

**MONTE CARLO SIMULATIONS FOR SURFACE SPUTTERING ANALYSIS AND
FIRST-PRINCIPLES CALCULATION OF STRUCTURAL AND ELECTRONIC
PROPERTIES OF SELECTED PEROVSKITES**

BY

AKINPELU AKINWUMI

(18PCE017293)

B.Tech Applied Physics, Ladoke Akintola University of Technology, Ogbomosho.

M.Sc Condensed Matter Physics, University of Ibadan, Ibadan

**A DISSERTATION SUBMITTED TO THE DEPARTMENT OF PHYSICS,
COLLEGE OF SCIENCE AND TECHNOLOGY IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE (M.Sc)
DEGREE IN INDUSTRIAL PHYSICS (RENEWABLE ENERGY AND MATERIAL
SCIENCE) OF COVENANT UNIVERSITY, OTA, NIGERIA**

OCTOBER, 2020

ACCEPTANCE

This is to attest that this dissertation is accepted in partial fulfillment of the requirements for the award of the degree of Master of Science in Industrial Physics (Renewable Energy and Material Science) in the Department of Physics, College of Science and Technology, Covenant University, Ota, Nigeria.

Mr. John A. Phillip

(Secretary, School of Postgraduate Studies)

Signature and Date

Prof. Abiodun H. Adebayo

(Dean, School of Postgraduate Studies)

Signature and Date

DECLARATION

I, **AKINPELU AKINWUMI (18PCE01793)**, declare that this research was carried out by me under the supervision of Dr. Oluwole E. Oyewande of the Department of Physics, College of Science and Technology, Covenant University, Ota, Nigeria. I attest that this dissertation has not been presented either wholly or partly for the award of any degree anywhere else. All scholarly materials used in the study are duly acknowledged and cited.

AKINPELU, AKINWUMI

Signature and Date

CERTIFICATION

We certify that this dissertation titled “MONTE CARLO SIMULATIONS FOR SURFACE SPUTTERING ANALYSIS AND FIRST-PRINCIPLES CALCULATION OF STRUCTURAL AND ELECTRONIC PROPERTIES OF SELECTED PEROVSKITES” is an original research work carried out by **AKINPELU, AKINWUMI (18PCE017293)** in the Department of Physics, College of Science and Technology, Covenant University, Ota, Ogun State, Nigeria under the supervision of Dr Oluwole E. Oyewande. We have examined and found this work acceptable as part of the requirements for the award of Master of Science in Industrial Physics.

Dr. Oluwole E. Oyewande

(Supervisor)

Signature and Date

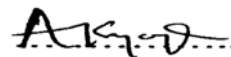
Prof. Ahzegbobor P. Aizebeokhai

(Head of Department)

Signature and Date

Prof. Olukayode D. Akinyemi

(External Examiner)



Signature and Date

Prof. Abiodun H. Adebayo

(Dean, School of Postgraduate Studies)

Signature and Date

DEDICATION

This project is dedicated to those individuals who have been adversely affected by epileptic power supply in Nigeria.

ACKNOWLEDGMENTS

First and foremost, I give all the glory and praise to God for His grace and provision throughout this work. I sincerely appreciate the Chancellor of Covenant University, Dr. David Oyedepo, for creating this platform. My thanks go to the entire Management of Covenant University, ably led by the Vice Chancellor, Prof. A. A. A. Atayero, for the resources provided and the opportunity to learn amongst erudite scholars, in this world-class institution.

I appreciate the Dean of school of post graduate studies, Prof. Abiodun H. Adebayo for the guidance enjoyed throughout this project. I deeply appreciate the assiduous efforts of the Dean, College of Science and Technology, Prof. Temidayo V. Omotosho, in making the work better. My profound gratitude goes to the Head, Physics Department, Prof. Ahzegbodor P. Aizebeokhai, for his tireless efforts, immense contribution and constructive criticisms in order to bring out the best from this project. Thank you so much.

I strongly recognize with gratitude, my project supervisor, Dr. Oluwole E. Oyewande, for his immense support, contributions and tireless efforts towards the success of this project. I am grateful for his encouragement and reassuring faith towards the success of the project. I acknowledge Prof. Marvel L. Akinyemi for her immense contribution to the dissertation. I like to appreciate Dr. Mojisola R. Usikalu for her positive input to the work. My gratitude goes to Dr. Moses E. Emetere and Dr. Maxwell Omeje for their helpful suggestions that helped to make the work come out this way. I also thank Dr. Olusegun Adewonyin and Dr. Charles O. Olawole for their helpful comments and suggestions. I appreciate Dr. Charity C. Enemuwe, Mr. Theophilus E. Arijaje, Miss Amanda Ndubuisi and all the members of Faculty and Staff of Physics Department who have contributed to the overall success of this project.

Finally, I will like to thank all members of Statistical Physics and Quantum Theory (SPaQ) group of the Theoretical Physics unit, Department of Physics, University of Ibadan, Ibadan for their contributions and efforts towards the success of this project.

My heartfelt appreciation goes to my wife, Mrs Bukola Akinpelu, for her prayers and encouragement. Also, I thank my mother, Mrs Ronke Akinpelu, and my siblings for their support and prayers towards the success of this study.

TABLE OF CONTENTS

CONTENT	Page
COVER PAGE	
TITLE PAGE	i
ACCEPTANCE	ii
DECLARATION	iii
CERTIFICATION	iv
DEDICATION	v
ACKNOWLEDGEMENTS	vi
TABLE OF CONTENTS	vii
LIST OF TABLES	x
LIST OF FIGURES	xi
LIST OF ABBREVIATIONS	xiii
ABSTRACT	xiv
CHAPTER ONE: INTRODUCTION	1
1.1 Background of the Study	1
1.2 Statement of Problem	4
1.3 Aim and Objectives	5
1.4 Significance of the Study	5
1.5 Scope of the Study	5
CHAPTER TWO: LITERATURE REVIEW	7
2.1 Perovskites	7
2.2 Perovskite Solar Cell	10
2.3 Hybrid Organic-Inorganic Halide Perovskites	10
2.3.1 Organic Cation Substitution	11
2.3.2 Inorganic Cation Substitution	12
2.3.3 Anions Substitutions	14
2.4 Sputtering	15
2.5 Sputtering Model	16
2.5.1 Sigmund Equation	16
2.5.2 Binary Collision Approximation (BCA)	17
2.6 Monte Carlo (MC) Method	18

2.6.1	Transport of Ions in Matter (TRIM)	19
2.6.2	Types of TRIM Calculation	19
2.7	Density Functional Theorem	21
2.7.1	Kohn-Sham Equation and the Exchange-Correlation Function	22
2.7.2	Pseudopotentials	22
2.7.3	Self Consistency Loop	23
2.7.4	Applications of Density Functional Theorem	23
2.8	Quantum opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization (ESPRESSO)	24
2.9	Toxicity of Lead	24
CHAPTER THREE: METHODOLOGY		25
3.1	Selected Perovskites	25
3.1.1	Choice of Perovskite	25
3.2	Methods	25
3.2.1	Stopping and Range of Ion in Matter and Transport of Ion in Matter	26
3.2.2	Surface Sputtering Process	30
3.2.3	Statistical Analysis	30
3.2.4	Principal Component Analysis Algorithm	31
3.2.5	Quantum Mechanical Calculations	32
3.2.6	Self-Consistent Calculation Details	34
CHAPTER FOUR: RESULTS		36
4.1	Projected Range and Sputter Yield	36
4.2	Principal Component Analysis (PCA)	43
4.3	Relationship between the Projected Range and Experimental Power Conversion Efficiencies	44
4.4	Structural and Electronic Calculation	45
4.4.1	Total Energy and Cutoff Energy	45
4.4.2	Structural Optimization and Bulk Modulus	46
4.4.3	Density of States (DOS) Calculations	46
4.4.4	Band Structure Calculations	50
CHAPTER FIVE: DISCUSSION		53

5.1	Sputtering Characteristics of Materials	53
5.2	Model Validation of Sputter Yield Results via Principal Component Analysis (PCA)	55
5.3	The Scree Test	56
5.4	The Structural and Electronic Analysis	56
5.4.1	Total Energy with Respect to Energy Cutoff	56
5.4.2	Structural Optimization Analysis	56
5.4.3	Density of States (DOS) Analysis	57
5.4.4	Band Structure Analysis	58
5.5	The Correspondence between Their Sputtering Characteristics and Electronic Properties	59
CHAPTER SIX: CONCLUSION AND RECOMMENDATION		61
6.1	Summary of Findings	61
6.2	Conclusion	62
6.3	Contributions to Knowledge	63
6.4	Recommendations	64
REFERENCES		65
APPENDIX A: ARGON BOMBARDMENT OF SELECTED PEROVSKITES		81
APPENDIX B: ARGON BOMBARDMENT OF SELECTED PEROVSKITES		91
APPENDIX C: QUANTUM MECHANICAL CALCULATIONS DATA		99

LIST OF TABLES

TABLE	CAPTION	PAGE
3.1	Input data for SRIM calculation	29
4.1	Descriptive statistics	43
4.2	Kaiser-Meyer-Olkin and Bartlett's test	43
4.3	Calculated equilibrium lattice constant, volume and bulk modulus of cubic $Pm\bar{3}m$ MALI, MATI, MALB and MATB	46
4.4	Calculated band-gap and Fermi energy of cubic $Pm\bar{3}m$ MALI, MATI, MALB and MATB perovskites	52

LIST OF FIGURES

FIGURE	CAPTION	PAGE
1.1	NREL efficiency chart (2020)	2
2.1	Crystal structure for ABX ₃ perovskite with space $pm\bar{3}m$ group	8
2.2	Phase transitions of perovskites	9
2.3	Flow chart of a self-consistency field (SCF) method	23
3.1	TRIM window interface	28
3.2	Output screen when SRIM is running	29
3.3	Structure of Quantum ESPRESSO calculation algorithm	33
3.4	Plane wave expansion as a function of pseudopotential	35
4.1	Projected range of Ne ⁺ ion in CH ₃ NH ₃ PbI ₃ , CH ₃ NH ₃ SnI ₃ and CH ₃ NH ₃ GeI ₃ perovskites targets for ion energies ranging from 1 keV to 10 keV.	37
4.2	Projected range of Ar ⁺ ion in CH ₃ NH ₃ PbI ₃ , CH ₃ NH ₃ SnI ₃ and CH ₃ NH ₃ GeI ₃ perovskites targets for ion energies ranging from 1 keV to 10 keV.	37
4.3	Sputter yield of A-site for the ejection of CH ₃ NH ₃ atoms from Ar ⁺ bombardment of CH ₃ NH ₃ PbI ₃ , CH ₃ NH ₃ SnI ₃ and CH ₃ NH ₃ GeI ₃ perovskites at different angles of incidence, for ion energy of 1 keV and 5 keV.	38
4.4	Sputter yield of B-site for the erosion of Pb/Sn/Ge atoms from Ar ⁺ bombardment of CH ₃ NH ₃ PbI ₃ , CH ₃ NH ₃ SnI ₃ and CH ₃ NH ₃ GeI ₃ perovskites at different angles of incidence, for ion energy of 1 keV and 5 keV.	38
4.5	Sputter yield of X-site for the erosion of I atoms from Ar ⁺ bombardment of CH ₃ NH ₃ PbI ₃ , CH ₃ NH ₃ SnI ₃ and CH ₃ NH ₃ GeI ₃ perovskites at different angles of incidence, for ion energy of 1 keV and 5 keV	39
4.6	Sputter yield of A-site for the ejection of CH ₃ NH ₃ atoms from Ne ⁺ bombardment of CH ₃ NH ₃ PbI ₃ , CH ₃ NH ₃ SnI ₃ and CH ₃ NH ₃ GeI ₃ perovskites at different angles of incidence, for ion energy of 1 keV and 5 keV	39
4.7	Sputter yield of B-site for the ejection of CH ₃ NH ₃ atoms from Ne ⁺ bombardment of CH ₃ NH ₃ PbI ₃ , CH ₃ NH ₃ SnI ₃ and CH ₃ NH ₃ GeI ₃ perovskites at different angles of incidence, for ion energy of 1 keV and 5 keV	40
4.8	Sputter yield of X-site for the ejection of CH ₃ NH ₃ atoms from Ne ⁺ bombardment of CH ₃ NH ₃ PbI ₃ , CH ₃ NH ₃ SnI ₃ and CH ₃ NH ₃ GeI ₃ perovskites at different angles of incidence, for ion energy of 1 keV and 5 keV	40
4.9	Range of in Ne ⁺ Cs ₃ Bi ₂ I ₉ , Rb ₃ Sb ₂ I ₉ and (CH ₃ (CH ₂) ₃ NH ₃) ₂ CuBr ₄ perovskites	

	for different ion energies from 1 keV to 10 keV	41
4.10	Sputter yield for the erosion of A cations from Ne ⁺ bombardment of Cs ₃ Bi ₂ I ₉ , Rb ₃ Sb ₂ I ₉ and (CH ₃ (CH ₂) ₃ NH ₃) ₂ CuBr ₄ perovskites at angles of incidence ranging from 0 ⁰ to 89 ⁰ , and ion energy 1 keV	41
4.11	Sputter yield for the erosion of B cations from Ne ⁺ bombardment of Cs ₃ Bi ₂ I ₉ , Rb ₃ Sb ₂ I ₉ and (CH ₃ (CH ₂) ₃ NH ₃) ₂ CuBr ₄ perovskites at different angles of ranging from 0 ⁰ to 89 ⁰ , and ion energy 1 keV	42
4.12	Sputter yield for the erosion of X anions from Ne ⁺ bombardment of Cs ₃ Bi ₂ I ₉ , Rb ₃ Sb ₂ I ₉ and (CH ₃ (CH ₂) ₃ NH ₃) ₂ CuBr ₄ perovskites at different angles of incidence and ion energy 1 keV	42
4.13	A Scree plot of the number of the principal components	44
4.14	Projected range of Ne ⁺ ion in CH ₃ NH ₃ PbI ₃ , CH ₃ NH ₃ SnI ₃ and CH ₃ NH ₃ GeI ₃ perovskites targets for 10 keV ion energy against their experimental PCE.	44
4.15	Projected range of Ne ⁺ in Cs ₃ Bi ₂ I ₉ , Rb ₃ Sb ₂ I ₉ and (CH ₃ (CH ₂) ₃ NH ₃) ₂ CuBr ₄ perovskites targets for 10 keV ion energy against their experimental PCE	45
4.16	Optimized plane-wave cutoff energy for lead and tin perovskite cubic $Pm\bar{3}m$ Phase	47
4.17	Calculated total energy - lattice constant and calculated total energy-volume in MALB and MATI cubic $Pm\bar{3}m$ phase.	47
4.18	Calculated total density of state for: (a) MALI (b) MATI (c) MALB and (d) MATB cubic $Pm\bar{3}m$ phase	48
4.19	Calculated total density of state (TDOS) and partial density of state (PDOS) for: (a) MALI (b) MATI, (c) MALB and (d) MATB	49
4.20	Calculated total density of state and integrated density of state for: (a) MALI (b) MATI (c) MALB and (d) MATB cubic $Pm\bar{3}m$ phase.	50
4.21	Orbital contributions to the band structures of: (a) MALI, (b) MATI, (c) MALB and (d) MATB cubic $Pm\bar{3}m$ phase	51

LIST OF ABBREVIATIONS

BCA	Binary Collision Approximation
CIGS	Copper Indium Gallium Selenide Solar
DFT	Density Functional Theorem
DOS	Density of State
ESPRESSO	opEn-Source Package for Research in Electronic Structure, Simulation and Optimization
HOIPs	Hybrid Organic Inorganic Perovskites
IBSS	Ion Beam Surface Sputtering
IHME	Institute of Health Metrics and Evaluation
KMO	Kaisers-Meyer-Olkin
MALI	Methylammonium Lead Iodide
MALB	Methylammonium Lead Bromide
MATB	Methylammonium Tin Bromide
MATI	Methylammonium Tin Iodide
MC	Monte Carlo
PCA	Principal Component Analysis
PCE	Power Conversion Efficiency
PDOS	Projected Density of State
PSC	Perovskite Solar Cell
QE	Quantum Espresso
SRIM	Stopping and Range of Ion in Matter
TDOS	Total Density of State
TRIM	TRansport of Ion in Matter
WHO	World Health Organization

ABSTRACT

Hybrid organic-inorganic perovskites (HOIPs) have become the fastest growing solar technology due to their power conversion efficiency of about 25.2%, competing with the conventional thin-film technology. Although unique and exceptional, instability and toxic behaviour of the perovskite hamper its commercialization. Therefore, this research was carried out to identify the best and less toxic material that can substitute for lead, by performing ion beam surface sputtering analysis of lead and certain lead-free perovskites and calculations of structural and electronic properties. The ion beam surface sputtering was carried out using both transport of ions in matter (TRIM) module and stoppage and range of ion in matter (SRIM) software package. Quantum opEn-Source Package for Research in Electronic Structure, Simulation and Optimization (ESPRESSO) was used to calculate the structural and electronic properties. The sputtering characteristics results showed similar sputtering pattern. The A-site of these perovskites recorded the highest sputter yields, with a maximum sputter yield around 78° ion incidence. Lattice constants, bulk moduli, density of states, projected and total density of states and band gaps results were compared with the experimental and theoretical values; good agreement was obtained. Tin perovskite ($\text{CH}_3\text{NH}_3\text{SnI}_3$) has the highest sputter yields amongst other less toxic perovskites and it has similar electronic structure to lead iodide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$). Therefore, this research suggests that optical properties be investigated to further examine the potential of tin to replace lead for photovoltaic applications.

Keywords: Band Structure; Density Functional Theory; Density of State; Lead-free Perovskite; Sputtering; Tin Perovskite