Investigating the optical and electronic properties of halide perovskite inspired antimony compounds

Padinhare Cholakkal Harikesh

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**INVESTIGATING THE OPTICAL AND ELECTRONIC
PROPERTIES OF HALIDE PEROVSKITE INSPIRED
ANTIMONY COMPOUNDS**

PADINHARE CHOLAKKAL HARIKESH

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

2019

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PROPERTIES OF HALIDE PEROVSKITE INSPIRED
ANTIMONY COMPOUNDS**

PADINHARE CHOLAKKAL HARIKESH

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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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

31st July 2019

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Date

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Assoc Prof Nripan Mathews

Authorship Attribution Statement

This thesis contains material from 2 papers published in the following peer-reviewed journals where I was the first author.

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The contributions of the co-authors are as follows:

- Prof. N. Mathews, Dr. H.K. Mulmudi and Dr. T.M. Koh provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
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- B. Ghosh performed and helped with the Density Functional Theory Analysis. Prof. S. Li helped with the analysis.
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- Prof. N. Mathews provided the initial project direction and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised together with Dr. R.A. John
- I performed all the materials' synthesis, collected X-ray diffraction patterns and visible light spectra, carried Scanning electron microscopy, and conducted electrical measurements and data evaluation.
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- K. Thirumal helped with the PESA analysis and provided inputs regarding the chemical reactions.
- Prof. S. Mhaisalkar provided direction to the project and helped with interpretations.

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Abstract

Lead halide perovskites have shown great promise as semiconductor for optoelectronic applications including solar cells, Light emitting devices, X-Ray detectors, Memristors and Neuromorphic devices. The origin of their exceptional properties are linked to their unique orbital character which enables a tunable band gap, large absorption coefficient, low exciton binding energies, long electron and hole diffusion lengths with sufficient mobilities and absence of deep traps in the band gap. The ionic-electronic coupling in the material emergent from the doping induced by ionic segregation is a double-edged sword which can be utilized positively in neuromorphic devices and should be avoided in solar cells and LEDs to avert injection barriers and hysteresis. Presence of an anti bonding valence band maximum induced by presence of ns^2 electrons and the high spin orbit coupling effect of Lead enable defect tolerance in this material by avoiding deep traps inside the band gap. This is the fundamental reason for their long carrier lifetimes and diffusion lengths and also the relatively shallow trap formation despite severe ionic migration. In addition, the p to p transitions equip them with a large absorption coefficient reducing the thickness of the layer required for complete absorption. The high electronic dimensionality enabled by the connected lattice structure also contributes to high mobilities and limiting the defects. Some of these properties like heaviness of lead, ionic migration induced doping (segregated +ve and -ve ions n and p doping the material locally) and solubility in common solvents could both be a boon or bane by enabling facile fabrication of a semiconductor with excellent properties but at the same time inducing toxicity, easy degradation and effects like hysteresis in solar cells. Hence, understanding the role of each these properties by exploring electronically similar materials will enable the understanding of halide perovskites, eliminating undesired properties and also sparking novel material discovery and applications.

This thesis focuses on Antimony based compounds due to its low toxicity, the presence of ns^2 electrons and the possible p to p transitions similar to halide perovskites with suitable anion combination. In addition, the lower atomic mass of Antimony compared to Lead is

beneficial to systematically investigate the role of heaviness of metal cation in halide perovskites. Two structurally dissimilar but electronically similar material systems – $\text{A}_3\text{Sb}_2\text{I}_9$ and NaSbS_2 were evaluated in this thesis because of the presence of the above mentioned properties. Firstly, the role of A cation in templating the layered structure of $\text{A}_3\text{Sb}_2\text{I}_9$ was studied. **The study was the first to unravel that a smaller A cation (Rb) can induce the formation of 2D layered structure** in $\text{Rb}_3\text{Sb}_2\text{I}_9$ opposed to a 0D dimer structure as in $\text{Cs}_3\text{Sb}_2\text{I}_9$. The 2D structured material had high absorption coefficients (10^5 cm^{-1}), low dark carrier densities ($10^{13} - 10^{14} \text{ cm}^{-3}$), decent mobilities ($1-10 \text{ cm}^2/\text{Vs}$) and resulted in better performance in solar cells compared to 0D form indicating the importance of electronic dimensionality in halide perovskites. However, the efficiencies (0.66%) were very low compared to lead halide perovskites.

Secondly, the effect of Atomic mass of metal cation on the optoelectronic properties of the layered $\text{A}_3\text{Sb}_2\text{I}_9$ compounds was evaluated by partially substituting Sb with Bi in $(\text{NH}_4)_3\text{Sb}_2\text{I}_9$. **The study showed, for the first time, the ability to tune the carrier type by just tuning the Atomic mass of the metal cation in $(\text{NH}_4)_3\text{Sb}_2\text{I}_9$.** This was achieved by changing the defects in the material. The heavy element Bismuth was shown to shift both the conduction and valence bands downward owing to its enhanced spin orbit coupling and ability to prevent ns^2 electrons from taking part in bonding respectively. This resulted in shallower conduction band side defects and deeper valence band defects on increased bismuth content hence changing the carriers from p to n type. The study proved the hypothesis that heaviness of the metal cation can influence defects in halide perovskites. In addition, the study also unraveled the role of a close direct-indirect band gap in the material in inducing long carrier lifetimes ($>100\text{ns}$). Furthermore, the ionic migration in the material was shown to induce doping in the material resulting in the **first report on Switchable Photovoltaic effect in Lead free halide perovskites.** This ionic-electronic coupling necessitates the need for alternative solar cell architectures to effectively harness carriers in these class of materials. The material also exhibited high absorption coefficients (10^5 cm^{-1}), low trap densities (10^{16} cm^{-3}), decent mobilities ($\sim 1 \text{ cm}^2/\text{Vs}$). However, the efficiency was still limited to 1.09% indicating that ns^2 electrons

and defect tolerance may not be a sufficient condition to achieve high efficiencies in solar cells.

Inspired by the conclusions from the above studies, the third work focused on effectively utilizing ionic-electronic coupling in a more structurally connected Sb based system – NaSbS₂ with similar electronic structure as lead halide perovskites. The material was found to have a tunable ionic conductivity based on the ambient and the Na ion content enabling super ionic conductivity in ambient (0.17mS/cm) with a 5% excess Na and mixed ionic-electronic conductivity in vacuum. In addition to that, it exhibited a suitable band gap (1.46eV) and high absorption coefficients (10^5 cm^{-1}) suitable for application in photovoltaic devices. The persistent Photo conductivity in the material was utilized to demonstrate potential application in artificial synaptic device with facile post fabrication tuning of synaptic plasticity enabled by electric field induced removal of Na ions. The study set up design rules for a novel area of Electrically re-configurable material which can be post-processed via electric field induced ionic insertion or removal.

Lay Summary

Lead halide Perovskites are compounds with formula AMX_3 where A is an organic or inorganic Cation like Cs or Methyl ammonium, B is usually Lead and X is a halogen (Iodine, Bromine or Chlorine). These materials are easily solution processable semiconductors and have found plethora of applications including Solar cells, Light Emitting Diodes, X-Ray Detectors and Memory devices. The reason for this versatility stem from their amazing properties like high light absorption capability, tunable band gap, ability to transport charges through a longer distance without recombination and their ability to retain properties despite slight compositional changes.

The fundamental reason for these properties are linked to their unique bonding characteristics. Different from other semiconductors, their valence bond is an anti-bonding orbital which enable defect tolerance in this material – i.e the ability to retain good semiconducting properties despite having crystallographic defects. They also have valence and conduction bands comprised of p orbitals which is the reason for the high light absorption. The ability to tolerate defects also allow the intrinsic ions to move without significantly deteriorating the material properties and resulting in local doping. Some of these properties have also been a bane, like when the heaviness of Lead is partly responsible for the defect tolerance in the material, it also is the origin of toxicity of this material. Similarly, the ionic migration induced property changes while being beneficial for memory devices, also lead to adverse effects in solar cells. Thus, investigating the role of each of these properties by exploring alternative material systems will enable deeper understanding of the material, enable methods to control it and spark discovery of novel materials and applications.

This thesis focused on Antimony based compounds because of their electronic similarity with Lead. In addition, its lower atomic mass compared to Lead enabled the systematic investigation of role of Atomic mass on properties of halide perovskite inspired materials. Two material systems $A_3Sb_2I_9$ and $NaSbS_2$ were investigated for their optoelectronic properties. The studies unraveled several interesting insights including the role of size of

A cation on structure of $A_3Sb_2I_9$, importance of Atomic mass in tuning charge carriers in the material, role of defect tolerance and ion induced doping in these materials and their implications on devices like solar cells and memristors. The investigations also lead to fascinating novel concept of semiconductors which can be post processed using electric fields after synthesis to enable desired properties.

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Abbreviations

0D	Zero Dimensional
1D	1 Dimensional
2D	2 Dimensional
3D	3 Dimensional
ALD	Atomic Layer Deposition
AFM	Atomic Force Microscopy
BSE	Back-scattered Electron
CL	Cathodoluminescence
CBM	Conduction Band Minimum
DFT	Density Functional theory
DSC	Differential Scanning Calorimetry
DOS	Density of States
ETL	Electron Transporting Layer
HTL	Hole Transporting Layer
IR	Infrared
LED	Light-emitting Diode
LIF	Leaky Integrate and Fire
LTP	Long Term Potentiation
LTD	Long Term Depression
IPCE	Incident Photon to Current Conversion Efficiency
MIEC	Mixed Ionic Electronic Conductor

NIR	Near-infrared
PBE	Perdew–Burke–Ernzerhof
PESA	Photoelectron Spectroscopy in Air
PL	Photoluminescence
PPF	Paired Pulse Facilitation
PC	Photoconductivity
SE	Secondary Electron
SEM	Scanning Electron Microscopy
SPV	Switchable Photovoltaic Effect
SNN	Spiking Neural Network
STP	Short Term Potentiation
STDP	Spike Timing Dependent Plasticity
TCSPC	Time-correlated Single Photon Counter
TAS	Thermal Admittance Spectroscopy
TA	Transient Absorption
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TRPL	Time-resolved Photoluminescence
UPS	Ultraviolet Photoelectron Spectroscopy
UV	Ultraviolet
VBM	Valence Band Maximum
VIS	Visible
XRD	X-ray Diffraction

XPS	X-ray Photoelectron Spectroscopy
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Chemical Names

DMF	N,N-dimethylformamide
DMSO	Dimethylsulfoxide
FTO	Flourine doped Tin Oxide
ITO	Indium Tin Oxide
PEO	Polyethylene oxide
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
PolyTPD	Poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine]
TiO ₂	Titanium dioxide

Physical Quantities

Abbreviation	Quantity	Unit
EQE	External Quantum Efficiency	%
FWHM	Full Width Half Maximum	nm
IQE	Internal Quantum Efficiency	%
Jsc	Current Density	mA/cm ²
PCE	Power Conversion Efficiency	%
PLQY	Photoluminescence Quantum Yield	%
RH	Relative Humidity	%
Voc	Open Circuit Voltage	V

R	Resistance	Ω
C	Capacitance	F
α	Absorption Coefficient	cm^{-1}
EPSC	Excitatory Post Synaptic Current	nA

Chapter 1

Introduction

This chapter elaborates the motivation and hypothesis behind this work. The scope and the objectives of the thesis are detailed followed by the overview and the implications of the work.

1.1 Motivation and Hypothesis

Lead halide perovskites have emerged as a wonder material with applications ranging from Solar cells^[1], LEDs^[2], Lasers^[3], X-Ray Detectors^[4], Memristors^[5] and Neuromorphic devices^[6,7]. Halide perovskite based solar cells have surpassed an unprecedented 24% power conversion efficiency^[8] within a decade. The reasons for the phenomenal performance of these class of materials in a variety of solar cell architectures and LEDs include a tunable band gap, large absorption coefficient^[9,10], low exciton binding energies^[11], long electron and hole diffusion lengths^[12,13] with sufficient mobilities^[14] and absence of deep traps^[9] in the band gap. Fundamental origin of these properties has been linked to the unique orbital characteristics of Pb^{2+} cation, with ns^2 electrons imparting defect tolerance^[15] ability to the perovskite semiconductor. This enables them to be manufactured without the need of strict and complex manufacturing protocols. In addition to this, these materials are mixed ionic-electronic conductors (MIECs)^[16]. But differing from other MIECs, the motion of ions do not deteriorate the electronic properties of this material owing to its defect tolerance property. This enables facile doping induced by electric fields to unlock novel phenomena like switchable photovoltaic effect^[17] and applications in memristors and neuromorphic devices. Despite these advantages, the presence of lead and the poor atmospheric stability of the material render the material unsuitable for commercial applications. However, they do serve as an archetype for how a solution processed semiconductor can achieve superior semiconducting properties. Hence, finding out novel solution processable non-toxic semiconductors with similar properties is of high interest to the research community.

In order to find out alternative semiconductor with similar properties, it is imperative to understand the origin of the exceptional properties exhibited by lead halide perovskites at a fundamental level. Lead based perovskites are considered ideal photovoltaic absorbers due to the suitable band gap with high absorption coefficients, decent electron and hole mobility, high minority carrier lifetimes and low intrinsic carrier concentrations. According to first-principle calculations, the reason for the phenomenal performance of the lead based perovskites is linked to the outermost s electrons in the metal cation^[9,15,18].

These s electrons can hybridize with the halogen (anion) p orbitals to give anti-bonding character to the valence band maximum as well as reducing the ionization energy. Pb being heavy causes significant spin orbit coupling which pushes the conduction band minimum downwards. Hence, the defects with high formation energies form only near or inside the band and do not form deep level traps. In addition, the I p to Pb p transitions coupled with high probability Pb s to Pb p transitions lead to high absorption coefficients.

Figure 1.1: (a) Structure of the standard MAPbI₃ perovskite (b) Bonding and antibonding orbitals in MAPbI₃ demonstrating the valence and conduction bands.

The role of the organic cation on the properties is highly debated. Even though it does not affect the valence and conduction band edges, the dipole moment associated with these organic cations are claimed to increase the dielectric constant which in turn help in lowering the exciton binding energy as well as contribute to defect screening^[15]. In addition, the high electronic dimensionality arising from the closely connected octahedral structure of perovskites is another contributing factor to its excellent charge transport and defect tolerance properties. The high ionic mobility of the material is linked to its soft and connected lattice. Thus, it is rational to look for highly connected structures containing elements with similar electronic configuration as Pb²⁺ (with outer s electrons) as potential candidates. Tin^[19–22] and Germanium^[23,24] belong to the same group as lead and hence are expected to show similar electronic properties. However, Sn and Ge are lighter compared to lead and the inert pair effect, deemed to be the reason for the stability of Pb²⁺ ion^[25], is weaker in them. Thus, the +2 states of these elements are unstable and are readily

oxidized to +4 states. The other immediate possibilities are Bi and Sb which are in the nearest group as lead in the periodic table and have the ability to form +3 ions with similar electronic configuration as Pb^{2+} . The good photovoltaic properties exhibited by Antimony Chalcogenides^[26] and the report on $\text{Cs}_3\text{Sb}_2\text{I}_9$ as a semiconducting material^[27] makes Sb based materials as favorable candidate for the present project. However, the +3 oxidation state prevents them from forming the perovskite structure. Hence, this work adopts a wider search for Sb^{3+} based materials incorporating perovskite derivatives and materials with similar electronic structures as perovskites. The study starts by exploring alternative semiconductors for solar cells but expands it to other applications involving ionic-electronic coupling based on the observed properties and limitations/strengths of the materials.

The hypothesis presented here are :

1. Antimony halides and chalcogenides can be promising optoelectronic materials due to ns^2 electrons, p to p transitions.
2. Connected octahedra and symmetry are critical in determining the optoelectronic properties of halide perovskites and perovskite like materials
3. Heavy elements can play key role in reducing the band gap and screening defects of the halide perovskites due to the spin orbit coupling effect which forces the donor type defects to be formed inside the conduction band.
4. The defect tolerance in the materials can enable ionic-electronic coupling leading to novel applications due to formation of shallow traps. This includes local doping and interfacial barrier formed by shallow traps introduced by ionic segregation.

1.2 Objectives and Scope

The objectives of this project are as follows:

1. To synthesize and characterize (optical, electrical, structural properties) $\text{A}_3\text{Sb}_2\text{I}_9$ structures and investigate them for solar cells and other optoelectronic applications. This includes understanding the effect of different A cations (Rb, Cs and Ammonium) on the structure and properties of these class of materials. Novel solution processing

strategies will be adopted to form phase pure thin films of these materials and will be characterized by X-Ray Diffraction, optical and electrical measurements.

2. Investigate the role of heavier elements in influencing optoelectronic properties and defects in $A_3Sb_2I_9$ structures. The effect of spin orbit coupling of heavy elements in tuning defects will be evaluated by partial substitution of antimony with a heavier Bismuth. The fundamental property changes will be evaluated using a combination of electrical (AC hall measurements, Admittance Spectroscopy, IV measurements) and optical (Steady state and Transient Absorption) techniques.

3. Based on the knowledge gained from the above investigations, extend the study to more structurally connected ns^2 electron containing systems and applications. The novel structures will be identified from the ICSD and Materials project database based on the conclusions from the above studies.

4. Understanding ionic electronic coupling in highly ionic conducting materials. The role of ionic migration and its role in doping the material systems will be studied by application in suitable applications.

1.3 Dissertation overview

Chapter 1 states the background for this investigation on ns^2 electron containing materials of Antimony outlining the motivations and hypothesis leading to it.

Chapter 2 presents a detailed literature review of the halide perovskite materials and the role of ns^2 electrons and other fundamental reasons for their exemplary optoelectronic properties.

Chapter 3 outlines the synthesis procedures used for the halide and chalcogenide compounds in this thesis. In addition, it explains the various experimental techniques used to evaluate the structural, optical, electronic and electrochemical properties of the synthesized materials.

Chapter 4 describes the role of A site cation on templating a structurally connected layered form of $A_3Sb_2I_9$. It is shown that this layered structure (2D) is superior to a dimer (0D) structure in terms of opto-electronic properties and defects highlighting the role of electronic dimensionality. The chapter is concluded with $Rb_3Sb_2I_9$ being tested in a solar cell architecture and showing better performances compared to the dimer form $Cs_3Sb_2I_9$.

Chapter 5 builds on the findings from Chapter 4 and investigates the effect of Heavy element substitution at the B site of layered $(NH_4)_3Sb_2I_9$. It is shown that the optoelectronic and defect properties of the material can be tuned by gradual substitution of Sb with Bi resulting in a change of carrier type from p to n.

Chapter 6 examines a more structurally connected novel Antimony chalcogenide ($NaSbS_2$) semiconductor containing ns^2 electrons. The opto-electronic and ionic properties of this material were investigated. The material exhibited a coupled ionic electronic transport and switchable Photovoltaic effect which was utilized for novel applications like neuromorphic devices.

Chapter 7 details the scientific insights from all the works discussed above and the possible future work in this field. The observations and interpretations from the thesis leads to a novel concept of electronically and ionically coupled semiconductors which can be post processed electrically to obtain desired electronic properties.

1.4 Findings and outcomes / Originality

The thesis presents the following conclusions :

1. The studies on the role of A cation in templating $A_3Sb_2I_9$ structures led to the first report on a solution processed layered $A_3Sb_2I_9$ compound – $Rb_3Sb_2I_9$ for photovoltaic applications. The layered form is superior in terms of mobility, lower bandgaps and defect tolerance compared to the dimer form of $A_3Sb_2I_9$.

2. The study on the role of heavy element on the optoelectronic properties in $A_3Sb_2I_9$ compounds is the first such comprehensive study on any halide perovskite material. The study on role of spin orbit coupling effect (depending on the atomic mass of metal cation) and the ns^2 electrons in determining the defect and opto-electronic properties of the material is novel. This resulted in the first report on tuning the carriers in a halide perovskite material by varying the Metal cation atomic mass.

3. The study presents a novel way to deposit thin films of $NaSbS_2$. It is also the first report on how to utilize the coupled ionic-electronic transport in this material to enable switchable photovoltaic effect for applications in neuromorphic devices. The study also resulted in a new class of materials which can be electrically reconfigured post deposition to obtain the desired electronic properties.

In conclusion, two novel class of compounds $A_3Sb_2I_9$ and $NaSbS_2$ were investigated in this thesis for their optoelectronic properties. The studies on $A_3Sb_2I_9$ compounds provided new insights on the role of A cation in templating the higher dimensionality layered structure and the role of atomic mass of B cation in determining the defect and opto-electronic properties of this material. $NaSbS_2$ turned out to be a mixed ionic-electronic conductor with switchable photovoltaic effect which enabled post-deposition tuning of the properties and application in neuromorphic devices. This study unlocks a new class of ionic-electronic materials which are electrically re-configurable after deposition to obtain desirable properties.

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Chapter 2

Literature Review

The emergence of lead halide perovskites as solution processable versatile semiconductors with applications in Solar cells, Light emitting devices, Lasers, Memristors and X-Ray detectors has spurred a lot of research activity. The following sections review the unique structural, electronic properties and applications of perovskites and related materials. The later sections review recent developments in similar but nontoxic solution processable semiconductors and analyze their potential limitations compared to lead based halides. The insights gained from these observations form the basis for the selection of ns^2 electron containing Antimony based compounds as suitable candidates for further studies.

2.1 Perovskite Halides and Related Structures

The Perovskite Structure refers to compounds having similar structure as CaTiO_3 . The first detailed study on perovskite structures was conducted by Victor Goldschmidt in his work on tolerance factors^[1]. The hybrid lead halide perovskites relevant to our work can be generally described by the general formula AMX_3 , where A is organic/inorganic cation, B is the metal cation (like Pb^{2+}) and X is the halide anion.

Figure 2.1: Crystal structure of AMX_3 perovskite

The relative radii of the A, M and X anions determine the stability of the perovskite structure defined by the tolerance factor:

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

The structure is stable for a t usually in the range 0.75-1.0. In case of hybrid lead halide perovskites, the A cations are usually Methylammonium (CH_3NH_3^+), Formamidinium ($\text{HC}(\text{NH}_2)_2^+$) or inorganic cations like Cs^+ , Rb^+ etc. The halide ions can be iodide, Bromide, Chloride or their mixtures. Continuous tuning of band gap is possible by tuning the composition of halides and even the A and M cations. These structures are characterized by presence of connected MX_6 octahedra. There are numerous other perovskite related structures with the MX_6 octahedra sharing corners, the edges or the faces^[2]. One of the structures that this thesis will focus on is trivalent metal ion based halides of Antimony. The most popular out of these are the $\text{A}_3\text{M}_2\text{X}_9$ compounds, which exhibit both face sharing (dimer phase) and corner sharing (layered phase) structures.

Figure 2.2: MX_6 systems sharing (a) corner (b) edge (c) face. Adapted from [2]

2.1.1. Multi dimensional Perovskites

Figure 2.3: Schematic Structure showing the crystalline structure of multidimensional perovskites including 2D perovskites and mixed dimensional perovskites and 3D perovskites. Adapted from [7].

A number of larger organic ammonium cations that cannot be accommodated within the octahedral cavities in the 3D perovskite structure, adopt the “two-dimensional” (2D) perovskite slabs with corner-shared octahedra, and conform to the Ruddlesden–Popper formulae of $A_{n-1}A'_2M_nX_{3n+1}$, where A' are typically bulkier organic ammonium cations^[3–5], whereas A , M , and X retain the same definitions. Consequently, along with the development of newer organic cations, numerous perovskite materials with the general formulae $(RNH_3)_2(A)_{n-1}M_nX_{3n+1}$ ($n = \text{integer}$) are now generally defined as 2D perovskites, while $(RNH_3)_2(A)_mM_mX_{3m+2}$ is categorized as a 1D perovskite, where RNH_3

is an aliphatic or aromatic alkylammonium cation^[6]. Hence, these perovskites can be broadly classified as multidimensional perovskites (Figure 2.3)^[7]

2.2 Optoelectronic applications of halide perovskites

2.2.1 Solar cell, LEDs and X-Ray Detectors

Figure 2.4: (a and c) Perovskite solar cell in mesoporous architecture (b and d) planar architecture.

The hype in perovskite as a novel semiconductor material came with their application in solar cells. The initial perovskite based solar cells were developed based on the concept of Dye Sensitized solar cells by replacing the organic dyes by the lead halide perovskite (Methyl ammonium lead iodide) as the absorber by Kojima et al^[8] in 2009. Later developments replaced the liquid electrolyte with Spiro-OMeTAD making the solar cells stable for a longer period^[9]. The configuration is usually referred to as n-i-p architecture where the active solar cell absorber layer is sandwiched between an n type material for

electron transport (ETL) and p type material for hole transport (HTL) as shown in Figure 2.4. The mesoporous TiO_2 acts as scaffold and also an n type contact. The presence of ETL is not a prerequisite for perovskite solar cells as devices with Insulating Al_2O_3 was later developed^[10]. It was also proved that perovskite devices can work efficiently without any hole transport layer as well^[11]. This indicates that the electron and hole can be separated in the perovskite itself and can be transported without the aid of other transporting layers. Further experimentation revealed long diffusion lengths for electrons and holes in perovskite^[12]. This aided the development of planar architectures of perovskite solar cells. Recent developments show use of multiple A and X site cations to improve stability and power conversion efficiency of perovskite based solar cells.

Figure 2.5 : (a) Linear attenuation coefficient of MAPbI₃, MAPbBr₃, CdTe, Se, and TlBr versus photons energy, (b) The voltage dependence of the photo-current generated by Cu K α X-ray in a single crystal of MAPbI₃ ; the red line is a fit with the Hecht model. Adapted from ^[14]

In addition to solar cells, investigations on perovskite materials spurred research in other areas like LEDs, Lasing, Transistors and X-Ray detectors. The high photoluminescence quantum yield of the material enabled their application in light emitting diodes. The first room temperature luminance from solution-processed perovskite-based LEDs was achieved in 2014, using $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ as the emitter layers^[13]. The possibility to tune the band gap of the material through compositional tuning and nanostructuring enable facile fabrication of multi color light emitting diodes.

The halide perovskites have also found applications in X-Ray radiation detectors because of their strong stopping power, large $\mu\tau$ product, large bulk resistivity and radiation hardness^[14]. Standard MAPbI₃ halide perovskite has a high density of around 4g/cm³, leading to a large linear attenuation coefficient of 10 cm⁻¹ to 100keV owing to its large atomic mass elements. The large bulk resistivity of this material is another important figure of merit in radiation detectors for attaining very small dark current and noise levels. The tolerance of the material towards defects as discussed later in text also provides radiation damage tolerance in these materials.

2.2.2 Memristors, Switchable Photovoltaic and Artificial Synaptic Devices

Ionic migration induced degradation and hysteresis has been one of the major problems to be addressed to address stability and reproducibility issues in most of the above mentioned applications^[15–17]. Nevertheless, the ionic migration has also been positively utilized in several applications like memristors^[18], Switchable photovoltaic^[19] and Neuromorphic devices^[20,21]. These devices mainly make use of the ionic segregation induced doping in the material and changes in conductivity of the material. The coexistence of ionic and electronic properties can also be attributed to its defect tolerance which is discussed in detail in the forthcoming sections.

In conventional semiconductors like Si, CIGS, GaSe or GaAs, the p-n junctions and hence the directions of internal electric field are formed by controlling the dopants during the fabrication stage of the device. Thus the generated carriers can only flow in one particular direction which is determined during the fabrication stage. Xiao et al^[19] showed that halide perovskites are an exception to this by forming an intrinsic p-n junction by segregating ions in the material to locally dope it leading to a field switchable photovoltaic effect. On electrical poling, +ve ions/vacancies (acceptor) move toward the negatively poled electrode making it p type and the other end with negative ions n type. This sets up an internal electric field inside the material driving the charge carriers. This

field was found to be reversible on switching the direction of the poling field resulting in a Switchable Photovoltaic Effect.

Figure 2.6 : (a and b) switchable Photovoltaic Effect in MAPbI₃ and (c and d) the changes in work function on +ve and -ve poling. Adapted from ^[19]

Halide perovskites have also found applications in neuromorphic computing systems that combine information storage and processing to beyond the von-Neumann computing architecture. Artificial synapses that can imitate biological synapses are considered building blocks for artificial neuromorphic systems^[22]. The resistive switching of the memristor can be made use to emulate the synaptic weight changes induced by stimuli. Memristors have been used to achieve several synaptic characteristics such as spike-timing-dependent plasticity (STDP), spike-rate-dependent plasticity (SRDP), paired pulse facilitation (PPF), excitatory postsynaptic current (EPSC), short-term plasticity (STP), long-term potentiation (LTP), and long-term depression (LTD)^[23–25]. This synaptic plasticity is usually achieved by gradual tuning of the memristive states. In these devices, usually the conductance of the memristive device represents the synaptic connection strength. Recently, Halide perovskites have become favorable candidates to emulate synaptic functions owing to their coupled ionic-electronic transport and ion induced doping.

Figure 2.7: (a) Schematic of the biological synapse and the (b) analogous device architecture. Four forms of STDP: C, asymmetric Hebbian rule, D, asymmetric anti-Hebbian rule, E, symmetric Hebbian rule, and F, symmetric anti-Hebbian rule. Adapted from ^[18]

Xiao et al reported the first halide perovskite based memristors mimicking the biological synapse^[18]. The device structure comprised of Au/MAPbI₃/ITO structure and utilized the switchable photovoltaic effect discussed earlier to demonstrate several synaptic functions like STDP, SRDP, STP, LTP and learning behavior (Figure 2.7). Later, similar behavior was also achieved in the LED architecture by positively utilizing the ionic motion of MA and halide ions in the material. The co-existence of the injection barriers in the device coupled with ion migration in perovskite layer defined the degree of synaptic plasticity which was tunable based on the type of the A site cation^[21].

2.3 Exceptional properties of hybrid lead halide perovskites and their origin

The reasons for the phenomenal performance and versatility of lead halide perovskites are due to its suitable bandgap^[26], large absorption coefficient, low exciton binding energies^[27], long electron and hole diffusion lengths^[12] and high mobilities^[28,29], and absence of deep defects in the band gap. The fundamental reasons for these observations

are linked to the unique orbital characteristics of Pb^{2+} cation. The high hole carrier mobility of the material is due to the Pb 6s state at the valence band maxima and the Pb 6p state at the conduction band minimum^[30]. The absorption coefficient of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is around $2 \times 10^5 \text{ cm}^{-1}$ at 450nm wavelength which is higher than most of the conventional semiconductors^[31].

Figure 2.8: (a) Absorption coefficient and (b) the band edge transition comparison of common semiconductors -Si, GaAs and Methylammonium lead iodide. Adapted from ^[61]

The absorption coefficient of a semiconductor is proportional to the Joint Density of States (JDOS) near the Valence band maximum and conduction band minimum. This depends on the orbital characteristics of VB and CB. Inter band p to p transitions are better compared to s to p transitions because the p orbitals are more localized and has higher JDOS. Thus I p to Pb p transitions in the lead halide perovskites lead to high absorption coefficients. In addition, the possibility of intra-atomic Pb s to Pb p transition with high probability also contributes to the high absorption coefficient. In addition to this the direct band gap of Methylammonium lead iodide (MAPbI_3) provides efficient transition near the band edges^[30].

MAPbI_3 based solar cells have excellent transport properties: long carrier diffusion lengths, low non radiative recombination as inferred from the high Photoluminescence quantum yield, long carrier lifetimes and high open circuit voltages. These observations are even more interesting given the perovskite films fabricated by solution processing

yields equal or higher similar properties compared to high vacuum processing techniques. This is explained based on the defect tolerant property of the material (Defect tolerance is the tendency of a semiconductor to keep its properties even in the presence of crystallographic defects)^[32].

Figure 2.9 : (a) Hybridization of Pb and I orbitals (b) representation of Donor and Acceptor defects.

The defect tolerance in lead perovskites is linked to the presence of dispersive anti bonding valence band maximum formed by the hybridization of Pb s and I p orbitals. This results in the acceptor type defects (D_a) to form only within the valence band. On the other hand, the conduction band is bonding in character owing to the ionic character of the perovskite which results in negligible coupling of Pb (p) with I(p) orbitals to form the conduction band. Thus, the donor type defects (D_d) are expected to form only shallow levels close to the conduction band^[32]. In addition, the spin orbit coupling interaction due to the heavy lead atom pushes the conduction band down further reducing the probability of forming deep states. The s electron contribution to the valence band maximum also makes it more dispersive resulting in lower hole effective masses^[33]. The defect tolerance property is also responsible for the unique coexistence of excellent semiconducting properties despite the motion of the ions. This enables doping by the segregated ions leading to effects like switchable photovoltaic effect where an intrinsic p-n junction can be formed inside the material just by segregating ions by application of a field.

The role of organic cation on the properties of the perovskite is however highly debated. The A cation does not contribute to the band edges of the perovskite and hence should not influence the optoelectronic properties much. However, the dipole moment associated with the organic cations is claimed to contribute to the dielectric constant of the material. A higher dielectric constant helps to reduce the exciton binding energy as well as reduce the defect capture cross sections.

2.4 Instability and Toxicity of Lead

Despite all the benign properties of lead based perovskite as an absorber, the toxicity of lead is a serious concern to commercial applications. The problem is aggravated by the low stability of the material in moist atmosphere. A potential failure of the encapsulation of perovskite solar cell will release the Pb^{2+} ions to the soil and ground water. This can be extremely dangerous to humans as well as aquatic life considering the bio-accumulation of lead^[34–36].

Most of the efforts to replace lead in Perovskite halides are focused on elements in the same group or adjacent group such as Sn, Ge, Bi and Sb assuming that similar electronic configurations will lead to similar optoelectronic properties. Suitable oxidation states, ionic sizes, the presence of ns^2 electrons and a connected lattice which result in the defect tolerant properties of lead halide perovskites are the major criteria in search for the search for novel materials. The following sections review alternative semiconductor inspired by halide perovskites.

2.5 Alternative Perovskite Inspired Semiconductors

2.5.1 Tin halide perovskites

Tin with an electronic configuration $[\text{Kr}] 4d^{10} 5s^2 5p^2$ is very similar to lead and hence is its most potential replacement. The first report on Tin based perovskites in a solar cell was on $\text{CH}_3\text{NH}_3\text{SnI}_3$ with an efficiency of 6.4 %^[37] However, the material was very

unstable in air due to oxidation of +2 Sn to +4 states. The presence of +4 Sn also resulted in variable self-doping of the material resulting in high hole doping density of $\sim 10^{18} \text{ cm}^{-3}$. The recombination with these self-doped carriers limited the diffusion lengths to only 30 nm and the mobility to $1.6 \text{ cm}^2/\text{VS}$ which is significantly low compared to MAPbI_3 . It was suggested that reducing these background carriers could be an effective strategy to improve the performances by improving the diffusion lengths.

Figure 2.10 : (a) A perspective of CsSnI_3 in the tetragonal phase and (b) orthorhombic phase, (c) The energy bandgap as a function of the cubic lattice a . The black circles represent the calculated band gap for a perfect cubic perovskite CsSnI_3 with different lattice parameters. The squares represent the bandgap of CsSnI_3 in the three phases, and the bandgap of MASnI_3 and of FASnI_3 in the cubic phase. Adapted from ^[59].

The first report on fully inorganic Sn based perovskite was on CsSnI_3 ^[38] with a power conversion efficiency of 2.02%. The study highlighted the importance of excess SnF_2 addition which resulted in reduction of carrier density from 10^{19} cm^{-3} in pristine sample to 10^{17} cm^{-3} with 20% SnF_2 addition. CsSnI_3 has also found application in Light Emitting

Diodes with electroluminescence around 950 nm and maximum EQE of 3.8%.^[39] Efficient EL from lead-free perovskites in the visible light regime is yet to be achieved.

2.5.2 Germanium based halide perovskites:

Moving even further up in the group, a smaller Germanium was also investigated as a potential candidate to form perovskites with photovoltaic properties^[40]. However, the solar cells of CsGeI₃ and MAGeI₃ suffered from a very low V_{oc} of 74mV and 150mV respectively restricting the efficiencies to 0.11% and 0.2% only. Germanium is even more unstable compared to Sn and gets easily oxidized to +4 state and is the reason for the poor performance. The problem is aggravated by its poor solubility in polar solvents which restricts good film formation.

Most of the research on lead replacement was focused on Sn or Ge in the same group. However, it is known that the inert pair effect responsible for the stability of the +2 state of lead reduces as we move up in the group. Thus, Sn²⁺ and Ge²⁺ are very unstable and gets oxidized to +4 ions. These +4 ions can act as traps leading to recombination and hence limiting the performances. Furthermore, reports show that Sn perovskites can be even more toxic compared to lead due to its potential oxidation to +4 oxidation state releasing HI into the environment^[36]. This necessitated the need for expanding the search to other group elements and other perovskite derivatives as well. Recently reported copper based perovskites were limited by low voltages and currents possibly due to defects owing to the absence of ns² electrons and the structural anisotropy^[41]. Another interesting study points out the possibility of a Sn-Ge mixed cation approach where the native oxide formed by oxidation of Ge protects further degradation of the system.^[42]

2.5.3 A₂SnX₆ as a stable alternative to ASnX₃

The use of tetravalent Sn is a strategy to enhance the stability of the Sn perovskite. However, a +4 Sn can only form compounds of structure A₂SnX₆ which is considered a 0D perovskite structure with isolated (SnI₆)²⁻ octahedra. There are several reports utilizing Cs₂SnI₆ as a hole transporting material in Dye sensitized solar cells due to its

exceptional p type conductivity^[43,44]. However, the reports on the band gap, carrier densities, mobility and type of charge carriers are still inconclusive as shown in Table 2.1. It is claimed that the pristine material is n type and reported p type behaviour is caused by doping with Sn^{2+} . Nevertheless, the optimum band gap of 1.3 to 1.6 eV of the material makes it a promising absorber for solar cells. The only report of Cs_2SnI_6 as a solar cell absorber material is by utilizing ZnO nanorods as electron transporting layer and P3HT as HTM reaching an efficiency $\sim 1\%$ ^[45].

Figure 2.11 : (a,b) Crystal structure of the vacancy ordered double perovskite Cs_2SnI_6 . Adapted from ^[60].

Table 2.1: Reported optoelectronic characteristics of Cs_2SnI_6

Reference	Band Gap(eV)	Carrier Density (cm^{-3})/type	Mobility (cm^2/Vs)
Lee et al ^[43]	1.3 (direct)	1×10^{14} (n)	310
Lee et al ^[43]	1.3 (direct)	1×10^{14} (p)	42
Saparov et al ^[46]	1.6 (direct)	6×10^{16} (n)	2.9

2.5.4 Towards +3 Metal Cations

Bi^{3+} and Sb^{3+} having the similar electronic configuration as Pb^{2+} are other viable alternatives. The presence of ns^2 electrons must also equip them with the defect tolerant property of lead. However, the +3 state constrains their ability to form a 3D corner sharing perovskite structure. Thus, the constraints for the search for lead free perovskites was expanded to materials which are inspired by the electronic structure of perovskites rather than the ABX_3 structure. They usually form $\text{A}_3\text{Sb}_2\text{X}_9$ compounds with a dimer

structure (with fused bi-octahedron) or a layered structure (with corner sharing octahedron). The first report on Bismuth based perovskite was on $\text{Cs}_3\text{Bi}_2\text{I}_9$ with an efficiency of $\sim 1\%$ ^[47]. The material consisted of fused bi-octahedral $(\text{Bi}_2\text{I}_9)^{3-}$ clusters surrounded by Cs atoms. The photoluminescence and photovoltaic performance of $\text{MA}_3\text{Bi}_2\text{I}_9$ was found to be very low compared to $\text{Cs}_3\text{Bi}_2\text{I}_9$ consistent with the other reports on $\text{MA}_3\text{Bi}_2\text{I}_9$ solar cells with a low efficiency of 0.19% ^[48]. $\text{MA}_3\text{Bi}_2\text{I}_9$ exhibited p type conductivity with a carrier density of 10^{16}cm^{-3} and mobility of $1\text{ cm}^2/\text{VS}$. This high background carrier density was suspected to have contributed to bulk recombination leading to a low V_{oc} of 0.35V . Other reports claim that the morphology of $\text{MA}_3\text{Bi}_2\text{I}_9$ layer and hence the efficiency are influenced by the underlying TiO_2 layer^[49]. A detailed material study on $\text{MA}_3\text{Bi}_2\text{I}_9$ ^[50] suggest that post treatment with pyridine can improve the PL lifetime of the material possibly by passivation of under coordinated bismuth ions on the surface. A maximum PL life time of 0.76ns was achieved which was dependent on the processing technique adopted. This is encouraging because materials with $< 1\text{ns}$ lifetimes has been reported to achieve efficiencies close to 10% ^[51]. $\text{Cs}_3\text{Bi}_2\text{Br}_9$ and $\text{Cs}_3\text{Sb}_2\text{Br}_9$ quantum dots has also been shown to yield high photoluminescence quantum efficiencies showing possibility of application in light emitting diodes^[52,53]. Interestingly, double perovskites (with a combination of +1 and +3 cation forming the B site of ABX_3) of the formula $\text{Cs}_2\text{AgBiBr}_6$ exhibited extraordinary PL lifetimes of 660ns which are on par with MAPbI_3 substantiating the defect tolerant property of Bismuth^[54]. In addition, the compound was found to exhibit extraordinary stability in moisture and light exposure even after one month. However, the presence of Ag seriously inhibits the solution processability of the material. The potential of bismuth halides as promising semiconductors is also corroborated by the decent efficiency of silver bismuth iodide solar cells exceeding 2.5% ^[55,56] and BiI_3 based solar cells with efficiency of 0.3% ^{5, 45}.

There are also reports on $\text{A}_3\text{M}_2\text{X}_9$ structures based on Sb as viable photovoltaic materials. However, the highest efficiency reported till date is only 0.5% with $\text{MA}_3\text{Sb}_2\text{I}_9$ as absorber^[57]. It is claimed that the layered structure of $\text{A}_3\text{Sb}_2\text{I}_9$ should exhibit better optoelectronic properties compared to the dimer form from First Principle Calculations^[58]. Recent reports on layered $\text{Cs}_3\text{Sb}_2\text{Br}_9$ quantum dots with PLQY around

46% substantiates the decent semiconducting behavior of the layered phase. However, the lack of solution processability of the iodides counterparts is a bottleneck to its formation and application in optoelectronic devices. In addition, the material is also susceptible to various defects which can induce deep traps limiting the photovoltaic performance. Thus, a strict control over the stoichiometry using optimum fabrication conditions will be necessary to obtain good performance with these classes of compounds.

2.6 Scope and Challenges

Based on the above review, it is clear that ns^2 electrons (contributing to dispersive valence band and defect tolerance), the p to p transitions (leading to high absorption coefficients) and presence of A cation with dipole moment are the most important properties which make lead halide perovskites as suitable candidates for optoelectronic applications.. However, replacement of Lead by Tin/Germanium with similar electronic configuration resulted in inferior photovoltaic performance due to their unstable +2 oxidation state. This necessitates need to expand the search to materials with closer electronic similarity to halide perovskites rather than just the structural similarity. Antimony (electronic configuration $[Kr] 4d^{10} 5s^2 5p^3$) can be a viable alternative due the presence of the above mentioned properties. In addition, the lower atomic mass of Sb compared to lead would help understand the role of atomic mass on optoelectronic properties of the material by suitable alloying with heavier elements like Bismuth. However, the +3 oxidation state of Sb deters the formation of AMX_3 perovskite phase, instead forming $A_3M_2X_9$ structures with dimer / layered variants (depending on how the metal halide octahedra are connected). The only report on $MA_3Sb_2I_9$ dimer as a photovoltaic absorber is limited by efficiencies $< 0.5\%$ ^[57]. The layered structure is reported to have better charge transport and optoelectronic properties compared to the dimer and hence forms starting point of the present study. However, the lack of solution processability is a major limiting factor to study the optoelectronic properties and to employ them as absorbers for solar cells.

The investigation of solution processable $A_3Sb_2I_9$ compounds is hence the starting point for this thesis. Followed by this, various factors like role of A cation, atomic mass of metal cation and ionic segregation are studied in detail to understand their influence on optoelectronic properties and defects in the material. The thesis then builds on these observations to propose and investigate novel materials which are different from perovskites but closely related to them in terms of electronic structure. The unique properties identified for each material is made use in viable electronic applications.

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Chapter 3

Experimental Methodology

This chapter describes the rationale for choosing the materials as well as the processing techniques adopted in this thesis. It explains the different characterization techniques utilized, their advantages and possible limitations in studying the particular phenomenon. The chapter also elucidates the fabrication and testing protocols adopted for various device configurations.

3.1 Rationale for method selection

This thesis studies the optoelectronic properties of ns^2 electron containing systems of Antimony. The preliminary scan for novel materials is based on existing compounds in ICSD database and band structures in Materials Project^[1]. The selection is bound to additional constraints including number of elements (less than or equal to 3), suitable band gap and solution processability. Since solution processability is one of the criteria, the search is limited to halides and chalcogenides as there are known facile solution processing techniques for them. Once the suitable material is identified, detailed Density Functional Theory computations are conducted on the material to evaluate its electronic band structure. This provides with the band gap, nature of transitions, and the contribution of different elements to valence and conduction bands. This is followed by identification of suitable solution processing strategies. In case of halides, the techniques are inspired from those developed for lead halide perovskites. The material is dissolved in polar solvents like Dimethylformamide (DMF) or Dimethyl sulfoxide (DMSO) and spin coated. In case of chalcogenides, an amine-thiol mixture is utilised to solubilize the materials. This is lower in toxicity compared to the conventional hydrazine/chalcogen synthesis route and also more flexible in terms of compositional tuning compared to thiourea based techniques. The deposited materials are characterized by X-Ray diffraction to ensure that the required phase is formed and to eliminate secondary phases. Scanning Electron Microscopy (SEM) imaging is utilized to understand the microstructure of the film. The composition of the materials is evaluated using Energy Dispersive X-Ray Spectroscopy (EDS) and X-Ray Photo-electron Spectroscopy (XPS). Suitable modifications are made to the solution processing route to avoid impurity phases and deviation from required composition. After identifying the suitable processing routes, the material is employed in functional devices or subjected to fundamental electrical and optical studies. For electrical characterization, special care is taken to choose suitable ohmic contacts which do not react with the materials. Experiences with halide perovskites reveal high reactivity of halides towards metal electrodes including gold. Hence, patterned Fluorine doped Tin Oxide (FTO) or Indium doped Tin Oxide (ITO) electrodes which are inert towards the materials are utilized for the studies. The energy

levels of the material are measured using techniques like UPS and PESA before choosing suitable charge selection layers for application in solar cell devices. Thin film formation strategies and the characterization techniques employed are discussed in the following sections.

3.2 Thin film formation

Glass, quartz, FTO or ITO are the substrates used in most of the studies. Substrates are cleaned by diluted detergent, deionized water and ethanol by sonication for 10 minutes in each. The substrates are then dried under Nitrogen gas and treated in ozone plasma for 30 minutes before spin coating. The following are the solution preparation and spin-coating procedure for the various compounds in this study.

3.2.1 $\text{Rb}_3\text{Sb}_2\text{I}_9$

RbI and SbI_3 are dissolved in 3:2 molar ratios to form 0.2 M, 1ml solution in N,N Dimethylformamide. The solution is heated at 70°C for 2hours and the filtered after cooling using a PTFE filter. The final solution is clear and dark red in colour and is heated again at 70°C before further processing. The films are formed by spin coating at 4000 rpm for 30s with the SbI_3 solution dripped after 3 s of the start of spin coating. The films are further cleaned by spin coating toluene solution at 4000rpm for 30s to remove any excess SbI_3 . The films are annealed at 120°C for 10 minutes.

3.2.2 $(\text{NH}_4)_3(\text{Sb}_{(1-x)}\text{Bi}_x)_2\text{I}_9$

NH_4I and $\text{SbI}_3/\text{BiI}_3$ are dissolved in 3:2 molar ratios to form 0.2 M, 1ml solutions in Dimethylformamide of $(\text{NH}_4)_3\text{Sb}_2\text{I}_9$ and $(\text{NH}_4)_3\text{Bi}_2\text{I}_9$. These solutions are stirred for 1 hour and then filtered using a PTFE filter. The solutions are mixed in appropriate volumes to get the required doping level of Bismuth. The spin coating is done with excess SbI_3 provided via anti-solvent dripping as reported previously^[2]. The films are annealed at 60°C for 10 minutes for all the measurements.

3.2.3 NaSbS₂

Solutions are prepared by dissolving Na, Sb₂S₃ and S in 1ml ethylene diamine and 0.1ml ethanedithiol to get a 1M solution at room temperature for 3 hours. The solution is then spin coated at 2000rpm for 30s followed by annealing at 320°C for 30 minutes. To form thicker films, the process is repeated several times with 320°C annealing for 10 minutes and a final annealing for 30 minutes. It is observed that on dropping the solution to the first layer, the film becomes transparent and redissolves. Hence a dynamic spinning is adopted with the solution dropped on the spinning substrate.

3.3 Characterization Techniques

3.3.1 X-Ray Diffraction

Figure 3.1 : Bragg's law of diffraction

X-Rays have a wavelength that is of the order of the inter-atomic spacing in crystals. Hence, they experience diffraction and interference upon incidence on the materials. This forms the basis for X-Ray diffraction measurements^[3]. In a system with long range order, the diffracted X-ray beams constructively interfere to produce diffraction beams. Hence, using an X-Ray with a known wavelength λ and knowing the angle between the transmitted and diffracted beams (2θ), the spacing between atoms arranged in various planes (d) can be discerned utilizing the Bragg's law

$$n \lambda = 2d \sin \theta \quad (3.1)$$

However, this method is not applicable to materials in which the atoms are periodically arranged as in crystalline samples which can induce diffraction corresponding to lattice spacing. Amorphous materials which have a random arrangement of atoms causes destructive interference and the patterns are not discernible. The recorded powder diffraction pattern contains a list of d values and relative intensities. This is compared with standard databases available from the International Centre for Powder Diffraction Data (ICDD)^[4]. This method can evaluate the relative quantities of different phases existing in the same sample by comparing the relative intensities peaks.

In this project, X-Ray diffraction is used to Identify the phase purity of the thin films and powders and to refine the crystal structure on doping and inclusion of secondary elements to the compounds. The powder XRD patterns are obtained on Bruker D8 Advance diffractometer in Bragg-Brentano configuration with Cu $K\alpha$ X-Rays of wavelength 1.54187 Å at 40kV and 40mA. The step size is kept at 0.02° with a step time of 2 s for all the powder samples to obtain sufficient intensity. The intensity of the strongest reflection is more than 10000 for the sample used for refinement of crystal structure. The experimental fitting is carried out using TOPAS V4.1 in a range of 10 to 80° 2 θ . The thin films are characterized at a higher step size of 0.04° and stepping time of 0.5s to match the obtained pattern with ICDD database to ensure phase purity.

3.3.2 Scanning Electron Microscopy

The Scanning electron microscope produces images by scanning the sample with a high-energy electron beam (1-20kV). It gives insight about the surface topography and composition of the film^[5]. On interacting with the sample, secondary electrons, back-scattered electrons and X-Rays are produced which are collected by dedicated detectors to get the required information. The incident electron beam usually penetrates a few microns into the sample as shown in figure 3.2. The Secondary electrons (SE) are produced by inelastic scattering and are of low energy(3-5eV) and provides topographical information with a resolution around 10nm. The backscattered electrons produced by

elastic scattering usually depend on the atomic mass of the elements. Hence, they can provide better compositional contrast.

The composition information about the sample is obtained using the X-Rays emitted from the sample using a technique called Energy Dispersive X-Ray Spectroscopy. When an electron beam hits the sample, electrons are emitted from the atoms. These vacancies are filled by electrons from a higher state resulting in emission of characteristic X-Rays. The X-Ray emitted is thus a characteristic of the element from which it is emitted.

Figure 3.2 : Schematic of electron beam interaction with sample

One of the issues encountered while imaging using an electron beam is the charging of the specimen. Hence, the sample needs to be conductive in order to give a better image. In the case of non-conducting samples, a thin layer of Pt or Au is usually sputtered followed by grounding the sample with a carbon or copper tape.

In this project, SEM is utilized to gain insight into the sample morphology and composition. The top view of the sample usually provides information about the packing of the grains, pinholes, and the existence of multiple phases in the film. The EDS analysis provides information about the composition of the semiconductor film. On analyzing the cross section of the sample, the thickness of each of the layers in the device is estimated. SEM measurements are performed using a field-emission scanning electron microscopy

(FESEM; Jeol 7600F) with an acceleration voltage of 5 kV. For EDS analysis, a higher accelerating voltage (15ev) is used.

3.3.3 Optical Spectroscopy

The electronic transitions from valence to conduction bands in semiconductors lie in the Ultraviolet (UV), Visible and Near Infrared Regions (NIR) of the electromagnetic spectrum. Hence, these regions of the spectrum are usually used to excite the materials and the absorption, reflection, transmission or emission are used to provide insights into the electronic band structure and defects in the material.

There are two type of spectroscopic measurements – (1) Steady state- where the sample is irradiated by a continuous beam of light and the response of the material is collected as a function of wavelength. (2) Transient – where usually a non-continuous light source like a pulsed laser is used to gain insight into the transient optical behavior of the material.

3.3.3.1 Steady-State Absorption Spectroscopy

The sample is irradiated by a continuous monochromatic beam of light and the attenuation of the intensity of this beam as it passes through a sample is measured over a range of wavelengths. The mathematical relation for the measurements is given by Bouguer-Lambert-Beer law as :

$$\log (I_0/I)_\lambda = \log (100/T(\%))_\lambda \equiv A_\lambda = \epsilon_\lambda \cdot c \cdot d \quad (3.2)$$

where $A_\lambda = \log (I_0/I)_\lambda$ is the absorbance, $T_\lambda = (I/I_0) \cdot 100$ is the transmittance, ϵ_λ is the molar extinction coefficient, I_0 is the intensity of incident monochromatic beam, I is the intensity of the transmitted beam, c is the sample concentration and d is the path length of the sample^[6]. This equation is only valid for dilute solutions where the ϵ_λ is independent of sample concentration. For a thin film sample, the absorption coefficient can be calculated based on the following equation :

$$\alpha_{\text{film}}(\lambda) = \frac{1}{d_{\text{film}}} \ln \left(\frac{1 - R_{\text{film}}(\lambda)}{T_{\text{film}}(\lambda)} \right) \quad (3.3)$$

where R_{film} and T_{film} are the film reflectance and transmittance and d_{film} is the thickness of the film^[7]. From the plot of absorption coefficient, one can obtain the band gap of the semiconductor using the tauc relation. A tauc plot has $h\nu$ (the energy of light) on the x axis and $(\alpha h\nu)^{1/r}$ on the y axis, where the exponent r depends on the nature of transition. $r = 1/2$ for direct transitions and $r = 2$ for indirect transitions. The band gap can be obtained by extrapolating the linear region of this graph to the x-axis.

Figure 3.3 : Schematic of a UV-Vis spectrometer

In this project, the absorption spectroscopy is used to calculate the absorption coefficients and band gaps of the novel semiconductor materials. The presence of excitons and mixed phases can also be detected from the absorption spectra. In semiconductors, the absorption coefficient at energies just below the band edge decreases exponentially with decreasing energy and this absorption tail is called the Urbach tail. The cause of the Urbach tail can be structural disorders, impurities, deep traps, phonon effects or excitons^[8–11]. The slope of this exponential tail can be used to calculate the Urbach energy^[8]. The Urbach energy can be an estimate of the deep traps and structural disorder in the synthesized material.

3.3.3.2 Transient Absorption Spectroscopy

Figure 3.4 : Principle of Pump-Probe spectroscopy. (a) The time delay between the pump and probe pulses can be adjusted using the delay stage. (b) Spatially overlapped pump and probe beam. Adapted from ^[28]

Transient Absorption (TA) spectroscopy (Pump-probe) yields time resolved observation of optical absorption with resolution as high as that of the laser pulse used. It works by splitting one laser beam into two – one pump beam (high intensity) which excites the sample and another probe beam (low intensity) which monitors the photo-excited dynamics. The delay between pump and probe can be controlled using a mechanical delay line and both are finally re-overlapped on the sample. The fundamental principle of the technique is to measure the change in the transmission or absorption of probe beam with respect to the probe delay. This gives information about the photo-excited species population. Hence, by varying the probe delay, one can map the time evolution of the photo-excited species. The resolution of the measurement is limited by the maximum possible delay between pump and probe.

The most common quantity measured by this technique is the change in transmittance of probe pulse due to pump pulse normalized to the total transmitted probe intensity ($\Delta T/T$). This can be related to pump-induced change in material absorption using the following relation :

$$\Delta A = \log\left(1 + \frac{\Delta T}{T}\right) \quad (3.4)$$

3.3.3.3 Steady-State Photoluminescence

Figure 3.5 : Steady-state photoluminescence setup. The emission from sample is collected by an optical fibre using couple of lenses and is directed to the monochromator coupled with CCD detector. Adapted from ^[28]

This technique helps to decipher the emission spectrum of the material after photo-excitation by a light source. The emission signal from the material is collected using two lenses which direct it to the optical fiber. The final signal is collected by the CCD detector. The photoluminescence peak shows the position of the electronic states which contribute to the radiative recombination. Sometimes emission can also occur from defect states where the energy of emission will be lower than the band gap. In this project, PL is used basically to gain insight into the nature of band gap of the materials under study. But owing to the indirect band gap of most of the materials, there was little or no emission recorded.

3.3.4 Cathodoluminescence spectroscopy

In cathodoluminescence (CL), the sample is excited by electrons instead of photons as in photoluminescence spectroscopy. Usually an electron beam of diameter 1-10 nm is used to excite the sample inside a scanning electron microscope which provides nanoscale

resolution to the excitation. The advantage of this method is that it allows spatial probing of different regions in a nanostructure. In addition, a map of the cathodoluminescence activity of the specimen can also be obtained.

Cathodoluminescence is slightly more complicated compared to photoluminescence and some additional factors need to be considered while obtaining and evaluating the spectrum. For example, the specimen can be damaged on prolonged illumination with electron beam or there can be vacuum induced defects which can lead to emission (surface defects, oxygen vacancies) which must be taken into account. CL emission occurs when the valence band electrons are excited to the conduction band by the incident beam which later recombine radiatively leading to emission. The CL emission originates from the interaction volume of the electron beam. However, carrier diffusion needs to be taken into account while evaluating samples with high mobility. Hence, although the excitation point may be highly localized, carrier recombination will induce a wider recombination volume.

In this study, CL is used because of the low photoluminescence quantum yield of the materials. The spectra is analyzed to understand the emission and nature of emission of the materials under study. The measurements are performed on FEI Verios scanning electron microscope equipped with a Gatan MonoCL4 Elite cathodoluminescence (CL) system. Samples are prepared in the similar procedure as described in thin film formation (methods section). To avoid any background luminescence signal from TiO_2/FTO , Samples are prepared on silicon substrate. Power resolved CL spectroscopy is performed by using accelerating voltage at 5kV and the beam current was varied 0.1-3.2nA

3.3.5 Photoelectron Spectroscopy

In this technique, the kinetic energy of the electrons emitted by photo excitation is analyzed. Electrons can be excited on absorption of photons and if the energy of the photon is high enough, the electron can be ejected out of the material into the vacuum.

Figure 3.6 : Schematic showing the principle of XPS

On its path, electrons usually collide elastically with other electrons to lose some part of the kinetic energy. However, some electrons which are ejected from the top 10 nm of the sample do not lose the energy by elastic collisions and can show distinct spectral features based on the binding energy. This technique is usually called X-Ray Photo-electron Spectroscopy (XPS) and uses soft X-rays (200-2000 eV) which are commonly produced by Al or Mg anodes. The kinetic energy of the ejected electron, (KE_{XPS}) is related to the binding energy, (BE_{XPS}), and the incident photon energy, (E_{ph}) as

$$KE_{XPS} = E_{ph} - \phi_{XPS} - BE_{XPS} \quad (3.5)$$

Here ϕ_{XPS} is the work function. This technique can be used to determine the elemental composition of the sample with sensitivity to elements from Li to U with up to 0.1 atomic percentage precision^[12]. The precision is higher for higher atomic weight elements. The work function of a metal can be extracted by only exciting the outer electrons. This can be done using a UV irradiation to excite the sample and the technique is known as Ultraviolet Photo-electron Spectroscopy (UPS). It generally uses a He discharge lamp with either 21.2 eV or 40.8 eV emission.^[13] The work function, ϕ , (or VBM) is :

$$\phi \text{ (or VBM)} = h\nu - W \quad (3.6)$$

Here W is the width of the UPS spectrum and $h\nu$ is the photon energy. UPS also requires a high vacuum environment for detection of the electrons. However, there are also techniques to detect photo-electrons in atmospheric pressure where photo-excited electrons are detected in air using two grids made of gold-plated stainless steel mesh^[14]. This technique is known as Photo Electron Spectroscopy in Air (PESA). The grids serve the purpose of protection of the sample from positive ions generated during discharge and also quench the counter discharge caused by incident electrons and hence enable detection of low energy electrons.

In this thesis, XPS is used to calculate the composition and oxidation states of elements as well as detect possible impurities and defects in the sample. The semiconductor film is spin coated on ITO substrates to avoid charging of the film during measurements. The XPS and UPS measurements are performed using Omicron EA-125 hemispherical electron analyzer under UHV conditions ($<1 \times 10^{-9}$ torr) with a 1486.6 eV monochromated Al K source for XPS, and monochromatic HeI 21.2 eV line source for UPS. XPS wide scans are measured in CAE mode using 50.0 eV pass energy, while elemental scans with 20.0 eV pass energy. All XPS elemental peaks are fitted with Gaussian-Lorentzian profile over Shirley background. UPS spectra are collected under -10 V bias, CAE mode with 2.00 eV pass energy. A Riken Photo-electron Spectrometer (Model AC 2) was used to perform the PESA measurements to obtain the Valence band maximum (VBM). The conduction band minima (CBM) is calculated by addition of VBM and the optical band gap obtained from UV-Vis measurements.

3.3.6 Thermal Admittance Spectroscopy

Thermal Admittance spectroscopy (TAS) is an effective technique to figure out the location of defect levels as well as defect density of states in a semiconductor. TAS yields the thermal emission rates, the thermal activation energy and the concentration of a deep level located in upper half of the band gap for an n type semiconductor or in the lower half for a p type semiconductor^[15,16]. It involves measuring the variation of capacitance as a function of frequency and Temperature T . The variation in capacitance is due to the

change in frequency with respect to the time constant of charge and discharge processes of deep levels around the point of space charge region where both time constants are equal. However, the Capacitance in a p-n junction solar cell can also be contributed by the dielectric capacitance of the layers as well. Hence, decoupling the chemical capacitance (caused by charging and discharging of defects) from other parasitic capacitance is necessary before analyzing the admittance data.

Figure 3.7: Schematic of a capacitance versus angular frequency (top) and $-\omega dC/d\omega$ versus angular frequency diagram (bottom), respectively. The inflection point in the C vs ω graph corresponds to the maximum in the $-\omega dC/d\omega$ vs. ω graph and represents the angular frequency that is about equal to 2 times the emission rate of the trap state investigated.

From the variation of capacitance across frequency at different temperature, the characteristic transition frequencies are calculated and are used to calculate the defect activation energies and the differentiated capacitance spectra to yield the energetic defect distribution. Assuming the occupied states are in thermal equilibrium, the thermal emission depth of the defects (E_a) is related to the transition frequency as :

$$\omega_0 = 2\pi f = 2\pi N_{c,v} v_{th} \exp\left(\frac{-E_a}{kT}\right) = 2\pi \xi_0 T^2 \exp\left(\frac{-E_a}{kT}\right) \quad (3.7)$$

where $N_{c,v}$ is the density of states of the conduction/valence band; v_{th} is the thermal velocity and σ is the electron/hole capture cross section. On approximating that $N_{c,v}$ and

v_{th} are proportional to $T^{3/2}$, the slope of $\ln(\omega/T^2)$ vs $1/KT$ gives the activation energy The trap density is extracted using the relation:

$$N_T(E\omega) = \frac{-V_{bi}}{qW} \frac{dC}{d\omega} \frac{\omega}{kT} \quad (3.8)$$

where V_{bi} is flat band potential, q is elementary charge, W is depletion layer thickness which is approximated as the thickness of perovskite layer assuming full depletion.

3.3.7 Hall measurements

When a magnetic field is applied perpendicular to the direction of current in a conductor, a voltage is induced in the transverse direction to the direction of current. This is called Hall effect (Figure. 3.8)^[17]. The ratio of the induced electric field to the product of the applied current density and the magnetic field divided by the sample thickness is termed as the Hall coefficient.

Figure 3.8 : Schematic showing principle of Hall effect

The Hall coefficient is dependent on the type, number and properties of charge carriers in the sample and hence can give useful information about the material. Charge transport mechanisms in the material can be deciphered by measuring the Hall effect at different temperatures. The Hall mobility is a very important electronic property of the material.

The induced Hall voltage is directly proportional to Hall coefficient (R_H) magnetic field (B) and current (I), and is inversely proportional to thickness (t). In the perfect case with accurate geometry, there should not be any voltage induced if the magnetic field is zero. However, in reality there are other parasitic voltages including misalignment voltage (V_o) and Thermal electric voltage (V_{TE}). The misalignment voltage is proportional to the

resistivity (ρ), the current and a factor (α) which depends on the geometry. The thermal electric voltage arises from the contact between two materials and is dependent on the thermal gradients present. Hence the voltage measured V_m is

$$V_m = \frac{\rho i}{t} (\mu B + \alpha) + V_{TE} \quad (3.9)$$

μB can be negligibly small compared to α in low mobility materials. Thus, any noise in the measured quantity can easily give erroneous results including inconsistent carrier signs.

3.3.7.1 AC Field Hall measurements

This method can remove the misalignment voltage by using an AC magnetic field. In this case where the magnetic field is a sinusoidal signal ($B(t) = B \sin(\omega t)$), the Hall voltage becomes time dependent as well, $V_H(t) = i \rho \mu / t B \sin(\omega t)$. This is usually generated by rotating magnets. Hence, the misalignment voltage which is independent of the magnetic field remains a DC voltage and can be easily removed. The total measured voltage thus becomes $V_m = (\mu B \sin(\omega t) + \alpha)$

Although a lock in amplifier can easily separate out the AC signal from DC signal, there is a new term in the total voltage. This is proportional to the derivative of the magnetic field and is proportional to inductance of sample and leads used in measurement. Assuming the proportionality constant as β , the measured voltage should be :

$$V_m = \frac{\rho i}{t} (\mu B \sin(\omega t) + \alpha) + \beta \frac{dB}{dt} \quad (3.10)$$

Since the final term is independent of the current, just like the thermal electric voltage, current reversal can be used to remove this term. The term is also 90° out of phase from the signal. Hence, phase resolution on the lock-in amplifier can be used to remove this component by combining current reversal and phase measurement.

3.3.8 Galvanostatic measurements

Figure 3.9: (a) Galvanostatic measurements on an MIEC with ion blocking electrodes showing the saturation and decay of the potential. (b) The nyquist plot of a mixed ionic electronic conductor sandwiched between ion blocking electrons and the (c) The equivalent circuit of the system.

DC polarization techniques are widely accepted for separating the ionic and electronic components of conduction in a mixed conductor. Sandwiching a Mixed Ionic Electronic Conductor (MIEC) in between suitable ion/electron blocking electrodes would lead to polarization of the material and development of a potential gradient inside (known widely as Wagner-Hebb or Yokota polarisation^[18]). Application of continuity equations for electronic and ionic current with suitable boundary conditions and approximating sufficiently weak current will give the relation for voltage current characteristics and its dependence on time. For purely electronic conducting (ion blocking) electrodes the characteristics are as shown in Figure 3.9a. Generally, there is an initial potential which gradually saturates with time. At the point of saturation, only the electrons contribute to

the conductivity (σ_{e0}) whereas at the instant of switching on the current, both electrons and ions contribute ($\sigma_{i0} + \sigma_{e0}$). In addition, at the point of switching off the current, the potential drops to the fraction σ_{i0}/σ of the stationary value. These relations can be utilized to decouple the electronic and ionic conductivity of the material. The time correlation of the change in potential (fits a $\sqrt{t}$ law for short times and exponential behavior for longer time) can be utilized to calculate the diffusion coefficient of the ions as well. In addition to this, temperature dependent measurements will enable to calculate both the electronic and ionic activation energies.

3.3.9 Impedance Spectroscopy to decouple ionic and electronic components

The DC polarization technique can be supplemented using variable frequency small signal AC methods to decouple electronic and ionic contributions to the current. The general configuration is the same as the DC polarization technique with pure electron conducting electrodes (ion blocking). In case of an MIEC with similar electronic and ionic conductivity, the following analysis can be applied^[19]. The ions are conducted through the bulk and blocked at the interface of the material/electrode whereas the transport of electrons are not. Such an interface can be modeled as a parallel plate capacitor (C_{int} combining effects of both the electrodes). The excess ionic charge is balanced by the electronic charge in the adjacent metal electrode. In an MIEC, the equivalent circuit must include components for electronic (R_e) and ionic path (R_i) in parallel. In addition to this, a capacitance (C_{geom}) acts parallel to the whole configuration due to the dielectric constant of the material. If the ionic transport through solid is impeded by internal interfaces like grain boundaries, this additional ionic impedance (R_{gb}) must act in series with the bulk ionic resistance. This is also associated with a parallel local capacitance (C_{gb}). The complete equivalent circuit and the generic curve associated with it is shown in Figure 3.9c. The intercepts on the real axis can be identified as follows :

1. The one at lowest frequency (R_3) is equal to the electronic shunt resistance R_e .

$$R_3 = R_e \quad (3.11)$$

2. The intercept at next highest frequency (R_2) is a combination of R_e and the sum of R_i and R_{gb} .

$$\frac{1}{R_2} = \frac{1}{R_e} + \frac{1}{(R_i + R_{gb})} \quad (3.12)$$

3. The one at highest frequency is due to the parallel combination of R_i and R_e as R_{gb} will be shunted out by the grain boundary capacitance C_{gb}

$$\frac{1}{R_1} = \frac{R_e R_i}{(R_i + R_e)} \quad (3.13)$$

The ionic conductance is $G_i = 1/R_{ionic} = 1/(R_i + R_{gb})$ (3.14)

The electronic conductance is $G_e = 1/R_e = 1/R_2 - 1/(R_i + R_{gb})$ (3.15)

Hence the total conductance is $G_{total} = G_e + G_i = 1/R_2$ (3.16)

Thus the ionic (t_i) and electronic (t_e) transference numbers can be found from

$$t_i = G_i/G_{total} = 1/(R_i + R_{gb}) \times R_2 = (1/R_2 - 1/R_e) \times R_2 = (R_3 - R_2)/R_3 \quad (3.17)$$

$$t_e = G_e / G_{total} = R_2/R_3 \quad (3.18)$$

It can be seen that the transference numbers can be obtained merely from the intercepts on the real axis. Thus, it is a relatively simple technique for samples with not a large difference in ionic and electronic impedance (The analysis may be altered when there is huge difference in ionic and electronic conductivity). It does not require high ionic conductivity nor imposition of thermodynamic conditions on the two sides of the sample and waiting for equilibrium of species within it as in the case of DC polarization technique. In addition, the technique also enables the decoupling the role of grain boundaries in the ionic migration. A temperature dependent measurement can extract further information regarding the activation energy of the carriers similar to the other techniques.

3.3.10 Density Functional Theory Calculations

Density functional theory (DFT) is a quantum mechanical computational technique used to understand the electronic structure of many body systems like atoms, molecules and

condensed phases. It uses functionals (function of a function) to determine the properties of the system. Here the function is spatially dependent electron density.

In this thesis, Density Functional Theory Calculations is used to calculate the band structure and Density of states of the suitable materials prior to experimental synthesis and characterization. The nature of band edges, contribution of the ns^2 electrons to valence band, the nature and value of band gap are the basic properties evaluated. The electronic structure calculations are realized through VASP with the standard frozen-core projected augmented-wave method (PAW) with 300 eV as the cut-off energy for basis set. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) functionals used for exchange correlation^[20–24]. The atomic positions are relaxed until force/atom is less than 0.05 eV. All structural relaxations are performed with Gaussian smearing of 0.01 eV. Considering the heavy elements, SOC relativistic correction is employed in electronic properties calculations.

3.3.11 Solar Cell fabrication and Characterization

The solar cells are fabricated in the n-i-p configuration with TiO_2 as the n type and PolyTPD as the p type layers. The FTO substrates are cleaned as discussed above and the blocking layer of TiO_2 is deposited by spray pyrolysis of 600 μl Titanium diisopropoxide bis (acetylacetonate) solution (75% in ethanol) and 400 μl Acetylacetone diluted with 9 ml ethanol. The substrates are then treated with 100mM TiCl_4 solution for 30 minutes at 70°C and annealed at 500°C for 30 minutes. TiO_2 paste (30NRD-Dyesol) is diluted with ethanol in the ratio 1: 3.5 and spin coated at 5000rpm for 30 seconds followed by annealing at 500°C for 30 minutes. The films are again treated with 20mM TiCl_4 solution at 70°C followed by 500°C annealing before depositing the perovskite films. The perovskite films are deposited as discussed previously. 10mg of poly-TPD dissolved in 1ml toluene and heated at 80°C was spin coated at 4000rpm for 30s to form the hole transporting layer. Finally, 100nm gold electrodes are thermally evaporated using shadow masking to define an active area of 0.2cm².

Photovoltaic characterisation is carried out using a AM 1.5G solar simulator equipped with a 450W xenon lamp (model 81172, Oriel). Its power output is adjusted to match AM 1.5G sunlight ($100\text{mW}/\text{cm}^2$) by using a reference Si photodiode. I-V curves are obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2612A digital source meter. The voltage scan is done at $160\text{mV}/\text{s}$ from -0.1 to 0.7V with 121 intermediate points. All devices are measured by masking the active area with a black tape mask of 0.2cm^2 area. Incident-photon-to-current conversion efficiency (IPCE) is measured using a PVE300 (Bentham), with a dual Xenon/ quartz halogen light source, measured in DC mode, with no bias light.

3.3.12 Switchable Photovoltaic Characterization

Figure 3.10 : Device configuration for Switchable Photovoltaic measurements

Switchable Photovoltaic Effect in this study refers to the formation of a reversible intrinsic p-n junction inside the material induced by ionic segregation induced doping. This phenomenon has been observed in lead halide perovskites recently and show the potential to form photovoltaic devices without additional charge transport layers. Application of a high electric field across the material induces segregation of positive and negative ions towards the contacts and to grain boundaries inducing a doping effect (positive ions n dope and -ve ions p dope the material). Interdigitated FTO electrodes (3 Fingers) with lateral spacing of 50 and $100\mu\text{m}$ and total effective length of 3.7cm is used in fabrication of lateral device as shown in Figure 3.10. For the electrode spacing study, Gold electrodes with lateral spacing of 2.5, 5, 10 and $20\mu\text{m}$ and length of 2mm are used.

A 2 nm layer of Al_2O_3 is deposited by ALD to prevent any diffusion of gold ions into the material. The measurements are conducted in a probe station chamber under mild vacuum of 10^{-3} mbar with the light incident through a quartz window. A monochromatic blue LED of wavelength 445nm and power 1400W/m^2 is used for poling as well as the photocurrent measurements. Electrical properties are measured using a Keithley 4200-SCS semiconductor characterization system. The electric field applied on the perovskite film is $2\text{V}/\mu\text{m}$ for 120s under illumination by Blue LED. After poling, the IV and I-t curves are measured using the Keithley 4200-SCS.

3.3.13 Artificial Synaptic Device Characterization

Figure 3.11 : A biological synapse and analogous artificial photonic synapse

A biological synapse is the connection between two neurons. The neurotransmitters are passed on from one neuron to another through the synapse. The permanent/temporary strengthening and weakening of the synaptic connections is responsible for the learning in human brain. Spike-timing dependent plasticity (STDP) is a biological process that adjusts the strength of synaptic connections based on the relative timing between the pre synaptic (input) and post-synaptic (output) neuronal ‘action potentials’^[25] (Action potential occurs when the membrane potential of a specific cell location rapidly changes).

It plays a key role in cell to cell communication). Continuous spikes results in cumulative strengthening known as Long Term Potentiation (LTP) whereas acausal spiking decreases the synaptic strength leading to Long-Term Depression (LTD). This spike time dependent Plasticity (STDP) forms the basis for associative learning.

Spiking Neural Networks (SNNs) try to implement this artificially via spike based synaptic weight plasticity with spikes of identical amplitude and duration^[26]. Information is encoded in the timing and frequency of the spikes. In the biological neuron, a spike at the presynaptic neuron modifies the membrane potential at the post synaptic neuron by an amount called synaptic weight and eventually leads to a post-synaptic spike through a leaky-integrate-and-fire (LIF) or other similar neuron model^[27]. Achieving analogous electronic circuits uses simulation of STDP based learning rules with memristors with the two terminals as the pre and post synaptic neurons. The change in electrical conductance of the channel on an optical/electrical pulse is taken as the synaptic weight.

Chapter 6 of this thesis tries to emulate the most common form of plasticity observed at excitatory synapses in the brain commonly known as Short Term Potentiation (STP). It refers to temporal strengthening of synaptic connection which lasts for tens of milliseconds to a few minutes. Paired pulse facilitation (PPF) is the most common form of STP and is a phenomenon in which synaptic weight change induced on the first spike is increased when the second spike closely follows it. It is essential to decode temporal information in the biological system and is the essential criteria for a synapse. The device configuration used is shown in Figure 3.11. The current between two lateral electrodes A and B form the post synaptic output and the light pulse to the device is the pre synaptic input. The ionic electronic coupling and the persistent photo conductivity of the material are utilized to emulate synaptic functions. The light pulses are provided using a blue LED (445nm) with varying power and the electrical characteristics are measured using Keithley 4200-SCS.

Figure 3.12 : The post synaptic current on application of two consecutive spikes. The PPF index is the ratio A_2/A_1

For the weight change analysis the following approach is used in the work :

1. Read the device conductance with an applied bias voltage. This voltage is varied to achieve the required initial conductance.
2. Apply the Photonic pulse of required power and monitor the transient change in conductance. The power of the pulse, number and pulse duration are varied to obtain the required STP or LTP behavior.
3. Monitor the conductance state after 80s after the pulse and compare it with the initial conductance state to obtain the weight change.
4. PPF index is calculated as the ratio of the peak conductance on application of the subsequent photonic pulse to the first pulse.

3.4 References

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Chapter 4*

Templating the Formation of Layered A₃Sb₂I₉ and its Opto-electronic Characteristics.

The presence of ns^2 electrons is deemed to be the reason for excellent semiconducting properties of lead halide perovskites. This chapter explores novel techniques to solution process layered A₃Sb₂I₉ compounds containing ns^2 electrons to evaluate their optoelectronic properties. It provides insights into the role of size of A cation in determining the structure of A₃Sb₂I₉ compounds. The Layered Rb₃Sb₂I₉ was found to be similar to lead halide perovskites in terms of electronic structure with the p to p transitions enabling high absorption coefficients (10^5) and a low background carrier density (10^{13}). It also exhibited superior opto-electronic properties compared to a lower dimensionality Cs₃Sb₂I₉ which was more defective and exhibited lower photovoltaic performance. However, the photovoltaic performance ($V_{oc} \sim 0.55V$, $J_{sc} \sim 2.12mA/cm^2$ and 0.66% efficiency) was inferior compared to the standard lead halide perovskites (~25%) and could be related to disconnected layered lattice of the compound and lower atomic mass of Antimony in comparison with Lead.

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4.1 Introduction

The unique orbital characteristics of lead halide perovskites discussed earlier serve as an archetype for the development of alternative low-toxic and stable semiconductors for similar applications. In this light, AMX₃ structures of tin^[1-5], germanium^[6,7] and A₃M₂X₉ type materials based on bismuth and antimony^[8-13] have attracted attention due to the presence of ns² electrons which may equip them with defect tolerant properties. However, the Sn and Ge are lighter compared to lead and the inert pair effect, deemed to be the reason for the stability of Pb²⁺ ion, is weaker in them. Thus, the +2 states of these elements are unstable and gets easily oxidized to +4 ions^[14]. The immediate alternatives are Bi and Sb which are in the nearest group as lead in the periodic table and have the ability to form +3 ions with similar electronic configuration as Pb²⁺. This hypothesis is strengthened by reports on Bi based perovskite like materials for solar cells^[8,10,15] and double perovskites exhibiting long carrier lifetimes^[16]. Even though most of the research has been focused on application in solar cells, these studies indicate superior semiconducting properties and will advance the fundamental understanding of the material leading to wider applications. Thus, we presume that Sb based perovskite structures could be excellent semiconductors too in this context with a good deal of reported antimony based materials exhibiting photovoltaic properties^[17,18]. However, the complication with Sb is that it can exist in a stable +3 state only in comparison to the +2 state of lead constraining their ability to form a 3D corner sharing perovskite structure. Instead, they form A₃Sb₂X₉ compounds with a dimer structure with fused bi-octahedron or a layered structure with corner sharing octahedron. It is also evident from density functional theory calculations that the layered structure is superior compared to the dimer form in terms of having a direct band gap, higher electron and hole mobilities and better tolerance to defects because of higher dielectric constants^[13]. However, the reported process to form the layered derivative of Cs₃Sb₂I₉ involves a high temperature annealing in SbI₃ vapour which is difficult to reproduce due to processing constraints. In addition, it is known that the compound could potentially form deep defects from the DFT calculations; and the lack of solution processability prevents us from tuning the chemical potentials of the precursors by changing their composition to passivate such defects. As a

result the efficiency of the solar cell fabricated by this process was limited by its V_{oc} of around 0.2V and currents $<0.2\text{mA/cm}^2$ indicating poor semiconductor quality^[13]. Hence, finding out a solution processable alternative to form the A₃Sb₂I₉ in layered phase can open up doors to improve the semiconductor quality by enabling defect passivation. Even though solar cells are used as an indicator to test the quality of the semiconductor in this chapter, the study will also spur research in related semiconductor based applications.

Thus, this chapter focuses on forming the layered derivative of A₃Sb₂I₉ via a novel solution based approach. It is achieved by adopting a rational approach by examining the reasons for the comparative stability of the dimer and layered phases of A₃Sb₂I₉ by Density Functional theory calculations. The conclusions from the study were successfully translated into an experimental procedure to fabricate solar cells based on layered antimony perovskites via solution processing.

4.2 Templating the formation of layered A₃Sb₂I₉

Figure 4.1. XRD of A₃Sb₂I₉ with various cations

It is known that the dimer form of Cs₃Sb₂I₉ has a preference over its layered derivative if formed via a solution process^[13]. This violates Pauling's rules on crystal structures^[19] because the layered structure has corner sharing octahedra and should be preferred over the dimer form with face sharing octahedra in order to maximize the distance between two adjacent Sb atoms. The exact reason for this contradiction is unknown and has not been studied systematically. Some authors attribute it to the processing conditions claiming that the dimer form is preferred in presence of a polar solvent^[13,20]. Previous reports suggest a link between the size of the A cation and the structure formed in case of ABX₃ compounds. There are reports on A₃Bi₂I₉ transforming from a 0 D dimer to 2 D layered form on reduction of the A cation size from Cs to Rb^[9].

Figure 4.2 : Absorption spectra of A₃Sb₂I₉ with various A cations

A combinatorial approach was followed to screen various A cations to understand the effect on the crystal structure of A₃Sb₂I₉. Cesium iodide, Rubidium iodide, Methyl ammonium iodide and Formamidinium iodide were used as the sources for the A cation and SbI₃ for the B cation. The suitable precursors were dissolved in the required molar ratio (3:2) to obtain 0.2M of the solution in Dimethyl formamide which was then spin coated at 4000 rpm and annealed at 70°C. The materials were then screened using X-Ray

diffraction patterns. The preliminary experiments on replacing Cesium (1.88Å, in XII coordination) in A₃Sb₂I₉ with Methylammonium, Formamidineum and their mixtures resulted in similar XRD peaks. The peaks could be indexed to the P *63/mmc* dimer phase of Cs₃Sb₂I₉ (Figure 4.1). However, a smaller Rb (1.72Å, in XII coordination) at the A cation site formed a structurally different phase indicating that the size of A cation could affect the structure of A₃Sb₂I₉. The formation of dimer structure by larger cations was also confirmed from the absorption spectra. Even combination of Cs, MA and The absorption spectra of the dimer shows a larger band gap and pronounced excitonic feature probably linked to the presence of discrete octahedra. From the study Rb was chosen as the suitable cation for formation and investigation of layered structure A₃Sb₂I₉.

4.3 Crystal Structure Refinement of Rb₃Sb₂I₉

Figure 4.3. Refinement of Rb₃Sb₂I₉

In order to identify the crystal structure of Rb₃Sb₂I₉ and calculate the lattice parameters, Pawley refinement was performed (Figure 4.3). Powder samples of Rb₃Sb₂I₉ were obtained by drop casting the stoichiometric ratio of precursors (0.2M, 2ml) and drying it at 120°C for 2 hours. The powder XRD patterns were obtained on Bruker D8 Advance diffractometer in Bragg-Brentano configuration with Cu K α X-Rays of wavelength 1.54187 Å at 40kV and 40mA. The step size was kept at 0.02° with a step time of 2 s for

all the powder samples. The crystal structure was determined starting from Rb₃Bi₂I₉^[9] by replacing Bismuth atoms with Antimony. *The final structure has a P1c1 space group with $a = 14.60\text{\AA}$, $b = 8.19\text{\AA}$, $c = 25.17\text{\AA}$ and $\beta = 125.05^\circ$.* Figure 4.3 shows the structure of Rb₃Sb₂I₉ and its comparison with the reported Cs₃Sb₂I₉ dimer^[21].

The latter has fused (Sb₂I₉)³⁻ bi-octahedra clusters surrounded by Cs atoms while Rb₃Sb₂I₉ has distorted corner sharing octahedra. The fused bi-octahedra in Cs₃Sb₂I₉ provide enough space to accommodate the Cs atoms hence stabilizing the dimer form (Figure 4.4). The same is true for larger cations like Methyl ammonium and Formamidinium which form the dimer structures.

Figure 4.4: Schematic showing the influence of A cation size on the structure of A₃Sb₂I₉
- Structures of Cs₃Sb₂I₉ (dimer, P 63/mmc) and Rb₃Sb₂I₉ (layered, P1c1)

4.4 Formation Energy of Dimer and Layered forms by Density Functional Theory Calculations

In order to understand the effect of A cation substitution on the A₃Sb₂I₉ structure, Density Functional Theory (DFT) analysis was carried out to compare the formation energies of the dimer and layered forms of A₃Sb₂I₉ with A = Cs and Rb. The electronic structure calculations are realized through VASP with the standard frozen-core projected augmented-wave method (PAW) with 300 eV as the cut-off energy for basis set. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE)

functionals was used for exchange correlation. The atomic positions are relaxed until force/atom is less than 0.05 eV. All structural relaxations were performed with Gaussian smearing of 0.01 eV. Rb, Sb and I atoms are described by 4p⁶5s¹, 5s²5p³, 5s²5p⁵ valence electrons respectively. A 3x4x1 Gamma K-point grid are applied for Brillouin zone integration. The formation energy of dimer and layered form of Cs₃Sb₂I₉ differed by only 0.1eV (as shown in Table 4.1), consistent with the experimental observation that both forms can exist depending on synthesis conditions.

Table 4.1: Formation Energy comparison of Dimer and Layered forms of A₃Sb₂I₉ with Cs and Rb cations

Compound	Formation Energy (eV)	
	Dimer	Layered
Cs₃Sb₂I₉	-12.80	-12.70
Rb₃Sb₂I₉	-12.40	-12.65

In case of the bigger Cesium (1.88Å), the space for accommodating the cation in between the corner sharing octahedra is limited. However, a face sharing bi-octahedron creates enough space for a larger cation at the expense of a lower Sb-Sb distances as discussed in reports on similar structures, thus making the dimer form preferable in case of Cs. However, the higher difference (0.25eV) in formation energy for the Rb based systems indicates an increased preference for the layered phase. This can be linked to the smaller ionic radius of Rb (1.72 Å) as shown schematically in Figure 4.4

4.5 Rb₃Sb₂I₉ Band Structure from DFT calculations

To understand the electronic structure of layered Rb₃Sb₂I₉, the band structure of Rb₃Sb₂I₉ was calculated using the Perdew–Burke–Ernzerhof (PBE) functional. This showed a direct bandgap of ~1.98 eV at the Γ point (Figure 4.5a). The partial density of states (PDOS) plots depicted in Figure 4.5b revealed that the VBM is mainly derived from I *p* states with a small contribution from Sb lone-pair *s* states at the top of the valence band.

On the other hand, the conduction band was found to be a mixture of I *p* and Sb *p* states. The nature of the density of states of the compound is very similar to methyl ammonium lead iodide. The material is also expected to have very high absorption coefficients due to the possible *p*-to-*p* transitions.

Figure 4.5: (a) The band structure and (b) the Density of states of Rb₃Sb₂I₉

4.6 Thermal stability of Rb₃Sb₂I₉

Rb₃Sb₂I₉ was thermally stable up to 250 °C as inferred from the TGA and DSC data given in Figure 4.6. It exhibited two-step decomposition with the first step starting at around 250°C associated with around 60% weight loss (loss of SbI₃). Even though a stability up to 250°C is high enough for processing the material, there is a possibility that SbI₃ can sublime from hot spots in the film at even lower temperatures when in thin films^[13]. Thus the temperature of processing was kept at 120°C for the thin film studies discussed later in the text. The DSC also showed no signs of phase change in between – 40°C to 200°C which is high enough range to operate a solar cell. The Cs₃Sb₂I₉ in its dimer structure exhibited similar stability as well (Figure 4.7).

Figure 4.6: (a) DSC and (b) TGA of Rb₃Sb₂I₉

Figure 4.7 : The (a) TGA and (b) DSC of the dimer structured Cs₃Sb₂I₉

4.7 Thin film formation and characterization by XRD and XPS

In order to form the thin films, stoichiometric ratios of the precursors were dissolved in DMF and spin coated after filtering as discussed in detail in the Chapter 3. The films were annealed at 120°C for 10 minutes for all the characterizations. XRD shows that the films formed were found to be single phase without traces of unreacted precursors as given in Figure 4.8b. However, a detailed examination using XPS revealed that the I/Sb and the I/Rb ratios were lower than the expected ratios as tabulated in Table 4.2 pointing to iodine deficiencies in the sample.

Table 4.2. Ratios of Sb and Rb in comparison with Iodine extracted from XPS

	I/Sb	I/Rb
Expected	4.5	3
Rb₃Sb₂I₉ pristine	4.1	2.8
Rb₃Sb₂I₉ - SbI₃ treated	4.33	3.0

Figure 4.8: (a) The procedure adopted to form Rb₃Sb₂I₉ films, (b) the comparison of XRD of untreated and SbI₃ treated films and (c) the XPS comparison of both films.

Furthermore, the elemental scan of Sb 3d reveals the presence of two doublets separated by a binding energy of around 0.8 ± 0.05 eV as shown in Figure 4.8c. This suggests the

existence of two different chemical states of antimony, the expected 3+ and possibly the oxidized 5+ oxidation state^[22]. Considering the fact that the films are phase pure from XRD, the stoichiometrically lower ratio of Iodine may be due to the presence of iodine vacancies at the sample surface. In light of previous theoretical calculations on layered Cs₃Sb₂I₉^[13] with a similar structure, these iodine vacancies are expected to create deep traps in the band gap. However, changing the chemical potentials of the reacting precursors by introducing excess of precursors is a possible strategy to passivate such vacancies by altering their formation energies^[13,23]. Thus, a possible route would be to add an excess of SbI₃ to the initial mixture. However, due to the limited solubility of RbI and SbI₃ in DMF, any excess of SbI₃ tends to be precipitated and removed during the filtering process before spin coating, thus severely limiting the ability to tune the composition of the reaction mixture.

Figure 4.9 : (a and c) The changes in XRD diffraction patterns with annealing temperature and time and (b and d) the corresponding changes in Full width at Half Maximum of peaks

To address this problem, we adopted a novel strategy to provide this excess of SbI₃ by dissolving it in toluene and dripping it while spin coating as depicted in Figure 4.7a. XPS measurements (Table 4.2 and Figure 4.8c) show that the films treated with excess of SbI₃ exhibited near ideal stoichiometry with a single +3 oxidation state of Sb as only one Sb 3d doublet is observed in XPS. Furthermore, XRD reveal that the untreated films were highly oriented along the (002), (004) and (006) planes which are parallel to the layers of corner sharing octahedra. Such a preferential orientation can hinder the charge transport across the films as the effective masses are higher in direction perpendicular to the layers as reported in similar materials. However, the films which were spin coated using the modified procedure, did not exhibit such preferred orientation probably because of faster crystallization of the perovskite. Increasing the annealing temperature and duration above 120°C and 10 minutes did not improve the film crystallinity as seen from the unchanged FWHM of the 006 and 220 peaks (Figure 4.9a to d).

Figure 4.10 : (a) Energy level alignment of Rb₃Sb₂I₉ obtained from (b) UPS and (c) PESA measurements

Figure 4.10 shows the valence band spectra and the work function of Rb₃Sb₂I₉ as obtained from UPS measurements. The schematic band diagram is obtained using the energy of the Valence band and the band gap calculated from the Tauc plot. The ionisation potential of 5.66 eV obtained from Photoelectron Spectroscopy in Air (PESA)

measurement is relatively close to the value of $5.54 \pm 0.04\text{eV}$ obtained from UPS measurements. The 10 minute annealed sample exhibited a steeper work function onset. This could be from the removal of any residual DMF from the film. The annealing temperature also changed the ionization potential of the material. The detailed XPS and UPS spectra of Rb₃Sb₂I₉ and Cs₃Sb₂I₉ are available in Appendix (Figures A1 and A2)

4.8 Characterization of Morphology by SEM

The morphology of the treated and untreated films was compared using scanning Electron Microscopy (SEM). The coverage of the perovskite films deposited using the SbI₃ treatment was better compared to the pristine films (Figure 4.11). The untreated films formed only islands of the perovskite on TiO₂, exposing significant amount of TiO₂

Figure 4.11: Comparison of morphology of untreated films (a) and films treated with SbI₃ in toluene (b) on mesoporous TiO₂

4.9 Optical characterization

The Rb₃Sb₂I₉ films were red in contrast to the orange colored films obtained in case of the Cs₃Sb₂I₉ dimer possibly arising from the direct nature of the band gap. Furthermore, the SbI₃ treated films were more reflective and smoother looking compared to the untreated films. To gain more insight into these observations, we carried out UV-Visible absorption spectroscopy. The absorption coefficient of the Rb₃Sb₂I₉, calculated from transmittance and total reflectance values, was found to be higher than $1 \times 10^5 \text{ cm}^{-1}$ at 2.5eV which is

comparable to the values for methyl ammonium lead iodide^[24] indicating that very thin layers of the material would suffice to provide adequate absorption (Figure 4.12). Such high values are expected based on the p-to-p direct transitions evident from the calculations discussed previously.

Figure 4.12: The absorption coefficient of the SbI₃ treated Rb₃Sb₂I₉ films

Figure 4.13: Tauc plot fitting

The Tauc plot fitting (Figure 4.13) of Rb₃Sb₂I₉ assuming direct and indirect band gaps yielded values of 2.24 eV and 2.1 eV respectively. In semiconductors, the absorption

coefficient at energies just below the band edge decreases exponentially with decreasing energy and this absorption tail is called the Urbach tail. The slope of this exponential tail (called Urbach Energy) represents structural disorders, impurities, deep traps, phonon effects and excitons^[25,26].

Figure 4.14: Urbach Energy of Rb₃Sb₂I₉

The extracted Urbach energies of Rb₃Sb₂I₉ were in the range 85-90meV for the SbI₃ treated samples for 3 different annealing temperatures considered (Figure 4.14). This value is very high compared to the conventional photovoltaic materials including Methyl ammonium lead iodide (which exhibits an Urbach Energy of around 15meV only^[27]) indicating the pronounced effect of the above mentioned effects. In addition, the Urbach energies of the pristine films were even higher (105 to 115 meV) compared to treated samples indicating that defects are more dominant in pristine films. The absorption spectrum of dimer structured Cs₃Sb₂I₉ exhibited more intense excitonic features compared to the layered structure. In addition, the absorption is blue shifted indicating a larger band gap (Figure 4.15).

Figure 4.15 : Comparison of absorption spectrum of dimer Cs₃Sb₂I₉ and layered Rb₃Sb₂I₉

4.10 Cathodoluminescence spectroscopy

Figure 4.16: Comparison of Cathodoluminescence of treated and untreated samples of Rb₃Sb₂I₉. The spectra were obtained at an accelerating voltage of 5KV and beam current of 0.2nA.

To further explore the optoelectronic properties, Cathodoluminescence spectroscopy was utilized. The CL intensity of the SbI₃ treated sample was found to be approximately twice as bright as the untreated sample (Figure 4.16) possibly due to a higher density of non-

radiative recombination centres in the untreated sample. The spectrum can be deconvoluted to 3 different peaks centred at 1.98eV, 1.63eV and 1.41 eV. To further understand the origin of these peaks, the variation of the intensities of the peaks with excitation power was plotted (Figure 4.17) and the saturation rate of the emissions found.

Figure 4.17 : The variation of Cathodoluminescence with fixed accelerating voltage (5KV) and varying excitation power (in log scale). I_b is the beam current and I_{CL} is the CL intensity.

From the power resolved measurements it was found that the 1.98eV emission (close to the absorption edge) has as a near linear dependence on excitation power ($I_{CL} \propto I_b^{0.82}$) indicating that it could be from band-to-band transition as reported in case of other perovskites. The slight shift of the emission from the band gap could be due to excitonic effects as observed in other layered materials. The 1.41 eV and 1.63 eV peaks saturated faster with increasing excitation powers ($I_{CL} \propto I_b^{0.61}$ and $I_{CL} \propto I_b^{0.71}$ respectively) indicating that these peaks may be associated with some recombination center with a long relaxation time, as observed in other materials^[28]. The CL spectrum of Cs₃Sb₂I₉ (Figure 4.18) could be deconvoluted into at least 4 peaks showing the possibility of defects in the material. The 2.25 eV peak could be from the band gap as it shows a near linear behavior ($I_{CL} \propto I_b^{0.9}$, where I_b is the beam current) with the excitation power. However, the highest intensity peak at 1.75eV shows saturation behavior at higher excitation powers ($I_{CL} \propto I_b^{0.5}$) showing that it is not from band-to-band transitions and must be associated with

some deep level defects. The higher intensity of this peak compared to the Band to band emission shows the pronounced effect of defects and explains why the material exhibits very low currents in the solar cells discussed later in text.

Figure 4.18 : The power dependent Cathodoluminescence of Cs₃Sb₂I₉

4.11 Hall measurements

Hall measurements suggested p type conductivity for Rb₃Sb₂I₉. However, the measurement gave variable values for the mobility and carrier densities at different magnetic fields (Table 4.3). This p type behavior may be caused by shallow traps near the valence band as observed from the CL spectrum.

Table 4.3. Hall measurement data

Field [G]	Resistivity [ohm cm]	Hall Coefficient [cm ³ /C]	Type	Carrier Density [1/cm ³]	Hall Mobility [cm ² /(VS)]
5.00E+02	8.01E+03	2.36E+05	p	2.64E+13	2.50E+01
1.50E+03	8.11E+03	1.01E+05	p	6.17E+13	1.07E+01
2.50E+03	8.18E+03	4.49E+04	p	1.39E+14	4.74E+00
3.50E+03	8.21E+03	9.29E+04	p	6.72E+13	9.82E+00
4.50E+03	8.39E+03	1.15E+05	p	5.41E+13	1.22E+01

4.12 Photovoltaic characterization

The optical and electronic characterization aided to choose the right device configuration for the material: TiO₂ as electron transport layer, Poly-TPD as hole transport layer and Gold as counter electrode for fabricating the solar cells. The devices were fabricated using the thin films formed by SbI₃ treatment with the SEM cross section as depicted in Figure 4.19. The thickness of TiO₂ was kept around 400nm to ensure sufficient absorption of above bandgap energy photons.

Figure 4.19 : SEM cross section of device

Several devices were fabricated and the statistical analysis is shown in Table A1 with the best device exhibiting a voltage of 0.55 V and a short circuit current density of 2.12mA/cm² (Figure 4.20a). The untreated devices showed lower Voc and Current Density compared to the SbI₃ treated samples (Appendix : Table A1 and A2). The external quantum efficiency (EQE)(Figure 4.16b) plot is in agreement with the absorbance spectrum with the onset of current from around 600 nm and the device exhibited a maximum of around 30 % EQE in its absorption range. The internal quantum efficiency (IQE) was calculated using the total reflectance and transmittance (IQE= EQE/(1-R-T)) of the device and exhibited values <32%. This shows that only <32% of the absorbed photons are converted to carriers and collected at electrodes. The device efficiencies were also severely limited by the open circuit voltages of <0.6V considering

the high band gap. This low V_{oc} and the low IQE is possibly caused by recombination occurring at the defect levels suggested by the CL measurements.

Figure 4.20: (a) The IV curve under forward and reverse scans of the best device with the Energy levels of Rb₃Sb₂I₉ shown in inset (b) and the corresponding IPCE spectrum with the integrated current density.

In order to get more insight into the recombination behaviour of the material, the variation of V_{oc} with natural logarithm of light intensity was studied as shown in Figure 4.21. In case of a bimolecular recombination requiring an electron and a hole, the slope of this plot must give a value of $K_b T/q$ ^[23,29]. The slope obtained from our analysis yielded a value of $1.95 K_b T/q$. This indicates that Shockley-Read-Hall like recombination through defect levels is dominant over bimolecular recombination. Furthermore, the variation of short circuit current with light intensity was also studied. Previous studies claim a power law dependence of J_{sc} with Intensity according to relation, $J_{sc} \propto I^\alpha$ where an $\alpha \sim 1$ is regarded as a system with weak bimolecular recombination^[29]. $\alpha < 1$ is generally associated with space charge effects, variation in mobility between carriers or energy barriers in the device. From the Figure 4.21, the fitting gave $\alpha = 1$ excluding the possibility of the above mentioned effects. Thus, the only possibility for the reduced V_{oc} is the recombination through defect levels in the material itself. Another possible factor limiting the performance could be the anisotropic charge transport arising from the layered nature of the material. The charge transport may be limited due to some grains oriented in unfavorable orientations. Studies on the same material reported after this work

show similar efficiencies with alternative HTM (spiro-OmeTAD) indicating intrinsic limitations with the material for application in solar cells^[30].

Figure 4.21: The variation of V_{oc} with natural logarithm of light intensity with the variation of J_{sc} with light intensity plotted in the inset.

4.13 Conclusion

The ability to form A₃Sb₂I₉ structures with the presence of valence shell s electrons and similar electron density of states and p-p transitions as lead halide perovskites make antimony a potential candidate for lead replacement. However, the photovoltaic properties are found to be highly dependent on the phase of A₃Sb₂I₉- Dimer or layered. Here a simple solution processable methodology was adopted to develop the desirable layered antimony perovskite with the structure A₃Sb₂I₉. The study demonstrates that a smaller cation like Rubidium can effectively stabilize the structure in its layered form. The findings from cathodoluminescence and XPS prove the need for carefully tuned fabrication methodologies in Antimony based and other lead free materials to obtain materials very close to stoichiometry to avoid deep defects. The high Urbach energy of the material compared to lead halide perovskites indicate pronounced effect of structural disorders, deep defects, excitons or phonons as an intrinsic limitation of the material. The dimer form Cs₃Sb₂I₉ with a lower electronic dimensionality due to the discrete octahedra

was found to be inferior for opto-electronic applications with the absorption spectrum showing more pronounced excitonic effects and the CL indicating presence of deep defects. This points to the conclusion that presence of ns² electrons may not be a sufficient criterion for defect tolerance and other factors like structural connectivity may play a role. Even though the layered form was better compared to dimer in a solar cell architecture, both suffered from low photovoltaic efficiencies. The charge transport anisotropy due to the layered nature of the material could also be a limiting factor for application in solar cells. Exploring alternative device architectures could also be a strategy to improve the performances of these materials in solar cells.

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Chapter 5*

Effect of Atomic Mass of Metal Cation on Defects and Optoelectronic Properties of Layered A₃Sb₂X₉

The previous chapter discussed the role of the A cation in the formation layered phase of A₃Sb₂I₉ and its superior properties over the 0D form. However, both structures were possibly limited by defects for optoelectronic applications. In this chapter, the effect of the Atomic mass of Metal Cation on the optoelectronic properties of the A₃Sb₂I₉ compounds is explored. It is investigated by replacing Sb partially with a heavier element Bi in (NH₄)₃(Sb_(1-x)Bi_x)₂I₉ which is a 2D layered perovskite system. It is shown that the heavier element significantly affects the band edges and the defect characteristics of the material allowing tuning of the carrier type and the band gap. All the materials in general exhibited excellent absorption coefficients (10⁵ cm⁻¹) and very low trap densities (10¹⁶ cm⁻³) similar to lead halide perovskites. The chapter also discusses the role of a close direct and indirect band gap in the material leading to long carrier lifetimes (>100ns) and the influence of ionic migration in self doping the material. Although, the Bismuth incorporation slightly improved the efficiency of the material (0.38% to 1.09%), the efficiencies were limited by ionic, excitonic and phonon effects in the material.

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5.1 Introduction

The fundamental origin of the exemplary properties of lead halide perovskites has been linked to the unique orbital characteristics of Pb²⁺ cation, with ns² electrons imparting defect tolerance^[1] ability to the perovskite semiconductor. And these unique orbital characteristics serve as an archetype for the development of alternative low-toxic and stable solar cell absorbers. In this light, AMX₃ structures of tin^[2-6], germanium^[7,8] and A₃M₂X₉ type materials based on bismuth and antimony^[9-14] have attracted attention due to the presence of ns² electrons which may equip them with defect tolerant properties⁸. However, the performance of these materials remain inferior compared to the lead perovskites till date. The layered Rb₃Sb₂I₉ discussed in the previous chapter suffered from low photovoltaic efficiencies despite the presence of ns² electrons.

The inferior performance of isoelectronic Sn and Ge can be linked to their low atomic masses which results in weaker inert pair effect^[15] and an unstable +2 oxidation state. In addition, the low atomic weight also results in reduced tolerance to defects close to the conduction band by limiting the Spin Orbit Coupling effect (SOC). A heavier atom like Lead or Bismuth with higher SOC would push down the conduction band edge making deep defects near the conduction band shallower^[1,16,17]. However, a heavy atom would also strongly hold the ns² electrons preventing them from effectively hybridising to form an anti-bonding valence band maximum^[18], increasing the possibility of deeper defects near the valence band. Such factors may be even more pronounced in structures like Bi based A₃M₂X₉ compounds despite the presence of ns² electrons.^[19,20] Their discontinuous structure limits the orbital overlap and increases the chance of deep defect formation. Hence, electronic dimensionality^[21] could also be a vital factor contributing to the good optoelectronic and defect tolerant properties of semiconductors. Recently, ionic migration also has been identified as a possible factor limiting the performance of perovskite based materials^[22-26]. Such diffusion of ions could also affect the local defect configuration in the material and hence the performance of the device. Thus, there is no single parameter which would ensure defect tolerance in a semiconductor; and systematic evaluation of the effect of different parameters like atomic weight of metal cation, the electronic

dimensionality of material, the presence of an anti-bonding valence band maximum and ionic migration would help create better models for screening of alternative semiconductors.

In this chapter, a combined theoretical and experimental approach is adopted to examine the effect of heavy element (Bismuth) addition and ion migration on the optoelectronic properties and defects in a novel 2D layered Antimony perovskite-(NH₄)₃Sb₂I₉. Gradual substitution of Sb with Bi results in controlled modulation of the band gap, carrier concentration and carrier types. It is shown for the first time, creating intrinsic p- and n-type materials by metal cation transmutation illustrating the relevance of the atomic mass of the metal cation in determining the defects and carrier properties of the halide perovskites. First principle calculations, AC hall measurements, thermal admittance spectroscopy and transient absorption measurements provide possible explanations for this observed behavior. The pristine and transmuted materials exhibit a direct-indirect band gap with low trap densities (10^{16} cm^{-3}) and carrier lifetimes $> 100 \text{ ns}$, the highest reported so far for any lead-free perovskite thin film. In addition, it is demonstrated for the first time, creating local switchable p and n type doping in the same film by inducing ionic drift under mild bias of $2 \text{ V}/\mu\text{m}$ resulting in a switchable photocurrent. This signifies the role of ionic migration in affecting the local defect configuration to alter the carrier properties of the material. Thus, this report critically analyses the influence of metal cation atomic weight and ionic migration on the defects in the material illustrating ways to engineer them appropriately.

5.2 Density Functional Theory Predictions

All the first principle calculations are carried out based on Generalized Gradient Approximation (GGA) of Density Functional Theory (DFT) using Perdew-Burke-Ernzerhof (PBE) exchange correlation functional as implemented in Vienna Ab-initio Simulation Package (VASP)^[27–32]. Projector Augmented-Wave (PAW) pseudopotentials were used to describe the valence state and the interaction between electrons and ions. A

Gamma-centered Brillouin zone integration with 2x4x2 meshes for 2x2x2 unit cell and 450 eV as cut-off energy were used for structural optimization and electronic properties calculations, respectively. The Bi 6s²6p³, Sb 5s²5p³, I 5s²5p⁵, N 2s²2p³, and H 1s states were considered for Valence configurations. Considering the heavy elements, SOC relativistic correction was employed in electronic properties calculations. The calculated Density-of-States (DOS) of the various compositions were aligned with respect to the Nitrogen atom in the ammonium cation.

Figure 5.1: (a) Schematic showing the contribution of individual elements to the band edges and the mid gap states. (b) and (c) The effect of increasing Bi content to the band structure and Density of states of (NH₄)₃Sb₂I₉. It can be seen that Bi(s) do not contribute significantly to the band edges.

To begin with, a 2D layered Antimony perovskite-(NH₄)₃Sb₂I₉ system (P121/n1)^[33] was chosen as the parent compound for investigation due to its stable higher electronic dimensionality with good orbital overlap and reduced probability of deep defect

formation, in comparison to the 0D form generally formed by other Sb/Bi perovskite-like halides^[9,14]. Ammonium being an organic cation, also increased the solubility compared to other inorganic cations like Rb or Cs, thus facilitating a wider window for compositional engineering. An isoelectronic heavier Bi cation (208.98 amu) was chosen to replace Sb (121.76 amu) to systematically analyse the influence of atomic weight of the metal cation on the optoelectronic properties and defect tolerance in lead-free halide perovskites. The compositional landscape was scanned and optimized by gradual substitution of Sb, resulting in mixed (NH₄)₃(Sb_{1-x}Bi_x)₂I₉ compositions with 0%, 12.5%, 25% and 37.5% Bismuth. The crystal structures were optimized based on their lowest energy configurations with complete unit cell relaxation after each substitution step for all the stoichiometry. The optimized unit cells are shown in Appendix in Figure A3 with lattice constants listed in Table A3. Partial substitution of Sb with Bi did not alter the crystal structure, but increased the optimized unit cell volume monotonically due to the larger radii of Bi. Spin orbit coupling (SOC) effect was included to fully understand the effect of the heavy Bismuth atom addition on the band edges. The band structure (Figure 5.1b) depicted a direct band gap of ~ 1.7 eV at Γ point, with a very close indirect transition. Increasing the bismuth content reduced the band gap of the compound primarily due to increased SOC of the heavier bismuth, shifting the conduction band downwards. Density of states calculation indicated strong contribution of the metal (s) and I(p) orbitals towards the valence band and metal (p) and I(p) orbitals towards the conduction band edge. Incorporation of bismuth shifted the valence band edge further downwards by tight capture of the s electrons, preventing hybridization with I(p) as evident from the reduced contribution of s orbital for higher concentrations of bismuth (Figure 5.1c, Appendix- Figure A4). This could adversely affect the defect tolerance property linked to the ns² electrons by shifting the valence band side defects deeper into the gap (as shown schematically in Figure 5.1a). It is interesting to note that even for a low 12.5% Bi, contribution of the Bi(p) orbitals to the conduction band edge was far higher compared to Sb(p) due to the higher SOC of Bi. Also, the DOS at the conduction band increased with increment in Bi content, which could result in higher absorption coefficients for increased Bi contents. Unlike lead perovskites where the conduction band is mainly contributed by Pb(p) orbitals, here I(p) also contributed equally to the

conduction band edge in addition to Sb(p) possibly due to the poor overlap of Sb(p) orbitals considering the layered structure of the compound. This hybridization with I(p) could be detrimental since the Sb dangling bonds defects (for example Iodine vacancies) can now induce deeper defects near the conduction band. However, increasing the bismuth (larger atom) concentration could be beneficial in increasing the orbital overlap and SOC, making the conduction band side defects shallower.

5.3 Thin film formation and Characterization

Figure 5.2 : The crystal structure of (NH₄)₃Sb₂I₉ (b) The UV-Vis Absorption and (c) XRD of the films with various Bismuth content

NH₄I and SbI₃/BiI₃ were dissolved in 3:2 molar ratios to form 0.2 M, 1ml solutions in Dimethylformamide of (NH₄)₃Sb₂I₉ and (NH₄)₃Bi₂I₉. These solutions were stirred for 1 hour and then filtered using a PTFE filter. The solutions were mixed in appropriate

volumes to get the required doping level of Bismuth. The spin coating was done with excess SbI₃ provided via anti-solvent dripping as reported previously^[13]. The films were annealed at 60°C for 10 minutes for all the measurements. Table A4 in appendix shows the stoichiometry of the final films measured using Energy Dispersive X-Ray analysis. Higher grain size samples for Switchable Photovoltaic study was obtained by waiting 1 minute before starting to spin.

The powder XRD patterns were obtained on Bruker D8 Advance diffractometer in Bragg-Brentano configuration with Cu K α X-Rays of wavelength 1.54187 Å at 40kV and 40mA. The thin films were characterized at a step size of 0.05° and stepping time of 1s. The sample stage was rotated to compensate for non-uniformities in film. X-Ray Diffraction pattern (XRD) of the pristine ammonium antimony iodide film matched well with the reference pattern^[33] with preferential orientation along (002), (004) and (006) planes (Figure 5.2c). The XRD pattern did not show any impurity phase with addition of Bismuth but the peaks shifted to lower angles with increasing bismuth content, indicating an increase in unit cell size as a result of the bulkier bismuth incorporation.

Figure 5.3: (a) Photoelectron Spectroscopy in Air (PESA) measurements showing downward shift of the valence band maximum with increased Bismuth content, (b) the Urbach energy calculations for the various compositions.

Table 5.1: The Urbach energy for the various compositions

	Urbach Energy (meV)
0 % Bi	114
10 % Bi	125
20 % Bi	102
30 % Bi	88
40 % Bi	83
50 % Bi	83

The pristine (NH₄)₃Sb₂I₉ films were extremely smooth and reflective and showed strong absorption above 2.27 eV (Figure 5.2b), a typical characteristic of direct transitions. However, the absence of photoluminescence with long carrier lifetimes (*vide infra*) suggested an indirect band gap. This is corroborated by the DFT calculations which predict very close direct and indirect band gaps (Figure 5.1b). High absorption coefficients similar to methyl ammonium lead iodide (MAPbI₃) enables the use of ultra-thin layers to achieve complete photon absorption. It was also observed that the absorption coefficient enhanced with increased Bi content (Figure 5.2b), indicating increased density of states in the conduction band side as predicted. Addition of bismuth also resulted in slight reduction of band gap, from 2.27eV for the pristine film to 2.16 eV for 50% Bi film, due to the higher SOC of Bi which pushed the conduction band downwards as predicted by the DFT calculations. However, the heavier Bismuth also caused a downward shift of the valence band, limiting the band gap tunability. This is verified by increased ionisation potential values (5.78 eV for the pristine film and 5.9 eV for the 50% Bi addition) obtained from Photo-Electron Spectroscopy in Air (PESA) measurements depicting downward shift of the valence band maximum, also validating the theoretical prediction of reduced ns² contribution to the valence band (Figure 5.1b, Figure 5.3a). The Urbach Energies of the different compositions were calculated and were found to be between 80 and 130 meV (Figure 5.3b, Table 5.1). The high values indicate that structural disorders, deep traps or phonon effects may be at play in the material. It was observed that the Urbach energies reduced with increased Bismuth content.

5.4 Transient Absorption measurements - Direct-Indirect Band Gap

In order to gain more insight into the optoelectronic properties of the materials, transient absorption (TA) from fs-ns and from ns- μ s time regimes was carried out. Transient absorption measurements were performed with an integrated Helios and EOS setup (Ultrafast Systems LLC). Briefly, the excitation laser beam (400 nm) was generated by passing the 800 nm laser pulses from a Ti-sapphire regenerative amplifier (Coherent Legend, 800 nm, 150 fs, 1 mJ) into a beta barium borate (BBO) crystal as frequency doubler. Although various intensity of pump beam was used, no significant shift of the TA profiles was observed. The intensity used in the figures is around 16 μ J cm⁻². The fs-ns TA data was collected using the Helios, in which the probe beam is generated by passing a small fraction of the 800 nm pulses from the regenerative amplifier through a sapphire crystal. The ns- μ s TA data was collected using the EOS, in which the probe beam was generated from a photonic fiber using a Neodymium doped Yttrium Aluminum Garnet (Nd:YAG) laser (1064 nm). A detailed description of the setup and measurement techniques can be found elsewhere.^[34]

The TA profiles for all the samples changed rapidly at the early time-scales ($t < 100$ ps, Figure 5.4a) but remained unchanged at longer time-scales ($t > 100$ ps)(Figure 5.4c). The origin of the photo bleach (PB) and the two photo induced absorption peaks (PA1 and PA2) when the TA profiles reached steady condition were first analysed. The TA profiles resembled first order derivative of the steady-state absorption profiles, indicating spectral red-shift in the presence of excited state species. A shift in the absorption edge can be attributed to Stark effect, Burstein-Moss effect or band gap renormalization. Burstein-Moss effect (band-filling) results in a blue-shift of the band edge, which can be excluded as the origin of the spectral red-shift here. The band gap renormalization effect leads to a red-shift of the band gap with increasing carrier density due to electron-electron and electron-ion interaction. Here we did not observe any change of the shift when we tuned the injected carrier concentration, through a modulation of the excitation power. Hence, it is most probable that this red-shift could originate from the modulation of absorption profile induced by the carriers generating a strong local field, i.e., the Stark shift. Since

$(NH_4)_3Sb_2I_9$ is an indirect semiconductor (no PL emission but long carrier lifetime discussed later), after the complete relaxation of the carriers to the indirect band edge, these carriers can generate a strong local field to modulate the absorption profile. This would mean that the PB, PA1 and PA2 should have the same decay kinetics after the relaxation of the ‘hot carriers’, and reflect the recombination dynamics of the indirect band edge carriers. This was confirmed by the similar decay curves at long time-window (ns- μ s) for these three peaks when the early time kinetics difference is smeared (Figure 5.4b).

Figure 5.4 : (a) The initial ps decay of the 0% Bi sample (b) The dynamics of the three peaks observed in the long time scale decay (c) The transient absorption profile of the $(NH_4)_3(Sb_{1-x}Bi_x)_2I_9$ at 100ps. (b) The early time kinetics of the TA profile indicating relaxation of carriers to direct band edge and the subsequent relaxation

On analyzing the early-time kinetics of all the three peaks, hot carriers were found to play

an important role in determining the transient absorption profile. The hot carriers strongly affected the absorption profile through state-filling as well as Stark effect. Utilizing multi-exponential decay fitting (Figure 5.4d), two fast components were observed (1) an ultrafast time constant $\tau_1 < 1$ ps, reflecting the relaxation of photoexcited carriers to the direct band edge and (2) a slower time constant $\tau_2 \sim 40$ ps reflecting carrier relaxation to the indirect band edge through inter-band scattering. Bi addition extended the excited state absorption edge to the red side, consistent with the steady-state absorption due to the higher SOC, also confirmed by DFT calculations. Carrier dynamics at the indirect band edge which accounts for the device performance, was monitored at PA2 as shown in Figure 5.4d. Bi-exponential decay model was used to extract the carrier recombination constants and an effective lifetime τ_{eff} was used to quantify their recombination lifetime, where τ_{eff} is:

$$\sum_i A_i \exp(-\frac{t}{\tau_{\text{eff}}}) = \sum_i A_i \exp(-\frac{t}{\tau_i})$$

in which τ_i is the i_{th} fitted lifetime component of the decay curve and A_i is its weighted amplitude. Carrier lifetimes decreased with Bi incorporation compared to the pristine (NH₄)₃Sb₂I₉ film: 184±8 ns (0% Bi), 94±25 ns (20% Bi), 149±12 ns (40%), 91 ±13 ns (50%). The Carrier lifetimes with increase in Bi content do not follow any particular trend. This may be because while Bismuth addition reduces the deep defects near the conduction band side, it induces defects near valence band. In addition to this Bismuth addition also may be altering the extent of Direct-Indirect nature of band gap thus affecting the lifetimes. Other possible reasons for the stark effect could include strong excitonic effects^[35] and photo induced ion movement^[36] and consequent structural changes leading to local fields which could cause the shift.

5.5 AC hall Measurements – Carrier Tuning

The long carrier lifetimes reflect low defect density in the material and motivated us to study the carrier properties by AC hall measurements. Hall measurements were performed on the samples which are deposited on the glass substrate with four point gold electrode contacts on each corner according to Van der Pauw technique^[37]. The hall system is using a rotating parallel dipole line magnet that generates AC field with pure

harmonic, unidirectional and strong magnetic field followed by Fourier spectral analysis and lock-in detection of the Hall signal^[37,38].

Figure 5.5 : Variation of carrier density and mobility with Bismuth content

The results depicted p-type conduction behaviour for the pristine (NH₄)₃Sb₂I₉ with a carrier concentration of $\sim 3.95 \times 10^{15} \text{ cm}^{-3}$ and mobility of $\sim 0.5 \pm 0.05 \text{ cm}^2/\text{Vs}$ (Figure 5.5). This background carrier density is close to the values reported for thin films of MAPbI₃^[39] and very low compared to Tin perovskites^[2] indicating low intrinsic defects in the material. With 10% and 20% incorporation of Bismuth, the carrier density further reduced, accompanied by an increase in mobility which doubled to $> 1 \text{ cm}^2/\text{Vs}$. Interestingly, the material exhibited a p to n transition for higher bismuth contents (40%, 50%). However, this was also associated with almost one order of increase in background carrier density and low mobility. The mobilities are comparable to the values of thin film photovoltaic semiconductors like CZTSSe ($\mu_h = 0.5 \pm 0.1 \text{ cm}^2/\text{Vs}$), but still lower than CIGS ($\mu_h = 4 \pm 0.4 \text{ cm}^2/\text{Vs}$), measured using similar technique^[37]. However, due to the layered nature of the material and the preferred orientation as evidenced by the XRD, the resulting hall mobility reflects carrier mobility along the 2D plane. The decent mobility coupled with the long majority carrier lifetimes suggest that the majority carrier properties are adequate to facilitate charge separation along the layers of octahedra. It would be the carrier diffusion lengths perpendicular to the layers which will determine

the final performance in a solar cell configuration. A proper addition of Bi may help in balancing majority and minority carrier diffusion properties to provide optimum semiconducting property.

5.6 Mott-Schottky analysis

Mott-schottky analysis was used to extract the flat band potentials of the materials in FTO/TiO₂/Perovskite/PolyTPD/Au configuration. The capacitance measurements were done at a frequency of 200Khz. The voltage scan was started from a positive bias of 1.2V to limit the effect of accumulation capacitance due to ionic motion etc as reported elsewhere^[40]. The extracted flat band potentials (V_{bi}) were in the range of 0.4 to 0.6V for all the compositions (Figure A6). The doping at the edge of the depletion region, N_D (ω) was also calculated from the Mott-Schottky analysis using the relation :

$$\frac{d(C^{-2})}{dV} = \frac{2}{qA^2 \epsilon N_D \omega}$$

where q is the elementary charge, ε is the dielectric constant and A is the area of the device. The dielectric constants were extracted from the high frequency range of the capacitances. The results are tabulated in Table 5.2. The results follow similar trend as the trap densities calculated from TAS discussed below where the 20% Bi sample shows the lowest doping density

Table 5.2 : The Doping densities calculated from Mott-Schottky analysis

Sample	Dielectric Constant	Doping Density (cm ⁻³)
0% Bi	7.04	2.41 x 10 ¹⁷
10% Bi	8.67	2.36 x 10 ¹⁷
20% Bi	7.44	8.12 x 10 ¹⁶
40% Bi	8.85	5.08 x 10 ¹⁷
50% Bi	7.14	9.97 x 10 ¹⁷

5.7 Admittance Spectroscopy for Analysis of Defects

The observed p to n transition of carrier characteristics indicate the changing nature of defects in the material on Bismuth addition. This was more clearly monitored using Thermal Admittance spectroscopy (TAS). TAS gives the defect density of states and their locations in a semiconductor

by measuring the variation of capacitance with frequency and temperature^[41–44]. The devices for TAS and Mott-Schottky Analysis were made on planar TiO₂ (50nm) and with polyTPD as hole transporting layer and 100nm evaporated gold as electrodes. The perovskite film (200nm) was spincoated as described previously. The capacitance–frequency response (C–f) was measured with an LCR meter (E4980A, Agilent), which probes from 20 Hz to 1 MHz at an ac voltage amplitude of 20 mV under dark conditions in the temperature range of 200–315 K, whereas capacitance–voltage (C–V) measurements were carried out at 200 kHz in Autolab PGSTAT302N. Temperature-dependent conductivity measurements were carried out with a Lakeshore-1200 cryogenic probe station at a pressure of 10^{−6} mbar

Figure 5.6 : The defect density of states for the various compositions determined using Admittance Spectroscopy

Table 5.3 : The Energetic distribution of defects and integrated defect densities

	Defect location	Integrated defect Density (cm ^{−3})	Peak defect density (cm ^{−3} eV ^{−1})
0% Bi	0.14 eV from VB	1.68 x 10 ¹⁶	2.01 x 10 ¹⁷
10% Bi	0.22 eV from VB	1.45 x 10 ¹⁶	1.51 x 10 ¹⁷
	0.31 eV from VB	3.63 x 10 ¹⁶	5.49 x 10 ¹⁶
20% Bi	0.24 eV from VB	1.12 x 10 ¹⁶	1.05 x 10 ¹⁷
	0.39 eV from VB	2.89 x 10 ¹⁵	3.74 x 10 ¹⁶
40% Bi	0.24 eV from CB	1.41 x 10 ¹⁶	1.41 x 10 ¹⁷
	0.24 eV from CB	5.5 x 10 ¹⁵	6.50 x 10 ¹⁶
50% Bi	0.10 eV from CB	1.83 x 10 ¹⁶	2.15 x 10 ¹⁷
	0.25 eV from CB	4.82 x 10 ¹⁵	5.92 x 10 ¹⁶

Figure 5.7 : Schematic showing the relaxation of carriers to the band edge followed by recombination and the changes in defect levels on cation transmutation

The dielectric constants of the materials extracted from the high frequency capacitance in vacuum were in the range of ~ 7 to 9 . This is close to the values reported for lead halide perovskites^[43] ($\epsilon_r \sim 20$) indicating low capture cross section of the defect states which contributes to defect tolerance. The detailed TAS calculations are available in Appendix (Figure A7- A11). Table 5.3 and Figure 5.6 illustrates the calculated location as well as the distribution of defects measured by TAS. In general, the defect densities were similar to that reported for MAPbI₃ using similar measurements^[43,44]. The comparable values again indicate potential defect tolerance in these systems. For the pristine sample, the defects were centred at 0.14 eV from the valence band with an integrated defect density of $1.68 \times 10^{16} \text{ cm}^{-3}$ corroborating the origin of p-type conduction in these films. On gradual addition of 10 and 20% bismuth, the defect level shifted deeper to 0.22 eV and 0.24 eV respectively with slightly reduced defect densities. This could be explained based on the downward shift of the valence band maximum as indicated by first principle calculations and PESA measurements. An additional deeper defect level was also observed in the samples with 10 and 20% Bi, although with much lower trap density ($\sim 3 \times 10^{15} \text{ cm}^{-3}$). Owing to the p-type nature of these films, TAS did not yield any information regarding

the acceptor type defects. However, for n-type 40% and 50% Bi samples, TAS enabled us to probe the changes in the acceptor type defects. The 40% Bi sample exhibited a shallow acceptor and a deeper defect level centred at 0.11 eV and 0.24 eV from the conduction band with defect densities of 1.41×10^{16} and $5.5 \times 10^{15} \text{ cm}^{-3}$ respectively. Increment of Bi to 50% pushed the conduction band further downwards causing the acceptor side defects to get shallower due to increased spin orbit coupling effect, resulting in an enhanced n-type behaviour (Figure 5.7).

5.8 Solar Cell Characterization

Solar cells were fabricated for all the compositions as described in the Experimental Methods Chapter. The 20% Bi sample exhibited the highest efficiency of 1.09 % with an open circuit voltage (V_{oc}) of 0.48 V and current density (J_{sc}) of 3.67 mA/cm^2 (Figure. 5.8a). All other samples were limited by lower J_{sc} and V_{oc} . Similar trend was also visible in the internal quantum efficiencies (IQE) of the devices (Figure. 5.8b) with the 20% Bi sample exhibiting the highest IQE $\sim 50\%$ in its absorption range. The IQEs also clearly indicated the band gap narrowing effect with the addition of bismuth. Lower IQE of the Bi rich samples also indicated lower collection of absorbed electrons.

Figure 5.8 : (a) IV characteristics and (b) the IPCE of the $(\text{NH}_4)_3(\text{Sb}_{(1-x)}\text{Bi}_x)_2\text{I}_9$ system

The low performance (especially V_{oc} of 0.48 V considering the high band gap) of these devices is surprising given the long carrier lifetimes of $\sim 100 \text{ ns}$ for all the samples. In

order to understand the recombination behaviour of these devices, the variation of open circuit voltage with natural logarithm of the light intensity was studied (inset of Figure 5.8a). Higher slope ($1.57K_bT/q$) obtained for the 20% Bi sample indicated dominant Shockley-Read-Hall like recombination through defect levels. The J_{sc} variation with light intensity is given by the relation,

$$J_{sc} \propto I^\alpha$$

where $\alpha \sim 1$ denotes a system with weak bimolecular recombination and $\alpha < 1$ is related to energy barriers and space charge effects in the device. The best fit value of $\alpha = 0.94$ confirmed absence of such effects and pointing to dominant trapping of carriers by defects underlying the device performances. The pronounced trapping by defects despite the calculated long carrier lifetimes and low trap densities may be related to low mobility of carriers perpendicular to the layers of octahedra although the mobility obtained along the layers is high enough for efficient charge extraction. Reports published after this study show the presence of high exciton binding energy and electron-photon coupling which makes it difficult to extract the carriers in layered A₃Sb₂I₉ compounds^[45]. In addition to this, ionic migration changing the local defect configuration of the material could also play a vital role in determining the device efficiencies as discussed below.

Table 5.4: The Photovoltaic parameters of the devices with various Bismuth content in reverse scan (Forward scan in brackets)

	J_{sc} (mA/cm²)	V_{oc} (V)	Fill Factor (%)	Efficiency (%)
0 % Bi	1.70 (1.66)	0.38 (0.39)	57.8 (62.6)	0.38 (0.40)
10 % Bi	3.16 (3.02)	0.39 (0.40)	48.4 (56.3)	0.59 (0.68)
20 % Bi	3.67 (3.67)	0.48 (0.48)	61.7 (61.2)	1.09 (1.08)
40 % Bi	2.26 (2.37)	0.37 (0.40)	36.8 (44.9)	0.31 (0.43)
50 % Bi	2.17 (2.47)	0.37 (0.39)	46.5 (45.7)	0.37 (0.44)

5.9 Switchable Photovoltaic Effect

Ionic conductivity leading to ionic segregation is known to induce self doping effect in Lead halide perovskites. Hence, we resorted to electrical poling as a possible strategy to understand the changes in the material properties by creating ionic drift. Lateral

interdigitated FTO electrodes (Figure 5.9a) with an interelectrode spacing of 100 μm was used to apply electric field to the material in order to create the ionic drift. The unpoled $(\text{NH}_4)_3\text{Sb}_2\text{I}_9$ (p type) based device showed linear photocurrent-voltage relationship demonstrating ohmic behaviour (Figure 5.9b). The device was then negatively poled by applying a bias of $-2 \text{ V}/\mu\text{m}$ to electrode B under illumination by a Blue LED (455 nm, power $1.4 \text{ mW}/\text{mm}^2$) for 2 minutes. The IV curves after the negative poling indicated photovoltaic effect with an open circuit voltage close to 200mV which flipped to -0.2 V on positive poling (Figure 5.9b). The material also exhibited measurable photocurrent densities at short-circuit conditions despite the large spacing (100 μm) between electrodes indicating decent diffusion lengths.

Figure 5.9 : (a) Schematic of the device configuration used for switchable photovoltaic study. (b) IV-curves of the device before and after negative and positive poling measured in illumination with 445nm LED with a power of $1.4 \text{ mW}/\text{mm}^2$. (c) The variation of the open-circuit voltage with electrode spacing and the applied poling field (d) The response of the device to 2s light pulses after poling in the absence of any external bias.

It was observed that the Switchable Photovoltaic Effect (SPV) persisted even at small electrode spacings of 2.5 μm (Figure A12). The opencircuit voltage (V_{oc}) increased with the increased spacing between electrodes at a constant applied poling field; and also with the magnitude of the initial poling field applied for a constant electrode thickness (Figure 5.9c). Similar effects were observed by Huang et al on lead based perovskites and attributed it to ionic accumulation^[46,47] and formation of local p-n junctions^[48] at grain boundaries. The effect of grains in influencing the SPV is also evident from the higher V_{oc} observed in the films with smaller grains (Figure A13). The similar effects were observed (Figure A14) in the intrinsically n type 40% Bi doped film. However, the fundamental origin of the SPV in the material and the role of ions and grain boundaries in modulating it is still unclear and offers scope for future investigations on this material. Similar ionic and doping effects may also be at play in a conventional solar cell architecture resulting in low efficiencies indicating the need for alternative device architectures to harness carriers in these novel halide based absorbers.

5.10 Conclusion

In summary, mixed Sb-Bi metal cation perovskites of the formula $(\text{NH}_4)_3(\text{Sb}_{(1-x)}\text{Bi}_x)_2\text{I}_9$ were evaluated for the opto-electronic properties. Direct absorption followed by an indirect nature of recombination was observed, which equips it with high absorption coefficients along with long carrier lifetimes. In addition, the presence of ns^2 electrons and a decent dielectric constant $\sim 7-9$ enabled defect tolerance in the material with low trap densities $\sim 10^{16}$ similar to MAPbI_3 . The effect of heavy element on the band structure and hence on the defects of $(\text{NH}_4)_3\text{Sb}_2\text{I}_9$ was also evaluated in detail. Heavy metal addition was observed to be a double-edged sword, which on one hand improved spin orbit coupling limiting the formation of deeper defects near conduction band side and narrowing the band gap; but on the other hand lead to creation of deeper defects near valence band side. However, through proper engineering of the composition of the metal cation, we show the possibility of creating intrinsically p- and n-type materials without sacrificing on the carrier lifetimes. In addition, the possibility of achieving switchable photovoltaic effect is demonstrated without additional extraction layers paving way for alternate architectures for extracting carriers in novel nontoxic semiconductors. The

insights from this study are also applicable to a broad class of semiconductors with similar band structures including Lead halide perovskites, sulfides of Sb and Bi etc. In case of Lead halide perovskites, metal cation transmutation with tin could be a possible strategy to engineer carriers to form intrinsic p and n-type materials paving way for alternative simple and cheaper device architectures with higher efficiencies in solar cells.

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Chapter 6

Synthesis and Investigation of NaSbS₂ as an Ionic-electronic Coupled Semiconductor.

Although the $A_3Sb_2I_9$ compounds failed to excel as suitable semiconductors for solar cells, the studies on Switchable Photovoltaic effect in the previous chapter unlocks the possibility of Ionic-Electronic coupling in Sb based ns^2 electron containing materials. In this chapter, alternative materials with a higher lattice connectivity and high ionic conductivity as well as defect tolerance are explored with a combined theoretical and experimental approach. NaSbS₂ is identified as a suitable candidate and suitable solution processing strategy was developed to form thin films of this material. Its opto-electronic and ionic characteristics are studied in detail. The material exhibited superionic conductivity (0.172mS/cm) in ambient atmosphere and Switchable Photovoltaic behavior in vacuum. In addition to that, it exhibits a suitable bandgap (1.46eV) and high absorption coefficients (10^5cm^{-1}) suitable for application in photovoltaic devices. The studies lead to potential applications in neuromorphic devices and the novel concept of electrically re-configurable materials.

6.1 Introduction

The previous chapters elucidated the role of ns^2 electron in instilling defect tolerance in Sb based perovskite derived semiconductors. However, the poor electronic dimensionality and ionic migration deterred its application in solar cell devices. Nevertheless, the study shows the possibility of utilizing similar materials but with higher ionic conductivity and defect tolerance for applications like memristors which require a coupled ionic-electronic transport. Although Mixed-Ionic Electronic Conductors (MIECs) have existed for long, interest has grown in recent years due to their applications as electrochemical energy storage materials, electrodes of fuel cells and batteries, bioelectronics, soft robotics, supercapacitors, electrochromics and separation membranes and catalysts with various requirements for chemical, electrical, thermal and mechanical properties^[1]. The most widely studied and understood MIECs have been oxide based materials with oxide ion diffusion. Devices based on them have utilized several favorable properties of MIECS such as ionic conductivity, ability to intercalate ions, capacitance changes on ion accumulation, structural and optical changes on ionic diffusion^[2]. However, all these devices treat electronic and ionic currents as separate entities without effectively utilizing a possible coupling between these two. However, there are some studies which indicate that ionic migration induced compositional changes can induce a coupling between ions and electrons as in the case of Y doped ZrO₂^[3], doped BaTiO₃^[4], doped SrTiO₃^[5], CuInSe₂^[6,7], and Hg_{0.3}Cd_{0.7}Te^[8] where a p-n junction is created by segregating the ions into different regions by applying an electric field. Such an ionic induced doping modulating the electronic properties of the semiconductor material (both prefabrication and in-operando) could open up new applications in electronics. However, fabricating functional devices based on these materials and understanding the mechanism of ionic-electronic coupling has been difficult due to high field required to enable the doping and the lack of solution processability of most of these materials limiting the ease of synthesis, investigation and modulation of the ionic-electronic coupling.

The recent emergence of Lead halide perovskites as solution processable semiconductors is highly promising in this respect. These ionic semiconductors have revolutionized the

field of photovoltaics and light emission due to their excellent electronic and photonic properties. Simultaneously they have found applications in memristive systems^[9] and switchable photovoltaics^[10] where excellent ionic properties are exploited. Similar effects were also observed in Sb systems^[11] as discussed in the previous chapter. This co-existence of ionic and electronic properties can be attributed to its defect tolerance – ie the ability of a semiconductor to retain its properties despite the presence of point defects. The presence of ns^2 electrons, a high dielectric constant and the presence of the heavy element for strong spin orbit coupling effect are deemed the fundamental reasons for this effect^[12]. In addition, a well-connected soft lattice enabling high electronic and ionic mobility and easily tunable grain microstructure play a major role in determining the ionic conductivity of these mixed conductors. The ionic migration can be assisted by grain boundaries aligned parallel to the flow of ions and impeded by those perpendicular to it^[13,14]. The ions which are blocked at the boundaries can help in local doping of the material by creation of shallow traps and inducing doping. These observations form the basis for our investigation into similar materials and setting up design rules to explore solution processable ionic electronic semiconductors which can be easily modulated and made into functional devices.

In this chapter, materials which have higher ionic conductivity compared to perovskite but still exhibit defect tolerance are explored to unlock useful applications. Cubic NaSbS₂ is identified as a potential candidate and its optoelectronic properties were evaluated with a combined experimental and theoretical approach. A novel solution processing strategy is developed to form thin films of this class of compounds. The material possess a high absorption coefficient with a band gap around 1.5 eV suitable for PV applications. In addition, it exhibits mixed electronic and ionic conductivity which can be modulated by the Na content and the ambient atmosphere. The material behaves as a superionic conductor on exposure to humidity enabling its application as humidity sensors and solid state electrolytes for thin film batteries. In addition, switchable photovoltaic effect was demonstrated for the first time in a Chalcogenide semiconductor by utilizing the ionic-electronic coupling. Finally, the Persistent photo-conductivity of the material is utilized to demonstrate Synaptic plasticity in a neuromorphic device with extremely simple

architecture. This device was then electrically reconfigured by removal of Na ions to change the hysteresis and also the synaptic weight change, thus opening up a novel field of electrically post processable semiconductors.

6.2 Search for Ionic-Electronic Coupled Semiconductors

Figure 6.1 : Design rules for an ionic-electronic coupled semiconductor

Based on the above mentioned initial design rules, the ICSD database^[15] and Materials Project^[16] was scanned for viable non toxic ternary compounds based on Sb and Bi with ns² electrons which possess a highly symmetric cubic and connected structure. Tin, Indium and Germanium were excluded from the search because of their inherent tendency to oxidise and lose the ns² electrons. Several compounds including NaSbS₂, LiSbS₂, AgSbS₂, K₃SbS₃, Rb₃SbS₃, Cu₁₂Sb₄S₁₃, NaBiS₂, AgBiS₂, LiBiS₂, KBiS₂, AgBiI₄

and CuBiI₄ were identified. Among these, Alkali metal Pnictide chalcogenides are fascinating because of their compositional variety^[17] and flexibility, high dielectric constants^[18] and semiconducting nature. Cubic NaSbS₂ was identified as the most suitable candidate because of its high symmetry and known high Na ion conductivity in similar Sodium Antimony chalcogenides^[19].

6.3 Density Functional Theory Calculations on Cubic NaSbS₂

Figure 6.2: (a) Crystal Structure of Cubic NaSbS₂, (b) Band Structure and (c) Density of States

The band structure and the Density of states of the material was analyzed in order to evaluate the optoelectronic properties. The structure of the material as shown in Figure 6.2(a) is similar to NaCl structure with Na/Sb having partial occupancy. This complicated the DFT analysis since there can be ordered and disordered arrangement for the Na and Sb atoms. The details of the DFT calculations are provided in Chapter 3. To begin with, the cubic (Fm -3m) NaSbS₂ with an ordered arrangement of Na and Sb atoms in the lattice was analyzed (Figure A15). The crystal structure was optimized based on the lowest energy configuration. Interestingly, the band structure showed metallic character which is contradictory to the experimental results discussed later suggesting that the Na and Sb atoms should have a random arrangement. On recalculating the band structure with a random arrangement of Na and Sb atoms in the lattice (Figure A16), the band gap increased significantly to 0.71 eV indicating such an arrangement in the Thin films. The density of states calculation indicated strong contribution of Sb(s) and S(p) orbitals in the valence band and Sb (p) and S(p) orbitals towards the conduction band edge (Figure

6.2c). The presence of an anti bonding valence band maximum results in the valence band side defects to form only within the valence band without inducing deep traps in the band gap similar to halide perovskites. In addition, the cross gap hybridization between S(p) and Sb (p) can result in high dielectric constants which would further assist defect screening. Furthermore, the material exhibits an indirect band gap with a very close direct transition(Figure 6.2b). However, the indirect band gap may not be detrimental in this case as the p to p transitions will enable a high absorption coefficient and the indirect recombination may prolong the carrier lifetimes. Most importantly, it is seen that Na has negligible contribution to the band edges. This is quite similar to the halide perovskites where the A site cation does not contribute to the band edges. This is very important since the material is expected to show high Na ion conductivity. Since Na does not take part in bonding, motion of the ion will not introduce deep defects in the band gap thus retaining the electronic properties despite local changes in Na ion concentration.

6.4 Thin Film Formation and Characterization

Figure 6.3: Schematic of the NaSbS₂ thin film deposition

Thin films of the material were fabricated by a novel solution processing route by dissolving Sb₂S₃, and elemental S and Na in amine-thiol mixtures^[20]. This technique has the advantage of using elemental precursors enabling facile compositional tuning and low toxicity compared to the conventional hydrazine/chalcogen processing route^[21]. Solutions were prepared by dissolving Na, Sb₂S₃ and S in 1ml ethylene diamine and 0.1ml ethanedithiol to get a 1M solution at room temperature for 3 hours. The solution was

then spin coated at 4000rpm for 30s followed by annealing at 320°C for 30 minutes. To form thicker films, the process was repeated several times with 320°C annealing for 10 minutes and a final annealing for 30 minutes. It was observed that on dropping the solution to the first layer, the film becomes transparent and redissolves. Hence, a dynamic spinning was adopted with the solution dropped on the spinning substrate.

Figure 6.4 : (a) Cross sectional and (b) Top view SEM of the NaSbS₂ films showing the nanoporous morphology

Figure 6.5 : XRD patterns of Pristine and 5% excess Na samples

The films were around 800nm thick and had a nanoporous morphology (Figure 6.4a and b). X-Ray diffraction Patterns were obtained as discussed in Chapter 3. X-Ray diffraction pattern of the cubic NaSbS₂ matched well with the reference pattern (Figure 6.5).

Annealing at higher temperatures above 320°C did not improve the crystallinity of the film as evident from the XRD (Figure A17). Addition of a 5% excess Na to the solution did not shift the XRD pattern indicating that excess Na ion may just be incorporated to the interstices without changing the crystal structure. A higher Na content in the precursor solution led to highly amorphous samples which are highly moisture sensitive (Figure A18).

Figure 6.6 (a) The Absorption coefficient and (b) Tauc plot of the pristine and 5% excess Na films, (c) PES measurements showing the valence band edge and (d) the photo-conductivity measurements at different energies confirming a 1.5 eV band gap

The material exhibited high absorption coefficients of around $1 \times 10^5 \text{ cm}^{-1}$ close to the values reported for lead halide perovskites^[22] indicating the potential of the material in Photovoltaic applications (Figure 6.6a). It was seen that a 5% Na excess in the precursor solution did not change the absorption onset significantly. Assuming an indirect transition as obtained from the first principle calculation, Tauc plot fitting yields an indirect band gap of 1.46 eV. The absence of a sharp absorption onset and also the photo-current measurements (Figure 6.6d) showing the increase in photocurrents at around 1.5 eV confirms that the band gap is most probably indirect (1.46 eV). Photoelectron spectroscopy in air (PESA) measurements indicate a valence band edge of 5.56 eV and conduction band edge of 4.1 eV which is compatible with most electron and hole extraction layers used in thin film photovoltaics (Figure 6.6c).

6.5 Investigation of Photoresponse

Figure 6.7 : (a) IV characteristics of pristine NaSbS₂ in Humid air and Vacuum, (b) The Persistent Photconductivity of the material in vacuum

The opto-electronic properties of the material was investigated in a lateral architecture with FTO interdigitated electrodes (Figure 6.10a). The material exhibited significant photoresponse in vacuum with an on off ratio of around 10 (Figure 6.7). The low on-off ratio might be associated with traps or high ionic conductivity of the sample. In addition, the photocurrent exhibited a long decay time possibly arising from the slow relaxation of the ionic charge carriers or trapped charged carriers resulting in persistent photoconductivity (PPC) (Figure 6.7b). Although this PPC behaviour may be detrimental in a photovoltaic device or a photodetector, the light induced memory behavior can be positively utilized in artificial Photonic synaptic devices as discussed later in text. The electronic properties of the material drastically changed with respect to the ambient with the dark conductivity increasing 3 orders of magnitude on exposure to humid air. This was accompanied by negligible photo response from the material in the ambient. This increase in dark current was not observed on measuring the sample in dry air indicating the role of moisture on the conductivity of the sample. (Figure 6.8). Thus, the material can be tuned as an excellent humidity sensor because of its selectivity to moisture. However, the fundamental reasons for this effect is elusive and needs to be investigated. Our preliminary studies point to increased ionic migration under humidity as a reason for the improved conductivity.

Figure 6.8 : Evolution of dark conductivity over time in different ambient

6.6 Impedance Spectroscopy Analysis to Decouple Ionic and Electronic Conductivity

Figure 6.9 : (a) The equivalent circuit used for analysis and (b) the Nyquist plot of the lateral NaSbS₂ device with the fitting

Impedance spectroscopy was used separate out the ionic and electronic components of current in the same lateral configuration using FTO electrodes. The ions are conducted through the bulk and blocked at the material/electrode interface whereas the transport of electrons are not. Such an interface can be modeled as a parallel plate capacitor (C_{int}

combining effects of both the electrodes). The resultant transport mechanism can be modeled using an equivalent circuit that include components for electronic (R_e) and ionic path (R_i) in parallel^[23]. In addition to this, a capacitance (C_{geom}) acts parallel to the whole configuration due to the dielectric constant of the material. In addition, the grain boundaries which are perpendicular to the ionic transport will impede the ionic migration and will introduce an additional ionic impedance (R_{i-gb}) that must act in series with the bulk ionic resistance. This is also associated with a parallel local capacitance (C_{gb}). The complete equivalent circuit and the generic curve associated with it is shown in Figure 6.9. The calculated resistances and the corresponding specific conductivity of are listed in Table 6.1. The bulk ionic conductivity of 2.55 mS/cm indicate superionic conductivity in the material and is one of the highest for Na ion conductors. However, the conductivity is impeded by the grain boundaries (or a slower component) which add additional resistance to the motion of ions resulting in an effective conductivity of 2.47×10^{-5} S/cm. The effective electronic conductivity was one order less than the ionic conductivity indicating the role of ions in the conduction mechanism.

Table 6.1 : The resistances obtained from Impedance fitting and Galvanostatic measurements for the pristine NaSbS₂

Component	Resistance (ohm)	Specific Conductivity S/cm (Impedance)	Specific Conductivity S/cm (Galvanostatic)
R_i	30×10^3	2.55×10^{-3}	-
R_{i-gb}	3.1×10^6	2.47×10^{-5}	2.35×10^{-5}
R_e	11×10^6	6.96×10^{-6}	2.13×10^{-6}

6.7 DC Polarization measurements : Na ion as cause of conductivity

The results from impedance analysis were corroborated using DC polarization measurements. Sandwiching the Mixed Ionic Electronic Conductor (MIEC) in between suitable ion/electron blocking electrodes and under a constant current bias would lead to polarization of the material and development of a potential gradient (known widely as Wagner-Hebb or Yokota polarisation¹¹). For purely electronic conducting (ion blocking)

electrodes, there is an initial potential which gradually saturates with time. At the point of saturation, only the electrons contribute to the conductivity (σ_{e0}) where as at the instant of switching on the current, both electrons and ions contribute ($\sigma_{i0} + \sigma_{e0}$).

Figure 6.10 : (a and c) Galvanostatic measurements on Pristine sample and 5% excess Na sample respectively. The inset (b and d) show the transient fits to the initial short time response of both to extract the diffusion coefficient.

The ionic conductivity of the pristine NaSbS₂ sample in humid air calculated from this relation (2.35×10^{-5} S/cm) is one order of magnitude higher than its electronic conductivity (2.13×10^{-6} S/cm) which is very close to the values obtained from the impedance spectroscopy. The investigation of the voltage transients prove that the observed polarization is caused by a chemical diffusion. As in case of chemical diffusion, the transient fits a $\sqrt{t}$ law for short times and exponential behavior for longer time. Both these time dependencies were verified from the excellent match of the time constants of 1519 s and 1418 s. The chemical diffusion coefficient of the ion ($D = L^2/(\pi\tau)$ where L is the distance between two electrodes) is calculated to be 7.14×10^{-9} cm²/s. Previous reports on similar materials point to the Na ion migration in this material. If sodium ions are responsible for the conduction mechanism, excess Na in the precursor solution should lead to films with enhanced ionic conductivity. The effective ionic conductivity of sample with 5% excess Na was found to be 0.17 mS/cm which is one order higher than the pristine sample. This value is one of the highest reported for any thin film sodium ion conductors indicating their potential application in solid electrolytes for thin film batteries^[19,24–26].

Figure 6.11 : Fits to the longer time response of the (a) Pristine (b) 5% excess Na samples to extract the diffusion coefficients

Table 6.2 : Comparison of Conductivity and diffusion coefficients of Pristine and 5% excess Na samples from galvanostatic measurements

Sample	Electronic Conductivity (S/cm)	Ionic Conductivity (S/cm)	Diffusion Coefficient (cm ² /s)
Pristine NaSbS₂ (Humid Air)	2.13×10^{-6}	2.35×10^{-5}	7.14×10^{-9}
5% excess Na (Humid Air)	2.37×10^{-5}	1.7×10^{-4}	2.6×10^{-9}

Interestingly, the diffusion coefficient of the sample with 5% Na excess ($2.6 \times 10^{-9} \text{ cm}^2/\text{s}$) was of the similar order as that observed for the pristine sample indicating that the improved ionic conductivity is caused by excess available ions rather than improved diffusion. Interestingly in vacuum, the ionic ($4 \times 10^{-9} \text{ S/cm}$) and electronic conductivity ($1.15 \times 10^{-9} \text{ S/cm}$) are four orders lower than that observed humid air as observed earlier in the IV characterizations. This is also associated with lower diffusion coefficients ($2.44 \times 10^{-10} \text{ cm}^2/\text{s}$) proving that diffusion of ions are moisture driven. The reduction of dark electronic conductivity in vacuum would also mean that there are lower traps in the material in vacuum and reduced availability ions in the form of defects in the film. Hence, this material is unique by being an ionic conductor in presence of moisture and a semiconductor with coupled ionic transport in inert atmosphere. This ion-electron

coupled transport observed in inert atmosphere can be made use in novel functional electronic devices.

Figure 6.12: (a) Galvanostatic measurements on Pristine NaSbS₂ in vacuum and fits to (b) short and (c) long time scale responses to extract diffusion coefficients and ionic and electronic conductivities

6.8 Switchable Photovoltaic Effect

During the electrical measurement in vacuum, the IV curves of the material slowly drifted away from the origin on repeated measurements. Similar effects are observed in halide perovskites and is attributed to ionic migration induced doping of the material which enables phenomena like switchable photovoltaic effect^[10]. Owing to the moderate ionic conductivity of the material in vacuum, we investigated switchable photovoltaic effects in the material in vacuum by electrical poling to create the ionic drift.

The unpoled NaSbS₂ film showed linear IV characteristics passing through origin demonstrating ohmic behavior. The device was then poled by application of -2V/ μ m to electrode B under illumination by a Blue LED (445nm) with a power of 1.4 mW/mm² for 200s. The IV curves after removing the negative poling resulted in a positive photocurrent from B to A with an open circuit voltage of around 0.2V (Figure 6.13b). The direction of photo-current and voltage flipped on positive poling at B resulting in a switchable direction of photocurrent. The photocurrent is stable and exhibits quick

response to light pulses at zero applied voltage (Figure 6.13c). Similar effects are also observed in ferroelectric materials like BiFeO₃^[27]. However, NaSbS₂ is cubic with a center of symmetry, hence ferroelectricity can be ruled out in this material. It is known that absence of center of symmetry is an essential criterion for Ferroelectricity. So the effect must be related to ion migration induced doping as observed in lead halide perovskites.

Figure 6.13: (a) Schematic of the device configuration for SPV study, (b) Switchable Photovoltaic behavior developed after electrical poling, (c) the response of the poled devices to pulsed light and (d) the temporal change in the short circuit current developed inside the material on poling by voltage pulses

However, the nature of doping and the ions responsible for it are still elusive and offer scope for further research in this field. Possibly, the positive Na ions may drift to the negatively poled electrode to n-dope the material leading to the formation of an intrinsic p-n junction capable of driving the electrons even in the absence of electron and hole

transporting layers. This hypothesis is supported by the recent theoretical studies on NaSbS₂ (in a lower symmetry P1 structure) showing the low formation energy of Na_i which can act as donor defects and n-dope the material^[28]. The Energy Dispersive X-ray Scattering (EDS) data shows lower concentration of Na near positively poled electrode supporting this hypothesis (Figure A19-appendix). For better investigation of the phenomenon, the lateral devices were subjected to varying poling duration. It was seen that the induced Short circuit current increased and saturated with the poling time (Figure 6.13d). Similar behavior has been observed in Lead^[10] and Antimony^[11] based perovskites and is a typical characteristic of ion migration where the migrating ions reach an equilibrium after a particular time. Similar ionic effects may be detrimental in a conventional solar cell architecture, but could be a boon in novel architectures.

Figure 6.14 : The variation of open circuit voltage with light intensity. The inset shows the variation of short circuit current with respect to light intensity

To get further insights into the recombination behavior in the device, intensity dependent IV measurements were carried out (Figure 6.14). The slope of V_{oc} vs natural logarithm of light intensity gives a value of $2.55K_B T/q$. The ideality factor higher than 2 might be related to nonuniform recombination currents in the device or tail states in the band gap. The J_{sc} usually show a power law dependence on light intensity according to relation : $J_{sc} = I^\alpha$. The value of α is found to be 0.85 indicating space charge effects in the device

which could be originating from ionic accumulation at the interfaces and grain boundaries.

6.9 Application in Neuromorphic Devices

Figure 6.15 : (a) Schematic of the operation of a biological synapse and the analogous artificial device, (b) EPSC after a single and (c) multiple pulses

In addition to the Switchable Photovoltaic behavior, the I-t measurements indicate a long decay time for the photo-currents. This Persistent Photo-conductivity was used to emulate artificial synaptic behavior in the material. Synapse is the connection between two neurons (pre and post neurons) in the brain, and permits the transfer of information in the form of electrical/chemical signal. The presence of slowly decaying current/voltage signals induced by an input pulse (electric or optical) and history dependent output signals are the fundamental requirements for an artificial synapse (The detailed scientific terms and the working of the synaptic device is detailed in Chapter 3). In our device, the light pulse is the presynaptic input and the current across the two lateral FTO electrodes is the post-synaptic output. A presynaptic input (Optical pulse of 35 mW/cm², 445nm) under a constant applied bias of 1V triggers an Excitatory post-synaptic current (EPSC) in the channel (Figure 6.15b). The EPSC reaches a peak value of 23pA which decays slowly on removal of the spike to the resting current of 14 pA in around 15 seconds. This EPSC behavior is quite similar to an EPSC process in a biological synapse. The energy

consumption per single pulse event is only 5.75 pJ (given by $I_{\text{peak}} \times t \times V$) and shows potential to reduce the energy consumption to femto joule levels on reduction of pulse width. The synaptic weight gradually decays over time and based on its lifetime, it can be categorized as Short-term synaptic plasticity (STP) or Long-term synaptic plasticity (LTP). The margin between STP and LTP is not clearly defined but usually it is ms to s and s to years respectively^[29].

Figure 6.16 : (a) PPF index variation with the increasing interval. (PPF index is the ratio between second (A2) and first (A1) post synaptic current). Variation of EPSC after a single photonic spike w.r.t (b) illumination intensity and (c) driving voltage

To modulate the plasticity behavior, different illumination intensities were applied to the device. It was seen that the synaptic weights increased on application of a higher intensity photonic pulse. With a low intensity (35mW/cm²) light pulse the current reduced back to its original state in around 15s which is quite similar to STP (Figure 6.16b). When the intensity was increased to 840mW/cm², the synaptic weight change persisted at a higher level showing potential to transition to LTP. This means the device can be shifted from an STP behavior to LTP behavior just by adjusting the intensity of the light pulse. Increasing the driving voltage from 1V to 3V did not however lead to an increased weight change.

Paired pulse facilitation (PPF) is a phenomenon in which EPSC induced on the first spike is increased when the second spike closely follows it. PPF is thus a form of short-term synaptic plasticity and is required to decode temporal information in the biological

system. This PPF behaviour can be successfully emulated in this artificial synaptic device. The current in the artificial synaptic device increased when a pair of successive optical signals were applied as required in case of a biological synapse (Figure 6.15c). The paired-pulse facilitation ratio (PPF) is the ratio of A_2 to A_1 where A_2 and A_1 are the current levels corresponding to the optical spikes. The PPF indices varied inversely with the pulse intervals with short pulse intervals (250ms) yielding high PPF indices. PPF index reached 100% for around 10000ms. Similar to the coupling of biological neurons, this behavior fits well with an exponential decay :

$$y = B_1 \cdot \exp\left(-\frac{x}{t_1}\right) + B_2 \cdot \exp\left(-\frac{x}{t_2}\right) + y_0$$

where x is the pulse interval, y_0 is the facilitation magnitude, B_1 and B_2 are facilitation constants, t_1 and t_2 are the characteristic time constants associated with it. The time constants t_1 and t_2 were calculated to be 5.52 s and 24.5 s respectively (Figure 6.16a).

6.10 Electrically Re-configuring the Material

From the band structure discussed in the first section of this chapter, it is clear that Sodium ion do not significantly contribute to the band edges and hence incorporation or removal of sodium ions should not greatly deteriorate the electronic properties. It is also clear from the subsequent sections that the increase in sodium content can improve the ionic conductivity of the sample and also potentially help in doping the sample. This opens up the unique possibility to remove some sodium ions from a deposited film by using an electric field to an ionic drain thus altering the electronic properties of the material after deposition. In order to investigate this, an FTO substrate with a PEO film was integrated on top of the the lateral device used for the artificial synapse study. Slight heating of the device at 70°C helped to melt the PEO thus forming intimate contact with NaSbS₂. The initial IV curve across the lateral electrodes show high hysteresis which is common for highly ionic conducting materials (Figure 6.17b). The device was then electrically poled vertically by applying a voltage of 20V for 200s to the PEO side inorder to extract the Na ions to the PEO layer (Figure 6.17a). This resulted in a significant reduction in hysteresis in the dark currents (Figure 6.17b) of the sample

possibly because of the reduction in concentration of free interstitial Sodium in the sample.

Figure 6.17 : (a) Device structure used for electrical reconfiguration study (b) The IV curves before and after re-configuring by removing Na ions

Figure 6.18 : The EPSC before and after re-configuring NaSbS₂

The synaptic device was tested before and after electrical re-configuration of the material. Initially the post-synaptic current decayed fast showing an STP behavior. Upon reconfiguration, the device retained significant weight change even after 80s showing transition to LTP behavior. The spatial non uniformity across several synaptic devices is

one of the major problem for developing neuromorphic circuits. This strategy offers a novel way to tackle this issue by correcting the synaptic weight changes across several devices by post deposition electrical poling.

6.11 Conclusion

In summary, a novel chalcogenide semiconductor – NaSbS₂ was synthesized and tested for its opto-electronic and ionic properties. A facile solution processing strategy was developed to form thin films of the material in its cubic structure. The material exhibited high absorption coefficients with a band gap suitable for photovoltaic applications. First Principle calculations point to high electronic dimensionality and similarity in Density of states of the material to lead halide perovskites which could equip it with superior optoelectronic properties. The material exhibited mixed ionic electronic conductivity with super-ionic conductivity for higher Na containing films in ambient atmosphere opening up applications in solid state electrolytes for Na ion batteries. This mixed-ionic electronic conductivity was also utilized to demonstrate switchable photovoltaic device and synaptic device paving way for alternative solar cell architectures and novel electronic applications of chalcogenide based semiconductors. Furthermore, the unique band structure and the high Na ion mobility in the material was utilized to demonstrate post deposition electrical reconfiguration of the material enabling facile tuning of synaptic weight changes. This ability to tailor compositions and internal electric fields is essential for applications that are relevant for both carrier injection and collection architectures, and would enable approaches to photovoltaics unbound by Shockley-Queisser limits, spectrally tunable photodetectors, efficient light emitting devices and neuromorphic memory architectures with continuously tunable weight changes. Electric field based post-fabrication processing can enable compensation of defects created by processes such as printing on non-ideal substrates, relevant for cost-effective electronics. The insights from the study are not limited to NaSbS₂ but can also be extended to other Alkali metal Antimony and Bismuth dichalcogenides which can be formed easily by the reported approach.

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Chapter 7

Conclusion and Research Outlook

This chapter draws together the threads of this dissertation. The general conclusions from the results and how they correlate with the hypotheses discussed in Chapter 1 is reflected. The limitations of the materials investigated, the broader scope of the study and possibilities for future work with relevant preliminary studies are discussed.

7.1 Summary and Implications

The thesis looked at the novel optoelectronic and ionic properties of ns^2 electron containing Antimony based compounds. A combined theoretical and experimental approach was adopted to explore fascinating compounds. Novel synthesis strategies and thin film formation techniques for each of the novel compounds were identified. The study was focused on $A_3Sb_2X_9$ structures and $NaSbS_2$. The opto-electronic characterization of the materials lead to the following exciting insights.

Figure 7.1 : Schematic showing the influence of size of A cation in forming the layered structure of $A_3Sb_2I_9$

Role of A cation in $A_3Sb_2X_9$ / Role of dimensionality.: The study detailed in the Chapter 4 unraveled the role of the size of A site cation in determining the structure and dimensionality of $A_3Sb_2I_9$ structures (Figure 7.1). ***It was the first report on solution processed thin film formation of a layered $A_3Sb_2I_9$ compound and its application in solar cell.*** The 2D $Rb_3Sb_2I_9$ was superior to 0D $Cs_3Sb_2I_9$ on application in a solar cell device. owing to its more connected structure. $Rb_3Sb_2I_9$ exhibited decent DC hall mobilities ($\sim 10 \text{ cm}^2/\text{VS}$) and low background carrier density ($\sim 5 \times 10^{13} / \text{cm}^3$). The low performance of 0D form in solar cells and the presence of defects as seen from cathodoluminescence measurements indicate that presence of ns^2 electrons may not be a sufficient condition for defect tolerance and factors like structural connectivity may play

in determining defects too. The p to p transitions enabled high absorption coefficients for the materials as hypothesized.

Table 7.1 : Comparison of Photovoltaic performance of $A_3Sb_2I_9$ structures

	J_{sc} (mA/cm ²)	V_{oc} (V)	Fill Factor (%)	Efficiency (%)
$(NH_4)_3Sb_2I_9$	1.70	0.38	57.8	0.38
$(NH_4)_3Sb_2I_9$ - 20 % Bi	3.67	0.48	61.7	1.09
$Rb_3Sb_2I_9$	2.11	0.55	56.97	0.66

Table 7.2 : Comparison of properties of $A_3Sb_2I_9$ and lead halide perovskites

	$A_3Sb_2I_9$	Lead Halide Perovskites
Absorption coefficient (cm ⁻¹)	$\sim 10^5$	$\sim 10^5$
Band gap (eV)	2-2.2eV	1.55eV (MAPbI ₃)
Dark Carrier Density (cm ⁻³)	10^{13} - 10^{14}	10^{12}
Trap Density (cm ⁻³)	10^{16}	10^{15} - 10^{16} (Thin films)
Mobility (cm ² /VS)	1-10	10 -100
Carrier type	p, n (Bismuth doped)	Intrinsic
Efficiency (%)	1.09%	$\sim 25\%$

Despite having good semiconducting properties in comparison to the Lead halide perovskites (Table 7.2), the $A_3M_2X_9$ structures studied in this thesis were limited by low efficiencies (Table 7.2). Several reports published during this thesis also revealed the role of exciton binding energy in determining the performance of $A_3Sb_2I_9$ compounds. Generally all of them are reported to exhibit high exciton binding energies^[1] which makes it difficult to dissociate the excitons and extract the charge carriers leading to poor photovoltaic efficiencies. This intrinsic limitation of $Rb_3Sb_2I_9$ limits its application in solar cells despite decent mobilities and potential tolerance to defects. Another reported limitation of the material is its strong electron-phonon coupling^[2]. Similar coupling in Sb_2S_3 is known to limit solar cell performance^[3]. Nevertheless, several layered $A_3Sb_2I_9$ materials have recently found alternative applications in neuromorphic devices and memristors.

Importance of Stoichiometry : Chapter 1 also revealed the importance of stoichiometry in determining properties of $A_3Sb_2I_9$ compounds. Iodide deficient compounds resulted in lower cathodoluminescence which translated into devices with poor photovoltaic efficiency. This is analogous to lead halide perovskites where vacancy of iodine is shown to result in lower performances^[4]. A novel technique was invented to avoid iodine deficiencies in $Rb_3Sb_2I_9$ compounds by modifying the anti-solvent dripping method used in perovskite deposition by including excess SbI_3 dissolved in toluene as anti-solvent.

Figure 7.2 : Schematic showing the influence of atomic mass of B cation in influencing defects and carriers in $(NH_4)_3Sb_2I_9$

Role of Atomic mass of B cation in $A_3Sb_2I_9$: The chapter 5 was an attempt to understand the role of atomic mass of metal cation on defects in antimony based perovskite. ***The study showed, for the first time, the ability to tune the carrier type by just tuning the Atomic mass of the metal cation in $(NH_4)_3Sb_2I_9$.*** Addition of Bismuth to $(NH_4)_3Sb_2I_9$ led to a change of carrier type from p to n type. Deeper investigations revealed the role of changing defect levels and role of spin orbit coupling in the phenomenon. A heavy element pushes the conduction band downwards causing the conduction band side defects to be shallower resulting in n type behavior. ns^2 electrons by default keeps the valence band side defects shallow. A heavy element can prevent participation of ns^2 electrons in bonding making valence band side defects deeper (Figure 7.2). Hence, the heaviness of metal cation can be a double-edged sword in case of layered $(NH_4)_3Sb_2I_9$. The study

proved the hypothesis that heaviness of the metal cation can influence defects in halide perovskites.

Figure 7.3 : Schematic showing direct-indirect band gap in $(\text{NH}_4)_3\text{Sb}_2\text{I}_9$

Role of direct indirect band gap : Chapter 5 also unraveled the presence of a direct-indirect band gap in $(\text{NH}_4)_3\text{Sb}_2\text{I}_9$. This provided high absorption coefficients to the material via a direct transition which then relax to the indirect band edge and recombining slowly. Transient absorption provided supporting evidence to this behavior showing an ultrafast time 1 ps component corresponding to relaxation of carriers to direct edge and a 40ps component showing inter-band scattering and relaxation to indirect band edge (Figure 7.3). This was followed by a long $>100\text{ns}$ carrier lifetime. ***This was the first report on such a direct-indirect band gap in lead free perovskites*** Similar effects are reported in lead halide perovskites, but are highly debated^[5].

Role of Switchable Photovoltaic Effect : Chapters 5 and 6 revealed the role of ionic migration in inducing Switchable Photovoltaic effect in $(\text{NH}_4)_3\text{Sb}_2\text{I}_9$ and NaSbS_2 . ***This was the first report on switchable Photovoltaic effect in a lead free halide perovskite.*** Similar effects have also been reported for lead halide perovskites^[6] indicating the electronic similarity of the materials with them. This increased ion migration induced doping necessitates need for alternative solar cell architectures to efficiently harness carriers from these class of materials.

Figure 7.4 : Design rules for electrically re-configurable materials

Design of ionic-electronic coupled materials : Drawing conclusions from all the above observations, Chapter 6 developed a novel concept of ionic electronic coupled materials which can be electrically post processed to obtain desired properties. Inducing compositional control through electric fields require controlled motion of charged ions and a material system that is compositionally flexible. The material system in addition to being compositionally flexible needs to possess a soft lattice capable of handling strain and have low formation energies. In order to utilize such materials for electronic applications, the charge transport properties need to be retained despite the stoichiometric variations induced by ionic segregation. The initial design rules to enable these properties included presence of ns^2 electrons (to induce defect tolerance), a connected lattice (to enable high electronic and ionic mobilities) and the mobile ion not contributing the band edges (to avoid deep defects on ionic motion) (Figure 7.4). These design rules were verified through the synthesis and evaluation of NaSbS_2 . The material exhibited high

ionic conductivity in ambient equaling superionic conductors. ***Switchable Photovoltaic Effects and Persistent Photo-conductivity were reported for the first time in this material enabling its application in artificial synaptic devices.*** In addition, the device was shown to be electrically re-configurable by removal of Na ions which reduced the hysteresis in IV curves and increased the persistence of photo-conductivity leading to higher synaptic weight changes.

7.2 Future work

7.2.1. Higher symmetric layered phase of $A_3Sb_2I_9$:

Figure 7.5 : The schematic showing the difference in crystal structures of $Rb_3Sb_2I_9$ and layered $Cs_3Sb_2I_9$

The symmetry of the crystal plays a role in influencing the overlap of the orbitals and hence the charge transport and even the defects in the material. A system with higher symmetry is expected to perform better than the low symmetric $Rb_3Sb_2I_9$ (monoclinic: $P1c1$) or $(NH_4)_3Sb_2I_9$. Thus a $A_3Sb_2I_9$ structure which has a higher symmetry (like layered $Cs_3Sb_2I_9$: hexagonal) should exhibit better optoelectronic properties (Figure 7.5). Synthesis of such structures can provide meaningful insights into role of structural symmetry on electronic properties, exciton binding energy, nature of band gap and ionic migration and hence the ionic-electronic coupling. It was known that A and X cation sizes can influence the crystal structure of the material. Hence a combinatorial approach can be followed to identify higher symmetric structures of the $A_3Sb_2I_9$ family.

7.2.2. Heavy element doping in Antimony based compounds

7.2.2.1 Bismuth doping in Antimony Chalcogenides to modify properties :

Figure 7.6 : (a) The changes in XRD pattern and (b) the UV-Vis absorption of Sb₂S₃ on incorporation of Bismuth

Antimony chalcogenides have been employed in solar cells in various architectures with efficiencies reaching 9%^[7,8]. However, defects and improper carrier collection has limited their efficiencies from advancing further. The studies on the effect of atomic mass of metal cation on defects and carrier types open up new possibilities in similar materials. As a preliminary study the effect of Bi inclusion in Antimony sulfide was evaluated and was shown to help in facile tuning of its band gap (Figure 7.6).

In addition to tuning the band gap of the material, Bismuth may help to passivate the conduction band side defects by pushing down the conduction band owing to its high spin orbit coupling effect. There is also a possibility of creating an intrinsic p-n junction inside Antimony sulfide by gradual local doping of Bismuth on the surface to enable facile carrier extraction. This principle is not limited to Antimony sulfide and may be applied to NaSbS₂ discussed in the chapter 5 or even the Lead halide perovskites. In lead halide perovskites, a Pb-Sn mixture might enable facile carrier tuning in addition to the reported band gap tuning^[9]. (cite)

7.2.2.2 Introduction of other heavy elements to $A_3Sb_2X_9$ compounds

The heavy elements are associated with an effect called spin orbit coupling which causes shifts in an electron's atomic energy levels due to electromagnetic interaction between the electron's spin and the magnetic field generated by the electron's orbit around the nucleus. The spin orbit coupling interaction is known to push the conduction band of the lead halide perovskites down reducing the band gap and also helping in screening the donor type defects near conduction band as discussed in case of Bi addition in Chapter 5. Thus addition of other heavier elements in combination with Antimony in $A_3Sb_2I_9$ will be an important study to understand the impact of dissimilar heavy metals in determining the defect and optoelectronic properties.

Table 7.1 : Comparison of viable heavy elements for doping

Atomic number	Name	Electronic configuration outside [Xe]/[Kr] core		Ionic radius (M^{3+}) pm
		M	M^{3+}	
51	Antimony (Sb)	$4d^{10} 5s^2 5p^3$	$4d^{10} 5s^2$	76
57	Lanthanum (La)	$5d^1 6s^2$	[Xe]	103
58	Cerium (Ce)	$4f^1 5d^1 6s^2$	$4f^1$	102
59	Praseodymium (Pr)	$4f^3 6s^2$	$4f^2$	99
60	Neodymium (Nd)	$4f^4 6s^2$	$4f^3$	98.3
61	Promethium (Pm)	$4f^5 6s^2$	$4f^4$	97
62	Samarium (Sm)	$4f^6 6s^2$	$4f^5$	95.8
63	Europium (Eu)	$4f^7 6s^2$	$4f^6$	94.7
64	Gadolinium (Gd)	$4f^7 5d^1 6s^2$	$4f^7$	93.8
65	Terbium (Tb)	$4f^9 6s^2$	$4f^8$	92.3
66	Dysprosium (Dy)	$4f^{10} 6s^2$	$4f^9$	91.2
67	Holmium (Ho)	$4f^{11} 6s^2$	$4f^{10}$	90.1
68	Erbium (Er)	$4f^{12} 6s^2$	$4f^{11}$	89
69	Thulium (Tm)	$4f^{13} 6s^2$	$4f^{12}$	88
70	Ytterbium (Yb)	$4f^{14} 6s^2$	$4f^{13}$	86.8
71	Lutetium (Lu)	$4f^{14} 5d^1 6s^2$	$4f^{14}$	86.1
83	Bismuth (Bi)	$4f^{14} 5d^{10} 6s^2 6p^3$	$4f^{14} 5d^{10} 6s^2$	103

However, the elements which may be incorporated will be limited by the Goldschmidt tolerance factors so that it can co-crystallise with Antimony. In addition, the presence of s electrons should be additional criteria to screen potential elements. The lanthanides exhibiting stable +3 oxidation states and having ionic radii between Bismuth and Antimony can be viable candidates. The outer ns electrons will be taking part in bonding in case of Lanthanides and probably making the conduction band dispersive (resulting in higher electron mobilities). A detailed computational and experimental study will reveal the effect of incorporating the Lanthanides on the optoelectronic properties of $A_3Sb_2I_9$.

7.2.3. Role of vacuum and light on creation of traps.

The thesis focused on understanding the optoelectronic properties and defects in halide perovskite inspired materials. However, the role of ambient and light in altering these properties were not evaluated systematically. It is known that traps in lead halide perovskites can be passivated on exposure to ambient^[10,11]. The preliminary studies using in situ Photoluminescence and Photo-conductivity reveal that illumination of lead halide perovskites in vacuum can induce traps in the perovskite material which can be healed on exposure to air (Figure 7.7). This was also associated with a contraction of lattice in vacuum and expansion in air. Since the materials investigated in this thesis were closely linked to lead halide perovskites in terms of band structure, they are expected to exhibit similar behavior as well. Hence, a detailed investigation on the effect of ambient and light on traps in these materials will unlock ideas to passivate them and enable novel applications.

Figure 7.7 : (a and b) The insitu PL and Photo-conductivity studies on Triple cation perovskite showing the trap creation in vacuum and healing in air, (c) The Transient PL measurements in different ambient and (d) The XRD diffraction measurements in vacuum and air showing lattice contraction in vacuum

7.2.4. Novel electrically re-configurable materials :

The presence of ionic induced doping and the switchable photovoltaic effect in $(\text{NH}_4)_3\text{Sb}_2\text{I}_9$ and NaSbS_2 unlock the possibility of post deposition electrical manipulation of electronic properties in similar class of materials. This methodology will pave the way towards synthesis of thin films that are synthetically inaccessible or non-equilibrium. This enables fine-tuning of the materials electronic structure and phase- independent of the processing route. By in-situ alteration of the energy levels, we can modulate local electronic structure, tailor electric field distribution, tune work functions and enable

processing methodologies that would typically induce electronic defects. This would have significant impact in electronic devices such as transistors, photo-detectors, light emitting diodes, sensors and photovoltaics, which needs to be fabricated through cost-effective methods. Some material systems identified based on the initial design criteria (presence of ns^2 electrons and high lattice connectivity) are LiSbS_2 , AgSbS_2 , K_3SbS_3 , Rb_3SbS_3 , $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, NaBiS_2 , AgBiS_2 , LiBiS_2 , KBiS_2 , AgBiI_4 and CuBiI_4 (Figure 7.8). The materials with higher ionic conductivity can be utilized for applications like memristors and neuromorphic devices and those with lower ionic conductivity for applications like photo-detectors and solar cells.

Figure 7.8 : The crystal structures of (a) LiSbS_2 (b) AgSbS_2 (c) Rb_3SbS_3 and (d) AgBiI_4

7.2.4.1 Altering internal electric fields through band structure modification

In case of solar cells, internal electric fields can be setup by creating segregation of +ve and -ve ions which can n and p dope the material respectively. This can enhance charge separation and improve the performance of the solar cell and can be a strategy in both lead and lead free halide perovskite solar cells. The major hurdle in achieving this will be the back diffusion of the ions after the poling electric field is removed. Some strategies in

this direction can be (a) Utilization of a removable contact with ion absorbing/donating capabilities to apply the poling field. This would enable the removal of the +ve or -ve ions from the perovskite layer to the contact resulting in p or n doping of the perovskite layer. PEDOT-PSS or poly(ethylene oxide) (PEO) which are good ionic conductors could be utilized for this purpose. The post processed perovskite layer can then be fabricated to a full device without need for additional p or n type layers (Figure 7.9).

Figure 7.9 : Application of Electric field to locally change the material properties (Top Left) to create internal electric fields for Transport layer free solar cells (Top Right) and to induce interfacial doping to improve charge injection efficiency (Bottom Right).

7.2.4.2 Altering charge injection and transport through interfacial ion insertion/ local doping

A large class of electronic devices derive their function from efficient injection of carriers into the active layer. These include light emitting diodes where efficient light emission requires facile injection of charge carriers through hole and electron transport layers. Another important and emergent application, which requires modulatable injection, is in

the area of diffusive memristors. This is the second category of functionality that can be explored through field induced electronic reconfiguration. Inspired by neural computing, the pursuit of ultra-low power neuromorphic architectures with highly distributed memory and parallel processing capability has recently gained more traction. Memristive devices emulating brain-like signal processing forms the foundation for development of efficient learning circuitry, but conventional drift-based memristors relying on stochastic metallic/defect filament formation fall behind in this regard due to their abrupt switching transitions^[12]. Very recently, diffusive memristors and second-order drift memristors have been engineered to approximate the biological synaptic dynamics based on metal atom diffusion, thermal dissipation, mobility decay and spontaneous nanoparticle formation^[13-15]. A common feature in all these systems is the insertion/extraction of mobile ions, directly or indirectly altering the electronic injection and conductivity in a continuous analog-like manner. Recent studies on halide perovskite-based memristive synapses show coupling fast electronic transitions with slow drift-diffusive ionic kinetics^[16]. Co-existence of carrier injection barriers and ion migration in the perovskite films defines the degree of synaptic plasticity (Figure 7.9). Similar to NaSbS₂ which was explored for synaptic plasticity in the chapter 6, all the above mentioned materials could be explored for similar functionality. The ability to tune the synaptic weight by post-deposition electrical treatment will be useful in correcting non uniformity across an array of synaptic devices.

7.2.5. Alkali Metal Dichalcogenides for solar cells

The band structure analysis of NaSbS₂ in the chapter 6 of this thesis revealed similarities with lead halide perovskites. In addition, the material was found to exhibit a close direct-indirect band gap with high absorption coefficients suitable for photovoltaic application. However, the high ionic conductivity of Na in the material inhibited its application in solar cells. Despite this there are reports on quantum dot based solar cells of the same material exhibiting 2 % efficiency^[17]. Hence, similar materials with lower ionic motion should hold potential to improve the efficiencies. Fortunately, this class of materials exhibit great compositional flexibility with Na being able to be replaced by other alkali metals. Rb or Cs (which is approximately 1.5 times larger than Na) could inhibit the

motion of ions leading to better performances (Figure 7.10). The novel amine-thiol based synthetic procedure discussed in the chapter 6 will enable facile solution processed thin film formation of all these materials.

Figure 7.10 : (a) Compositional variety in Alkali metal Chalcogenides and (b) Structure of CsSbS₂

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APPENDIX

A.1 Appendix for Chapter 4

Figure A1 : The detailed XPS spectra of $\text{Rb}_3\text{Sb}_2\text{I}_9$

Figure A2 : UPS and XPS of $\text{Cs}_3\text{Sb}_2\text{I}_9$

Table A1 : IV Characteristics of SbI₃ treated devices

Device	Voc (V)	Jsc (mA/cm ²)	FF (%)	Efficiency (%)
1	0.50	1.73	50.53	0.44
2	0.52	1.48	58.75	0.45
3	0.50	1.66	54.33	0.45
4	0.53	1.78	56.96	0.53
5	0.53	1.91	56.09	0.57
6	0.49	1.24	57.34	0.35
7	0.50	1.86	55.82	0.52
8	0.52	1.75	56.70	0.51
9	0.54	1.63	59.15	0.52
10	0.52	1.48	59.00	0.45
11	0.50	1.35	58.87	0.40
12	0.55	2.11	56.97	0.66
13	0.52	2.09	57.42	0.63
14	0.53	1.18	53.90	0.34
Average	0.52	1.66	56.56	0.49
Standard Deviation	0.02	0.28	2.29	0.09

Table A2 : IV characteristics of the untreated devices

Device	Voc (V)	Jsc (mA/cm ²)	FF (%)	Efficiency (%)
1	0.28	0.77	38.85	0.08
2	0.29	0.78	38.42	0.09
3	0.13	0.83	36.15	0.04
4	0.11	0.79	36.21	0.03
5	0.30	1.08	35.40	0.11
6	0.29	1.07	34.78	0.11
7	0.24	1.09	33.62	0.09
8	0.33	0.91	38.65	0.11
9	0.23	0.89	36.40	0.07
10	0.20	0.89	37.47	0.07
Average	0.24	0.84	36.59	0.08
Standard Deviation	0.07	0.26	1.74	0.03

A.2 Appendix for Chapter 5

Figure A3: Optimised unit cells with various percentages of Bi. The blue colored octhedra are the ones including Bi.

Table A3 : Lattice constants with various Bi content predicted using DFT

	a	b	c	α	β	γ
0% Bi	14.68	8.20	20.99	90	90.55	90
12.5% Bi	14.73	8.24	21.06	90	90.59	90
25% Bi	14.75	8.26	21.09	90	90.58	90
37.5% Bi	14.75	8.33	21.15	89.97	90.67	90

Figure A4: The Valence and Conduction band charge densities with 0% and 12.5% Bismuth. The charge density around Bismuth in the VBM is feeble compared to Sb showing the reduced ns² contribution from Bismuth.

Table A4: Composition of films calculated using Energy Dispersive X Ray Analysis (EDS)

	Sb	Bi	I	Bi (%)
0%	18.21	0	81.16	0
10%	16.39	2.58	81.03	13.6
20%	15.21	4.46	80.32	22.6
30%	14.63	4.97	80.40	25.3
40%	14.54	6.78	78.68	31.8
50%	11.12	7.92	80.96	41.6

Figure A5: SEM images of films with various content of Bismuth

Figure A6: The flat band potential extracted from the configurations with varying bismuth content

Figure A7 : (a) The variation of capacitance across temperatures from 200K to 315K, (b) the differentiated capacitance spectra used to obtain the characteristic frequencies, (c) the calculation for the activation energy and (d) the Defect distribution of the 0% Bi sample

Figure A8: (a) the variation of capacitance and differentiated capacitance with varying temperature, Arrhenius plot of the characteristic frequencies to extract the (b) shallow defect and (c) deep defect activation energies, (e) the calculated defect energy distribution of the 10% Bi sample

Figure A9 : (a) the variation of capacitance and differentiated capacitance with varying temperature, Arrhenius plot of the characteristic frequencies to extract the (b) shallow defect and (c) deep defect activation energies, (e) the calculated defect energy distribution of the 20% Bi sample

Figure A10 : (a) the variation of capacitance and differentiated capacitance with varying temperature, Arrhenius plot of the characteristic frequencies to extract the (b) shallow defect and (c) deep defect activation energies, (e) the calculated defect energy distribution of the 40% Bi sample

Figure A11: (a) the variation of capacitance and differentiated capacitance with varying temperature, Arrhenius plot of the characteristic frequencies to extract the (b) shallow defect and (c) deep defect activation energies, (e) the calculated defect energy distribution of the 50% Bi sample

Figure A12 : The IV characteristics of 2.5 μm spaced gold electrodes after 4V/ μm poling in presence of light.

Figure A13 : The IV (a) and I-t (b) characteristics of the small and big grained films on 50 μm spaced FTO electrodes after poling at 4V/ μm . (c) and (d) shows the SEM images of the small and big grained films.

Figure A14 : (a) The initial and stabilized photo voltages of the 40% Bi sample. (b) The photo-response at zero bias. (c) The voltages measured between electrode B and A at zero current for 40%Bi sample with (c) negative and (d) positive poling at electrode B.

A4 Appendix for Chapter 6

Figure A15 : (a) Ordered arrangement of Na and Sb in NaSbS₂ and (b) the corresponding band-structure

Figure A16 : The disordered NaSbS₂ super cell (2x2x2) used for band structure calculations

Figure A17: The XRD of the NaSbS₂ films annealed at different temperatures

Figure A18 : XRD of NaSbS₂ films with 40 and 80% excess Na

Figure A19: The elemental distribution of the electrically poled sample showing a depletion in Na ion concentration near positively poled side