Investigation of Structural, Optical and Electronic Properties of Modified Methylammonium Lead Iodide Perovskites

Rasanjali Jayathissa

Western Michigan University, rasanjalijayathissa@ymail.com

Follow this and additional works at: https://scholarworks.wmich.edu/dissertations

Part of the Physics Commons

Recommended Citation
https://scholarworks.wmich.edu/dissertations/3497
INVESTIGATION OF STRUCTURAL, OPTICAL AND ELECTRONIC PROPERTIES OF MODIFIED METHYLAMMONIUM LEAD IODIDE PEROVSKITES

by

Rasanjali Jayathissa

A dissertation submitted to the Graduate College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics
Western Michigan University
August 2019

Doctoral Committee:

Clement Burns, Ph.D., Chair
Lisa Paulius, Ph.D.
Asghar Kayani, Ph.D.
Ramakrishna Guda, Ph.D.
© 2019 Rasanjali Jayathissa
ACKNOWLEDGMENTS

I would like to begin by expressing my deepest gratitude to my research advisor and the thesis committee chair, Prof. Clement Burns, for his constant guidance, encouragement, immense knowledge and for always making himself available for discussion. He has done so much to foster my capability in conducting an experimental research and thesis writing. I could not have imagined having a better advisor for my Ph.D. work than him.

I would like to show my great appreciation to Graduate College and Department of Physics, WMU, for the financial support given to me to fulfill my Ph.D. studies and for making my stay in USA a great memory in my life. I thank Dr. Paul Pancelia and all the faculty members for their knowledge, guidance and support given to me during my career in Department of Physics, WMU.

I greatly appreciate the support provided by my committee members in numerous ways. Specially, Dr. Lisa Paulius for letting me work in her lab, Dr. Asghar Kayani for his support in RBS measurements with valuable discussions, and Dr. Ramakrishna Guda for sharing his knowledge on optical spectroscopy. Also, I thank all of them for their valuable time in reviewing this thesis.

I also want to express my special thanks to Dr. Gellert Mezei and his research group for the initial guidance given to me on synthesizing materials for my research, Dr. Ekkehard Sinn for his support on SCXRD analysis and Dr. Pnina Ari-Gur for letting me use the PANalytical XRD facility in her lab at Department of Mechanical and Aerospace Engineering, WMU. I gratefully acknowledge Rick Welch and Josh Byers for promptly preparing parts for my experimental setups,
Acknowledgement-Continued

and Benjamin Gaudio for his immense support on resolving issues I had with software or an instrument, and Allan Kern for his technical tips and advices. They taught me lot of things which I could not learn in my classroom.

Finally, I would to like to dedicate this dissertation to my parents to express my sincere gratitude for giving me life and making me the person who I’m today, to my husband Charuka for his endless support, love, patience and trust on me and to my son Abises for his unconditional love. It would have been impossible to complete this journey without all your support.

Rasanjali Jayathissa
Owing to their high-power conversion efficiency (PCE), easy processability, and low fabrication cost, organic lead halide perovskites (OLHP) are emerging as a most promising photovoltaic technology. However, toxicity of lead (Pb) is a major concern for further development. Therefore, it is essential to explore nontoxic metals to replace lead in these materials. In the current research work, nontoxic \( \text{Mn}^{2+}, \text{Na}^{+} \) and \( \text{Ba}^{2+} \) are doped at 1, 5 and 10% mole concentrations to partially substitute \( \text{Pb}^{2+} \) in methyl ammonium lead iodide (\( \text{CH}_3\text{NH}_3\text{PbI}_3 \) or MAPbI\(_3\)) perovskite systems, and the effects of doping on structural, optical, electronic and dielectric properties are investigated.

In the first part of the work, thin films of \( \text{Mn}^{2+} \) and \( \text{Na}^{+} \) doped MAPbI\(_3\) are fabricated from perovskite precursor solutions containing metal acetates, using a single step spin coating technique. They are characterized using Rutherford back scattering spectroscopy (RBS), x-ray diffraction (XRD) and ultraviolet-visible spectroscopy (UV-Vis spectroscopy). RBS shows a reduction of surface roughness upon addition of dopants to the perovskite films, which is favorable for solar cell performances. XRD data confirms that the room temperature tetragonal structure of the pristine material is preserved, but there is a shrinkage of the lattice as smaller sized \( \text{Mn}^{2+} \) and \( \text{Na}^{+} \) dopants are introduced. In addition, formation of smaller grains with \( \text{Mn}^{2+} \) doped samples are observed whereas with the \( \text{Na}^{+} \) dopants such effects are not observed at the studied dopant levels.
UV-Vis absorption measurements confirm that these metals can be used to replace Pb in pristine material at 1, 5 and 10% dopant concentrations without significantly altering the remarkable absorption property of the pristine material. Furthermore, a procedure is optimized to fabricate solar cells with FTO/c-TiO$_2$/mp-TiO$_2$/Perovskite/P3HT/Au configuration and a PCE of 16.7 % with short circuit current density ($J_{sc}$) of 28.3 mA/cm$^2$, open circuit voltage ($V_{oc}$) of 0.99 V and fill factor of (FF) of 0.58 for pristine material is obtained.

In the second part of the research, Ba$^{2+}$ doped MAPbI$_3$ polycrystals (MAPb$_{1-x}$Ba$_x$I$_3$ with x=1%,5% and 10%) are successfully synthesized and their structural, calorimetric, ionic conductivity, and dielectric properties are investigated using XRD spectroscopy, differential scanning calorimetry (DSC) and impedance spectroscopy (IS). No new structures are formed upon doping with Ba$^{2+}$ ions, however it results a lattice expansion as shown by the XRD study. Moreover, as deduced from DSC study on the doped crystals, Ba$^{2+}$ shows no effect on the tetragonal to cubic phase transition temperature of the pristine material. The IS measurements are used to find the dark conductivity and the dielectric constants of the doped crystals at different temperatures. The conductivity arises mainly from vacancy mediated iodide ion (I$^-$) migration and the increase in ionic conductivity with dopants is ascribed to lattice distortion caused by the isovalent ion doping. The possibility of an increase in the number of I$^-$ vacancies due to lowering of defect formation energies in the distorted lattice is suggested to explain the observed conductivity. In addition, the bulk dielectric constant increases with increasing Ba$^{2+}$ dopant amounts. This phenomenon is correlated to the ordering of MA dipoles and the distortions of the Ba sites in the lattice. Finally, the temperature dependence of the dielectric constants is observed for all the samples and it is attributed to thermal effects on orientation polarization of MA molecules.
TABLE OF CONTENTS

ACKNOWLEDGEMENTS....................................................................................................................... ii

LIST OF TABLES.................................................................................................................................. vii

LIST OF FIGURES............................................................................................................................... viii

CHAPTER

1. INTRODUCTION

1.1. Need for renewable energy sources ......................................................................................... 1

1.2. Solar energy .............................................................................................................................. 3

1.3. Photovoltaics (PV) and solar cells ............................................................................................. 4

1.4. Perovskites in photovoltaics ........................................................................................................ 9

1.4.1. Structure and evolution of perovskite photo absorber .......... 9

1.4.2. Electronic structure of OILH perovskites ......................... 12

1.4.3. High optical absorption of OILH perovskites ............... 15

1.4.4. Superior ambipolar carrier conductivity of OILH perovskites .............................................. 18

1.4.5. Ferroelectric effect ................................................................. 21

1.4.6. Inexpensive fabrication .............................................................. 22

1.4.7. Device architecture and working principle of OILH perovskite based solar cell ................. 24

1.4.8. Issues and challenges in OILH perovskites ................... 27

1.4.9. Progress on lead-free OIMH perovskites ......................... 28
1.5. Thesis aims and scope ................................................................. 30

2. Mn$^{2+}$ AND Na$^+$ ION INCORPORATED CH$_3$NH$_3$PbI$_3$ THIN FILMS FOR SOLAR CELLS

2.1. Introduction .............................................................................. 32
2.2. Methodology ........................................................................... 34
  2.2.1. Materials ........................................................................... 34
  2.2.2. Perovskite precursor solution preparation ....................... 35
  2.2.3. Substrate preparation ...................................................... 35
  2.2.4. TiO$_2$ anode preparation ............................................. 35
  2.2.5. Perovskite thin films deposition and solar cell fabrication .............................................. 36
2.3. Instruments and procedure utilized for sample characterization .............. 37
  2.3.1. Ultraviolet-visible (UV-Vis) spectroscopy .................... 37
  2.3.2. Rutherford backscattering spectrometry (RBS) .......... 38
  2.3.3. X-Ray diffraction (XRD) ........................................... 43
  2.3.4. Solar cell characterization ........................................... 46
2.4. Results and discussion .................................................................. 51
  2.4.1. Perovskite films preparation and morphology ............. 51
  2.4.2. Structural properties of perovskite films ..................... 55
  2.4.3. Optical properties of perovskite films ......................... 66
  2.4.4. Solar cells fabrication and characterization .......... 70
Table of Contents-Continued

CHAPTER

2.4.5. Conclusions ................................................................................. 76

3. Ba\textsuperscript{2+} DOPED CH\textsubscript{3}NH\textsubscript{3}Pbl\textsubscript{3} CRYSTALS

3.1. Introduction .................................................................................... 78

3.2. Methodology .................................................................................. 79

3.2.1. Materials .................................................................................... 79

3.2.2. MAPb\textsubscript{1-x}Ba\textsubscript{x}I\textsubscript{3} crystal preparation .................. 79

3.3. Instruments and procedure for sample characterization ................. 80

3.3.1. X-Ray diffraction (XRD) ................................................................. 80

3.3.2. Differential scanning calorimetry (DSC) ....................................... 81

3.3.3. Impedance spectroscopy ................................................................. 82

3.4. Results and Discussion .................................................................. 80

3.4.1. Structural properties of MAPb\textsubscript{1-x}Ba\textsubscript{x}I\textsubscript{3} crystals ........... 86

3.4.2. Calorimetric properties of MAPb\textsubscript{1-x}Ba\textsubscript{x}I\textsubscript{3} crystals ........... 89

3.4.3. Impedance analysis of MAPb\textsubscript{1-x}Ba\textsubscript{x}I\textsubscript{3} crystals ............... 90

3.5. Conclusions ................................................................................... 109

REFERENCES .......................................................................................... 110

APPENDIX .............................................................................................. 126
LIST OF TABLES

1.1. Calculated effective masses for electrons ($m^*_e$) and holes ($m^*_h$). (SOC-Spin orbit coupling) .......................................................... 19

2.1. Variation of unit cell parameters with dopant %. The average of 3 sets of data were used and the average deviation from the each data set from the net average values were presented as the uncertainties ......................................................... 63

2.2. Variation of bandgap energy of MAPbI$_3$ with dopant %.70

2.3. Solar cell parameters recorded for the best two devices obtained for MAPbI$_3$ perovskite .... 74

3.1. Variation of unit cell parameters a, c with Ba%. .......................................................... 88
LIST OF FIGURES

1.1. Projected world energy demand for the year 2030 [1] ................................................................. 1

1.2. Comparison of global energy potential with renewable and nonrenewable energy sources (Terawatts per year). ........................................................................................................... 2

1.3. Global horizontal solar irradiation map [3]. .................................................................................... 3

1.4. Schematic of Si solar cell ................................................................................................................... 4

1.5. Energy band diagram of p-n junction in equilibrium ......................................................................... 5

1.6. Basic classification of photovoltaics (Adapted with permission from [6]). ................................. 6

1.7. Best Research-Cell Efficiency Chart for a research cells for a range of PV technologies , plotted from 2000 -present ............................................................................................................... 8

1.8. (a) Cubic perovskite crystal structure (Adapted with permission from [16]) and (b) comparison of cubic, tetragonal and orthorhombic perovskite structures ........................................ 10

1.9. Calculated t and μ factors for some OIMH perovskites ................................................................. 11

1.10. Bonding diagram for [PbI₆]⁺ cluster representing MAPbI₃ perovskite ....................................... 13

1.11. (a) Electronic band structure with (left) and without (middle) the MA cation and contributions of MA, Pb and I on the DOS (right) of low temperature orthorhombic phase (adapted with permission from [24]); Band structure and energy gap for (b) cubic (c) tetragonal and (d) orthorhombic phases (adapted with permission from [26]) of MAPbI₃ perovskite .............................................................................................................. 14

1.12. The schematic optical absorption mechanisms of (a) 1st generation (Si), (b) 2nd generation (GaAs) and (c) perovskite halide (MAPbI₃) photo absorbers (adapted with permission From [28]) ............................................................................................................................... 15

1.13. (a) Electronic density of states (DOS), (b) Joint density of states (JDOS) (c) optical absorption coefficient for MAPbI₃ and GaAs and (d) Calculated maximum efficiencies of MAPbI₃, CIS, CZTS and GaAs as a function of film thickness. ................................................................. 17

1.14. Schematics of (a) Bandgap tuning by compositional engineering of elements in OILH perovskites (adapted with permission from [29]), (b) four-terminal and (c) two-terminal tandem designs for perovskite solar cells ................................................................................................................. 18

1.15. Schematic diagrams for (a) bulk PV effect in a ferroelectric thin film and (b) a multidomain ferroelectric thin-film as hypothesized for hybrid halide perovskite solar cells. ......................................................... 22
List of Figures-Continued

1.16. Representative fabrication methods for perovskite thin films: (a) One-step spin coating method (b) Two-step spin coating method (c) Doctor blade method (d) Dual source vapor deposition method (e) Sequential vapor deposition method and (f) Vapor-assisted solution method ((a), (b), (d), (e) and (f) are adapted with permission from [54]). ........................................23

1.17. Schematic diagrams of perovskite solar cells in the (a) n-i-p mesoscopic, (b) n-i-p planar, (c) p-i-n planar, (d) p-i-n mesoscopic structures and (e) Schematic of band diagram and working principle of PSC: 1 Photon absorption and free charge generation, 2 charge transport and 3 charge extraction by electrodes. ((a), (b), (c) and (d) are adapted with permission from [56]). .................................................................25

1.18. Schematic diagram showing the energy levels, from left to right, for representative cathode, ETM, absorber, HTM and anode material (copyright [56]). .........................................................26

2.1. Semitransparent TiO$_2$ anode with compact and mesoporous layers on FTO substrate. ......36

2.2. A schematic of the double beam UV-Vis spectrometer. .........................................................38

2.3. A schematic of a classical collision and scattering of particle by an incident particle. ......39

2.4. Schematic of backscattering event from a thick elemental sample and a resulting spectrum. ..........................................................................................................................41

2.5. Geometries use in RBS: left: IBM and right: Cornell...............................................................42

2.6. A schematic of Bragg’s reflection from a crystal. ..............................................................44

2.7. A schematic of the components and the geometry of the X-ray diffractometer. .................44

2.8. Labeled diagram of the PANalytical Empyrean X-ray Diffraction System used in this research work .........................................................................................................................................45

2.9. A schematic of J-V curves of solar cell under dark and illumination conditions. .............47

2.10. An equivalent circuit model for solar cells with a single diode under illumination. ............47

2.11. Laboratory I-V measurement setup with the homemade vacuum chamber used to test PSCs. ..........................................................................................................................................50

2.12. A perovskite film on glass substrate obtained in this experiment using single step deposition process. .........................................................................................................................51

2.13. The experimental and simulated RBS spectra and fitted curves obtained using SIMNRA for all elements present in the sample consisting of pristine film and glass substrate........52
List of Figures-Continued

2.14. The experimental and simulated (fitted) RBS spectra for Mn$^{2+}$ and Na$^+$ doped MAPbI$_3$ thin films on glass substrate...............................................................54

2.15. Simulated powder XRD pattern for pristine sample with labeled peaks for tetragonal I4/mcm space group at room temperature (Cu K$_{\alpha 1}$ (1.54060 Å). .........................................................55

2.16. XRD patterns obtained for Mn$^{2+}$ incorporated MAPbI$_3$ thin films at 294 K........................................56

2.17. XRD patterns obtained for Na$^+$ incorporated MAPbI$_3$ thin films at 294 K ........................................57

2.18. Comparison plot of peak intensity variation for (110) peaks in the simulated PXRD patterns obtained for Mn$^{2+}$ and Na$^+$ incorporated MAPbI$_3$ at 294 K........................................59

2.19. XRD peak shift for (110) peaks (left) and (224) peaks (right) for Mn$^{2+}$ incorporated MAPbI$_3$ thin films on glass at 294 K .................................................................60

2.20. XRD peak shift for (110) peaks (left) and (224) peaks (right) for Na$^+$ incorporated MAPbI$_3$ thin films on glass at 294 K .................................................................61

2.21. A schematic of room temperature tetragonal unit cell of MAPbI$_3$ perovskite. ...............................62

2.22. Variation of unit cell parameters a,c with increasing dopant % for Mn$^{2+}$ (a,b) and Na$^+$ (c,d) incorporated MAPbI$_3$ perovskite thin films. .........................................................64

2.23. UV–Vis absorption per unit thickness for Mn$^{2+}$ incorporated MAPbI$_3$ thin films on glass substrate.................................................................67

2.24. UV–Vis absorption per unit thickness for Na$^+$ incorporated MAPbI$_3$ thin films on glass substrate.................................................................67

2.25. Tauc plot for Mn$^{2+}$ incorporated MAPbI$_3$ thin films on glass substrate... .................................69

2.26. Tauc plot for Na$^+$ incorporated MAPbI$_3$ thin films on glass substrate. ........................................69

2.27. (a) A schematic of solar cell device and (b) Some of solar cells prepared in this research...71

2.28. The contribution from each layer to UV-Vis absorption spectra of the solar cell consists of pristine MAPbI$_3$ perovskite. .................................................................72

2.29. J-V curves obtained for the two solar cells with highest efficiencies in this study. ....................73

3.1. Polycrystals of MAPb$_{1-x}$Ba$_x$I$_3$ with x= 0,1, 5 and 10 obtained in this study....................79
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.</td>
<td>(a) The DSC Q100 calorimeter (TA instruments) setup used to collect data and (b) the enlarged view of thermoelectric disk where sample and reference pans placed, surrounded by a furnace inside the instrument.</td>
</tr>
<tr>
<td>3.3.</td>
<td>Physical representation of Maxwell’s layered dielectric model for electrode/sample system.</td>
</tr>
<tr>
<td>3.4.</td>
<td>(a) and (d) show two common RC circuits. Parts (b) and (e) show their impedance plane plots.</td>
</tr>
<tr>
<td>3.5.</td>
<td>PXRD profiles with indexed peaks for Ba$^{2+}$ doped MAPbI$_3$ crystals with Si peaks aligned together.</td>
</tr>
<tr>
<td>3.6.</td>
<td>Peak shift of (110) peak for Ba$^{2+}$ doped MAPbI$_3$ crystals.</td>
</tr>
<tr>
<td>3.7.</td>
<td>The variation of Ba% with the Lattice constants a (left) and c (right).</td>
</tr>
<tr>
<td>3.8.</td>
<td>DSC profiles for Ba doped MAPbI$_3$ samples.</td>
</tr>
<tr>
<td>3.9.</td>
<td>Temperature dependence Nyquist plots for MAPb$_{1-x}$Ba$_x$I$_3$ pellets sandwiched between two Cu electrodes.</td>
</tr>
<tr>
<td>3.10.</td>
<td>Temperature and frequency dependence Capacitance of MAPb$_{1-x}$Ba$_x$I$_3$ pellets sandwiched between two Cu electrodes.</td>
</tr>
<tr>
<td>3.11.</td>
<td>Temperature and composition dependence of dark conductivity of Ba$^{2+}$ doped MAPbI$_3$ pellets.</td>
</tr>
<tr>
<td>3.12.</td>
<td>Variation of dark conductivity at room temperature with Ba % in Ba$^{2+}$ doped MAPbI$_3$ pellets.</td>
</tr>
<tr>
<td>3.13.</td>
<td>Schematic atomic arrangement in the Pb-I plane in a) MAPbI$<em>3$ and b) MAPb$</em>{1-x}$Ba$_x$I$_3$ Lattice.</td>
</tr>
<tr>
<td>3.14.</td>
<td>Variation of bulk dielectric constant with Ba % and temperature of Ba$^{2+}$ doped MAPbI$_3$ pellets.</td>
</tr>
<tr>
<td>3.15.</td>
<td>Temperature dependence of real part of dielectric constant for Ba$^{2+}$ doped MAPbI$_3$ pellets.</td>
</tr>
<tr>
<td>3.16.</td>
<td>Temperature dependence of imaginary part of dielectric constant for Ba$^{2+}$ doped MAPbI$_3$ pellets.</td>
</tr>
<tr>
<td>3.17.</td>
<td>Temperature and frequency dependence of loss tangent for Ba$^{2+}$ doped MAPbI$_3$ pellets.</td>
</tr>
</tbody>
</table>
List of Figures-Continued

3.18. Temperature and frequency dependence of peak of loss tangent for 5% and 10% Ba\textsuperscript{2+} doped MAPbI\textsubscript{3} samples where the peaks can be seen.........................................................108
CHAPTER 1
INTRODUCTION

1.1. Need for renewable energy sources

The increased demand of energy [1] with industrialization, urbanization, technological boom and growing world population (Figure 1.1) has caused negative impact on the life of this planet already. The main methods of generating energy, which includes combustion of fossil fuels (coal, natural gas and petroleum) and nuclear fission of uranium, have shown noticeable negative effects such as global warming and nuclear catastrophes (E.g. Fukushima) respectively. In addition, fossil fuels are not renewable, they will deplete eventually. Also, due to the safety concerns and the unsolved question of nuclear waste disposal, nuclear energy is not an effective energy source for the future. Therefore, it is essential to find clean and renewable energy sources for a sustainable development of human society.

Figure 1.1. Projected world energy demand for the year 2030 [1]
Renewable energy sources are energy sources that are naturally replenishing. The main types of renewable energy sources include biomass, hydropower, geothermal, tidal power, wind and solar energy. Biomass, which is organic materials from plants and animals, can be burned directly or converted to liquid biofuels or biogas that can be burned as fuels. Hydro power is where the force of water flowing in rivers and streams produce mechanical energy which is later converted to electrical energy. The geothermal energy, which is the heat continuously produces inside the earth core, can be used to generate power. Naturally occurring tides and ocean waves are also producing power. The wind, which is caused by uneven heating of the earth surface, can be used to produce electricity too. Solar energy, the direct radiation energy from the sun, which is the ultimate source for most energy sources, can be converted to electricity.

![Figure 1.2. Comparison of global energy potential with renewable and nonrenewable energy sources (Terawatts per year). Total recoverable reserves are shown for the finite resources. For renewable sources, yearly potential is shown. (Adapted with permission from [2])]
once the technologies and the infrastructures are enhanced for each renewable energy sources. Figure 1.2 shows the comparison of global energy potential in terawatts per year for both renewable and nonrenewable energy sources [2].

1.2. Solar energy

Among all the aforementioned renewable energy sources, free, clean and inexhaustible solar radiation is most promising source to consider for a sustainable human society. It is carbon free and available all over the world. The sun rising and setting is remarkably consistent, and we have decent seasonal and daily projections for sunlight receive in different locations globally. Figure 1.3 shows the solar irradiation received by the earth [3]. Depends on the location, some countries receive long hours of solar irradiance and make ideal locations to take advantage of solar energy. Even though the weather conditions affect the use of solar energy, as given in Figure 1.2, solar power could theoretically supply the world with all its energy needs.

![Global horizontal solar irradiation map][3]

Figure 1.3. Global horizontal solar irradiation map [3]
Generation of electricity using solar energy can be done by two methods: concentrated solar power (CSP) and photovoltaics (PV). CSP uses mirrors and lenses to concentrate a large area of sunlight to generate heat and steam to rotate conventional turbines [4]. In PV, sunlight is directly transformed into electricity and this method is the most popular.

1.3. Photovoltaics (PV) and solar cells

PV is the direct conversion of light into electricity using a phenomenon called the “photovoltaic effect”, the generation of an electrical potential difference at the junction of two different materials upon exposure to light, which was discovered by French scientist Edmond Becquerel in 1839 [5]. The solar energy conversion into electricity takes place in an electrical device called a solar cell (or photovoltaic cell). A PV system employs solar panels, each consists of several solar cells. The solar cell requires three basic attributes for its operation: 1) Absorption of light and generation of electron-hole pairs, 2) Separation of opposite charge carriers and 3) Extraction of charge carriers to an external circuit. The conventional solar cells are made of semiconductor materials, usually p-type and n-type doped crystalline silicon (c-Si).

Figure 1.4. Schematic of Si solar cell.
Figure 1.4 shows the components and basic operation of conventional p-n junction Si solar cell and Figure 1.5 shows the corresponding energy band diagram. In n-type semiconductor majority of charge carriers are negatively charged electrons which are compensated by positively charged ionized donor atoms, whereas in p-type semiconductor holes are the majority carriers which are compensated by negatively charged ionized acceptor atoms.

When p-type and n-type semiconductors are bought together, the difference in carrier concentrations between p and n type regions makes a diffusion current of electrons from n-side to p-side and a diffusion current of holes from p-side to n-side. This happens through the interface between p and n-type regions and due to the diffusion process, this region becomes depleted of mobile charge carriers and gives rise to a space charge created by the charged donor and acceptor atoms that are no longer compensated by mobile charges. The space charge results an electric field in the p-n junction. Figure 1.5 shows the energy band diagram of p-n junction under equilibrium. In there, the average energy of electrons, Fermi energy $E_f$, has a constant position.
in the band diagram and the distance between Fermi level and conduction \((E_C)\) and/or valence \((E_V)\) bands does not change in the quasi-neutral regions and is the same as in isolated n or p-type semiconductors. But conduction and valence bands inside the space-charged region are represented by curved lines, which is an indication of the electric field presence in this region. When a p-n junction is illuminated, additional charge carriers are generated (photo generated e-h pairs) and the internal electric field in the space charge region makes them separate and gives rise to flow of photo-generated current and as given in Figure 1.4, this current can be used to power a load. The efficiency (also called Power Conversion Efficiency- PCE), which is defined as the ratio of energy output from solar cell to input energy from the sun, is the most commonly used parameter to compare the performance of one solar cell to another.

![Figure 1.6. Basic classification of photovoltaics (Adapted with permission from [6]).](image)

PV technologies can be classified [6] based on their historical development which was intended to explore ways to make PV a reliable, cheaper and durable way to generate power (Figure 1.6). The first generation, silicon wafer solar cells are the most commercially widespread as well as the oldest PV
technology. Due to their relatively high conversion efficiency and long lifetime, they currently control over 80% of the PV market and currently are at ~26% in the efficiency chart [7]. The second-generation PV cells include thin film and building integrated PV technology (BIPV) [8]. They are thinner, more flexible and cost-effective than their early generation counterparts. A variety of semiconductor materials are used from amorphous silicon (a-Si) to cadmium telluride (CdTe), gallium arsenide (GaAs) and copper-indium-gallium-selenide (CIGS). Laboratory testing has shown efficiencies equal to or greater than Si solar cells (Figure 1.7), but their flexibility and cost has not been enough to overtake the conventional Si solar cells. The use of polymer, photo electrochemical and dye-sensitized (DSSC) solar cells rose in the era of third generation PV technology. Compared to Si and other inorganic material-based cells, they have incredibly cheap production costs but the issues with durability, stability and low efficiency made them the least chosen products for commercialization [9,10,11]. The fourth generation is the future of the PV technology, which includes new photo absorber material, perovskites, with such cutting-edge technology as quantum dots [12] and nanowires [13]. Perovskites evolved in 2009 to transform PV technology and currently displays an outstanding potential with solar cell efficiencies 23.7% [7].

It is worth mentioning that the key factors need to be considered when moving PV technology from laboratory to commercial products are low cost, high power conversion efficiency and longer lifetime. Si PV technology hold more than 80% of the current PV market, because it delivers a package of high PCE as 21% with long life time of >25 years for a low cost of 0.3 $W^{-1}. In comparison, the emerging perovskite technology hold promise of reaching PCE of ~23% and above with low manufacturing cost, which has been estimated to be able to reach half of the that for crystalline Si, but still it struggles with lifetime issues, which seems more likely to be the last technological barrier for its commercialization [14].
Best Research-Cell Efficiencies

Figure 1.7. Best Research-Cell Efficiency Chart for a range of PV technologies, plotted from 2000 - present. This plot is courtesy of the National Renewable Energy Laboratory, Golden, CO [7].
1.4. Perovskites in photovoltaics

1.4.1. Structure and evolution of perovskite photo absorber

Perovskite compounds commonly adapt a 3-dimensional (3D) crystal structure which consists of three primary ions exhibiting a stoichiometry ABX₃ similar to the mineral, calcium titanate (CaTiO₃) also known as perovskite. A German mineralogist, Gustav Rose, discovered CaTiO₃ and it was named after a Russian mineralogist, Lew A. Perovski [15]. The A, B and X ions are typically represented by a large metal cation, a smaller metal cation and anion respectively. In the idealized cubic perovskite structure, the ions are arranged in such a way that the cation A forms 12-fold cuboctahedra coordination and cation B forms 6-fold octahedral coordination of anion X as shown in Figure 1.8(a) [16].

The structural stability is deduced by considering the Goldschmidt’s tolerance factor (t) and octahedral factor (μ) given by,

\[ t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)} \]  \hspace{1cm} \text{Eq.1.1} \\
\[ \mu = \frac{R_B}{R_X} \]  \hspace{1cm} \text{Eq.1.2}

where \( R_A, R_B \) and \( R_X \) are radii of cation A, cation B and anion X respectively. The t factor evaluates whether the A cation can fit within the cavity formed by BX₃ framework and the factor μ assesses the fit of the cation B in the BX₆ octahedron [17,18]. For an example, for halide perovskites (where X= F, Cl, Br, I), t and μ lie in the ranges 0.81 < t < 1.11 and 0.44 < μ < 0.90. For t values in the range 0.89-1.00 results cubic structure and less symmetric tetragonal and orthorhombic structures are likely to form for lower t values. On the other hand, for t > 1 3D network would not stands and results 2D layer structure [18]. However, for any given perovskite, transitions between such structures are possible upon heating (Figure 1.8 (b)).
The hybrid perovskite family of organic-inorganic metal halide perovskite (OIMH) (where A is an organic molecule, B is an inorganic post-transition metal and X is a halide) is the present interest of perovskites in PV applications. The A cation is generally considered to be for charge compensation in the lattice and does not contribute to the band structure. However, size variation of A will strongly influence the optical properties due to deformation of the BX₆⁴⁻ octahedral network. In 1978 Weber used methyl ammonium (CH₃NH₃⁺) and formamidinium (CH(NH₂)₂⁺) ions for A cation to form Sn and Pb halide perovskites [19] and the structure-property relationship in CH₃NH₃PbI₃ and CH₃NH₃SnI₃, was explored by an IBM researcher, David B. Mitzi, in 1999 [20]. It was evident that in above ABX₃ geometries, lead halide perovskites with 0.84 < t < 0.86 have higher tolerance than their Sn counterpart with 0.91 < t < 0.95 and use of Pb over Sn was justified.
Using CH$_3$NH$_3$PbX$_3$ (X = Br, I) as photo absorbers in solar cells was first published in 2009 by Akihiro Kojima et al [21]. Since then, OILH (Organic-Inorganic Lead Halide) perovskite based solar cells have revolutionized the field of photovoltaics with excellence cell performance benefits from their inherited material properties such as stronger and broader light absorption, high dielectric constants, ultrafast carrier charge separation, high carrier mobility and optimized carrier diffusion lengths and factors related to ease of processing with inexpensive fabrication costs compare to other PV technologies [16] (which will be discussed later in the chapter). It is also important to mention that, as given in Figure 1.7, the rapid progress towards high solar cell efficiencies has been achieved within just a few years, along with the rapid developments of device architectures, processing techniques and novel OIMH perovskites [22].

Figure 1.9. Calculated t and μ factors for some OIMH perovskites. The corresponding formamidinium (CH(NH$_2$)$_2^+$) based halides are expected to have intermediate values between those of methyl ammonium (CH$_3$NH$_3^+$ or MA) and ethyl ammonium (CH$_3$CH$_2$NH$_3^+$ or EA) compounds shown. (Adapted with permission from [16]).
1.4.2. Electronic structure of OILH perovskites

In OILH perovskites, the electronic structure is mainly dominated by PbX$_6^{4-}$ octahedral blocks. Unlike most cations whose outer s orbitals are empty, Pb has an occupied 6s orbital which can interact with p-orbitals of a suitable x-anion to generate Pb 6s states close to the Fermi level ($E_F$) of the perovskite. In the case of PbI$_6^{4-}$ units, the conduction band (LUMO - lowest unoccupied molecular orbital) is determined by (i) Pb 6p-I 5p $\pi$-antibonding and Pb 6p-I 5s $\sigma$-antibonding orbitals and the higher occupied states, the valence band, can be decomposed into three parts: HOMO - highest occupied molecular orbital is determined by (ii) Pb 6s-I 5p $\sigma$-antibonding which is at the top of the states, (iii) I 5p orbitals in the middle energy region, and (iv) Pb 6p–I 5s $\sigma$-bonding and Pb 6p–I 5p $\pi$-bonding orbitals in the bottom of the state. In the lower-energy region (v) Pb 6s–I 5p $\sigma$-bonding orbital is situated [23].

The valence band maximum (VBM) has strong Pb s and I p antibonding character whereas the conduction band minimum (CBM) is dominated by Pb p state which reflects the unique and dual ionic and covalent nature of electronic structure of the perovskite. The detailed band diagram is given in Figure 1.10. The density of state (DOS) and the band structures for orthorhombic ($\gamma$-phase), tetragonal ($\beta$-phase) and cubic ($\alpha$-phase) structures are shown for MAPbI$_3$ perovskites in Figure 1.11. The DOS shows that the electronic states associated with the MA cation are located far from the band gap, therefore it does not contribute to the band gap electronically [24]. The optical absorption OILH perovskites is believed to be typical of direct band gap semiconductors. In the undistorted ideal structure, the axial orbital overlaps between I-p and Pb- s and Pb-p orbitals is most favorable and leads to a significant broadening of the s type valance band and consequently increases the width of the band and narrows the bandgap significantly. As the octahedra begin to tilt, the axial overlaps weaken, and bandwidth decreases [25].
The band structures for each phase looks the same for MAPbI$_3$, indicating that the Pb-I-Pb bond angle distortions do not significantly change the electronic structure [26]. Even though the MA cation does not play a direct role in electronic structure, it indirectly contributes through steric and Coulombic interactions which deforms the lattice in specific ways. For an example the Pb-I-Pb angle decreases from $\alpha$-FAPbI$_3$ (179.9$^\circ$) to $\beta$-MAPbI$_3$ (163.6$^\circ$) and to $\gamma$-CsPbI$_3$ (153.2$^\circ$), then the electronic structure close to the band edge changes due to octahedral tilting and the bandgap increases from 1.48 eV in $\alpha$-FAPbI$_3$ to 1.67 eV in $\gamma$-CsPbI$_3$[25].
Figure 1.11. (a) Electronic band structure with (left) and without (middle) the MA cation and contributions of MA, Pb and I on the DOS (right) of low temperature orthorhombic phase (adapted with permission from [24]; Band structure and energy gap for (b) cubic (c) tetragonal and (d) orthorhombic phases (adapted with permission from [26]) of MAPbI$_3$ perovskite.
1.4.3. High optical absorption of OILH perovskites

The optical absorption of a semiconductor is primarily determined by two factors; the transition matrix elements between valence and conduction band states, which measures the probability of each photoelectric transition and their joint density of states (JDOS), which measures the total number of possible photoelectric transitions [27]. Therefore, the optical absorption coefficient of a material depends on its electronic structure. The comparison of mechanisms of optical absorption for 1st, 2nd generation solar cell absorbers with perovskite halide absorbers are schematically depicted in Figure 1.12. The 1st generation Si is an indirect bandgap semiconductor making its transition probability between band edges (from Si p orbital to Si p and s orbitals), about two orders of magnitude lower than that of direct bandgap, thus requiring its absorber layer to be two orders of magnitude thicker and increasing the material cost.

![Figure 1.12](image)

Figure 1.12. The schematic optical absorption mechanisms of (a) 1st generation (Si), (b) 2nd generation (GaAs) and (c) perovskite halide (MAPbI$_3$) photo absorbers (adapted with permission from [28]). $E_g^i$ and $E_g^d$ represent indirect and direct bandgaps respectively.
Both 2nd generation photo absorber, GaAs and current generation MAPbI₃ perovskite have direct bandgaps and thus their optical absorption is high in comparison to Si. However, their electronic structures are very different; the halide perovskite exhibit inverted electronic band structure (Figure 1.12 (b) and (c)). In GaAs, CBM dictates from dispersive s band (delocalized s orbitals) whereas in MAPbI₃ it is from degenerated Pb p bands (less dispersive p orbitals of Pb), thus in the latter the DOS is significantly higher and consequently leading to higher JDOS as shown in Figure 1.13(a, b). Furthermore, the intra-atomic transitions between VB to CB is higher in MAPbI₃ due to Pb s to Pb p transitions and results stronger absorption coefficient than that of GaAs. The comparison for calculated absorption coefficient of GaAs to that of MAPbI₃ is give in Figure 1.13 (c) and it can be seen that for perovskite, it is up to an order of magnitude higher within the visible light range, which accounts for the major usable portion of the solar spectrum (~1.8 eV–3.1 eV), and hence relatively lower thickness is needed to obtain high efficiency for MAPbI₃ compared to current high efficiency thin film photo absorbers as shown in Figure 1.13(d) [26, 28].

Another remarkable feature of OILH perovskite is the ability to tune the bandgap over a wide range of the solar spectrum which leads to considerable improvement in device performance. Compositional engineering of MAPbI₃ perovskite can be achieved by exchanging organic, metal or halide ions (Figure 1.14) [29]. Partial replacement of MA by FA to obtain MAₓFA₁₋ₓPbI₃ was an effective way to extend the absorption to longer wavelengths and enhance the thermal stability. Introducing mixed halides (I and Br) has also led to bad gap tuning to cover almost the entire visible spectrum (1.5-2.3 eV) and by adopting mixed cation and mixed anion like in (FAPbI₃)₁₋ₓ(MAPbI₃)ₓ absorber, over 19% high efficiencies have been reported with a high degree of reproducibility [30, 31, 32, 33]. Likewise, Pb was also replaced by divalent metal cations and system MAPb₁₋ₓSnₓI₃ has achieved ~14% solar cell efficiency [34].
Moreover, this ability to tune the bandgap makes them valuable in tandem devices (Figure 1.14 (b-c)) with Si or CIGS cells and cell efficiencies of 19.5% and 21% have been reported for four-terminal-perovskite/CIGS and two-terminal-perovskite/Si devices respectively [35, 36]. Most recently it has been reported that a tandem with ytterbium-doped perovskite on ~14 cm Si solar cells was able to convert the blue light that falls on the perovskite layer to near-infrared (near-IR) photons, which the Si cell below then turns into electricity [37]. The researchers also predict that this design could boost Si efficiency by nearly 20%.
1.4.4 Superior ambipolar carrier conductivity of OILH perovskites

The OILH perovskites exhibit high charge carrier mobilities with small effective masses for both electrons and holes, which makes them the best candidates for solar cells [38]. The effective mass \( m^* \) is an important parameter pertaining to carrier transport of a semiconductor and near the band edge it is approximately fitted by,

\[
m^* = \frac{\hbar^2}{\left| \frac{\partial^2 \varepsilon(k)}{\partial k^2} \right|^{-1}}
\]

where \( \varepsilon(k) \) are the energy dispersion relation functions, which are described by band structures [28]. Thereby, the more dispersive the band near the band edge is the lighter the effective mass is. In conventional
thin film photo absorbers, like GaAs, VBM is dominated by anion p orbital and CBM is contributed mostly by cation and anion s orbitals (p-s semiconductors) (see Figure 1.12).

In Figure 1.12, the lowest conduction band (LCB) is more dispersive than highest valence band (HVB) and therefore has a much smaller electron effective mass than that of holes, hence solar cells on those materials rely on the formation of p-n junctions. In contrast, as mentioned earlier the electronic structure of MAPbI₃ is inverted compared to conventional p-s semiconductors. Its CBM is dominated by Pb p orbital and has a much higher energy level than anion p orbitals, as in p-s semiconductor and therefore the LCB is more dispersive in MAPbI₃ than the HVB in p-s semiconductors. In addition, the strong s-p coupling enhances the dispersion of HVB of MAPbI₃ and thereby results in a small effective mass for holes. A comparison of theoretically calculated electron and hole effective masse for different PV generations and α-MAPbI₃ is given in Table 1.1. This unique feature of small effective masses for both electrons and holes, makes OILH perovskites ideal for thin film p-i-n (p-type, intrinsic, n-type semiconductors) solar cells.

<table>
<thead>
<tr>
<th></th>
<th>mₑ*</th>
<th>mₕ*</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-MAPbI₃ (SOC)</td>
<td>0.18</td>
<td>0.23</td>
</tr>
<tr>
<td>Si</td>
<td>0.26</td>
<td>0.29</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.07</td>
<td>0.34</td>
</tr>
</tbody>
</table>

In thin film absorbers shallow defect levels close to band edges are responsible for p or n type doping. However deep level defects can trap carriers and become Shockley-Read-Hall non radiative recombination centers in the absorber, which are mainly responsible for short minority carrier lifetime. In halide perovskites shallow defects are dominant due to high formation energies for deep transition level defects [26] and are
closely related to the dual-nature electronic structure. For an example, the strong s-p coupling makes VBM in halide perovskites energetically higher than 1 5p (Figure 1.10) indicating lower defect levels or shallow defect states. Hence the charge carrier recombination is much lower for MAPbI₃ like absorbers [28]. Moreover, it has been shown that, depending on the solution processing or deposition techniques used, in OILH perovskites thin films, carrier mobilities and diffusion lengths can be optimized and thereby promotes its ambipolar carrier transportation [29, 38, 40].

Furthermore, in comparison to conventional organic PV in which low dielectric constants contributes to poor charge transport, OILH perovskites yield superior charge transport due to high dielectric constants. In any photo absorber, absorption of photons lifts electrons out of the VB into the CB, generating free carriers and small number of excitons can also be formed. Excitons are fundamental quasi-particles that consist of bound electron -hole pair due to coulomb attraction and the excitons levels form within the bandgap. The exciton binding energy ($E_b$) and the Bohr radius ($r_B$) are given by,

$$E_b = 13.6 \frac{\mu}{\varepsilon^2} \text{ (eV)}$$  

$$r_B = 0.529 \frac{\varepsilon}{\mu} \text{ (Å)}$$

where, $\varepsilon$ and $\mu$ are the dielectric constant and exciton pair mass respectively. $E_b$ compared with the thermal energy ($\sim kT$) determines if the photo-created carriers will dissociate or will need to be separated by an additional junction in a PV device. Excitons are generally described as two types, Frenkel and Wannier. Typically, the excitons in organic molecules are the Frenkel type, with stronger binding energies (0.3-1.0 eV) which consequently leads to a smaller Bohr radius due to low dielectric constants of the organic molecule [41]. Conversely the exciton binding energy of OILH perovskites is low ($\sim 37$meV MAPbI₃) due to organic-
inorganic behavior of the material resulting in high dielectric constants, so the nature of the excitons in halide perovskites are more Wannier-like, in which e-h pairs are loosely bounded and easily become free carriers [42, 43].

1.4.5. Ferroelectric effect

Compare to conventional inorganic photo absorbers, OILH perovskites have non-centrosymmetric organic cations (e.g. the MA ion in MAPbI$_3$) which gives rise to a unique property of ferroelectric domains within the material which aid e-h separation and transportation [44]. Ferroelectric materials exhibit spontaneous polarization even in the absence of an electric field and the local field increases in proportion to the polarization. Thus, these materials must possess permanent dipoles. In the case of MAPbI$_3$, MA ion has a permanent dipole which shows ferroelectric behavior. In a conventional semiconductor solar cell, the electric field only exists in the space charge region of the p-n junction (See Figure 1.5) and this region is responsible for separation of the charge carriers. In contrast, in a ferroelectric thin film electrical polarization results in internal electric fields throughout the bulk region that are not completely canceled out by screening charges. Hence, PV effects are not limited to an interfacial region (Figure 1.15(a)) and fields can be generated without forming complex structures [45].

Theoretical calculations for bulk polarization of MAPbI$_3$ was reported by Frost et al. [46] and the calculated magnitude was 38 μC cm$^{-2}$, which is comparable to the value of ferroelectric oxide perovskites such as KNbO$_3$ (30 μC cm$^{-2}$). They also proposed that the boundaries of ferroelectric domains may form “ferroelectric highways” which facilitates the carrier transportation as shown in Figure 1.15(b) for halide perovskite based solar cells. Due to a fixed direction of polarization within each domain, e and h can effectively separate along the direction of electric field before they can recombine, and these ferroelectric boundaries are peak and troughs of electrostatic potential where e and h can select energetically favorable “highways” avoiding and “collisions” with the opposite charge carriers [46]. Also, direct observation of
ferroelectric domains in tetragonal MAPbI$_3$ was reported [47] and can be regarded as another unique property of OILH perovskite absorbers.

![Diagram](image)

Figure 1.15. Schematic diagrams for (a) bulk PV effect in a ferroelectric thin film and (b) a multidomain ferroelectric thin-film as hypothesized for hybrid halide perovskite solar cells. The diffusion highways for electrons and holes are shown by blue and red lines with arrows respectively (adapted with permission from [46]).

1.4.6. Inexpensive fabrication

Conventional Si solar cells require an expensive, multi-step manufacturing processes, conducted at high temperatures (> 1000°C) in a high vacuum in special clean room facilities. In contrast, OILH perovskites, can be manufactured using a simple wet chemistry technique in a traditional lab environment at low cost and requiring less energy. The simplest and economical solution-based fabrication method can be divided into one step and two step methods depending on the number of deposition steps used. In one-step method of preparing MAPbI$_3$ thin films, a solution containing PbI$_2$ (inorganic component) and MAI (organic component) is spin-coated on a substrate followed by annealing (~100°C) to form perovskite whereas in the two-step method, a solution of inorganic component is spin-coated on a substrate first and subsequent spin-coating (or immersing) of a solution containing the organic component is followed by annealing (Figure 1.16 (a), (b)). Even though these methods are cost effective and straight forward to implement, each method has
some drawbacks. For one step method, poor film quality and choice of a solvent that can simultaneously dissolve both components are major concerns. For the two step method the major issue is less control over the film thickness. However, power conversion efficiencies (PCE) of over 17% has been achieved using solution-based fabrication methods [48, 49, 50]. The doctor blade method (Figure 1.16 (c)) which has the advantage of using ~90% less material than spin coating, was also used to fabricate perovskite thin films and was able to achieve PCE~15% [51].

Vacuum deposition methods, such as dual source vapor deposition and sequential vapor deposition are (Figure 1.16 (d), (e)) also used to deposit thin films of halide perovskites, which provide the advantage of producing pin-hole free uniform films and eliminate the problem of one step co-depositions. Nevertheless,
vacuum processing requires a high-vacuum environment and involves high energy consumption [52]. The vapor-assisted solution method integrates the advantages of the solution method and the evaporation method (Figure 1.16 (f)). At a lower vacuum, the perovskite materials with fewer internal defects can be synthesized [53, 54].

1.4.7. Device architecture and working principle of OILH perovskite solar cells

OILH perovskite was first used in DSSC, which has a mesoscopic structure, replacing the light harvesting dye and later the liquid electrolyte was replaced with a solid-state hole conductor [55]. This later improvement attracted much interest in the PV community and given rise to development of device structures as given in Figure 1.17 (a)-(d) [56]. In each device structure perovskite layer is sandwiched between the electron (ETM) and hole (HTM) transporting materials. The variation of device structure is depending on the position of the ETM and HTM. Normal device structure is so called n-i-p structure and p-i-n structure is called the inverted device structure. The mesoscopic layer is used to enhance the charge collection by decreasing the carrier transport distance, preventing direct current leakage between the selective contacts and increasing the photon absorption by light scattering. The pore filling fraction and morphology of the perovskite layer is critically dependent upon the thickness of the mesoporous layer and for n-i-p mesoscopic structure thickness < 300 nm is recommended [57]. The n-i-p planar device, without a mesoporous layer is formed by carefully controlling the formation of perovskite layer and the interfaces at carrier transport layers and electrodes and was able to achieve PCE ~19.3 % to date [58].
However, the state-of-the-art n-i-p devices use a thin mesoporous buffer layer filled and capped with the perovskite as planar device exhibit more severe J-V hysteresis, (current-voltage hysteresis is observed by varying the direction and the rate of voltage sweep.) which undermines the reporting accuracy of PCE [59]. For the p-i-n structure, in which HTM layer is deposited on the transparent electrode, PCEs of 18.9 % and 17.3 % were reported for planar and mesoscopic devices respectively [60, 61].
A schematic of the band diagram and the transport process of e and h in a perovskite solar cell (PSC) is given in Figure 1.17 (e). Upon exposure to sunlight, the perovskite layer absorbs photons and produces excitons which create free carriers immediately. These free e and h drift and diffuse through the absorber and transport layers (ETM (donor) and HTM (acceptor)) and are finally collected by anode and cathode respectively. The charge selective layers and contacts influence the charge transport and extraction properties [62] and Figure 1.18 shows energy levels for some notable components used in most common types of perovskite solar cells.

Figure 1.18. Schematic diagram showing the energy levels, from left to right, for representative cathode, ETM, absorber, HTM and anode material (copyright [56]).
1.4.8. Issues and challenges in OILH perovskites

OILH perovskite solar cells have shown remarkable progress in PV technology owing to the above highlighted properties. However, there are some critical factors that affect the development of OILH solar cells. From the commercialization perspective, stability, toxicity issues and challenges in the scaling of solar cell fabrication for large scale deployment are the major concerns.

OILH perovskites are greatly affected by external environmental factors such as humidity, temperature and ultraviolet radiation [63, 46] and proper protecting coatings and encapsulation techniques such as glass sealing have improved the device stability to over 3000 hours at 60°C under simulated sunlight [64]. Nevertheless, long-term stability that is comparable to 30 years’ standard of commercial PV panels has yet to be demonstrated. It has been determined that in order to enhance the stability of OILH perovskites, several factors need to be considered including crystal structure design, ETM, HTM and electrode material preparation, composition of the perovskite absorber, interfacial engineering, fabrication methods and encapsulating methods [65, 66, 67].

For successful commercialization, fabrication of large-area perovskite films with high quality and incorporated it in PV modules is essential. Thus far, most of the best reported efficiencies > 20% were reported for miniature devices with are < 1 cm². However, reports on an area of 10.1 cm² with efficiency 10.3% and 36.13 cm² with an efficiency 12.1% have been published [68, 69] and the researchers in the former publication were able to fabricate 100 cm² area showing that the possibility of overcoming this scalability issue. Further development of large area perovskite solar cells should also focus on reducing series resistance and conductivity issues with electrodes and finding suitable alternatives to replace gold and silver which could prove to be uneconomical for large scale deployment.

Since the Pb employed in this technology is highly toxic, acceptance of this technology has become debatable. Exposure to even very low levels of Pb has been associated with significant health problems
affecting almost every organ and system in the body [70]. Recent studies based on life cycle analysis (LCA), and environmental impact analysis (EIA) for perovskite solar cells have revealed that only a small fraction of Pb contributes to overall environmental impact during the manufacturing process [71, 72]. The potential Pb pollution from 1GW plant is insignificant compared to other Pb emission sources such as fossil fuels, mining industries, battery and other electronic technologies [73]. Moreover, recent reports have shown the possibility of fabricating perovskite solar cells using recycled Pb from car batteries, which opens new ways to reduce Pb contamination associated with other technologies by reusing in perovskite PV technology [74]. However, it would be very valuable to find a low toxic or non-toxic constituent to replace Pb for the future of this PV technology. In this regard, many efforts have been made up to date and will be discussed in the forthcoming section.

1.4.9. Progress on lead-free perovskites

Many research groups are working on finding solutions to reduce or eliminate Pb from most promising OIMH perovskite absorbers. Monovalent substitution of Pb with cations with stable 2+ oxidation state is a one approach that has been considered. The suitable candidates can be found among elements in group-14, alkaline-earth metals, transition metals, lanthanides and p-block of the periodic table. However, the selection rules include, the ability to form perovskite structure with bandgaps suitable for photovoltaic applications, being less toxic than Pb and not being radioactive. This excludes some of the elements. Out of the most promising candidates, Sn$^{2+}$ [75, 76, 77], Mg$^{2+}$ [76, 82, 84], Ca$^{2+}$ [77, 84, 112], Ba$^{2+}$[154, 155, 156], Sr$^{2+}$[76, 77, 112], Co$^{2+}$, Fe$^{2+}$, Ni$^{2+}$, Zn$^{2+}$[75, 76], Cu$^{2+}$ [76, 78], Mn$^{2+}$[76,79] have been studied as replacements in perovskites solar cells. Sn-based solar cells have been most investigated so far and show highest PCE ~6% for ASnI$_3$ with A = MA and FA [80, 81, 82, 83]. For Mg-halide perovskites, theoretical calculations predicted that to be stable despite the smaller ionic radii than Pb and the possibility of bandgap tunability within 0.9-1.7
eV, but the sensitivity towards humidity become an issue [84,85]. Ca halide perovskites have been reported as stable but due to high band gaps they are not suitable for PV applications, but it was predicted to be suitable for charge selective contacts [86, 177]. Nontoxic and relatively inexpensive Sr has been reported to form high band gap halide perovskites which exhibit poor stability due to its hygroscopic nature [126]. Reports on Ba replacement for Pb at low concentrations which led to improved PV performance has also been reported [154, 155, 156]. Partially substitution of Pb with Fe has introduced trap states which diminishes PV performance and Co, Ni and Zn are reported to be not disrupting the PV performance at low level of Pb replacement [76]. Partial replacement of Pb in mixed halide (I, Cl) perovskites with Mn at very low level has been reported to result high open circuit voltage of 1.19 V with fill factor 87.9% [79]. Cu halide perovskites are reported to form low dimensional structure and reported efficiency was low as 0.63% even though it exhibits ambient stability and high absorption coefficient in the visible region [78].

Substitution of Pb with heterovalent cations is another approach taken towards forming less or nontoxic perovskites suitable for PV applications. However, charge neutrality cannot be obtained with these ions in the ABX₃ structure and they can switch the majority charge carrier from n to p type or vice versa. Heterovalent ions like Al³⁺ [87], Bi³⁺ [75, 88, 89], Au³⁺, In³⁺, Ti⁴⁺ [75,89] have been studied in the perovskite structure so far. Al partial substitution for Pb has resulted in enhancement of the thin film quality with reduced density of crystal defects and PCE ~19% was reported for p-i-n solar cells. Alivonalent substitution of Bi³⁺, In³⁺ and Ti⁴⁺ has reported to decrease the PV performance by disturbing the fundamental mechanisms of the charge generation and transport [75] and however, controlled incorporation of tri valent ions has led to enhance the electrical conductivity while preserving the 3D perovskite structure [89]. Furthermore, Pb substitution of monovalent ions like Cu⁺, Na⁺ and Ag⁺ which have comparatively similar ionic radii to Pb²⁺ has been studied and enhanced PV performance which was attributed to formation of uniform film and enhancement in bulk transport, has been reported [90].
All above efforts were performed to reduce toxicity of Pb while preserving the 3D OILH perovskite structure. However, efforts have also been made to form lead free 3D double perovskite structure (also called elpasolites) and other low dimensional structures (0D, 1D and 2D). The 3D double perovskite structure has a general formula $A_2B'B''X_6$ with B site substituted for a pair of $B'$ and $B''$ cations with mono and trivalency. Cs$_2$Sn$^{4+}$I$_6$ adopts this structure and has been explored as HTM in DSSCs [91]. Theoretical predictions for double perovskites with A= Cs, $B'$= Au, Cu, $B''$=Bi and X= Cl, Br have been proposed but working solar cells based on this structure have not been reported [92]. The size, shape and functionality of organic cations alter the 3D inorganic network of ABX$_3$ to form extended 2D layers, 1D chains and 0D isolated octahedra. These compositional and structural changes affect the optical and electronic properties as well. Recently, experimental works on 2D Pb free perovskite photo absorbers such as Cs$_3$Bi$_2$I$_9$, MA$_3$Bi$_2$I$_9$ and Rb$_3$Sb$_2$I$_9$ were reported but with low PCEs as 1.09%, 0.26% and 0.66% respectively [93, 94, 95]. An effort to make thin films of 0-D MA$_3$Bi$_2$I$_9$ and incorporate them in a solar cell to get ~0.1% PCE has also been reported [96]. Even though their PCEs are very small at this stage, above work illustrate the potential of accessible Pb-free perovskite systems in solar driven optoelectronics.

The aforementioned research works have provided a foundation to further research on possible Pb-free perovskite absorber materials and to integrate them into tailored device structures which give rise to significant enhancement in solar cell efficiencies for the near future.

1.5. Thesis aim and scope

Organic inorganic lead halide perovskite (OILHP) is emerging as a most promising photovoltaic technology owing to its high-power conversion efficiency (PCE), easy processability and low fabrication cost. 3D methyl ammonium lead halide (CH$_3$NH$_3$PbI$_3$ or MAPbI$_3$) is the most extensively investigated perovskite material in the family of OILHP. Hence it can be introduced as a standard and a model perovskite compound
used in solar cells. However, toxicity of lead is a major concern for its further development. Therefore, further exploring nontoxic metals to replace lead in the MAPbI$_3$ system is essential. It is also interesting to see how the substituted ions affect the material and device properties.

In this research, different nontoxic metal cations with iso and mono valences were introduced to partially substitute the lead cation in MAPbI$_3$ perovskite and their effects on structural, optical, electronic and dielectric properties were investigated.

Chapter 2 of this thesis presents the research work on Mn$^{2+}$ and Na$^+$ incorporated MAPbI$_3$ thin films for solar cells. In this work, thin films of MAPb$_{1-x}$M$_x$I$_3$ (M= Mn and Na, x= 1, 5 and 10) are formed and structural and optical absorption properties are investigated. Further, a procedure to obtain high efficient solar cells with the configuration FTO/c-TiO$_2$/mp-TiO$_2$/Perovskite/P3HT/Au is optimized.

In Chapter 3, the research work on Ba$^{2+}$ doped MAPbI$_3$ polycrystals is presented. The work primarily focuses on synthesis and investigation of structural, calorimetric, ionic conductivity and dielectric properties of MAPb$_{1-x}$Ba$_x$I$_3$ polycrystals (x= 1%, 5% and 10%).
CHAPTER 2

Mn$^{2+}$ AND Na$^+$ ION INCORPORATED CH$_3$NH$_3$PbI$_3$ THIN FILMS FOR SOLAR CELLS.

2.1. Introduction

Compositional engineering of the crystal structure in OIMH perovskites is a one way of achieving highly stable and efficient perovskite solar cells (PSC). Currently, the highest efficient PSCs are achieved by optimization of APbX$_3$ structure with mixed A cation and mixed X halides (PCE= 22.1 % for (FAPbI$_3$)$_{0.95}$(MA$_{0.15}$PbBr$_3$)$_{0.05}$) [7, 97]. For the purpose of reducing Pb, several efforts have been made to partially replace Pb with other suitable cations as mentioned in the previous chapter. But this technique remains a relatively a less explored path for using less toxic mono or divalent cations in partial replacement of Pb in MAPbI$_3$ perovskites. For this research work, the divalent and monovalent ions of interest are Mn$^{2+}$ and Na$^+$.

Manganese (Mn) is a transition metal with low toxicity and known to be one of the most abundant metals in the earth’s crust [98]. Partially replacing Pb with Mn in MAPbI$_3$ and its effects on photovoltaic devices [76, 99, 100, 101] as well as possibilities of incorporating its magnetic properties in magneto-optical data storage devices [102] have been explored by a few research groups. Klug et al showed, that at low levels (~1.5% of Pb replacement) Mn incorporation leads to modest improvement of PCE due to an increase in open circuit voltage for p-i-n devices and the observed result was ascribed to dopants causing energy level shifting to more favorable energetic alignment with HTM as observed in Co$^{2+}$ incorporation systems [76]. Mn doping into mixed halide MAPb$_x$Mn$_{1-x}$I$_{1.5}$I$_{1+2x}$Cl$_{2-2x}$ (for x=0.1-1) has been studied and for x=0.9, a high open circuit voltage of 1.19 V was reported, which was ascribed to the pin hole free morphology of the Mn doped perovskite film [100]. Zheng et al showed that, 3% partial substitution of Pb by Mn could improve PCE by
6% and found high reproducibility in the device performance for n-i-p device with spiro-OMeTAD as HTM [99]. The extension of PV into magnetism was reported by Nafradi et al, for 10% Mn doped MAPbI$_3$ system, which showed a unique combination of ferromagnetism ($T_c = 25K$) and high efficiency of photoelectron generation. They observed a decrease in $E_g$ and strong photocurrent response for photons with wavelength $< 830$ nm and a change in magnetism of the Mn doped sample [102]. An experimental and theoretical study of structural and electronic properties of Mn doped MAPbI$_3$ thin films has been reported by Bartesaghi et al who showed enhancement of charge carrier lifetime for $\sim 3$% Mn doping, which positively affects PV device performance [101]. Moreover, Pb was partially replaced by Mn in nanocrystal and Nano platelets of the CsPbX$_3$ systems and resulted in an intense sensitized Mn luminescence and thermal stability benefiting high performance perovskite LEDs (light emitting diodes) [103, 104, 105].

Sodium (Na), is an alkali metal with low toxicity and is known to be the sixth most abundant in the earth’s crust [106]. Also, alkali metals are good additives to be consider owing to their stability against oxidation and reduction [107]. Effects of incorporation of Na$^+$ ions to partially replace Pb in MAPbI$_3$ for PV applications have been studied by several research groups. Using NaI salt as the Na$^+$ source, an enhancement of photocurrent density ($\sim 23$ vs 21 mA cm$^{-2}$ for pristine) has been shown for n-i-p device with spiro-OMeTAD as HTM and it has been attributed to the enhancement of bulk charge transport upon Na doping [108]. Similar enhancement of device current density and enhancement of fill factor (from pristine 0.74 to doped 0.79) have been also reported for partial substitution Pb with 0.25 mol % of NaI in solar cells with p-i-n structure, and the results were attributed to dopant effect in increasing crystallinity and crystal size of the perovskite absorber [109]. Reduced trap states enhanced luminescent intensity and lengthened lifetime in Na$^+$ doped MAPbI$_3$ thin films solar cells have also been reported [110]. Unlike divalent dopants, Na$^+$ can generate holes in the valence band in the perovskite due to its monovalency compared to Pb$^{2+}$ and enhancement of hole concentration can be attributed upon doping perovskite with Na$^+$. However, a significant decrease in hole
mobility with an order of magnitude enhancement of hole concentration has been reported for NaI based MAPbI₃ system when increasing dopant concentrations from 0.11 - 0.22 M [111] and the reduction of mobility was attributed to dopant served as scattering centers for carriers.

As mentioned above, various investigations have been performed to study Mn²⁺ and Na⁺ additives effects on material and PV device performance of MAPbI₃ perovskite. Each investigation is unique, especially due to the differences in thin film preparation methods, dopant concentrations, deposition method, etc.), the solar cell device structure and its components used (ETM, HTM, etc.) and characterization techniques used to study the properties of the material and PV devices. Hence, it still remains interesting to further investigate Mn²⁺ and Na⁺ ions doping effects on the MAPbI₃ perovskite material at different dopant concentrations, in different device architectures.

In this research work, thin films of MAPb₁₋ₓMₓI₃ (M= Mn and Na, x= 1, 5 and 10) were formed using metal acetates and morphological, structural and optical absorption properties of the modified perovskite materials were investigated using RBS spectroscopy, UV-Vis spectroscopy and XRD spectroscopy respectively. Furthermore, a procedure to fabricate high efficiency solar cells with n-i-p device structure with mp-TiO₂/ c-TiO₂/ perovskite/P3HT/ Au configuration was optimized.

2.2. Methodology

2.2.1. Materials

Methyl ammonium iodide (CH₃NH₃I, 98%) was purchased from Dyesol and used as received. Lead acetate trihydrate (Pb (CH₃CO₂)₂.3H₂O) (≥99%, CAS 6080-56-4) was purchased from Alfa Aesar. Manganese (II) acetate tetra hydrate (Mn (CH₃CO₂)₂.4H₂O) (≥99%, CAS 6156-78-1), anhydrous sodium acetate(NaCH₃CO₂) (≥99%, CAS 127-09-3), anhydrous N, N-Dimethylformamide (DMF) (CAS 68-12-2), titanium(IV) isopropoxide (TTIP) (97%, CAS 546-
68-9), hydrochloric acid (HCl) (37 wt.% (aq.), 99.999%, CAS 7647-01-0) and FTO (fluorine doped tin oxide)-coated glass (7 Ω/square) were purchased from Sigma-Aldrich. Anhydrous silver acetate (AgCH$_3$CO$_2$) (ACS grade) was purchased from Fisher Scientific. Ti-nanoxide HT paste was purchased from Solaronix.

2.2.2. Perovskite precursor solution preparation

To prepare the pristine perovskite precursor solution, CH$_3$NH$_3$I and Pb-acetate were dissolved in anhydrous DMF at a molar ratio of 3:1 to form 1M solution of golden yellow color. For the alien cation incorporated precursor solutions, the molar ratio of CH$_3$NH$_3$I, Pb-Acetate and Metal-Acetates was chosen to be 3:1-x:x (x=0.01, 0.05 and 0.1). The solutions were sonicated at 70°C for about an hour and filtered with PTFE (0.2 μm) syringe filter prior to the deposition.

2.2.3. Substrate preparation

For the optical and structural studies of the perovskites, thin films were deposited on glass slides. The solar cells were fabricated on FTO-coated glass in which the FTO layer under the anode side contact was etched out using Zn powder and 2M HCl initially. All the substrates were then cleaned with 15 minutes’ sequential sonication in detergent, DI water, acetone and ethanol. Oxygen plasma treatment was performed on the substrates for 10 minutes and the thin layers were deposited on substrates within 15 minutes of the plasma treatment.

2.2.4. TiO$_2$ Anode preparation

On the pre-cleaned FTO substrate, a hole blocking layer of compact TiO$_2$ (c-TiO$_2$) was deposited by spin coating a mildly acidic solution of titanium isopropoxide in ethanol at 3000rpm for 30 s. After that, the substrate was annealed in a closed oven at 500°C for 45 minutes. To prepare the above-mentioned solution, 1ml of TTIP, 0.15 ml of HCl and 14.5 ml of absolute ethanol (95%)
[112] were stirred overnight at room temperature. The obtained milky solution was filtered using PTFE syringe filter of pore size 0.2μm prior to use. Next, the mesoporous TiO₂ (mp-TiO₂) layer was deposited on compact layer at 3000 rpm for 30 s from diluted (150 mg/ml) Ti-nanoxide HT paste (Solatronix) in ethanol following an annealing at 475°C for 30 minutes in a closed oven.

Figure 2.1. Semitransparent TiO₂ anode with compact and mesoporous layers on FTO substrate.

2.2.5. Perovskite thin films deposition and Solar cell fabrication

For the optical and structural studies of the thin films, perovskite solution was deposited on pre-cleaned glass slides at 2000 rpm for 40 s and annealed at 100°C on a hotplate for 5 minutes inside a nitrogen filled glove box. Before the deposition the glass slides were heated on a hotplate at 100°C for a minute.

For the solar cells, perovskite solution was deposited on FTO/c-TiO₂/mp-TiO₂ anode at 2000 rpm for 40 s. Prior to the deposition the perovskite solution and the anode were heated on a hotplate at ~70°C for a few minutes. After spin-coating, the films were transferred on to a hotplate
to anneal at 100°C for 5 minutes. Then a hole transporting layer of P3HT (Poly(3-hexylthiophene-2,5-diyl) was deposited from a 10 mg/ml solution in chlorobenzene at 2000 rpm for 30s and the films were annealed at 70°C for 5 minutes on a hotplate to remove the solvent effect. The solution was filtered using PTFE syringe filter of pore size 0.45μm prior to use. The above procedure was performed inside a nitrogen filled glove box. Finally, 30 nm gold (Au) electrodes were deposited using the Cressington Sputter coater under vacuum of ~0.045 Torr, at a rate of 0.1 nm/s, to complete the device.

2.3. Instruments and procedure utilized for sample characterization

2.3.1. Ultraviolet-visible (UV-Vis) spectroscopy

The wavelength dependence of absorbance of the perovskite films deposited on the glass slides were measured using a Lambda-35 UV-Vis double beam spectrophotometer with spectral band width of 1nm (fixed slit) for a wavelength range from 200-1100 nm at room temperature. In a double beam UV-Vis spectrometer (Figure 2.1), first a beam of light from the source lamp (halogen lamp for visible and deuterium lamp for UV radiation) is separated into its component at the diffraction grating (monochromator) to produce a spectrum. Each monochromatic (single wavelength) beam in turn is then split into two equal intensity beams by a beam splitter, and one beam passes through the sample (perovskite film on a glass slide) whereas the other passes through the reference (glass slide). The intensities of these light beams are then measured by electronic detectors (photodiodes) and compared. If the intensity of the reference beam is I₀ and that of sample beam is I, the absorbance (A) can be given by [113],

\[ A = \log_{10}(\frac{I_0}{I}) \]

Eq. 2.1
The absorbance values can be recorded as a function of wavelength. At least three samples from each group were tested to reduce the sample variance and the average of similar spectra were presented.

2.3.2. Rutherford backscattering spectrometry (RBS)

Rutherford backscattering spectrometry (RBS) has been widely used for near-surface analysis of solids, identification of elemental compositions and depth profiling of individual atoms. This technique is based on the scattering of particles in a central force field. The fundamentals of ion scattering in solids can be explained by classical mechanics, i.e. elastic scattering of a particle by another particle (Figure 2.3). The ratio of energy $E_1$ of particles backscattered from an atom is related to the incident energy $E_0$ via the principles of conservation of energy and momentum by the following equation,
\[ \frac{E_1}{E_0} = K = \left[ \frac{M_2^2 - M_1^2 \sin^2 \theta}{M_1 + M_2} \left( \frac{1}{2} \cos \theta \right) \right]^2 \]  

Eq.2.2

Where \( M_1, M_2, \theta \) and \( K \) are mass of incident particle, mass of target particle, scattering angle and kinematic factor respectively\[114, 115\].

The kinematic factor determines the elastic energy transfer from a projectile to a target atom and thus identifies the target atom. The ion scattering technique involving elastic and inelastic scattering can be divided into three categories: low-energy, medium-energy and high-energy ion scattering; RBS falls into the high-energy ion scattering category. The elastic scattering of a particle with charge \( Z_1 e \) and mass \( M_1 \) from a nucleus with charge \( Z_2 e \) and mass \( M_2 \) by the Coulomb interaction is known as Rutherford scattering and the Rutherford cross section (\( \sigma \)) is given by,

\[ \sigma(E_0, \theta) = \frac{Z_1 Z_2 e^2}{4E_0} \left[ \frac{4[(M_2^2 - M_1^2 \sin^2 \theta)(\frac{1}{2}) + M_2 \cos \theta]^2}{M_2 \sin^4 \theta (M_2^2 - M_1^2 \sin^2 \theta)} \right] \]  

Eq.2.3

Figure 2.3. A schematic of a classical collision and scattering of particle by an incident particle. For the scattering of light incident particle like He from heavy target atoms like Pb, \( \varphi \) dependence (recoiling) can be neglected.
Where $Z_1$ and $Z_2$ are the atomic numbers of incident and target atoms respectively [114, 115]. The cross section characterizes the probability of collisions between incident ion and target atom and contributes to the signal amplitude of the RBS spectrum. For heavier elements like Pb, $\sigma$ (= 9821.60 mb/sr for 2.0 MeV He$^{++}$ at $\theta=150^0$) is high and for the light elements in the target like C and N, $\sigma$ (=46.13 mb/sr and 62.78 mb/sr respectively) is low. Thus, RBS is more sensitive for detecting heavy elements rather light elements [116]. Since the $\sigma$ is inversely proportional to the square of the initial energy $E_0$, for the scattering below the surface due to the energy loss within the sample, the cross section is higher for a respective target atom.

Due to the electronic interactions with the target atoms, incident ions can lose energy when the energetic ions penetrate into solid material. If $\Delta E$ is the energy difference observed for ions scattered from the surface and from depth $x$, the parameter, stopping cross section ($S$) can be defined as

$$S(E) = \frac{\Delta E}{N_x} \quad \text{Eq.2.4}$$

$$\Delta E = KE_0 - E_1 \quad \text{Eq.2.5}$$

Where $N$ is the areal density (atoms/cm$^2$) within of the target material within distance $x$ and $KE_0$ and $E_1$ are exit energies of the scattered ions from surface and depth $x$ respectively. The stopping cross sections have been established for many materials as a function of energy, so the film thickness of a material can be determined. Figure 2.4 shows a schematic of backscattering event from a thick elemental sample and a resulting RBS spectrum. The energy of backscattered ions depends on the target atoms and the backscattering yield is related to the number scattering events.
of target atoms in the material. The film thickness can be determined using the width of the peaks in RBS spectrum.

Depending on the placement of the detector with respect to the target and incident beam directions, two different geometries are defined for RBS: IBM and Cornell as shown in figure 2.5. IBM geometry uses a simple setup with all incident beam, exit beam and surface normal are in the same plane with,

$$\alpha + \beta + \theta = 180^0$$  \hspace{2cm} \text{Eq. 2.6}

Where $\alpha$, $\beta$, $\theta$ are incident, exit and scattering angles respectively. The Cornell geometry is a 3-dimensional scattering geometry in which incident beam, exit beam and rotational axis of the sample are in same plane with,

$$\cos \beta = -\cos \alpha \cos \theta$$  \hspace{2cm} \text{Eq. 2.7}
and it has the advantage of a large scattering angle, which optimizes mass resolution and grazing incident and exit angles which optimizes depth resolution. In this study, RBS measurements on metal ion doped MAPbI$_3$ films on glass substrate were carried out in the IBM geometry using the 6.0 MV tandem Van de Graaff accelerator in the Department of Physics at Western Michigan University [117]. The backscattering spectra for a 2.0 MeV He$^{++}$ ion beam was collected at a scattering angle of 150$^0$ using a silicon surface barrier detector placed at an exit angle of 30$^0$. The data were simulated and analyzed using the SIMNRA [118, 119] program and the thickness of each sample was estimated in atoms/cm$^2$. The areal density atoms/cm$^2$ is the characteristic of RBS measurement, however, if the density of the material is known, this can be readily converted into

Figure 2.5: Geometries use in RBS: left: IBM and right: Cornell. $\alpha$, $\beta$, $\theta$ are incident, exit and scattering angles respectively. Pink color box shows the plane of incident and exit beams and blue color rectangle represents the target material.
the depth scale. The densities for thin films under investigation were calculated using XRD data and used to find the thickness of the films.

2.3.3. X-Ray diffraction spectroscopy (XRD)

X-ray diffraction is based on constructive interference of monochromatic x-rays and a crystalline sample. X-rays are generated in a cathode ray tube by heating a filament to produce electrons which are accelerated towards a target using an applied voltage. Characteristic x-rays are produced when the electrons have sufficient energy to dislodge inner shell electrons in the target material (e.g. Cu, Fe, Co, Mo). The spectra consist of several components like $K_{\alpha}$ and $K_{\beta}$, the most common. $K_{\alpha}$ further consists of $K_{\alpha 1}$ and $K_{\alpha 2}$, where $K_{\alpha 1}$ with a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The wavelengths are characteristic of the target material. These x-rays are filtered to produce monochromatic radiation, collimated and directed onto sample. The incident x-rays photons are elastically scattered by atoms in the sample and scattered monochromatic x-rays that are in phase produces constructive interference which satisfy Bragg’s law [120] given by,

$$n\lambda = 2d \sin \theta$$

Eq.2.8

where, $n$ is the integer called the order of reflection, $\lambda$ is the wavelength of the x-rays, $d$ is the characteristic spacing between the crystal planes of the sample specimen and $\theta$ is the angle between the incident beam and the reflecting lattice plane (Figure 2.2). These diffracted x-rays are then detected by the detector. By scanning the sample through a range of $2\theta$ angles all possible diffractions occurred due to randomly oriented crystallites of the samples, can be detected. The detector records the number of x-rays observed at each angle $2\theta$ and processes this x-ray signal to a count/count rate which is then output as an intensity plot of counts against the $2\theta$ angles.
Many diffractometers use the Bragg-Brentano geometry with the incident angle (ω) between the incident beam and the sample and the diffracted angle (2θ) is between the incident beam and the diffracted beam. To keep the x-ray beam properly focused, ω changes in conjunction with 2θ and this can be accomplished by rotating the sample or by rotating the x-ray tube. A schematic of the components and the geometry of the X-ray diffractometer is given in Figure 2.7. The Soller slits are used to improve the peak shape and resolution in 2θ type scans, especially at low scattering angles, by limiting the axial divergence of the incident and diffracted x-ray beams. Divergence slits match the diffraction geometry and the sample size, assuring beam does not exceed the sample size at any angle. The mask in the incident beam path adjust the beam width on the sample. Anti-scatter slit on the diffracted beam path reduces the background signal from air scattering assuring only the reflected beam reaches the detector.
Figure 2.8. Labeled diagram of the PANalytical Empyrean X-ray Diffraction System used in this research work. The x-rays from Cu target were used with β-Ni filter. The values for Soller slits, divergence slit, anti-scatter slit, and incident beam masks were 0.04 rad, 1/32°, 2° and 10 mm respectively.
Filters (β-filter) are usually used in the diffracted beam path to reduce the influence of sample florescence. The filter suppresses the Kβ radiation while keeping as much as possible of Kα radiation from the tube. For an example Ni filter used with Cu radiation absorbs >99% of Kβ but also lowers the Kα by ~50% [121]. 2θ X-ray diffraction scans on the perovskite thin films deposited on glass slides were obtained using PANalytical Empyrean X-ray Diffraction System (Figure 2.8) with Cu Kα1 (1.54060 Å). The applied voltage and current were 45kV and 40mA respectively. The samples were tested at 294K under vacuum (~5.2x10⁻² Torr) using the TTK-600 low temperature chamber (sample stage with Z-axis feature and which allows a vacuum). The geometry was such that ω = θ and both the detector and the X-ray tube were moved in a circle around the sample, which was fixed in position. Scanned 2θ range was 10⁰ to 50⁰ with the step size and the time per step were 0.008⁰ and 11s respectively. The collected data was analyzed using High Score Plus software.

2.3.4. Solar cell characterization

The most fundamental way to characterize the perovskite solar cell (PSC) performance is measuring current-voltage (I-V) measurements, in which the illuminated cell is put under a reverse bias voltage and the generated photocurrent is recorded. In general, current density (J) is used instead of current when characterizing solar cells because the area of the cell will have an effect on the magnitude of the output current. The characteristic J-V curves for a solar cell under dark and illumination are given in Figure 2.9. The J-V properties of heterojunction PSC can be analyzed using diode models [122, 123, 124].
Figure 2.9. A schematic of J-V curves of solar cell under dark and illumination conditions. The blue curve represents the ideal solar cell. The blue arrows represent how $R_{sh}$ and $R_s$ affect the J-V curve. The terms $J_{sc}$, $V_{oc}$, MPP, $V_{MPP}$, $J_{MPP}$, $R_{sh}$ and $R_s$ represent short circuit current density, open circuit voltage, maximum power point, voltage at MPP, current density at MPP, shunt resistance and series resistance respectively.

Figure 2.10. An equivalent circuit model for solar cells with a single diode under illumination.
In the most common single diode model, the electrical behavior of an ideal device can be modeled using the Shockley diode equation [125],

\[ J_D = J_0 \left\{ e^{\frac{qV}{nKT}} - 1 \right\} \]  \hspace{1cm} \text{Eq.2.9}

where, \( J_D \) is the dark current, \( V \) is the applied voltage \( J_0 \) is the reverse saturation current density at dark and is directly related to the recombination rate, indicating the thermal emission rate of electrons from VB to CB in photo absorber, \( q \) is the elementary charge, \( n \) is the ideal factor of a heterojunction, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. Under the ideal condition of sunlight, photocurrent can be added into the Eq.2.9:

\[ J_D = J_{ph} + J_0 \left\{ e^{\frac{qV}{nKT}} - 1 \right\} \]  \hspace{1cm} \text{Eq.2.10}

where \( J_{ph} \) is the photocurrent. However, no device is ideal in reality and hence, Eq.2.10 should be further modified to account for potential losses that may arise from internal resistance and leakage current in solar cells. Figure 2.6 presents the equivalent circuit diagram for solar cell, from which the JV curve (under illumination) of heterojunction PSC can be further described by

\[ J_D = J_{ph} + J_0 \left\{ e^{\frac{qV}{nKT}} - 1 \right\} - \frac{V + JR_s}{R_{sh}} \]  \hspace{1cm} \text{Eq.2.11}

Where \( J \), \( R_s \) and \( R_{sh} \) are the output current, series and shunt resistances respectively [126]. \( R_s \) accounts for the resistances arise from energetic barriers at interfaces and bulk resistances within layers. To prevent efficiency losses due to increased charge carrier recombination, this must be minimized, and it can be achieved by ensuring good energy alignment of the material used in the PSC. \( R_{sh} \) accounts for the existence of alternate pathways through the PSC and unlike \( R_s \), it must be high as possible to prevent leakage current through these alternate paths.
The values for $R_{sh}$ and $R_s$ can be found by the reciprocal of the gradient of the J-V curve at $J_{sc}$ and $V_{oc}$ (parameters which will be explained next) respectively. The short circuit current density ($J_{sc}$), is the photo generated current density of the cell when there is no applied bias and only the built-in electric field within the cell is used to drive charge carriers to the electrodes. This parameter is dependent on the absorption characteristics of the photoactive layer, charge generation, transport and extraction efficiency. The open circuit voltage ($V_{oc}$), is the voltage at which the applied electric field cancels out the built-in electric field so that no driving force for the charge carries resulting in zero photocurrent density. This matric is affected by energy levels of the photoactive materials, work function of the electrode materials and charge carrier recombination rate. Another important parameter which can be defined using the J-V curve is the fill factor (FF), which is defined as the ratio of the actual power of the PSC to the power if there were an infinite $R_{sh}$ and no $R_s$ (ideal case) and is given by,

$$FF = \frac{J_{MPP}V_{MPP}}{J_{sc}V_{oc}}$$  \hspace{1cm} \text{Eq.2.12}$$

Where $J_{MPP}$ and $V_{MPP}$ are the current density and bias voltage at maximum power point (MPP) for the PSC. FF is also defined as the area ratio of A and B which describe how square the J-V curve is (see Figure 2.9) and ideally it is as close as to 1. If $R_{sh}$ decreases the part closes to the $J_{sc}$ on the J-V curve will drop and if $R_s$ increases, the part closes to $V_{oc}$ will tilt to the left as given in Figure 2.9 and affect the FF. The most important parameter, power conversion efficiency (PCE), is given by,

$$PCE = \frac{P_{\text{max}}}{P_{\text{irradiated}}} = \frac{J_{MPP}V_{MPP}}{0.1 \text{ (cm}^{-2})} = \frac{J_{sc}V_{oc}FF}{0.1 \text{ (W cm}^{-2}) \times \text{cell area}}$$  \hspace{1cm} \text{Eq.2.13}$$
which is the ratio of maximum power output ($P_{\text{max}}$) of the PSC to the total input power ($P_{\text{irradiated}}$).

The current–voltage (I-V) data were measured using Keithley 2400 Source Meter under simulated sunlight at 1000 w/m$^2$ irradiance generated by Air Mass 1.5 simulator connected to Xenon Lamp power supply (Model XPS400, Solar Light Co.). The I-V curves were obtained by Green Mount IV-Stat 3.1 Software. The cells were tested inside a homemade vacuum chamber to avoid any humidity effect on layers of the solar cells. The devices were masked with an opaque mask to define an active area of 0.52 cm$^2$ and to avoid over illumination.

![Laboratory I-V measurement setup with the homemade vacuum chamber used to test PSCs.](image)
2.4. Results and discussion

2.4.1. Perovskite films preparation and morphology

\(\text{Mn}^{2+}\) and \(\text{Na}^+\) cations incorporated \(\text{CH}_3\text{NH}_3\text{PbI}_3\) thin films were successfully prepared from single step deposition from perovskite precursor solutions. In order to prepare the perovskite precursors, the molar ratio of MAI: Metal acetate was selected to be 3:1 based on previous reports where it was found that large excess of organic component results much larger crystalline domains and smoother films than those with 1:1 ratio [127]. It is also found that the anion in the Pb source determines the kinetics of perovskite crystal growth and hence affects the film morphology and device performance. Lead Iodide (PbI\(_2\)) is known to be the common Pb source for the MAPbI\(_3\) precursors. But it was found that the acetates form more volatile byproducts during the perovskite formation process than iodides which in turn results in much smoother films with no or fewer pinholes, and reduced annealing temperature and time [128]. So, within 5 minutes of annealing at 100\(^\circ\)C a shiny dark brown film was obtained from acetates as metal (Pb and other cations) sources. The spinning speed and time were optimized to get a streaks free smooth perovskite films on glass plates. It was also found that the glass slides need to be pre heated prior to the deposition of perovskite solution to get optimum coverage of the film (see methods for optimized values).

Figure 2.12. A perovskite film on glass substrate obtained in this experiment using single step deposition process.
The thickness of the thin films was estimated using RBS spectrometry. RBS spectra obtained for metal ion doped MAPbI$_3$ films on glass substrate were fitted using the atomic concentrations of the unit cell for all the elements in each composition. For an example, for pristine MAPbI$_3$ film, the tetragonal unit cell consists of 48 atoms with 4 atoms each of Pb, C and N, 12 atoms of I and 24 atoms of H. The corresponding atomic concentrations were then found to be 8% for Pb, C and N, 25% for I and 50% for H. Since for the heavy Pb and I atoms, the backscattering yield were high, therefore during the fit, concentrations corresponding to Pb and I atoms were approximated to be fixed to have a more realistic solution. If the mass of the probing particle is heavier than target particle, forward scattering occurs. Therefore, H atoms could not be quantified by RBS. The composition for the glass substrate for all the samples were fixed with atomic concentrations of 24% for Si, 62% for O, 10% for Na and 4% for Ca.

Figure 2.13. The experimental and simulated RBS spectra and fitted curves obtained using SIMNRA for all elements present in the sample consisting of pristine film and glass substrate. The grey color area on the main peak represents the energy dispersion due to the roughness of the film.
Figure 2.13 shows the experimental and simulated RBS spectra and fitted curves obtained for all elements present in the sample consisting of pristine film and glass substrate. The peak appears within the energy range from ~350 keV - ~500 keV is mainly composed of backscattering for Pb and I atoms. The step like feature in the low energy region (~200 keV) corresponds to the backscattering yield from the elements in the glass substrate. The extra contribution of energy spread (grey color area) in the main peak is due to the roughness of the perovskite film [129].

For all other compositions only the experimental and simulated (with best fit) curves are presented for clarity. The energy spread due to roughness of the perovskite layer was found to be decreasing with increasing dopants amounts compared to pristine film (Figure 2.14). This implies that the dopants increase the smoothness of the films. Lowering of surface roughness for 1% NaI incorporated MAPbI$_3$ film was previously reported in the literature using atomic force microscopy (AFM), which is in agreement with this present finding [110]. It is known that smoother MAPbI$_3$ thin films can effectively contribute to better contacts with its capping layer which is beneficial for the performances of solar cells [130]. Increase of roughness can slightly enlarge the interface area with HTL, which can increase the number of trap states at the interface causing reduction of $J_{sc}$ giving poor device performance [131]. Using the areal density values obtained from the RBS spectra and the density values derived from unit cell parameters obtained through XRD analysis of thin films, thickness of the thin films was found to be in the range of 0.48 μm - 0.36μm. The uncertainty of the thickness measurement can be related to the roughness of the films. Furthermore, it was found that the RBS technique is a powerful method to identify the morphology, elemental concentration and qualitative measure of the roughness of thin films on substrates.
Figure 2.14. The experimental and simulated (fitted) RBS spectra for Mn$^{2+}$ and Na$^+$ doped MAPbI$_3$ thin films on glass substrate. The energy spread at the left side of the main peak indicates the roughness of the films.
2.4.2. Structural properties of perovskite films

The structural properties of perovskite thin films with and without dopants was investigated by x-ray diffraction (XRD). The ideal powder diffraction patterns for the samples at room temperature (294 K) were first simulated using Rietveld modeling with High Score Plus software. The simulation for the pristine sample was obtained using the available theoretical structural data [132] (space group symmetry, unit cell dimensions, and relative coordinates of atoms in unit cell, atomic site occupancies, and atomic thermal displacement parameters) and for Mn$^{2+}$ and Na$^+$ ions doped samples, the simulations were obtained by varying Pb site occupancies in the pristine sample accordingly (for an example for Mn$^{2+}$ 1% sample, Pb site occupancy was changed to 99% Pb and 1% Mn). These simulations were used to indexing the XRD peaks (hkl) (Figure 2.15) and to predict the changes in peak intensities when a dopant is introduced to the sample. However, change in interatomic distances due to dopants cannot be predicted by the Rietveld modeling (which requires empirical calibration or advanced ab-initio simulation).

![Simulated powder XRD pattern for pristine sample with labeled peaks for t tetragonal I4/mcm space group at room temperature (Cu Kα1 (1.54060 Å)).](image-url)
The experimental X-ray diffraction patterns show no new peaks with the addition of dopants, hence the room temperature tetragonal structure (I4/mcm space group) is preserved without additional phases and the experimental data contain the major peaks listed in the simulation. The simulations assumed the ideal powder XRD (PXRD) in which crystallites are randomly oriented, whereas the actual samples were thin films which are textured (i.e. they have a preferred crystalline orientation) and thus they may show more pronounced peaks for one lattice plane, and all the other have substantially lowered or even absent peak intensities. The most intense peak for the samples which is located at ~14° was found to be consists of (002) and (110) peaks and they were not fully resolved as in PXRD simulated pattern. This may be mainly due to instrument resolution which does not allow these close two reflections to be resolved.

Figure 2.16. XRD patterns obtained for Mn^{2+} incorporated MAPbI₃ thin films at 294 K.
Figures 2.16 and 2.17 show the indexed XRD patterns obtained for Mn$^{2+}$ and Na$^+$ doped MAPbI$_3$ thin films respectively. Depending on the relative strength of the diffraction from different lattice planes, which depends on scattering intensity of the components of the crystal structure and their arrangement in the lattice, each peak has an intensity ($I_{hkl}$) which differs from other peaks in the pattern. In general, the structure factor ($F_{hkl}$) quantifies the intensity of the light scattered by a crystal and is given as,

$$I_{hkl} \propto \| F_{hkl} \|^2$$  \hspace{1cm} \text{Eq.2.14}$$

$$F_{hkl} = \sum_{j=1}^{m} N_j f_j \exp[2\pi i (hx_j + ky_j + lz_j)]$$  \hspace{1cm} \text{Eq.2.15}$$

Figure 2.17. XRD patterns obtained for Na$^+$ incorporated MAPbI$_3$ thin films at 294 K.
Where $x_j, y_j, z_j$ are the fractional coordinates which represent the atomic positions in the atomic planes with Miller indices h,k and l in the lattice, $N_j$ is the fraction of every equivalent position that is occupied by atom $j$ and $f_j$ is the scattering factor (also known as atomic form factor) which quantifies the relative efficiency of scattering at any angle by the group of electrons in each atom.

The scattering factor is given by,

$$f_j = f_0 \exp \left[ -\frac{B \sin^2 \theta}{\lambda^2} \right]$$

Eq.2.16

where, $f_0$ is the scattering amplitude at zero Bragg angle ($\theta$) which equals to number of electrons ($Z= \text{the atomic number}$) and B is the Debye-Waller temperature factor ($= 8\pi^2 U^2$, $U^2$ is the mean square amplitude of the vibration) which accounts for thermal vibrations of atoms.

The simulation results show the decrease in peak intensities (heights) with the increase in dopants of the samples. This variation in intensity can be ascribed to difference between scattering factor ($f$) between Pb$^{2+}$ (80 electrons) and dopant ion (Mn$^{2+}$ (23 electrons) or Na$^+$ (10 electrons)). Figure 2.18 shows the enlarged (110) peak from the simulation and it can be seen that for Na$^+$ incorporated samples the intensities are less than that of Mn$^{2+}$ incorporated samples. The intensity of the experimental XRD profiles are not clear like the ideal patterns. This may be due to differences in film thicknesses and due to the fact that the grains in the thin film tend to be preferentially oriented. These two things affect the XRD intensity for each plane in each film. The single step deposition method used in this experiment was earlier found to nucleate from an ordered intermediate phase and the crystallite orientation of the perovskite thin films has been found to be highly dependent on annealing temperature [133]. Also, the thickness of the films is mainly dependent on the concentration of the precursor solution and the spin rate. The presence of
different dopants in precursor solutions can have effect on the viscosity of the solution with the same concentration. Even though the experimental conditions for thin film growth process were kept constant, in practical, small variations in the conditions might have led to variation in thicknesses and the orientation of lattice planes which made it difficult to see the intensity drop as

Figure 2.18. Comparison plot of peak intensity variation for (110) peaks in the simulated PXRD patterns obtained for Mn$^{2+}$ and Na$^+$ incorporated MAPbI$_3$ at 294 K.
However, the peak shift with increasing dopant amounts in the samples are clearly visible with the experimental data. According to Bragg’s equation (Eq.2.8), the diffraction peak position (diffraction angle) is a function of the average atomic distances ($d_{hkl}$) between reflection planes (hkl) when wavelength is fixed. Thus, anything that changes the average bond distances such as temperature, substitutional doping and stress, will change $d_{hkl}$ and therefore change the diffraction peak position [134].

Figure 2.19. XRD peak shift for (110) peaks (left) and (224) peaks (right) for Mn $^{2+}$ incorporated MAPbI$_3$ thin films on glass at 294 K. The shoulder peak of (224) is ascribed to the (400) peak. At 10% concentration, the peak intensity was low, and the peak becomes broader and the shoulder peak was hard to identify. The (224) peaks have low intensity compared to (110) peaks and here the normalized intensities were presented to clearly show the peak shift.
In the case of doping, a difference in ionic radii will produce a change in the average interatomic distances. For both \( \text{Mn}^{2+} \) and \( \text{Na}^+ \) incorporated thin films, the experimental peaks were shifted towards high 2\( \theta \) values (Figure 2.19 and 2.20). This can be ascribed to relatively smaller size of dopant ions, \( \text{Mn}^{2+} \) (0.86 Å) and \( \text{Na}^+ \) (1.02 Å), than that of \( \text{Pb}^{2+} \) (1.19 Å) under the experimental conditions used.

Figure 2.20. XRD peak shift for (110) peaks (left) and (224) peaks (right) for \( \text{Na}^+ \)-incorporated MAPbI\(_3\) thin films on glass at 294 K. The shoulder peak of (224) is ascribed to the (400) peak. The (224) peaks have low intensity compared to (110) peaks and here the normalized intensities were presented to clearly see the peak shift.
On the other hand, \( d_{hkl} \) can be correlated to the unit cell dimensions. For the tetragonal unit cell the relationship between \( d_{hkl} \) and the unit cell dimension \( a \) and \( c \) is given by,

\[
\frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2}
\]

Eq.2.17

Figure 2.21 shows the room temperature tetragonal unit cell for MAPbI\(_3\) which consists of 4 units of MAPbI\(_3\) [135]. Using the above relation, unit cell parameters “a” and “c” were calculated considering (110) and (224) peaks for all the samples and the values are given in Table 2.1.

Figure 2.21. A schematic of room temperature tetragonal unit cell of MAPbI\(_3\) perovskite. [Adapted with permission from [135]]
Table 2.1. Variation of unit cell parameters with dopant %. The average of 3 sets of data were used and the average deviation from the each data set from the net average values were presented as the uncertainties.

<table>
<thead>
<tr>
<th>Dopant %</th>
<th>Mn$^{2+}$</th>
<th>Na$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
</tr>
<tr>
<td>0</td>
<td>8.8861 ± 0.0001</td>
<td>12.5721 ± 0.0001</td>
</tr>
<tr>
<td>1</td>
<td>8.8781 ± 0.0031</td>
<td>12.5650 ± 0.0008</td>
</tr>
<tr>
<td>5</td>
<td>8.8714 ± 0.0032</td>
<td>12.5563 ± 0.0007</td>
</tr>
<tr>
<td>10</td>
<td>8.8691 ± 0.0047</td>
<td>12.5160 ± 0.0115</td>
</tr>
</tbody>
</table>

From the above data, it is evident that the lattice parameters shrink with increasing dopants amounts for smaller ionic radii than that of Pb$^{2+}$. As Vegard’s law states, the lattice parameters should vary linearly with the dopant concentrations [136]. However, the linear fit for the experimental data shows $R^2$ values in the range of ~0.85-~0.96 ($R^2=1$ for the best linear fit) (Figure 2.22). This may be due to the approximation of peak position made on the not resolved (110) and (224) peaks. It is also observed that for Mn samples, the peaks broaden with increasing dopant amounts (Figure 2.19). For the Na samples this is not significant (Figure 2.19). The peak broadening can be caused by non-uniform strain and defects. Peak broadening due to micro strain ($B_s(2\theta)$) is given by,

$$B_s(2\theta) = 4\varepsilon \frac{\sin \theta}{\cos \theta}$$

Eq.2.18

$$\varepsilon = \frac{\Delta d}{d} \ %$$

Eq.2.19
Figure 2.22. Variation of unit cell parameters $a, c$ with increasing dopant % for Mn$^{2+}$ (a,b) and Na$^+$ (c,d) incorporated MAPbI$_3$ perovskite thin films. R$^2$ values for the linear fit lines are also presented.
Where, $\theta$ is the Bragg angle, $d$ is the lattice spacing, $\Delta d$ is the upper limit of deviation from $d$, and $\varepsilon$ is the strain.

Since the size of the Mn$^{2+}$ ions are smaller, it may be possible to introduce interstitial defects upon increasing Mn$^{2+}$ ions in the sample and thereby introducing non-uniform lattice distortions resulting in peak broadening. Compared to Mn$^{2+}$, Na$^+$ ions are bigger and have closer ionic radii to host Pb$^{2+}$ hence the interstitial defects with increasing Na$^+$ amounts may not be a dominant effect within the used dopant concentrations. These distortions in the lattice can also reduce the XRD peak intensities by affecting the constructive interference of lattice planes. The peak broadening also depends on the size of the crystallites/grains (B(2$\theta$)) in the thin film and is given by Scherrer equation,

$$B(2\theta) = \frac{K\lambda}{L \cos \theta}$$  \hspace{1cm} \text{Eq. 2.20}

where, $K$ is the Scherer constant which defines the contribution due to crystallite shapes (E.g. For spherical crystallites $K= 0.89$ if $B(2\theta)$ defined as FWHM), $L$ is the crystallite/grain size, $\lambda$ is the wavelength and $\theta$ is the Bragg angle [137]. According to above equation small crystallites/grain results in peak broadening.

If the peak broadening presence in the Mn samples are due to only crystallite size effect, then it can be assumed that Mn$^{2+}$ incorporation results in smaller crystallite formation by inhibiting the crystallite formation. This may be due to migration of Mn$^{2+}$ ions to grain boundaries and neutralizing the free energy, stabilizing the boundary. Yang et al reported that decrease in grain size for NaI incorporated MAPbI$_3$ thin films at higher concentration of dopant levels (>10%) [111]. So, it can be assumed that at higher concentration the peak broadening could be visible for Na$^+$ incorporated thin films. Thus, within the 1, 5 and 10% doping levels Na$^+$ ions may not have much
effect on the crystallite / grain sizes compare to pristine sample. The poor resolution of peaks in the experimental xrd profiles made it difficult to accurately find the peak breadth or full width at half maxima thus the estimation of strain vs. crystallite sizes were unable to be performed.

2.4.3. Optical properties of perovskite films

The UV-Vis absorption data was plotted against the wavelength (λ) for each metal-mixed composition (Figure 2.23 for Mn and Figure 2.24 for Na). To compare the effect of dopants, absorption per unit thickness is presented. For the pristine MAPbI$_3$ film, broad absorption band (black curves in both figures 2.23 and 2.24) which covers the entire visible spectral range (~450 nm-750 nm) exists with a band edge at around 780 nm which is in good agreement with the literature [138]. The optical absorption mechanisms in solid state materials are caused by transition processes between occupied and unoccupied bands in the band structure of the material. According to the previous findings the absorption peak near 760 nm is mainly attributed to a direct band gap transition from VBM (Pb 6s-I 5p σ-antibonding which is more extended within the PbI$_3$ framework) to CBM (Pb p state) [139, 140, 141]. The higher energy absorption peak around 480 nm is ascribed to the optical transitions from non-bonding states of Ip (mainly localized at the I atoms) to the Pb p orbitals [142]. For Mn incorporated thin films the absorption drops with increasing dopant amounts (Figure 2.23). A similar drop in absorption was reported in the literature for 3% MnI$_2$ doped MAPbI$_3$ films [99]. But for Mn 1% sample the absorption for wavelengths ~ 480 nm shows an enhancement of the absorption compared to other compositions. As shown in Figure 2.24, with 1% of Na added the absorption enhancement for the visible range can be observed. A similar trend was reported for 1% NaI doped films in the literature [108, 109]. They ascribed this increase in absorption intensity to the increase in crystallinity of the pristine
Figure 2.23. UV–Vis absorption per unit thickness for Mn$^{2+}$ incorporated MAPbI$_3$ thin films on glass substrate.

Figure 2.24. UV–Vis absorption per unit thickness for Na$^+$ incorporated MAPbI$_3$ thin films on glass substrate.
material with Na\textsuperscript{+} doping. As the amounts increase further, the absorption reduces in comparison to the pristine film. The electronic configurations for Pb, Mn, and Na atoms are Pb [Xe] 6s\textsuperscript{2} 4f\textsuperscript{14} 5d\textsuperscript{10} 6p\textsuperscript{2}, Mn [Ar] 3d\textsuperscript{5} 4s\textsuperscript{2} and Na [Ne] 3s\textsuperscript{1} respectively. For Mn and Na, the outer orbitals are s type which are dispersive and Pb p orbitals are less dispersive. Hence compared to p orbitals s has less DOS. So, when dopants are introduced the reduction of DOS may be the reason for observed drop in absorption.

However, for both Mn and Na doped thin film compositions the absorption intensities are strong with the same order of magnitude of absorption as in the pristine films. So, without altering the remarkable absorption property of the pristine material, these nontoxic metal ions can be used to replace Pb in pristine material at 1, 5 and 10\% dopant concentrations. Furthermore, to see if the presence of dopants has any influence on the band gap position of the pristine material, band gap values were evaluated using the measured spectra. For direct allowed transitions, the relation between $\alpha$ and the incident photon energy $h\nu$ is given by the Tauc relation,

$$\alpha h\nu = \beta (h\nu - E_g)^{0.5}$$

Eq.2.21

where $\beta$ is a constant and $E_g$ is the band gap energy which can be estimated by the plot of $(\alpha h\nu)^2$ vs $h\nu$. The Tauc plots for both Mn (Figure 2.25) and Na (Figure 2.26) doped thin films show a slight blue shift at the absorption edge. From these plots optical band gap of all synthesized films was estimated and the results are given in Table 2.2. In the literature, for MAPbI\textsubscript{3} thin films the band gap energy is reported to be in the range of 1.55-1.60 eV [90, 143, 144, 166]. Hence it can be concluded that the variation in the band gap energy (~2-4\%) upon dopants is negligible. However, lattice distortion can affect metal –halide orbital overlap and cause changes in band gaps [145]. As mentioned earlier, CBM is derived from p orbitals with poor orbital overlap (more
nonbonding character) whereas the VBM is derived from metal s and iodine p orbitals (antibonding character).

Figure 2.25. Tauc plot for Mn$^{2+}$ incorporated MAPbI$_3$ thin films on glass substrate. The dotted lines show the extrapolation to the linear part of the absorption edge.

Figure 2.26. Tauc plot for Na$^+$ incorporated MAPbI$_3$ thin films on glass substrate. The dotted lines show the extrapolation to the linear part of the absorption edge.
Table 2.2. Variation of bandgap energy of MAPbI$_3$ with dopant %.

<table>
<thead>
<tr>
<th>Dopant %</th>
<th>$E_g$ (eV)</th>
<th>For Mn$^{2+}$</th>
<th>For Na$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.5580 ± 0.0005</td>
<td>1.5597 ± 0.0004</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.5918 ± 0.0001</td>
<td>1.5763 ± 0.0003</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.5957 ± 0.0002</td>
<td>1.5765 ± 0.0004</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.5896 ± 0.0002</td>
<td>1.5873 ± 0.0002</td>
<td></td>
</tr>
</tbody>
</table>

Hence the CB is expected to respond less strongly to lattice distortions than the VB. Thus, the structural change to perovskite structure may cause shift in VBM and thereby affect the energy gap. From the observed trend of band gap energies, it looks like the lattice contraction (as observed in XRD analysis) has reduced the metal-halide overlap and increased the band gap by small amount. As seen in the Mn samples, the increasing trend slightly deviates at 10% dopant concentration. This may be due to formation of Mn-clusters at high concentrations with high band gaps which cause no further effect on changes to band gap [101].

2.4.4. Solar cell fabrication and characterization

Solar cells with n-i-p mesoscopic structure with the configuration FTO/c-TiO$_2$/mp-TiO$_2$/Perovskite/P3HT/Au, were fabricated in the laboratory using the metal doped perovskite systems (Figure 2.27).
The mesostructured solar cell with porous TiO$_2$ layer was the choice for this study because it was reported that the variation of TiO$_2$ layer morphology provides high surface area with the perovskite absorber and enhanced electron mobilities via a well-connected nanostructured path [59, 146]. In addition, the compact TiO$_2$ layer acts as a blocking layer to avoid the short circuit problems in the cell by preventing the holes created in the perovskite layer from reaching the FTO electrode and obstructing the flow of electrons from FTO to HTM or holes from HTM to FTO, avoiding heavy recombination. The P3HT was reported to be a cost effective and stable HTM material for perovskite solar cells which also acts as a protective layer from humidity due to its hydrophobic nature [147]. Hence laboratory available P3HT was used as the HTM for the solar cells in this study. Figure 2.28 shows the contribution from each layer to overall UV-Vis optical absorption for the solar cell. In particular, the perovskite layer strongly absorbs from 350 nm to 800 nm, verifying it is responsible for the majority of light harvesting while P3HT layer contributes absorption of the solar cell in 400 – 650 nm region and TiO$_2$ contributes absorption near 300 nm. This additional light absorption from ETM and HTM apparently increases the generation of photo-excited electrons and improves overall cell efficiency.

Figure 2.27. (a) A schematic of solar cell device and (b) Some of solar cells prepared in this research.
Many attempts were taken to obtain optimized layer morphologies and thicknesses for the final design of the solar cell in this study (refer to methods for optimized values). Most importantly, the TiO$_2$ anode must be semitransparent to assure the maximum amount of light gets to the perovskite absorber. The perovskite layer most has the correct thickness to get the maximum number of photo generated carriers while controlling the charge recombination and obtaining full surface coverage of the TiO$_2$ anode. The P3HT layer thickness should be optimized to assure perfect coverage of the perovskite layer preventing direct contact between perovskite and electrode and contributing as small a series resistance as possible across the solar cell. The Au layer should also be thick enough to have small series resistance to the cell. Using the optimized procedure discussed in the method section, solar cells were fabricated in the laboratory for this study.
Figure 2.29 shows the J-V curves obtained for two solar cells with the highest achieved efficiencies for pristine MAPbI₃ perovskite. Table 2.3 shows the derived solar cell parameters from the plots. The best cell efficiency obtained was 16.5% for the pristine perovskite and this is higher than the reported efficiency found in the literature for the same device architecture in which they achieved PCE of 6.7%, but with a c-TiO₂ layer obtained via spray pyrolysis [148]. The other reasons for differences of achieved cell efficiencies compared to the reference can be due to differences in layer thickness. Our work thus implies that with the optimized procedure used to obtain solar cells in this study has the potential to yield high efficiency solar cells. However, the method did not consistently reproduce the high efficiency cells, due to variations in the manufacturing process.
Table 2.3. Solar cell parameters recorded for the best two devices obtained for MAPbI$_3$ perovskite.

<table>
<thead>
<tr>
<th>Cell</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.99</td>
<td>28.3</td>
<td>0.58</td>
<td>16.5%</td>
</tr>
<tr>
<td>2</td>
<td>1.01</td>
<td>25.6</td>
<td>0.48</td>
<td>12.4%</td>
</tr>
</tbody>
</table>

However, due to the difficulty in consistently obtaining the high efficiency the effect of Mn$^{2+}$ and Na$^+$ dopants on the MAPbI$_3$ perovskite solar cell was unable to be studied and discussed in details in this thesis. However, this work will be part of future studies.

But from the results obtained for morphology, optical and structural properties of the MAPbI$_3$ perovskite thin films with Mn$^{2+}$ and Na$^+$ dopants, some predictions can be made about the effect of these dopants on solar cell device performance. From the RBS study it was found that the dopants improve the smoothness of the perovskite layer. As mentioned earlier, smoother films can contribute to better contact with the HTM layer, reduce trapping states at the interface and promote charge transfer to achieve high photocurrent. Hence it can be predicted that the dopants may cause enhancement of photocurrent by decreasing the roughness of the perovskite film. From XRD studies on thin films, it was found that the Mn$^{2+}$ doped films may form smaller crystallites compared to pristine films. Formation of smaller grains may lead to charge loss by recombination at grain boundaries in the device and thereby decrease the photocurrent [149]. Hence as the Mn$^{2+}$ amount increases in the perovskite layer; reduction of photocurrent can be predicted. From absorption data it was found that 1%, 5% and 10% Mn$^{2+}$ doping and 5% and 10% Na$^+$ doping result in a decrease in photo absorption while 1% Na$^+$ causes little enhancement of absorption of the MAPbI$_3$ thin film. Hence it can be predicted that solar cells with MAPbI$_3$ perovskite thin film with1% Na$^+$ may have enhancement of photocurrent while other compositions mentioned above
may result in the opposite. On the other hand, due to the monovalancy of Na\(^+\) compared to Pb\(^{2+}\), enhancement of hole concentration can be predicted for the MAPbI\(_3\) perovskite with Na\(^+\) dopants. It is worth mentioning that in reality it takes many trials and a long time to perfect the materials and techniques that make highly efficient solar cells. As mentioned earlier, even though a procedure was optimized and achieved a few high efficiency solar cells, reproducibility could not be achieved due to several factors. The main issue was many devices fabricated were short-circuited. This problem arises when the Au coated cathode makes contacts with the bottom FTO layer. The use of compact TiO\(_2\) layer should have avoided this problem, but it was found that dust particles can adhere to wet TiO\(_2\) layers (which were deposited in the normal lab environment and annealed in a high temperature ceramic furnace) which were later cause formation of pinholes with the top perovskite and P3HT layer. These pinholes may form conductive paths upon deposition of Au on top of P3HT. Removal of dust particles on the annealed TiO\(_2\) electrodes could have achieved using clean room fabrication techniques.

Another issue was that a number of fabricated solar cells that functioned well suffered from very low efficiencies. Lower efficiency solar cells even with the uniform and dark perovskite layers were also reported in the literature [150] and they hypothesized that temperatures above 280\(^\circ\)C in the glove box may induce crystallites within the precursor before the solution is deposited on the substrate, compatible with the inverse temperature crystallization of perovskites [151], which impacts the morphology and quality of the perovskite film. During the perovskite layer deposition in the glovebox it was found that temperature raises to 32\(^\circ\)C and that may be the cause achieving low cell efficiencies as suggested by the above-mentioned study. This problem could have avoided by not making many samples at the same time and by letting sufficient time to cool the glove box before the next sample is made. Overheating the samples during gold evaporation
to make gold metal contacts may be the other possibility that could cause low device performances as suggested by studies in the literature. Their findings suggested that temperatures exceeding 70°C during the metal deposition causes metal ions to easily pass through the HTM layer and accumulate within the perovskite layer and degrades the performance of devices [150, 152]. It was found that the solar cells were hot when they were taken out from the Au deposition chamber and the exact temperature during the deposition process inside the chamber could not be found. The maximum deposition time that can be achieved by the laboratory available Au sputter is 300s which resulted 30nm thick layer on the device and it was found that for lower sputtering time than that resulted in a very thin Au layer which was easily removed when making other contacts with the IV testing apparatus. The temperature effects on sputtering Au could have avoided by step wise layer deposition by sputtering Au for a few seconds and giving sufficient time to cool down before sputtering the next layer until the desired thickness is obtained.

So, the above-mentioned issues which occurred during the solar cell preparation resulted in an underperforming batch of devices even with similar optimized steps. Also, it was found that the practical experience is highly important to realize highly efficient solar cells reproducibly. Future work will aim to fabricate solar cells with reproducible efficiencies avoiding errors linked to bad device performance and compare the effects of Mn$^{2+}$ and Na$^+$ dopants effects at 1, 5, 10 % dopant concentrations on MAPbI$_3$ perovskite solar cells.

2.4.5. Conclusions

In conclusion, thin films of MAPb$_{1-x}$M$_x$I$_3$ (M= Mn and Na, x= 1,5 and 10%) perovskites were formed from single step spin coating of perovskite precursor solutions containing metal acetates. From RBS spectra it was found that the roughness of the perovskite layer reduces with addition of both Mn$^{2+}$ and Na$^+$ dopants which is beneficial for obtaining better contacts with its
capping layers and thereby favorable for the performance of solar cells. The room temperature tetragonal structure of pristine MAPbI$_3$ perovskite was found to be preserved for the metal doped thin films using XRD spectroscopy. However peak shifts towards high 2θ values were observed for the metal doped perovskite films implying a lattice size change for smaller dopant cation in the host MAPbI$_3$ lattice. The lattice parameters were calculated using the XRD data and the lattice shrinkage upon addition of smaller size dopants was observed. In addition, peak broadening with increasing Mn$^{2+}$ dopant amounts were observed in the XRD profiles which indicated smaller grain size with addition of Mn$^{2+}$ as was predicted. Peak broadening due to Na$^+$ for the used dopants levels could not be observed. From the UV-Vis absorption measurements it was found that nontoxic Mn$^{2+}$ and Na$^+$ metal ions can be used to replace Pb in pristine material at 1, 5 and 10% dopant concentrations without altering the remarkable absorption property of the pristine material. Furthermore, a procedure was optimized to fabricate solar cells with FTO/c-TiO$_2$/mp-TiO$_2$/Perovskite/P3HT/Au configuration and we were able to obtain a PCE of 16.7 % with Jsc= 28.3 mA/cm$^2$, Voc= 0.99 V and FF= 0.58 for pristine material. However, due to the difficulty in consistently obtaining the high efficiency the effect of Mn$^{2+}$ and Na$^+$ dopants on the MAPbI$_3$ perovskite solar cell could not be studied and discussed in detail in this thesis. Nevertheless, the possible effects of Mn$^{2+}$ and Na$^+$ dopants in MAPbI$_3$ based solar cell were anticipated using the findings from morphology, optical and structural analysis of thin films. In addition, the issues that causes poor reproducibility of solar cells with consistent efficiencies with the perovskite materials formed in this study were considered and future work will be aimed at fabricating solar cells with reproducible efficiencies to compare Mn$^{2+}$ and Na$^+$ dopants effects in MAPbI$_3$ based solar cell at 1, 5, 10 % dopant concentrations.
CHAPTER 3
Ba\(^{2+}\) DOPED CH\(_3\)NH\(_3\)PbI\(_3\) CRYSTALS

3.1. Introduction

As the toxicity of lead (Pb) in the CH\(_3\)NH\(_3\)PbI\(_3\) (MAPbI\(_3\)) perovskite has become a major concern towards its further development, exploring ways to replace lead or reduce lead in the perovskite structure is essential. The selection of suitable candidate to replace Pb should be done considering Goldschmidt’s tolerance factor (Eq. 1.1) and the octahedral factor (Eq.1.2) to form stable perovskites [16, 17]. In this regard, if we replace the selected cations in Pb site of MAPbI\(_3\), their tolerance factors and octahedral factors must lie in the ranges 0.8 < t < 1 and 0.442 < μ < 0.895 respectively to form stable perovskites. The ability to form divalent cations and closely related ionic radii to Pb suggest alkaline-earth metals to be considered to use in MAPbI\(_3\) to replace Pb. In this regard, the predictions of stable perovskite crystals of MABI\(_3\) with B = Ca, Sr and Ba with similar formation energies to that of MAPbI\(_3\) using Density Functional Theory (DFT) has been reported previously [177]. They have predicted enlarged bandgap and poor optical absorption in visible and infrared wavelengths with fully replacing Pb with the above ions. However, partial replacement of Pb with Sr showed a decrease in the bandgap [153]. Few studies where the Pb is partially replaced with nontoxic Ba in MAPbI\(_3\) thin films have been reported in the literature. Ba doping has shown decrease in the photovoltaic characteristics in MAPbI\(_3\) solar cells compare to pristine, but an increase compares to Sr doped cells [154] whereas low doping level of (1-5%) Ba resulted improved photovoltaic performance in thin film solar cells [155, 156]. All the above mentioned experimental works are related to Ba doped MAPbI\(_3\) thin films and their effect on photovoltaic properties. In this research, nontoxic Ba doped MAPbI\(_3\) polycrystals (MAPb\(_{1-x}\)Ba\(_x\)I\(_3\) with x= 1%,5% and 10%) were synthesized and their structural, calorimetric, ionic conductivity and dielectric properties were investigated.
3.2. Methodology

3.2.1. Materials

Lead acetate trihydrate (Pb(CH₃CO₂)₂·3H₂O) (≥99%, CAS 6080-56-4), barium acetate (Ba(CH₃CO₂)₂) (99%, CAS 543-80-6), methylamine (CH₂NH₂) (40 wt.% (aq.), CAS 74-89-5) and hydro iodide acid (HI) (57 wt.% (aq.), CAS 10034-85-2) were purchased from Alfa Aesar and used as received.

3.2.2. MAPb₁₋ₓBaₓI₃ crystal preparation

Slightly modifying the method described by Poglitsch and Weber [157], polycrystalline MAPb₁₋ₓBaₓI₃ was synthesized as follows. To prepare the pristine sample (x=0), 0.625 g of Pb-acetate was dissolved in 2.5 ml of concentrated aqueous HI in a Pyrex round bottom flask heated in a silicon oil bath using a magnetic stirrer. To prepare Ba doped samples, the molar ratio of Pb-acetate to Ba-acetate was chosen to be 1-x:x (x=0.01,0.05 and 0.1). The obtained solution was pale yellow in color.

![Figure 3.1. Polycrystals of MAPb₁₋ₓBaₓI₃ with x= 0, 1, 5 and 10 obtained in this study. (Green color square = 1 x 1 mm²)](image-url)
In a separate container, another 0.5ml of HI was mixed with 0.1664 ml of aqueous methylamine in an ice bath and the mixture was added to the first solution dropwise. Upon cooling from 110°C to 50°C, a black color precipitate was formed, and it was dried overnight at 70°C in a vacuum after filtering. Black color polycrystals were obtained upon slow cooling for 5 days. Pure Ba sample, where x=1, was also attempted; initially it was a colorless transparent solution which turned to brown around 80°C upon cooling. With this sample no precipitate was formed. All the samples were placed in the same oil bath during crystallization.

3.3. Instruments and procedure for sample characterization

3.3.1. X-Ray diffraction spectroscopy (XRD)

A detailed discussion of XRD spectroscopy was given in Chapter 2. For the present study, powdered samples of perovskite crystals were prepared by manually grinding using a mortar and pestle. 2θ X-ray diffraction scans on the Ba doped perovskite powdered samples deposited on Si zero background holder were obtained using PANalytical Empyrean X-ray Diffraction System equipped with Cu Kα1 (1.54060 Å) x-rays. The applied voltage and current were 45kV and 40mA respectively. Scanned 2θ range was 10° to 50° with the step size and the time per step were 0.008° and 11s respectively. The samples were tested at 294K under vacuum using the TTK-600 low temperature chamber. A small amount of Standard Si (NIST) powder was mixed with the perovskite powders to avoid confusions of the peak.

The data was analyzed using Xpert High Score Plus software. First, the ideal powder diffraction patterns for the pristine sample at room temperature (294 K) were simulated using Rietveld modeling with High Score Plus software to index the PXRD peaks as mentioned in Chapter 2- section 2.3.2. Then, for all the samples PXRD profiles were fitted using the available default profile fitting function to obtain more precise peak information about position, intensity,
width and shape of the diffraction peaks in the profile, and Si peaks were aligned together using reference profile ICDD 00-027-1402 for Si. Then the obtained data were used to calculate unit cell dimensions which is correlated to interatomic distances using Eq.2.17.

3.3.2. Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a thermo-analytical technique that is used to measure heat capacities of condensed phases. It determines the temperature and heat flow associated with the materials transitions as a function of time and temperature. It also provides quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes during physical transitions that are caused by phase changes, melting, oxidation and other heat related changes.

In the instrument, the sample which is encapsulated in a pan and an empty reference pan sit on a thermoelectric disk surrounded by a furnace (Figure 3.2). As the temperature of the furnace is change at a linear rate, heat is transferred to the sample and reference through the thermoelectric disk. The differential heat flow to the sample and the reference is measured by area thermocouples using the thermal equivalent of Ohm’s law,

$$q = \frac{\Delta T}{R}$$

Eq. 3.1

where, q is the sample heat flow, \(\Delta T\) is the temperature difference between the sample and the reference and R is the resistance of the thermoelectric disk [158].
For the Ba doped samples, DSC measurements were performed on a DSC Q100 calorimeter (TA instruments) at a rate of 10 °C min⁻¹ over a range of 35°C to 100°C under nitrogen gas flow. Approximately 7mg of crystal samples was mounted on Al pans in each experiment. The reference sample was an empty Al pan. The profile of heat flow associated with each sample as a function of temperature was obtained.

3.3.3. Impedance spectroscopy (IS)

AC impedance Analysis is a widely used method to characterize electrical properties of materials. The most common method is to study the ac response of a test system (electrode-material-electrode system) by the direct measurement of the impedance in the frequency domain. For any system, the impedance is defined as,
where, $V_0$ and $I_0$ are root mean square (rms) values of voltage and current respectively. Usually $Z$ contains both resistive (R) and reactive (L and/or C) components, which need to be determined. By applying a single frequency ($\omega$) voltage ($V$),

$$V = V_0 \sin \omega t$$  \hspace{1cm} \text{Eq. 3.3}$$
across the system, the resultant current ($I$),

$$I = I_0 \sin(\omega t + \phi)$$  \hspace{1cm} \text{Eq. 3.4}$$

So the phase shift ($\phi$) can be determined. Except for a system which behaves as an ideal resistor, there will be a $\phi$ phase difference between the applied voltage and the resultant current and it is related to the reactive component of the system. The $Z$ is a vector quantity and can be defined as a complex number,

$$Z = Z' - jZ''$$  \hspace{1cm} \text{Eq. 3.5}$$

where, $j=\sqrt{-1}$. $Z'$ and $Z''$ represent the real (resistive) and imaginary (reactive) parts of $Z$ respectively [159]. The representation of impedance data in the complex impedance plane plot, i.e. Nyquist Diagram, the grains and grain boundaries can be easily identified. Hence bulk electrical properties can be studied without any interference from grain boundary effects [160]. In the Nyquist plots $Z''$ is plotted against $Z'$ for decreasing frequencies ($\omega$). The materials with capacitive and resistive components show semicircles in their Nyquist plots. These components are represented by parallel RC equivalent circuit models which can be assigned to the appropriate
regions of the test system. As in Maxwell’s model of the layered dielectric [161], the physical features in the test system can be represented by layers of various thickness as given in Figure 3.3.

![Figure 3.3. Physical representation of Maxwell’s layered dielectric model for electrode/sample system.](image)

A high frequency semicircle in the complex impedance plane reflects the bulk contribution and an additional low frequency arc is caused by grain boundaries [162]. Figure 3.4 shows two common RC circuit models and their complex impedance plots [163]. Using these plots, the parameters R1 (charge transfer resistance) and C1 (double layer capacitance) can be determined and hence values found for the conductivity and capacitance of the basic material. The bulk resistance ($R_b$) of the sample can be found by the second intercept of the high frequency semicircle with the real axis. Hence, the bulk electrical conductivity ($\sigma_b$) can be determined by,

$$\sigma_b = \frac{l}{R_b A}$$  \hspace{1cm} Eq.3.6

where, $l$ is the thickness of the sample and $A$ is the area of the electrode. The RC product is usually independent of the geometry of the region which implies the RC element.
The Apex frequency ($f_p$) of the Nyquist Semi-circle is given by the relation

$$2\pi f_p R_b C_b = 1 \quad \text{Eq. 3.7}$$

and $f_p$ is a fundamental parameter which is independent of the geometry known as the relaxation frequency of the material [163]. Using this relation, the bulk capacitance ($C_b$) can be determined and the bulk dielectric constant ($\varepsilon_b$) of the material can be found by,

$$C_b = \varepsilon_0 \varepsilon_b \frac{A}{l} \quad \text{Eq. 3.8}$$

where $\varepsilon_0$ is the permittivity of free space. For the IS measurements, the samples were prepared by pressing powdered crystals using a hydraulic pressing system to form thin pellets. The pellets were annealed at 70°C for about an hour to remove the effect of the applied pressure. A cylindrical pellet
was sandwiched between two copper (Cu) electrodes and the impedance data was collected using a QuadTech1920 precision LCR meter. The sample was kept inside an oven and dark measurements of capacitance (C) and complex impedance (Z) were carried out in the frequency range from 20 Hz to 1MHz with 1V AC signal under 0V DC bias for the temperature range of 25°C – 65°C. The Nyquist plots were created from the obtained data and the components for RC parallel equivalent circuit were identified. The above equations were used to calculate the electric and dielectric properties for the samples.

3.4. Results and discussion

3.4.1. Structural properties of MAPb$_{1-x}$Ba$_x$I$_3$ crystals

Figure 3.5 shows the PXRD profiles for the Ba doped samples and standard Si (NIST) powder sample. The tetragonal phase (I4/mcm space group) was confirmed by the Reitveld modeling using the Xpert High Score plus software and hkl values for peaks were identified. No new peaks arise upon doping indicating that the tetragonal structure of the pristine is preserved. Si peaks were aligned together (ICDD 00-027-1402) and the peak shift towards low 2θ angles was observed with increasing Ba%. As given in Figure 3.6 the magnified (110) peak clearly shows the peak shift towards small 2θ angles. The shoulder peak is ascribed to (002). The most intense peak (110) was used to calculate the variations in lattice parameters upon doping. The lattice parameters are expanded with increasing Ba%. This lattice expansion is due to the replacement of Pb$^{2+}$ with Ba$^{2+}$ which has a little larger ionic radius (1.19 Å) than Pb$^{2+}$(1.35 Å).
Figure 3.5. PXRD profiles with indexed peaks for Ba$^{2+}$ doped MAPbI$_3$ crystals with Si peaks aligned together.

Figure 3.6. Peak shift of (110) peak for Ba$^{2+}$ doped MAPbI$_3$ crystals. The shoulder peak is ascribed to (002).
Table 3.1. Variation of unit cell parameters a, c with Ba%.

<table>
<thead>
<tr>
<th>Ba %</th>
<th>a(Å)</th>
<th>c(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.8471 ± 0.0001</td>
<td>12.6218 ± 0.0002</td>
</tr>
<tr>
<td>1</td>
<td>8.8702 ± 0.0001</td>
<td>12.6298 ± 0.0002</td>
</tr>
<tr>
<td>5</td>
<td>8.8740 ± 0.0001</td>
<td>12.6388 ± 0.0002</td>
</tr>
<tr>
<td>10</td>
<td>8.9085 ± 0.0001</td>
<td>12.7138 ± 0.0002</td>
</tr>
</tbody>
</table>

According to the Goldschmidt’s tolerance factor(t), Ba$^{2+}$ (t = 0.871) is compatible in the MAPbI$_3$ perovskite structure in place of Pb$^{2+}$. Hence Pb$^{2+}$ can be substitute by Ba$^{2+}$ without forming new structures [17]. The calculated lattice parameters were used to find the dopants amounts of
the samples using the Vegard’s law. The Vegard’s law states that the change of the lattice constant is proportional to the concentration of the dopant for a crystal whose lattice reacts as an elastic medium [164]. The lattice parameters for pristine MAPbI$_3$ [157] and MABaI$_3$ [165] were obtained from the literature and were used to find the linear relationship of lattice constant and Ba %. As shown in the Figure 3.7 and the Table 3.1, the experimental lattice constants are in good agreement with the trend and hence the dopant amounts were more likely to be the amounts that were in the mother solution.

3.4.2. Calorimetric properties of MAPb$_{1-x}$Ba$_x$I$_3$ crystals

Figure 3.8 shows the DSC curves for Ba$^{2+}$ doped MAPbI$_3$ samples with tetragonal to cubic transition with peaks at nearly 57 °C and nearly 56 °C for heating and cooling curves respectively.

![DSC profiles for Ba doped MAPbI3 samples. The downward peak represents the endothermic (heating) curve whereas upward peak is for exothermic (cooling) curve.](image)

Figure 3.8. DSC profiles for Ba doped MAPbI3 samples. The downward peak represents the endothermic (heating) curve whereas upward peak is for exothermic (cooling) curve.
The transition temperature for pristine sample is in good agreement with previously reported transition temperatures [166] and for the doped samples this is almost the same. That means the used Ba amounts in the samples have no effect on the phase transition temperature. No additional peaks in the DSC profile within the used temperature range also implies that there are no other structural transitions occur. The origin of difference in transition temperatures for heating and cooling curve is uncertain.

3.4.3. Impedance analysis of MAPb$_{1-x}$Ba$_x$I$_3$ crystals

The plotted Nyquist plots show single distorted semicircular arcs whose radii become smaller as the temperature increases (Figure 3.9). The arcs emerge at high frequencies and hence corresponds to a bulk effect. As the Ba amounts increases in the sample (from 5-10%) a low frequency arc starts to emerge which corresponds to grain boundary effect. Even though the grain boundary effect is not fully detectable within the range of the frequency studied, it can be concluded that the high number of dopants can modify the grain boundary behavior.

The frequency and temperature dependence of capacitance for different Ba% varies as in Figure 3.10. The data for empty cell capacitance is plotted in Ba 0% graph for comparison. At high frequencies (~1MHz) the capacitance reaches the bulk capacitance which is frequency independent.

Furthermore, as given in the Figure 3.11, the dark conductivity of the Ba$^{2+}$ doped MAPbI$_3$ samples increases with increasing Ba content. Figure 3.12 shows the dark conductivity variation for room temperature with increasing Ba content.
Figure 3.9. Temperature dependence Nyquist plots for MAPb$_{1-x}$Ba$_x$I$_3$ pellets sandwiched between two Cu electrodes.
Figure 3.10. Temperature and frequency dependence Capacitance of MAPb$_{1-x}$Ba$_x$I$_3$ pellets sandwiched between two Cu electrodes.
Figure 3.11. Temperature and composition dependence of dark conductivity of Ba$^{2+}$ doped MAPbI$_3$ pellets.

Figure 3.12. Variation of dark conductivity at room temperature with Ba % in Ba$^{2+}$ doped MAPbI$_3$ pellets.
From previous studies it is shown that the dark conductivity in MAPbI$_3$ is ionic to a substantial degree [167]. Therefore, it can be assumed that this conductivity contribution is coming from ions in the samples. Moreover, it is also reported that the ionic conductivity arises from point defect mediated ion migration of MA$^+$ [168, 169] and I$^-$ [170, 171, 172]. Theoretical studies from first principle calculations suggested that the activation energies for ion migrations of I$^-$ (0.58 eV) is smaller than that for MA$^+$ (0.84 eV) and Pb$^{2+}$ (2.3 eV) [173] and it is shown that iodine vacancy is the most favorable point defect for ionic migration in bulk MAPbI$_3$ in comparison to the cost of energy of interstitial migration. Also, the I$^-$ ions in the edge of PbI$_6^{4-}$ octahedron have a shorter distance to the nearest I$^-$ vacancy (~4.46 Å) than Pb$^{2+}$ (~6.28 Å) ions, hence the majority of mobile ions were suggested to be I$^-$ ions [174] By successive motion of negative iodine ions into neighboring vacancies, a unit of negative charge can be moved with relative ease across the lattice. Thus, in the pristine sample, it can be assumed that the ionic conductivity arises mainly from vacancy mediated by I$^-$ migration.

Since the Ba$^{2+}$ is isovalent to Pb$^{2+}$, the observed conductivity behavior can be related to the observed lattice distortion by the isovalent ion doping. When Pb$^{2+}$ site is replaced by larger Ba$^{2+}$ ion, atoms locally rearrange their positions resulting a tensile strain near the Ba site and leaving the neighboring Pb site under compression. Energy minimization can be achieved by lattice relaxation and may introduce a net change in lattice parameter. This effect can be seen in the xrd data as the lattice expansion grows upon Ba incorporation. We propose that strain increases the defect concentration thereby increasing the ionic conductivity.

To discuss further, let’s consider defect formation in a perfect lattice. The Gibbs free energy (G) of the lattice is given by,
\[ G = U - TS + PV = H - TS \]  \hspace{1cm} \text{Eq. 3.9}

where \( U \) is the internal energy, \( H \) is the enthalpy, \( T \) is the absolute temperature, \( V \) is the volume \( P \) is the pressure and \( S \) is the entropy. The structural stability of the lattice is achieved by minimization of \( G \). At thermodynamic equilibrium, a lattice consists of atoms on the regular lattice sites and the intrinsic point defects randomly distributed on some lattice sites. Vacancies and interstitials are known to be intrinsic point defects of real crystals. Formation of such defects is often constrained by charge neutrality. This can be achieved by several ways. There can be essentially equal number of positive and negative ion vacancies (Schottky defects) or there can be equal numbers of vacancies and interstitials of the same ion (Frenkel defects).

Vacancy formation (empty sites) in a perfect lattice leads to distortions of the lattice and thereby increases the potential energy of the system. Hence the enthalpy \( (H) \) of the lattice increases compared to the perfect lattice. Then the work requires to form such a point defect or the enthalpy of formation of one vacancy \( (\Delta H_v) \) can be given by the following equation.

\[ \Delta H_v = (H_{\text{crystal with one vacancy}} - H_{\text{perfect crystal}}) \]  \hspace{1cm} \text{Eq.3.10}

Also, as the vacancy is introduced into a perfect crystal the orderliness of the system reduces. That means, configurational entropy \( (S_{\text{configurational}}) \) of the system increases upon vacancy formation. Then the change in entropy \( (\Delta S) \) can be given by,

\[ \Delta S = \Delta S_{\text{configurational}} = (S_{\text{state with vacancies}} - S_{\text{state without vacancies=perfect crystal}}) \]  \hspace{1cm} \text{Eq. 3.11}

But,
\[ S_{\text{perfect crystal}} = 0 \]  \hspace{1cm} \text{Eq. 3.12}

Hence,

\[ \Delta S_{\text{configurational}} = S_{\text{state with vacancies}} \]  \hspace{1cm} \text{Eq. 3.13}

Then the change in free energy due to putting \( n \) number of vacancies in a perfect lattice can be given by,

\[ \Delta G = (G_{\text{crystal with vacancies}} - G_{\text{perfect crystal}}) = \Delta H - T \Delta S = n \Delta H_v - T \Delta S_{\text{configurational}}. \]  \hspace{1cm} \text{Eq. 3.14}

Therefore, the Gibbs free energy can be lowered by accommodating some vacancies into the lattice, at a cost of energy to put vacancies into a lattice and at the gain of configurational entropy due to vacancies.

Moreover, the probability of finding a lattice site in vacant is given by,

\[ P = \frac{1}{1 + e^{\frac{-\Delta H_v}{kT}}} \]  \hspace{1cm} \text{Eq. 3.15}

If there are \( N \) sites and \( n \) vacancies and for \( n \ll N \), the above relation can be approximated by,

\[ P = \frac{n}{N} \approx e^{\frac{-\Delta H_v}{kT}} \]  \hspace{1cm} \text{Eq. 3.16}

In the case of Frenkel defects, if \( n_f \) is the number of Frenkel defects (which is equals to number of interstitial atoms) the above relationship is given by,
\[
\frac{n_f}{N} \approx e^{-\frac{\Delta H_f}{2kT}} \tag{3.17}
\]

where, \( \Delta H_f \) is the energy required to displace an atom from a regular lattice site to an interstitial site. Hence, the defect formation within the lattice can be enhance by lowering the defect formation energy. So, at thermal equilibrium, the concentration of point defects is governed by the energy of defect formation and the existence of point defects in the lattice is represent by the configurational entropy.

In the case of pristine MAPbI\(_3\), the lattice consists of some number of intrinsic vacancies other than the atoms in their regular lattice sites. The MAPb\(_{1-x}\)Ba\(_x\)I\(_3\) lattice where Ba atoms partially replace the Pb atoms, is a strained lattice compare to the pristine one. We suggest that in this lattice, the defect formation energy is low and thereby the number of vacancies presence is higher than that of the pristine lattice.

As mention earlier, the ionic conductivity arises mainly from vacancy mediated I\(^-\) migration. Hence, to enhance I\(^-\) migration, the vacancy sites available for I\(^-\) must be increased. Also, as previously mention, the enhancement of defect formation should be related to the lattice distortion by the Ba ions. In this regard the defect formation in Ba doped lattice can be ascribed to the change in atomic interactions at Ba sites. The interactions in ionic and heteropolar crystals like MAPbI\(_3\) is influenced by the Madelung electrostatic potential [175]. Then the electrostatic interaction (\(u^{coul}(r)\)) per ion pair has the form,

\[
u^{coul}(r) = -\alpha \frac{e^2}{r} \tag{3.18}
\]

where \( \alpha \) known as Madelung constant, depends only on the crystal structure, \( r \) is the nearest neighbor distance and \( e \) is the electron charge.
The \( \alpha \) depends on the coordination number, i.e., the number of nearest neighbors (of opposite charge) [176] in the pristine lattice, iodine in the Pb-I plane is only affected by interaction by Pb ions (Figure 3.13 (a)). On the other hand, iodine ions in MAPb\(_{1-x}\)Ba\(_x\)I\(_3\) lattice should have a different interaction due to neighboring Ba and Pb ions (Figure 3.13 (b)). Note that the coordination number for I in both lattices is same. But the Ba-I bond length (3.23 Å) is larger than that of Pb-I (3.11 Å) [177]. Consequently, the absolute value for the Madelung potential is smaller for iodine in Ba doped lattice. This may cause displacement of an iodine atom from the lattice site into a nearby interstitial site forming an iodine vacancy and interstitial at a given temperature (Frenkel pair). Due to the spatial availability near the Ba site, the interstitial can be in close proximity with the vacancy. In the case of pristine lattice such Frenkel pairs may cost more energy to form due to spatial unavailability nearby as in MAPb\(_{1-x}\)Ba\(_x\)I\(_3\) lattice. Hence other than the regular intrinsic vacancies in regular Pb sites, Ba sites may introduce extra vacancies to the lattice by Frenkel defect formation and as a result it enhances the ionic conductivity for increasing Ba amounts in the samples.

Moreover, as seen in the Figure 3.11, the conductivity increases with the temperature. This can be explained according to the Eq.3.17, which represents the enhancement of defect concentration with increasing temperature. The increase in thermal energy increases the atomic vibrations and may cause bond breaking and thereby increase the defects. On the other hand, thermal vibrations make it easier for an iodine atom to move to nearby vacancy and enhance the ionic motion.
Also, there is an increase in dark conductivity an order of magnitude from 0-5 % (10\(^{-6}\) -10\(^{-5}\) Sm\(^{-1}\)) Ba\(^{2+}\) doping and then as higher dopant concentration is approached (10%) it looks as it starts to saturate (Figure 3.12). This can be due to formation of Ba clusters at high concentrations which may saturate the number of defects in Ba sites and the clusters can act as scatters for the ionic motion thereby decreasing the ionic conductivity. Furthermore, the bulk dielectric constant of the Ba\(^{2+}\) doped MAPbI\(_3\) samples increases with increasing Ba content as given in Figure 3.14. The dielectric constant of a material directly depends on the dipoles and their behavior within the material.

If we place a dielectric material in an electric field, the electric field polarizes the molecules in the material and turns them into dipoles. The average electrical dipole moment \(\bar{p}\) is given by,

\[
\bar{p} = rq
\]

Eq.3.19
where, \( r \) is the radius of the dipole and \( q \) is the charge of the dipole. It can also be written as,

\[
\vec{p} = \alpha \vec{E}
\]

Eq. 3.20

where, \( \alpha \) is the polarizability of the material, which is the ability to form instantaneous dipoles in an electric field and \( \vec{E} \) is the applied electric field. Then the polarization \( \vec{P} \) or net electric dipole moment density is given by,

\[
\vec{P} = N\vec{p} = N\alpha \vec{E}
\]

Eq. 3.21

where, \( N \) is the number of dipoles per unit volume. Also, the electric flux density \( \vec{D} \), of a dielectric material is given by,

\[
\vec{D} = \varepsilon_0 \vec{E} + \vec{P}
\]

Eq. 3.22

where, \( \varepsilon_0 \) is the permittivity of free space, \( \vec{E} \) is the applied electric field and \( \vec{P} \) is the polarization. The dielectric constant \( \varepsilon \) is defined as the ratio of electric flux density to electric field intensity and is given by,

\[
\varepsilon = \varepsilon_0 + \frac{P}{E}
\]

Eq. 3.23

where \( P \) and \( E \) are the magnitudes of polarization \( \vec{P} \) and electric field \( \vec{E} \) vectors. Hence, for a given electric field, polarization determines the dielectric constant of the material. Note that \( \vec{P} \) is the contribution from both induced and permanent dipoles in the material.
In MAPbI₃, the MA⁺ ion has a permanent electric dipole moment; thus, a dynamic process changing the orientation of this ion can contribute to the dielectric properties of the substances [178, 179, 180]. Specially within the frequency range where the bulk properties were determined (MHz regime), the polarization response is reported to be the contribution from MA⁺ rotation and its associated dipole moment along C-N bond axis [181]. Near room temperature the entropy associated with MA⁺ orientation is high and upon lowering the temperature, entropy of MA⁺ dipole orientation decreases reflecting an increase in dielectric constant [182]. In that low temperature orthorhombic phase MA⁺ are well oriented to maximize the hydrogen bonding with I in PbI₆ octahedral [183]. In contrast, in the tetragonal phase MA molecules are randomly oriented and shows no orientational correlation between them resulting high orientational disorder [182]. Considering the above facts, reduction of orientational disorder of MA molecules in the tetragonal

Figure 3.14. Variation of bulk dielectric constant with Ba % and temperature of Ba²⁺ doped MAPbI₃ pellets.
lattice can enhance the dielectric constant. To explain the observed behavior of dielectric constant with the Ba incorporation, we can suggest that the distortion of the Ba sites causes the orientation of MA molecules to be ordered to some extent and thereby increases the dielectric constant. Since the orientation of MA molecules depends on the hydrogen bonds it forms with iodides in octahedron [184], displacement of I due to lattice distortion may introduce a preferred orientation of MA molecules within the Ba site. In the literature, similar increasing behavior in dielectric constant with the dopant was reported for Fe$^{2+}$ doped MAPbI$_3$ films and the behavior was attributed to the creation of larger grains during the crystallization due to the high residual stress cause by the Fe$^{2+}$ dopants [185]. On that account, within that large grains there is a possibility for MA molecules to be ordered. In our case, this can be related to the expanded Ba sites.

Also, there is an observed variation of the dielectric constant with the temperature. This can be due to the thermal effect on the orientational polarization. As the molecules receive more thermal energy the random motion become greater and molecules align less closely with each other making less orientational polarization and hence dielectric constant can be lowered. This effect is observed experimentally up to a certain temperature, more likely 55$^\circ$C as given in above plot (Figure 3.14). After that the trend shows a discontinuity and that can be due to the tetragonal to cubic phase transition of the materials which agrees with DSC data. From the DSC curve the transition temperature was calculated to be 57$^\circ$C. During the phase change, the structural change will affect the orientation of the dipoles and hence the dielectric constant will change.

Further, from the impedance data that were collected, the frequency and temperature dependence of dielectric constant of Ba doped MAPbI$_3$ can be analyzed as follows. For a material, the dielectric constant ($\varepsilon$) can be written as a complex number,
\[ \varepsilon = \varepsilon' - j\varepsilon'' \]  

Eq. 3.24

where, \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary part of the dielectric constant. The \( \varepsilon' \) represents the dispersion, which is the dependence of \( \varepsilon \) of the material on the frequency of an applied field, and the \( \varepsilon'' \) represents the loss characteristic of the dielectric response of dipolar materials, which quantifies the dissipation of electrical energy in the form of heat. Also, the ratio between, \( \varepsilon' \) and \( \varepsilon'' \) is known as the loss tangent,

\[ \tan \delta = \frac{\varepsilon''}{\varepsilon'} \]  

Eq.3.25

Since the complex dielectric constant is related to complex impedance by,

\[ \varepsilon = \frac{1}{j\omega C_0 Z} \]  

Eq. 3.26

with

\[ C_0 = \frac{d}{2\pi f A \varepsilon_0} \]  

Eq. 3.27

then, \( \varepsilon' \) and \( \varepsilon'' \) can be expressed as,

\[ \varepsilon' = \frac{d}{2\pi f A \varepsilon_0} \left[ \frac{-\varepsilon''}{Z'^2 + \varepsilon''^2} \right] \]  

Eq. 3.28

\[ \varepsilon'' = \frac{d}{2\pi f A \varepsilon_0} \left[ \frac{Z'}{Z'^2 + \varepsilon''^2} \right] \]  

Eq. 3.29
where \( d \) is the thickness of the pellet, \( A \) is surface area of the electrode used in IS measurements and \( \varepsilon_0 \) and \( f \) are the vacuum permittivity and the frequency respectively [186].

Figure 3.15 shows the, frequency and temperature dependence of the real part of the dielectric constant (\( \varepsilon' \)) for different Ba %. Towards the low frequency end there is a clear increase in the dielectric function which agrees with the previously published reports for pristine samples [171,187,188,189]. This change is attributed to the slow ionic migration of I\(^-\) [190]. From the same plots it is also evident that with increasing Ba%, \( \varepsilon' \) also increases. This agrees with the assumption we made earlier about more defects formation with increasing Ba % in the sample, which leads to enhancement of I\(^-\) in motion thereby increase the polarization response in this low frequency regime. Also, at low frequencies the value of \( \varepsilon' \) increases with temperature whereas towards high frequencies \(-\)MHz the increase is at smaller rate. In that high frequency region, the polarization response is mainly from reorientation of MA\(^+\) ion with a permanent dipole and the increase in \( \varepsilon' \) can be ascribed to the lattice distortion with Ba incorporation minimize the orientational disorder of MA\(^+\) giving increase polarization response as described in a previous section. As shows in the Figure 3.16, the dielectric loss (\( \varepsilon'' \)) shows 1/f dependence below 10 kHz region, a phenomenon known as ‘Jonscher’s law’ and it reveals the ionic conductivity nature of the material [189, 191].

Moreover, the loss tangent (tan \( \delta \)) plotted against frequency for different temperatures shows high values at low frequencies and the peak value shifts toward the high frequency (shown by an arrow) as the temperature is increased (Figure 3.17). While we do not have an explanation for this behavior; similar behavior for MAPbI\(_3\) thin films was reported in the literature; they were also unable to explain this phenomenon [192].
Figure 3.15. Temperature dependence of real part of dielectric constant for $\text{Ba}^{2+}$ doped MAPbI$_3$ pellets. (Temperatures are given in °C)
Figure 3.16. Temperature dependence of imaginary part of dielectric constant for Ba$^{2+}$ doped MAPbI$_3$ pellets. (Temperatures are given in °C)
Figure 3.17. Temperature and frequency dependence of loss tangent for Ba$^{2+}$ doped MAPbI$_3$ pellets. (Temperatures are given in °C)

In addition, with increasing Ba% in the samples, the value and the peak frequency of tan δ also increases. Towards high frequencies (~MHz), there is almost no loss. As mentioned earlier at low frequencies the dielectric response is coming from I$^-$ ion motion. So, this loss can be attributed to conduction loss of the iodide ions. As more I$^-$ ions are present with the increased doping, they may cause more collisions in ion conduction hence result in conduction loss and thereby increase
the value of loss tangent for one particular temperature. However, the origin of shift of loss tangent peak towards high frequencies with increasing Ba % and temperature (Figure 3.18) is uncertain.

Figure 3.18. Temperature and frequency dependence of peak of loss tangent for 5% and 10% Ba$^{2+}$ doped MAPbI$_3$ samples where the peaks can be seen. (The numbers next to data points represent the sample temperature in °C during the measurements)
3.5. Conclusions

In conclusion, nontoxic Ba doped MAPbI$_3$ polycrystals (MAPb$_{1-x}$Ba$_x$I$_3$ with x= 1.5 and 10) were successfully synthesized and their structural, calorimetric, ionic conductivity and dielectric properties were investigated. From PXRD spectroscopy it was found that the room temperature tetragonal structure of pristine MAPbI$_3$ perovskite was preserved upon Ba$^{2+}$ doping at 1, 5 and 10% dopant concentrations. In addition, lattice expansion was observed with increasing Ba% and it was ascribed to the replacement of Pb$^{2+}$ with Ba$^{2+}$ which has a little larger ionic radius (1.35Å) than Pb$^{2+}$(1.19Å). From the DSC studies it was found that, within the used dopant concentrations, there is no effect on the tetragonal to cubic phase transition temperature. Also using AC impedance spectroscopy, dark conductivity of prepared perovskite samples was found to be increasing with increasing Ba content in the samples. Furthermore, it was found that the conductivity arises mainly from vacancy mediated I$^-$ migration and the observed conductivity behavior with dopants was ascribed to lattice distortion caused by the isovalent ion doping. It was suggested that the lowering of defect formation energies in the distorted lattice may increase the number of vacancies and thereby enhance the I$^-$ migration. Moreover, the bulk dielectric constant was found to be increasing with increasing dopant amounts in the samples and it was correlated to the ordering of MA dipoles and the distortions of the Ba sites in the lattice. Additionally, the temperature dependence of dielectric constants was observed for all the samples and it was attributed to thermal effects on orientation polarization of MA molecules.
REFERENCES


[34]. Liu, C., Li, W., Li, H., Zhang, C., Fan, J., & Mai, Y. (2017). C 60 additive-assisted crystallization in CH 3 NH 3 Pb 0.75 Sn 0.25 I 3 perovskite solar cells with high stability and efficiency. *Nanoscale, 9*(37), 13967-13975.


[117]. "Western Michigan University: Department of Physics, “[Online]. Available: https://wmich.edu/physics/accelerator


120


[158]. DSC Q Series Getting Started Guide (2007), TA Instruments_Waters LLC.


APPENDIX

Permissions from the Copyright Holders to use the following figures in this Ph.D. dissertation

1. Figure 1.2: Comparison of global energy potential with renewable and nonrenewable energy sources (Terawatts per year). Total recoverable reserves are shown for the finite resources. For renewable sources, yearly potential is shown. (Adapted with permission from [Error! Bookmark not defined.])

SPRINGER NATURE LICENSE
TERMS AND CONDITIONS

This Agreement between Mrs. Rasanjali Jayathissa ("You") and Springer Nature ("Springer Nature") consists of your license details and the terms and conditions provided by Springer Nature and Copyright Clearance Center.

License Number: 455964141414
License date: Mar 25, 2019
Licensed Content Publisher: Springer Nature
Licensed Content Publication: Springer eBook
Licensed Content Title: Introduction
Licensed Content Author: Miodam Tariq Chaichan, Hussein A. Kazem
Licensed Content Date: Jan 1, 2018
Type of Use: Thesis/Dissertation
Requestor type: academic/university or research institute
Format: print and electronic
Portion: figures/tables/illustrations
Number of figures/tables/illustrations: 1
Will you be translating? no
Circulation/distribution: <501
Author of this Springer Nature content: no
Title: Investigation of Structural, Optical and electronic properties of modified Methyliammonium Lead Jodide Perovskites
Institution name: Western Michigan University
Expected presentation date: Aug 2019
Portions: Fig. 1.2 Comparing renewable and nonrenewable energy sources
Requestor Location: Mrs. Rasanjali Jayathissa
5950 Beckley Rd
APT 3D
KALAMAZOO, MI 49069
United States
Attn: Mrs. Rasanjali Jayathissa

Total: 0.00 USD

Terms and Conditions

Springer Nature Terms and Conditions for RightsLink Permissions
Springer Nature Customer Service Centre GmbH (the License) hereby grants you a non-exclusive, worldwide licence to reproduce the material and for the purpose and requirements specified in the attached copy of your order form, and for no other use, subject to the conditions below:

1. The Licensor warrants that it has, to the best of its knowledge, the rights to license reuse of this material. However, you should ensure that the material you are requesting is

https://s0263.copyright.com/CustomerAdmin/PLF.jsp?ref=b1df87c3-893b-42b9-bb506-e41cd9f87ef
original to the Licensor and does not carry the copyright of another entity (as credited in the published version).

If the credit line on any part of the material you have requested indicates that it was reprinted or adapted with permission from another source, then you should also seek permission from that source to reuse the material.

2. Where print only permission has been granted for a fee, separate permission must be obtained for any additional electronic re-use.

3. Permission granted free of charge for material in print is also usually granted for any electronic version of that work, provided that the material is incidental to your work as a whole and that the electronic version is essentially equivalent to, or substitutes for, the print version.

4. A licence for ‘post on a website’ is valid for 12 months from the licence date. This licence does not cover use of full text articles on websites.

5. Where 'reuse in a dissertation/thesis' has been selected the following terms apply:
   Print rights of the final author's accepted manuscript (for clarity, NOT the published version) for up to 100 copies, electronic rights for use only on a personal website or institutional repository as defined by the Sherpa guideline (www.sherpa.ac.uk/romeo/).

6. Permission granted for books and journals is granted for the lifetime of the first edition and does not apply to second and subsequent editions (except where the first edition permission was granted free of charge or for signatories to the STM Permissions Guidelines http://www.stm-assoc.org/copyright-legal-affairs/permissions/permissions-guidelines/), and does not apply for editions in other languages unless additional translation rights have been granted separately in the licence.

7. Rights for additional components such as custom editions and derivatives require additional permission and may be subject to an additional fee. Please apply to Journalpermissions@springernature.com/bookpermissions@springernature.com for these rights.

8. The Licensor’s permission must be acknowledged next to the licensed material in print. In electronic form, this acknowledgement must be visible at the same time as the figures/tables/illustrations or abstract, and must be hyperlinked to the journal/book’s homepage. Our required acknowledgement format is in the Appendix below.

9. Use of the material for incidental promotional use, minor editing privileges (this does not include cropping, adapting, omitting material or any other changes that affect the meaning, intention or moral rights of the author) and copies for the disabled are permitted under this licence.

10. Minor adaptations of single figures (changes of format, colour and style) do not require the Licensor’s approval. However, the adaptation should be credited as shown in Appendix below.

Appendix — Acknowledgements:

For Journal Content:
Reprinted by permission from [the Licensor]: [Journal Publisher (e.g. Nature/Springer/Palgrave)] [JOURNAL NAME] [REFERENCE CITATION (Article name, Author(s) Name), [COPYRIGHT] (year of publication)]

For Advance Online Publication papers:
Reprinted by permission from [the Licensor]: [Journal Publisher (e.g. Nature/Springer/Palgrave)] [JOURNAL NAME] [REFERENCE CITATION (Article name, Author(s) Name), [COPYRIGHT] (year of publication), advance online publication, day month year (doi: 10.1038/s[.JOURNAL ACRONYM];)]

https://s100.copyright.com/Customer/Admin/PLF.jsp?ref=4b9fe7c3-85f8-452b-8556-a4fbc0c9c79ef
2. Figure 1.6: Basic classification of photovoltaics (Adapted with permission from [Error! Bookmark not defined.])
RE: REQUEST FOR THE PERMISSION TO USE YOUR COPYRIGHTED WORK IN MY DOCTORAL THESIS

Katie Sinclair <katies@spie.org>
Wed 3/27/2019 5:37 PM
To: Rasanjali Jayathissa <rasanjali.jayathissa@wmich.edu>


Best,
Katie

From: Rasanjali Jayathissa <rasanjali.jayathissa@wmich.edu>
Sent: Wednesday, March 27, 2019 2:35 PM
To: Katie Sinclair <katies@spie.org>
Subject: Re: REQUEST FOR THE PERMISSION TO USE YOUR COPYRIGHTED WORK IN MY DOCTORAL THESIS

Dear Katie,

Thank you so much for giving me permission from SPIE. I already contacted the first author of the publication and I have copied his email reply regarding his permission on the matter below for your reference.

From: Ashwith Chilvery <achilver@xula.edu>
Sent: Wednesday, March 27, 12:42 PM
To: Rasanjali Jayathissa
Subject: Re: REQUEST FOR TO USE YOUR COPYRIGHTED WORK IN MY DOCTORAL THESIS

Hello Rasanjali,

Sure, you may use it for publication in your dissertation provided you give the due credit to the article as mentioned in the journal guidelines.

Good Luck!
Ashwith

On Wed, Mar 27, 2019 at 9:03 AM Rasanjali Jayathissa <rasanjali.jayathissa@wmich.edu> wrote:

Dear Dr. A.K.Chilvery,

I am Rasanjali Jayathissa, a final year graduate student at the Department of Physics, Western Michigan University, MI, USA. I am in the process of preparing my doctoral dissertation and seeking your permission to include the following materials in my dissertation titled "Investigation of Structural, Optical and electronic properties of modified Methylammonium Lead Iodide Perovskites ".

Title of the publication:
Perovskites: transforming photovoltaics, a mini-review, Ashwith Kumar Chilvery, Ashok K. Batra, Bin Yang, Kai Xiao, Padmaja Guggilla, Mohan D. Aggarwal, Raja Surabhi, Ravi B. Lal, James R. Currie, Benjamin G. Penn

Journal: Journal of Photonics for energy
Vol. and year: vol 5 2015

Materials of interest: Fig. 1 Basic classification of photovoltaics.

https://outlook.office.com/mail/inbox/idAAQqAGYzOT2MGQwLtkwMjATNDowMi95NTltlWm0n2QytYTBntfT1M9AQAPfuQio0nTfHI8iW9ySq%2F...
I would like to request your permission to include the above figure, published in the above-mentioned article, in my doctoral dissertation. The source will receive full credit in the work. This figure will be used to explain the main classification of solar cells in the introduction section of my work.

By agreeing to the use of the item in my dissertation, you give ProQuest Information and Learning (PQIL) the right to supply copies of this material on demand as part of my doctoral dissertation. Please attach any other terms and conditions for the proposed use of this item.

Thank you for your time and attention to this matter.

Sincerely,
Rasanjali Jayathissa

---

Regards,
Ashutosh Chalvery, Ph.D.
Assistant Professor
Department of Physics and Materials Engineering
Xavier University of Louisiana
1 Drexel Dr, New Orleans, LA 70125
Ph: 504-520-5149
Fax: 504-520-7992

Sincerely,
Rasanjali

---

Rasanjali Jayathissa
Graduate Teaching Assistant
Department of Physics
Western Michigan University

https://outlook.office.com/mail/inbox/id/AAQiAGYzOTAzMGQwLTkwMjA5NTdhLM0NjZ2Q0YTlhNTl1MFAQPrUOIn1TIHIBWrSx%2F...
From: Katie Sinclair <kates@spie.org>
Sent: Wednesday, March 27, 2019 5:18 PM
To: Rasanjali Jayathissa
Subject: RE: REQUEST FOR THE PERMISSION TO USE YOUR COPYRIGHTED WORK IN MY DOCTORAL THESIS

Dear Rasanjali,

Thank you for seeking permission from SPIE to reprint material from our publications. Publisher’s permission is hereby granted under the following conditions:

1. you obtain permission of one of the authors;
2. the material to be used has appeared in our publication without credit or acknowledgment to another source; and
3. you credit the original SPIE publication. Include the authors’ names, title of paper, volume title, SPIE volume number, and year of publication in your credit statement.

Best,
Katie Sinclair
Editorial Assistant, Publications
SPIE
+1 350 685 5436
kates@spie.org

SPIE is the international society for optics and photonics
http://SPIE.org

From: Rasanjali Jayathissa <rasanjali.jayathissa@wmich.edu>
Sent: Wednesday, March 27, 2019 1:50 PM
To: reprint_permission <reprint_permission@spie.org>
Subject: REQUEST FOR THE PERMISSION TO USE YOUR COPYRIGHTED WORK IN MY DOCTORAL THESIS

To whom it may concern,

I am Rasanjali Jayathissa, a final year graduate student at the Department of Physics, Western Michigan University, MI, USA. I am in the process of preparing my doctoral dissertation and seeking your permission to include the following materials in my dissertation titled "Investigation of Structural, Optical and electronic properties of modified Methylammonium Lead Iodide Perovskites ".

**Title of the publication:**
Perovskites: transforming photovoltaics, a mini-review, Ashwith Kumar Chilvery, Ashok K. Batra, Bin Yang, Kai Xiao, Padmaja Guggilla, Mohan D. Aggarwal, Reja Surabhi, Revi B. Lai, James R. Currie, Benjamin G. Penn

**Journal:** Journal of Photonics for energy
**Vol., year and page no:** vol 5, 2015, 057402-2

**Materials of interest:** Fig. 1 Basic classification of photovoltaics.

https://outlook.office.com/mail/inbox/idAAQkAGYzOTAzMSQwTkxwMjATNDcwMi05NTdLWM0NQ0YTbHNTIT1MQA0APnOIXr1TIHbWIrSQt%2F...
I would like to request your permission to include the above figure, published in the above-mentioned article, in my doctoral dissertation. The source will receive full credit in the work. This figure will be used to explain the main classification of solar cells in the introduction section of my work.

By agreeing to the use of the item in my dissertation, you give ProQuest Information and Learning (PQIL) the right to supply copies of this material on demand as the part of my doctoral dissertation. Please attach any other terms and conditions for the proposed use of this item.

Thank you for your time and attention to this matter.

Sincerely,
Rasanjali Jayathissa

Rasanjali Jayathissa
Graduate Teaching Assistant
Department of Physics
Western Michigan University
3. Figure 1.8 (a) Cubic perovskite crystal structure. (Adapted with permission from [Error! Bookmark not defined.]) and Figure 1.9: Calculated $t$ and $\mu$ factors for some OIMH perovskites. The corresponding formamidinium (CH(NH$_2$)$_2$)$^+$ based halides are expected to have intermediate values between those of methyl ammonium (CH$_3$NH$_3^+$ or MA) and ethyl ammonium (CH$_3$CH$_2$NH$_3^+$ or EA) compounds shown. (Adapted with permission from [16]).
Springer Nature Customer Service Centre GmbH (the Licensor) hereby grants you a non-exclusive, world-wide licence to reproduce the material and for the purpose and requirements specified in the attached copy of your order form, and for no other use, subject to the conditions below:

1. The Licensor warrants that it has, to the best of its knowledge, the rights to license reuse of this material. However, you should ensure that the material you are requesting is original to the Licensor and does not carry the copyright of another entity (as credited in the published version).

   If the credit line on any part of the material you have requested indicates that it was reprinted or adapted with permission from another source, then you should also seek permission from that source to reuse the material.

2. Where print only permission has been granted for a fee, separate permission must be obtained for any additional electronic re-use.

3. Permission granted free of charge for material in print is also usually granted for any electronic version of that work, provided that the material is incidental to your work as a whole and that the electronic version is essentially equivalent to, or substitutes for, the print version.

4. A licence for 'post on a website' is valid for 12 months from the licence date. This licence does not cover use of full text articles on websites.

5. Where 'reuse in a dissertation/thesis' has been selected the following terms apply: Print rights of the final author's accepted manuscript (for clarity, NOT the published version) for up to 100 copies, electronic rights for use only on a personal website or institutional repository as defined by the Sherpa guideline (www.sherpa.ac.uk/romeo/).

6. Permission granted for books and journals is granted for the lifetime of the first edition and does not apply to second and subsequent editions (except where the first edition permission was granted free of charge or for signatories to the STM Permissions Guidelines http://www.stm-assoc.org/copyright-legal-affairs/permissions/permissions-guidelines/), and does not apply for editions in other languages unless additional translation rights have been granted separately in the licence.

7. Rights for additional components such as custom editions and derivatives require additional permission and may be subject to an additional fee. Please apply to Journalpermissions@springernature.com/bookpermissions@springernature.com for these rights.

8. The Licensor's permission must be acknowledged next to the licensed material in print. In electronic form, this acknowledgement must be visible at the same time as the figures/tables/illustrations or abstract, and must be hyperlinked to the journal/book's homepage. Our required acknowledgement format is in the Appendix below.

9. Use of the material for incidental promotional use, minor editing privileges (this does not include cropping, adapting, omitting material or any other changes that affect the meaning, intention or moral rights of the author) and copies for the disabled are permitted under this licence.

10. Minor adaptations of single figures (changes of format, colour and style) do not require the Licensor's approval. However, the adaptation should be credited as shown in Appendix below.

**Appendix — Acknowledgements:**

**For Journal Content:**
Reprinted by permission from [the Licensor]: [Journal Publisher (e.g. Nature/Springer/Palgrave)] [JOURNAL NAME] [REFERENCE CITATION (Article name, Author(s) Name), [COPYRIGHT] (year of publication)]

**For Advance Online Publication papers:**
Reprinted by permission from [the Licensor]: [Journal Publisher (e.g. Nature/Springer/Palgrave)] [JOURNAL NAME] [REFERENCE CITATION (Article name, Author(s) Name),

https://s100.copyright.com/CustomerAdmin/PLF.jsp?ref=0179d3c4-fc7f-40a6-922d-0059b9c703
2/3

135
4. Figure 1.11 (a) Electronic band structure with (left) and without (middle) the MA cation and contributions of MA, Pb and I on the DOS (right) of low temperature orthorhombic phase (adapted with permission from [Error! Bookmark not defined.])
requirements specified in the attached copy of your order form, and for no other use, subject
to the conditions below:

1. The Licensor warrants that it has, to the best of its knowledge, the rights to license reuse
   of this material. However, you should ensure that the material you are requesting is
   original to the Licensor and does not carry the copyright of another entity (as credited in
   the published version).

   If the credit line on any part of the material you have requested indicates that it was
   reprinted or adapted with permission from another source, then you should also seek
   permission from that source to reuse the material.

2. Where print only permission has been granted for a fee, separate permission must be
   obtained for any additional electronic re-use.

3. Permission granted free of charge for material in print is also usually granted for any
   electronic version of that work, provided that the material is incidental to your work as a
   whole and that the electronic version is essentially equivalent to, or substitutes for, the
   print version.

4. A licence for 'post on a website' is valid for 12 months from the licence date. This licence
   does not cover use of full text articles on websites.

5. Where 'reuse in a dissertation/thesis' has been selected the following terms apply:
   Print rights of the final author's accepted manuscript (for clarity, NOT the published
   version) for up to 100 copies, electronic rights for use only on a personal website or
   institutional repository as defined by the Sherpa guideline (www.sherpa.ac.uk/romeo/).

6. Permission granted for books and journals is granted for the lifetime of the first edition and
   does not apply to second and subsequent editions (except where the first edition
   permission was granted free of charge or for signatories to the STM Permissions Guidelines
   http://www.stm-assoc.org/copyright-legal-affairs/permissions/permissions-guidelines/),
   and does not apply for editions in other languages unless additional translation rights have
   been granted separately in the licence.

7. Rights for additional components such as custom editions and derivatives require additional
   permission and may be subject to an additional fee. Please apply to
   Journalpermissions@springernature.com/bookpermissions@springernature.com for these
   rights.

8. The Licensor's permission must be acknowledged next to the licensed material in print. In
   electronic form, this acknowledgement must be visible at the same time as the
   figures/tables/illustrations or abstract, and must be hyperlinked to the journal/book's
   homepage. Our required acknowledgement format is in the Appendix below.

9. Use of the material for incidental promotional use, minor editing privileges (this does not
   include cropping, adapting, omitting material or any other changes that affect the meaning,
   intention or moral rights of the author) and copies for the disabled are permitted under this
   licence.

10. Minor adaptations of single figures (changes of format, colour and style) do not require the
    Licensor's approval. However, the adaptation should be credited as shown in Appendix
    below.

Appendix — Acknowledgements:

For Journal Content:
Reprinted by permission from [the Licensor]: [Journal Publisher (e.g.
Nature/Springer/Palgrave)] [JOURNAL NAME] [REFERENCE CITATION
(Article name, Author(s) Name), [COPYRIGHT] (year of publication)
For Advance Online Publication papers:
Reprinted by permission from [the Licensor]: [Journal Publisher (e.g. Nature/Springer/Palgrave)] [JOURNAL NAME] [REFERENCE CITATION (Article name, Author(s) Name), [COPYRIGHT] (year of publication), advance online publication, day month year (doi: 10.1038/sj.[JOURNAL ACRONYM].)

For Adaptations/Translations:
Adapted/Translated by permission from [the Licensor]: [Journal Publisher (e.g. Nature/Springer/Palgrave)] [JOURNAL NAME] [REFERENCE CITATION (Article name, Author(s) Name), [COPYRIGHT] (year of publication)

Note: For any republication from the British Journal of Cancer, the following credit line style applies:

Reprinted/adapted/translated by permission from [the Licensor]: on behalf of Cancer Research UK: [Journal Publisher (e.g. Nature/Springer/Palgrave)] [JOURNAL NAME] [REFERENCE CITATION (Article name, Author(s) Name), [COPYRIGHT] (year of publication)

For Advance Online Publication papers:
Reprinted by permission from [the Licensor]: on behalf of Cancer Research UK: [Journal Publisher (e.g. Nature/Springer/Palgrave)] [JOURNAL NAME] [REFERENCE CITATION (Article name, Author(s) Name), [COPYRIGHT] (year of publication), advance online publication, day month year (doi: 10.1038/sj.[JOURNAL ACRONYM])

For Book content:
Reprinted/adapted by permission from [the Licensor]: [Book Publisher (e.g. Palgrave Macmillan, Springer etc)] [Book Title] by [Book author(s)] [COPYRIGHT] (year of publication)

Other Conditions:

Version 1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-645-2777.
5. Figure 1.11 Band structure and energy gap for (b) cubic (c) tetragonal and (d) orthorhombic phases (adapted with permission from [Error! Bookmark not defined.]) of MAPbI$_3$ perovskite.
This Agreement between Mrs. Rasanjali Jayathissa ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

<table>
<thead>
<tr>
<th>License Number</th>
<th>4560310061217</th>
</tr>
</thead>
<tbody>
<tr>
<td>License date</td>
<td>Apr 01, 2019</td>
</tr>
<tr>
<td>Licensed Content Publisher</td>
<td>John Wiley and Sons</td>
</tr>
<tr>
<td>Licensed Content Publication</td>
<td>Advanced Materials</td>
</tr>
<tr>
<td>Licensed Content Title</td>
<td>Unique Properties of Halide Perovskites as Possible Origins of the Superior Solar Cell Performance</td>
</tr>
<tr>
<td>Licensed Content Author</td>
<td>Wan-Jian Yin, Tingting Shi, Yanfa Yan</td>
</tr>
<tr>
<td>Licensed Content Date</td>
<td>May 15, 2014</td>
</tr>
<tr>
<td>Licensed Content Volume</td>
<td>26</td>
</tr>
<tr>
<td>Licensed Content Issue</td>
<td>27</td>
</tr>
<tr>
<td>Licensed Content Pages</td>
<td>6</td>
</tr>
<tr>
<td>Type of use</td>
<td>Dissertation/Thesis</td>
</tr>
<tr>
<td>Requestor type</td>
<td>University/Academic</td>
</tr>
<tr>
<td>Format</td>
<td>Print and electronic</td>
</tr>
<tr>
<td>Portion</td>
<td>Figure/table</td>
</tr>
<tr>
<td>Number of figures/tables</td>
<td>1</td>
</tr>
<tr>
<td>Original Wiley figure/table number(s)</td>
<td>Figure S3. The band structures of CH3NH3PbI3 at (a) Pm3m, (b) I4/mcm, (c) Pbnn</td>
</tr>
<tr>
<td>Will you be translating?</td>
<td>No</td>
</tr>
<tr>
<td>Title of your thesis / dissertation</td>
<td>Investigation of Structural, Optical and electronic properties of modified Methylammonium Lead Iodide Perovskites</td>
</tr>
<tr>
<td>Expected completion data</td>
<td>Aug 2019</td>
</tr>
<tr>
<td>Expected size (number of pages)</td>
<td>100</td>
</tr>
</tbody>
</table>
| Requestor Location   | Mrs. Rasanjali Jayathissa  
5050 Beckley Rd  
APT 2D  
KALAMAZOO, MI 49009  
United States  
Attn: Mrs. Rasanjali Jayathissa |
| Publisher Tax ID     | EU826007151   |
| Total                | 0.00 USD      |

**TERMS AND CONDITIONS**

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a "Wiley Company") or handled on behalf of a society with
which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at http://myaccount.copyright.com).

Terms and Conditions

- The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.

- You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, and any CONTENT (PDF or image file) purchased as part of your order, is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.

- With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner. For STM Signatory Publishers clearing permission under the terms of the STM Permissions Guidelines only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts. You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.

- The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you
shall not assert any such right, license or interest with respect thereto

- NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.

- WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.

- You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.

- IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, Provisioning, viewing or use of the Materials regardless of the form of action, whether for breach of contract, breach of warranty, tort, negligence, infringement or otherwise (including, without limitation, damages based on loss of profits, data, files, use, business opportunity or claims of third parties), and whether or not the party has been advised of the possibility of such damages. This limitation shall apply notwithstanding any failure of essential purpose of any limited remedy provided herein.

- Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.

- The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.

- This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY’s prior written consent.
Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.

These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.

In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.

WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.

This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License

The Creative Commons Attribution License (CC-BY) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-commercial uses.

Creative Commons Attribution Non-Commercial License

The Creative Commons Attribution Non-Commercial (CC-BY-NC) License permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes (see below).

Creative Commons Attribution-Non-Commercial-NoDerivs License

The Creative Commons Attribution Non-Commercial-NoDerivs License (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

Use by commercial "for-profit" organizations
6. Figure 1.12: The schematic optical absorption mechanisms of (a) 1\textsuperscript{st} generation (Si), (b) 2\textsuperscript{nd} generation (GaAs) and (c) perovskite halide (MAPbI\textsubscript{3}) photo absorbers (adapted with permission from [Error! Bookmark not defined.]). \( E_{g}^{i} \) and \( E_{g}^{d} \) represent indirect and direct bandgaps respectively.
7. Figure 1.13: (a) Electronic density of states (DOS), (b) Joint density of states (JDOS) (c) optical absorption coefficient for MAPbI$_3$ and GaAs and (d) Calculated maximum efficiencies of MAPbI$_3$, CIS, CZTS and GaAs as a function of film thickness. (Adapted with permission from [26]). CIS and CZTS represent copper-indium-gallium-selenide and copper-zinc-tin-selenide solar cell absorbers respectively.
TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a “Wiley Company”) or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively “WILEY”). By clicking “accept” in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., (“CCC’s Billing and Payment terms and conditions”), at the time that you opened your RightsLink account (these are available at any time at http://myaccount.copyright.com).

Terms and Conditions

- The materials you have requested permission to reproduce or reuse (the “Wiley Materials”) are protected by copyright.

- You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, and any CONTENT (PDF or image file) purchased as part of your order, is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.

- With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner. For STM Signatory Publishers clearing under the terms of the STM Permissions Guidelines only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts. You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.

- The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc., the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right,
license or interest to any trademark, trade name, service mark or other branding
("Marks") of WILEY or its licensors is granted hereunder, and you agree that you
shall not assert any such right, license or interest with respect thereto.

- NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR
  REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY,
  EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS
  OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE
  MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED
  WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY
  QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY,
  INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES
  ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED
  BY YOU.

- WILEY shall have the right to terminate this Agreement immediately upon breach of
  this Agreement by you.

- You shall indemnify, defend and hold harmless WILEY, its Licensors and their
  respective directors, officers, agents and employees, from and against any actual or
  threatened claims, demands, causes of action or proceedings arising from any breach
  of this Agreement by you.

- IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR
  ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY
  SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR
  PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN
  CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR
  USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION,
  WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT,
  NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT
  LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE,
  BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER
  OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH
  DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY
  FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED
  HEREIN.

- Should any provision of this Agreement be held by a court of competent jurisdiction
to be illegal, invalid, or unenforceable, that provision shall be deemed amended to
achieve as nearly as possible the same economic effect as the original provision, and
the legality, validity and enforceability of the remaining provisions of this Agreement
shall not be affected or impaired thereby.

- The failure of either party to enforce any term or condition of this Agreement shall not
constitute a waiver of either party's right to enforce each and every term and condition
of this Agreement. No breach under this agreement shall be deemed waived or
excused by either party unless such waiver or consent is in writing signed by the party
granting such waiver or consent. The waiver by or consent of a party to a breach of
any provision of this Agreement shall not operate or be construed as a waiver of or
consent to any other or subsequent breach by such other party.

- This Agreement may not be assigned (including by operation of law or otherwise) by
you without WILEY's prior written consent.
• Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.

• These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.

• In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.

• WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

• This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.

• This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS
Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License
The Creative Commons Attribution License (CC-BY) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

Creative Commons Attribution Non-Commercial License
The Creative Commons Attribution Non-Commercial (CC-BY-NC)License permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes (see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License
The Creative Commons Attribution Non-Commercial-NoDerivs License (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

https://s1000.copyright.com/CustomerAdmin/PLF.jsp?ref=28f9b33ca0d44e9f8b8989251212bd92
Use by commercial "for-profit" organizations
Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee. Further details can be found on Wiley Online Library [http://olabout.wiley.com/WileyCDA/Section/id-410895.html](http://olabout.wiley.com/WileyCDA/Section/id-410895.html)

Other Terms and Conditions:

v1.10 Last updated September 2015
Questions? [customercare@copyright.com](mailto:customercare@copyright.com) or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.
8. Figure 1.14: Schematics of (a) Bandgap tuning by compositional engineering of elements in OILH perovskites (adapted with permission from [Error! Bookmark not defined.])
This Agreement between Mrs. Rasanjali Jayathissa ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

<table>
<thead>
<tr>
<th>License Number</th>
<th>4564261405704</th>
</tr>
</thead>
<tbody>
<tr>
<td>License date</td>
<td>Apr 08, 2019</td>
</tr>
<tr>
<td>Licensed Content Publisher</td>
<td>Elsevier</td>
</tr>
<tr>
<td>Licensed Content Publication</td>
<td>Joule</td>
</tr>
<tr>
<td>Licensed Content Title</td>
<td>ABX3 Perovskites for Tandem Solar Cells</td>
</tr>
<tr>
<td>Licensed Content Author</td>
<td>Miguel Anaya,Gabriel Lozano,Mauricio E. Calvo,Herrán Mígez</td>
</tr>
<tr>
<td>Licensed Content Date</td>
<td>Dec 20, 2017</td>
</tr>
<tr>
<td>Licensed Content Volume</td>
<td>1</td>
</tr>
<tr>
<td>Licensed Content Issue</td>
<td>4</td>
</tr>
<tr>
<td>Licensed Content Pages</td>
<td>25</td>
</tr>
<tr>
<td>Start Page</td>
<td>769</td>
</tr>
<tr>
<td>End Page</td>
<td>793</td>
</tr>
<tr>
<td>Type of Use</td>
<td>reuse in a thesis/dissertation</td>
</tr>
<tr>
<td>Intended publisher of new work</td>
<td>other</td>
</tr>
<tr>
<td>Portion</td>
<td>figures/tables/illustrations</td>
</tr>
<tr>
<td>Number of figures/tables/illustrations</td>
<td>1</td>
</tr>
<tr>
<td>Format</td>
<td>both print and electronic</td>
</tr>
<tr>
<td>Are you the author of this Elsevier article?</td>
<td>No</td>
</tr>
<tr>
<td>Will you be translating?</td>
<td>No</td>
</tr>
<tr>
<td>Original figure numbers</td>
<td>Figure 3. Bandgap Tunability of ABX3 Perovskites</td>
</tr>
<tr>
<td>Title of your thesis/dissertation</td>
<td>Investigation of Structural, Optical and electronic properties of modified Methylammonium Lead Iodide Perovskites</td>
</tr>
<tr>
<td>Publisher of new work</td>
<td>Western Michigan University</td>
</tr>
<tr>
<td>Expected completion date</td>
<td>Aug 2019</td>
</tr>
<tr>
<td>Estimated size (number of pages)</td>
<td>100</td>
</tr>
<tr>
<td>Requestor Location</td>
<td>Mrs. Rasanjali Jayathissa 5059 Beckley Rd APT 2D KALAMAZOO, MI 49009 United States Attn: Mrs. Rasanjali Jayathissa</td>
</tr>
<tr>
<td>Publisher Tax ID</td>
<td>98-0397604</td>
</tr>
</tbody>
</table>
INTRODUCTION
1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS
2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol./edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all
claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. Translation: This permission is granted for non-exclusive world English rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. Posting licensed content on any Website: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxx or the Elsevier homepage for books at http://www.elsevier.com. Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. For journal authors: the following clauses are applicable in addition to the above:

Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.). Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of

https://s100.copyright.com/Customer/Admin/PLF.jsp?ref=5e2df9c3-35b6-4f74-b552-891f174edceeb

3/6
articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.

Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement

- After the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (PJA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.

Policies for sharing publishing journal articles differ for subscription and gold open access articles:

Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others’ research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossRef logo, the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier’s posting policy for further information.

https://s100.copyright.com/CustomerAdmin/PLF.jsp?ref=0e2f09c3-3eb0-41f4-b0d2-f9f74edc6eb

4/5/2019

RightsLink Printable License
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

19. **Thesis/Dissertation:** If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PIs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

**Elsevier Open Access Terms and Conditions**

You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our [open access license policy](#) for more information.

**Terms & Conditions applicable to all Open Access articles published with Elsevier:**

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated. The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their use complies with the terms and conditions determined by the rights holder.

**Additional Terms & Conditions applicable to each Creative Commons user license:**

**CC BY:** The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at [http://creativecommons.org/licenses/by/4.0](http://creativecommons.org/licenses/by/4.0).

**CC BY-NC-SA:** The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at [http://creativecommons.org/licenses/by-nc-sa/4.0](http://creativecommons.org/licenses/by-nc-sa/4.0).

**CC BY-NC-ND:** The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at [http://creativecommons.org/licenses/by-nc-nd/4.0](http://creativecommons.org/licenses/by-nc-nd/4.0).

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:
• Associating advertising with the full text of the Article
• Charging fees for document delivery or access
• Article aggregation
• Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. Other Conditions:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.
9. Figure 1.15: (b) a multidomain ferroelectric thin-film as hypothesized for hybrid halide perovskite solar cells. The diffusion highways for electrons and holes are shown by blue and red lines with arrows respectively (adapted with permission from [46]).
Dear Sir/Madam,

I am Rasanjali Jayathissa, a final year graduate student at the Department of Physics, Western Michigan University, MI, USA. I am in the process of preparing my doctoral dissertation and seeking your permission to include the following materials in my dissertation titled “Investigation of Structural, Optical and electronic properties of modified Methylammonium Lead Iodide Perovskites”.

Details of the publication:

Atomistic Origins of High-Performance in Hybrid Halide Perovskite Solar Cells


DOI: 10.1021/nl500930f
Publication Date (Web): March 31, 2014
Copyright © 2014 American Chemical Society

Materials of interest:
Figure 5. (c,f) a multidomain ferroelectric thin-film. In the multidomain ferroelectric, which we propose for hybrid perovskites, electrons will move along minima in the potential, while holes will move along maxima (i.e., antiphase boundaries).

I would like to request your permission to include the above figure, published in the above-mentioned article, in my doctoral dissertation. The source will receive full credit in the work. This figure will be used to explain the ferroelectric effect in the introduction section of my work.

By agreeing to the use of the item in my dissertation, you give ProQuest Information and Learning(PQI) the right to supply copies of this material on demand as part of my doctoral dissertation. Please attach any other terms and conditions for the proposed use of this item.

Thank you for your time and attention to this matter.

Sincerely,
Rasanjali Jayathissa

Rasanjali Jayathissa
Graduate Teaching Assistant
Department of Physics
Western Michigan University

[CML: MCI661757]
10. Figure 1.16: Representative fabrication methods for perovskite thin films: (a) One-step spin coating method (b) Two-step spin coating method (c) Doctor blade method (d) Dual source vapor deposition method (e) Sequential vapor deposition method and (f) Vapor-assisted solution method. (a), (b), (d), (e) and (f) are adapted with permission from [54].
INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol / edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all
claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC’s Billing and Payment terms and conditions. These terms and conditions, together with CCC’s Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC’s Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. Translation: This permission is granted for non-exclusive world English rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. Posting licensed content on any Website: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu. Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. For journal authors: the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author’s own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.). Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of
articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement

- After the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (PJA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.

Policies for sharing publishing journal articles differ for subscription and gold open access articles:

Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others’ research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier’s posting policy for further information.

https://s100.copyright.com/CustomerAdmin/PLF.jsp?ref=39244a20-ficc-45c-ab13-f55faa6ae0e8

165
18. For book authors the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. Posting to a repository: Authors are permitted to post a summary of their chapter only in their institution's repository.

19. Thesis/Dissertation: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PIs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated. The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.

CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.

CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0.

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

https://s100.copyright.com/CustomerAdmin/PLF.jsp?rel=39244a26-fdbc-4f5c-ab13-f5fa6ae6e8
Associating advertising with the full text of the Article
Charging fees for document delivery or access
Article aggregation
Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. Other Conditions:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.
11. Figure 1.17: Schematic diagrams of perovskite solar cells in the (a) n-i-p mesoscopic, (b) n-i-p planar, (c) p-i-n planar, (d) p-i-n mesoscopic structures (adapted with permission from [56]) and Figure 1.18: Schematic diagram showing the energy levels, from left to right, for representative cathode, ETM, absorber, HTM and anode material (copyright [56]).
Rasanjali Jayathissa

Graduate Teaching Assistant

Department of Physics

Western Michigan University

From: Song, Zhaoning <Zhaoning.Song@utoledo.edu>
Sent: Friday, April 5, 2019 7:48 PM
To: Rasanjali Jayathissa
Subject: Re: REQUEST FOR THE PERMISSION TO USE YOUR COPYRIGHTED WORK IN MY DOCTORAL THESIS

Hi Rasanjali,

Thank you for your interest in our paper. You are granted the right to use the figures in your thesis. Best luck for your dissertation.

Regards,

Zhaoning Song
Research Assistant Professor
Department of Physics and Astronomy
University of Toledo
2500 Dorr St, B1 Building, Toledo, OH 43606
https://sites.google.com/site/zhaoningsong/

From: Rasanjali Jayathissa <rasanjali.jayathissa@wmich.edu>
Sent: Friday, April 5, 2019 13:43
To: Song, Zhaoning
Subject: REQUEST FOR THE PERMISSION TO USE YOUR COPYRIGHTED WORK IN MY DOCTORAL THESIS

Dear Dr. Zhaoning Song,

I am Rasanjali Jayathissa, a final year graduate student at the Department of Physics, Western Michigan University, MI, USA. I am in the process of preparing my doctoral dissertation and seeking your permission to include the following materials in my dissertation titled "Investigation of Structural, Optical and electronic properties of modified Methylammonium Lead Iodide Perovskites".

**Details of the publication:**

Pathways toward high-performance perovskite solar cells: review of recent advances in organo-metal halide perovskites for photovoltaic applications

Zhaoning Song, Suneth C. Watthage, Adam B. Phillips, Michael J. Heben

*J. of Photonics for Energy, 6(2), 022001* (2016). [https://doi.org/10.1117/1.JPE.6.022001](https://doi.org/10.1117/1.JPE.6.022001)

**Materials of interest:**

- Fig 2. Schematic diagrams of perovskite solar cells in the (a) n-i-p mesoscopic, (b) n-i-p planar, (c) p-i-n planar, and (d) p-i-n mesoscopic structures.
- Fig 5. Diagram showing the energy levels, from left to right, for representative cathode, n-type (ETM), absorber, p-type (HTM), and anode materials.
4/6/2019

I would like to request your permission to include the above figures, published in the above-mentioned article, in my doctoral dissertation. The source will receive full credit in the work. These figures will be used to explain perovskite device architecture in the introduction section of my work.

By agreeing to the use of the item in my dissertation, you give ProQuast Information and Learning (PQL!) the right to supply copies of this material on demand as part of my doctoral dissertation. Please attach any other terms and conditions for the proposed use of this item.

Thank you for your time and attention to this matter.

Sincerely,

Rasanjali Jayathissa

Rasanjali Jayathissa
Graduate Teaching Assistant
Department of Physics
Western Michigan University

---------------------------------------------------

Thank you!

Sincerely,

Rasanjali

Rasanjali Jayathissa
Graduate Teaching Assistant
Department of Physics
Western Michigan University

From: Katie Sinclair <kats@pql.org>
Sent: Wednesday, March 27, 2019 5:37 PM
To: Rasanjali Jayathissa
Subject: RE: REQUEST FOR THE PERMISSION TO USE YOUR COPYRIGHTED WORK IN MY DOCTORAL THESIS


Best,

Katie

From: Rasanjali Jayathissa <rasanjali.jayathissa@wmich.edu>
Sent: Wednesday, March 27, 2019 2:35 PM
To: Katie Sinclair <kats@pql.org>
Subject: Re: REQUEST FOR THE PERMISSION TO USE YOUR COPYRIGHTED WORK IN MY DOCTORAL THESIS

Dear Katie,

Thank you so much for giving me permission from SPIE. I already contacted the first author of the publication and I have copied his email reply regarding his permission on the matter below for your reference.

From: Ashwath Chilvery <ashwath@pql.org>
Sent: Wednesday, March 27, 12:42 PM

https://outlook.office.com/mail/inbox/id/AQ4kAGYzOTAzMGQxLTMkJTl8Mj1MNjI5MTM3MDQyMDM5NzEwMDIyMjMwNjI1MzA1NTI1MgQAPhIiM1THI8bW15%2F...
12. Figure 2.21: A schematic of room temperature tetragonal unit cell of MAPbI$_3$ perovskite. [Adapted with permission from [Error! Bookmark not defined.]]

Materials of interest:
Figure. 1 Structure models of CH3NH3PbI3 with (a) cubic, (b) tetragonal and (c) orthorhombic structures.

I would like to request your permission to include the above figure, published in the above-mentioned article, in my doctoral dissertation. The source will receive full credit in the work. This figure will be used to show the structure models of MAPbI3.

By agreeing to the use of the item in my dissertation, you give ProQuest Information and Learning (PQIL) the right to supply copies of this material on demand as the part of my doctoral dissertation. Please attach any other terms and conditions for the proposed use of this item.

Thank you for your time and attention to this matter.

Sincerely,
Rasanjali Jayathissa

Rasanjali Jayathissa
Graduate Teaching Assistant
Department of Physics
Western Michigan University
13. Figure 3.4: (a) and (d) show two common RC circuits. Parts (b) and (e) show their impedance plane plots. Arrows indicate the direction of increasing frequency. (Adapted with the permission from [Error! Bookmark not defined.]).
transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., (“CCC’s Billing and Payment terms and conditions”), at the time that you opened your RightsLink account (these are available at any time at http://myaccount.copyright.com).

Terms and Conditions

- The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.

- You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, and any CONTENT (PDF or image file) purchased as part of your order, is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.

- With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner. For STM Signatory Publishers clearing permission under the terms of the STM Permissions Guidelines only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts. You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.

- The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto

https://s100.copyright.com/CustomerAdmin/PLF.jsp?ref=a9330b65-a368-474c-bfa9-8c094e19e047c
• NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.

• WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.

• You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.

• IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.

• Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.

• The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party’s right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.

• This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY’s prior written consent.

• Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.
These terms and conditions together with CCC’s Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.

In the event of any conflict between your obligations established by these terms and conditions and those established by CCC’s Billing and Payment terms and conditions, these terms and conditions shall prevail.

WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC’s Billing and Payment terms and conditions.

This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.

This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

**WILEY OPEN ACCESS TERMS AND CONDITIONS**

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The **Creative Commons Attribution License** (CC-BY) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

The **Creative Commons Attribution Non-Commercial (CC-BY-NC) License** permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.(see below)

The **Creative Commons Attribution-Non-Commercial-NoDerivs License** (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

**Use by commercial "for-profit" organizations**

Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee.
Further details can be found on Wiley Online Library
http://olabout.wiley.com/WileyCDA/Section/id-410895.html

Other Terms and Conditions:

v1.10 Last updated September 2015
Questions? customeercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.