stabilities, making them potential starting materials towards designing an efficient air-stable eco-friendly solar cell. Overall, the results of this study demonstrate some promise of tin(IV)-based perovskite compounds for solar cell applications, in a good agreement to the recent studies on Cs_2SnI_6 based solar cells from different groups.^[6, 7]

4. *The correlation between A-site cations and optoelectronic properties and ambient and thermal stabilities in the germanium(II) and tin(IV) iodide perovskites.*

The studies of AGeI_3 and $A_2\text{SnI}_6$ perovskite materials both have shown that the careful choice of A-site cation allows a fine tuning of optoelectronic properties for the metal-halide perovskites as well as their stabilities against heat and air. In the AGeI_3 system, the substitution of Cs with MA and FA molecules shifts the valence band level downwards which is responsible for the bandgap broadening. On the other hand, A-site cations are electronically inactive in the $A_2\text{SnI}_6$ system, leading to similar bandgap values of $A_2\text{SnI}_6$ compounds with different A-site cations ($A = \text{Rb}, \text{Cs}, \text{MA}, \text{or FA}$). In both perovskite systems, the perovskites with small organic A-site cations degraded at lower temperature upon heating than those with relatively stable inorganic cations. Additionally, hybrid FA_2SnI_6 powders suffered more severe deterioration in ambient environment in comparison to inorganic Rb_2SnI_6 powders, due to the high affinity towards humidity of FA cations.

In conclusion, all the aforementioned hypothesis have been proved successfully to different extents in this thesis work. From a broad fundamental standpoint, the findings presented in this dissertation highlight the essential role of chemical compositions on altering structural, morphological and optoelectronic properties of perovskite materials as well as their ambient and thermal stabilities. The germanium(II) substitution of lead in APbX_3 perovskites broadened the bandgap and depressed the ambient stability; the partial tin(II)

incorporation in the $\text{APb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ mixed-halide system lowered the bandgap and suppressed the charge recombination process within the perovskite layer; the complete tin(IV) substitution reduced the dimensionality but enhanced the ambient stability. Moreover, the replacement of inorganic cations with small organic cations at A-sites improved the film formation and altered the band edge positions, and nevertheless reduced the ambient and thermal stabilities.

7.2 Future prospects

In this thesis work, two classes of lead-free perovskites (AGeI_3 and A_2SnI_6) and a series of $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ binary perovskites have been used as the model materials for studying the relationship among perovskite composition, optoelectronic properties and photovoltaic applications, establishing the bases for the rational design and development of nontoxic and stable perovskite materials for photovoltaic applications in future. To identify new perovskite-type compounds as nontoxic and stable solar-harvester candidates, theoretical screenings based on the thermodynamic stabilities, bandgaps, and other critical electronic or optical properties are necessarily adopted in the first place. Recent studies have suggested that substituting lead(II) with one or two non-divalent metal cation results in the formation of new perovskite-derivate candidates with chemical formulae such as $\text{A}_3\text{M}_2^{3+}\text{X}_9$, $\text{A}_2\text{M}^{4+}\text{X}_6$, $\text{A}_2\text{M}^{1+}\text{M}^{3+}\text{X}_6$, and AM^{5+}X_6 .^[8, 9] In comparison with the standard AM^{2+}X_3 perovskites, these perovskite derivatives exhibit new crystal structures and electronic features and favorable stability for photovoltaic applications. In the near future, these suggested perovskites and derivatives are expected to be synthesized and experimental investigations will be performed to validate their applications in photovoltaic devices.

From the synthetic point of view, the main challenge consists in the careful combination of inorganic or organic A-site cations and single or mixed halide anions with the selected nontoxic metal cation. To modify the perovskite crystal structure and optimize the chemical composition for desired properties, ion replacement, doping or alloying can be adopted. For instance, two-dimensional germanium(II)-based perovskites are expected to be designed by replacing small MA^+/FA^+ cations with more complex organic cations and their

associated solar cells might achieve higher efficiency and stability. In terms of the processing steps, there are several outstanding questions to be considered: (i) how to form a uniform stoichiometric phase without impurities throughout the perovskite film? (ii) how to choose electron and hole transporting materials with appropriate band alignment and without interfacial chemical reaction to the designed perovskite? (iii) how to deposit a smooth and continuous perovskite film layer on the selected charge transporting layer? In particular, these questions need to be solved for the further improvement of tin(IV)-based perovskite solar cells. Overall, the theory-experiment-integrated approach discussed above should be adopted through the discovery and development of truly functional lead-less perovskite-type materials for the employment in a solar device with measurable performance, which starts from the theoretical calculation, followed by synthesis of the predicted compounds, deposition of perovskite thin films, characterizations of photovoltaic-related properties, and device fabrication and evaluation.

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APPENDIX

Figure A.1 Predicted bandgap values of the 360 AMX_3 halide perovskite compositions. The top, middle and bottom section correspond to X-site species with halogens $X = \text{Cl}$, Br and I , respectively, and in each session, the x and y axes correspond to M and A-site components.

(a)

(f)

(b)

(g)

(c)

(h)

Figure A.2 XPS spectra of non-etched samples with (a) $x = 0.2$, (b) $x = 0.4$, (c) $x = 0.6$, (d) $x = 0.8$, (e) $x = 1.0$ (pure Sn), and etched samples with (f) $x = 0.2$, (g) $x = 0.4$, (h) $x = 0.6$, (i) $x = 0.8$, (j) $x = 1.0$ (pure Sn)

Figure A.3 Top-view SEM images of $\text{FAPb}_{1-x}\text{Sn}_x(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskite thin-films depending on the amount of Sn: (a) $x = 0$ (pure Pb); (b) $x = 0.2$; (c) $x = 0.4$; (d) $x = 0.6$; (e) $x = 0.8$; (f) $x = 1.0$ (pure Sn).

Figure A.4 Time-resolved UV-Vis absorption measurements to probe the ambient stability of FAPb_{1-x}Sn_x(I_{0.8}Br_{0.2})₃ perovskite thin-films: (a) $x = 0$ (pure Pb); (b) $x = 0.2$; (c) $x = 0.4$; (d) $x = 0.6$; (e) $x = 0.8$; (f) $x = 1.0$ (pure Sn).

Figure A.5 The UPS spectra of (a) Cs_2SnI_6 , (b) Rb_2SnI_6 , (c) MA_2SnI_6 , and (d) FA_2SnI_6 ; The valence band edge against the Fermi level of (e) Cs_2SnI_6 , (f) Rb_2SnI_6 , (g) MA_2SnI_6 , and (h) FA_2SnI_6 .