

Table of Contents

DECLARATION	iii
CERTIFICATE FROM SUPERVISOR	v
Plagiarism Report.....	vii
Dedication	ix
Preface.....	xi
Acknowledgements.....	xiii
ABSTRACT.....	xv
List of Abbreviations and Symbols.....	xix
List of Figures	xxvii
List of Tables	xxxii
CHAPTER 1	1
Introduction to photovoltaic technology and theoretical background of Perovskite Solar Cells	1
Introduction	3
1.1 Solar Cell Technologies	4
1.2 Photovoltaic Generation	6
1.2.1 1st generation: Crystalline Silicon (Poly-silicon or mono-silicon) solar cells	6
1.2.2 2nd generation: Thin-film Solar Cell (TFSC).....	7
1.2.3 3rd generation Solar Cells.....	8
1.3 PEROVSKITE SOLAR CELLS	10
1.3.1 Introduction to Perovskite material.....	10
1.3.2 Organic-inorganic Sn-based halide perovskites.....	13
1.3.3 Inorganic Sn-based halide perovskites.....	15
1.3.4 Inorganic Ge-based halide perovskites	16
1.4 Different components of a Perovskite solar cell	17
1.4.1 Transparent Conducting Oxide (TCO)	17
1.4.2 Electron Transport Layer (ETL)	17
1.4.3 Hole Transport Layer (HTL)	18
1.4.4 Counter Electrode	19
1.4.5 Device Architecture of Perovskite Solar Cells	19
1.5 Working Principle of Solar Cells	20

1.5.1	Absorption of Incident Photons	20
1.5.2	Generation of Free Electrons and Holes	22
1.5.3	Transport of Photo Generated Carriers	23
1.5.4	Collection of Photogenerated Carriers.....	23
1.6	Scope of the Thesis	25
References.....		26
CHAPTER 2.....		35
Experimental and characterization methods		35
Introduction.....		39
2.1	Experimental Procedures.....	39
2.1.1	Materials and Synthesis	39
2.1.2	Substrate cleaning	40
2.1.3	Thin Film Fabrication Techniques.....	41
2.2	Characterization Techniques	43
2.2.1	Optical characterization	44
2.2.2	Structure and Surface characterization	49
2.2.3	Electrical Characterization.....	57
References.....		67
CHAPTER 3.....		71
Theoretical framework and modeling approaches		71
Introduction.....		73
3.1	What is DFT	73
3.2	Fundamentals of DFT.....	74
3.2.1	Hohenberg-Kohn theorem	75
3.2.2	Kohn-Sham Density Functional Theory	75
3.2.3	Kohn-Sham equations (KS)	77
3.2.4	Self-consistency with single electron Kohn-Sham orbitals	77
3.3	The exchange-correlation functionals	80
3.3.1	Local (Spin) Density approximation (L(S)DA).....	81
3.3.2	Generalized Gradient Approximation (GGA)	84
3.4	Methods for the estimation of various properties using WIEN2k	86
3.4.1	The augmented plane wave method (APW)	86
3.4.2	The LAPW method	87
3.5	Procedure for the estimation of various properties using WIEN2k	89

3.5.1	Structure generation	89
3.5.2	Input generation	89
3.5.3	The Self-Consistent-Field (SCF) cycle	90
3.5.4	Electronic Properties	93
3.5.5	Defect Calculations	97
3.5.6	Thermodynamic Stability	98
3.5.7	Optical Properties	99
3.6	Numerical Modelling of PSCs	100
3.6.1	SCAPS-1D tool for device modeling	101
3.6.2	SCAPS input parameters	103
3.6.3	SCAPS input start-up panel interface	104
3.6.4	SCAPS solar cell definition panel	106
	References	108
	CHAPTER 4	71
	Enhancing lead-free Perovskite Solar cells efficiency using DMSO and activated carbon as counter electrodes: An Experimental and DFT Analysis	71
	Introduction	115
4.1	Experiment section	116
4.1.1	Chemical and materials	116
4.1.2	Device Fabrication	117
4.1.3	Characterization and Measurement	119
4.2	Result and discussion	120
4.2.1	Scanning electron microscope (SEM) study	120
4.2.2	Fourier-transformed infrared (FTIR) analysis	121
4.2.3	UV-Vis absorption spectra analysis	122
4.2.4	XRD Study	123
4.2.5	Power Conversion efficiency	125
4.2.6	Electrochemical impedance spectroscopy analysis	127
4.3	Computational details	131
4.3.1	Structural properties of the lead-free MASnI_3 perovskite material	132
4.3.2	Electronic properties of the light absorber MASnI_3	133
4.3.3	Absorption Spectra of the light absorber MASnI_3	135
4.4	Experimental validation of Theoretical results	135
4.5	Conclusion	136
	References	137

CHAPTER 5	143
Impact of Bromine substitution on band gap broadening and blue shift in lead-free Cs-based Perovskite Solar Cells	143
Introduction	145
5.1 Modeling and Methods.....	146
5.1.1 Device Architecture	146
5.1.2 DFT Calculations	147
5.1.3 Device Modeling.....	147
5.2 Results and Discussion.....	148
5.2.1 Structural properties.....	148
5.2.2 Electronic band structure and density of states.....	150
5.2.3 Optical properties.....	153
5.3 Solar cell characteristics.....	157
5.4 Effect of thickness of the perovskite absorber layer	159
5.5 Effect of defect density of the perovskite absorber layer.....	160
5.6 Effect of Br addition on Electronic and Optical Properties	162
5.7 Conclusion.....	163
References	165
CHAPTER 6	145
Theoretical analysis of metal doping effect on the performance of lead-free RbSnI₃-based Perovskite Solar Cells	145
Introduction	175
6.1 Theoretical approach	177
6.2 Results and discussion.....	178
6.2.1 Structural Properties and Phase Stability.....	178
6.2.2 The Electronic band structure and density of states.....	182
6.2.3 Optical properties.....	186
6.2.4 Calculation of Exciton Binding Energy	190
6.2.5 Insight of metal-doping from HOMO LUMO analysis	191
6.3 Device Architecture.....	193
6.4 Device Modeling	194
6.5 Solar cell characteristics.....	195
6.6 Effect of Metal Doping on the Efficiency of the Devices.....	198
6.7 Conclusion.....	198
References	200

CHAPTER 7	207
Investigating the efficiency of lead-free CsSnI₃/CsSnBr₃ heterostructure Perovskite Solar Cells: A Combined Experimental and DFT Approach	207
Introduction	209
7.1 Chemicals and Materials	211
7.2 Device Fabrication	211
7.3 Theoretical and Experimental Methods	213
7.4 Results and Discussion.....	215
7.4.1 Structure and morphology.....	215
7.4.2 Stability calculation	220
7.4.3 Electronic band structure and density of states.....	221
7.4.4 FTIR analysis	225
7.4.5 XPS study.....	226
7.4.6 Optical properties.....	228
7.4.7 Calculation of Exciton Binding Energy.....	232
7.4.8 PL spectra.....	233
7.4.9 Kelvin probe force microscopy (KPFM) analysis	233
7.4.10 Ultraviolet Photoelectron Spectroscopy (UPS) study.....	234
7.4.11 I-V Characteristics	237
7.4.12 EIS study.....	240
7.5 Experimental validation of Theoretical results	242
7.6 Conclusion.....	242
References	244
CHAPTER 8	253
Summary and Conclusions	253
Appendix	263
List of Journal Publications	265
List of Conference Presentations	267
List of Workshop attended	269
Reprint of Published Papers	271