Compositional Engineering of Perovskite Materials to Replace Toxic Lead (Pb) in Photovoltaic Applications

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Doctor of Philosophy

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Thesis/Dissertation submitted in partial fulfillment of the requirements for the degree

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August 2025

DECLARATION

I declare that this is my own work and this thesis/dissertation does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any other University or Institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text. I retain the right to use this content in whole or part in future works (such as articles or books).

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The above candidate has carried out research for the PhD/MPhil/Masters thesis/dissertation under my supervision. I confirm that the declaration made above by the student is true and correct.

Prof. G. A. Sewvandi

Name of Supervisor:

11/08/2025

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Signature of the Supervisor: Date:

Dedicated to

…to my loving husband and my son,

….to my parents and my parents-in-law

ACKNOWLEDGEMENT

I would like to express my sincere and deepest gratitude to my supervisor Prof. G. A. Sewvandi for giving me the opportunity to conduct this research as well as her continuous support, excellent motivation and constructive guideline throughout my PhD. Her timely feedback greatly helped me stay on track and progress smoothly on this research journey toward achieving my goals.

I sincerely thank Dr. Pasan Henadeera (Senior Lecturer, University of Moratuwa) and Mr. H.A.T. Vimukthi Nanayakkara of the Department of Solid State Materials Processing, Institute of Material and Process Design, Germany, for their invaluable support in the installation and configuration of VASP and related software during my research.

I also acknowledge Mr. M.M. Kumarasinghe for his support in initiating my VASP simulation work, and Mr. W. Satheekshana for his assistance in troubleshooting on my workstation.

In addition, I would like to express my sincere thanks to Mr. V. Sivahar (former Head, Department of Materials Science and Engineering) and all academic staff members of the Department of Materials Engineering, University of Moratuwa, for their valuable support during my research.

I am indebted to Senate Research Committee Grants (SRC) for the awarding of a research grant to carry out my research successfully.

In conclusion, I would like to express my pardon if I have inadvertently omitted the name of those to whom thanks is due.

Jayawardane J.T.S.T

ABSTRACT

Solar energy is a renewable and environmentally friendly power source that is free from pollution and noise, making it a promising alternative to conventional non-renewable energy sources. Solar cells are extensively used to efficiently harness and convert sunlight into electricity, offering substantial potential for sustainable energy generation. Among the various types of solar cells, Organolead halide perovskite solar cells have garnered considerable attention in recent years due to their superior optoelectronic properties. However, Pb is highly toxic, and the dissolution of lead (Pb) in water poses serious environmental and health risks and long-term instability, hindering commercialization. Thus, the development of stable, lead-free perovskites is critical.

The thesis presents a first-principles Density Functional Theory (DFT) investigation of the structural, electronic, and optical properties of bismuth-based halide perovskites, chalcogenide halide perovskites, and chalcohalides as Pb alternavites. A detailed theoretical and numerical analysis is conducted on materials including $CH_3NH_3BiI_2Se$, $CH_3NH_3BiI_2S$, $Sb_{1-x}Bi_xSeI$, $Cs_3Bi_2I_9$ and $CH_3NH_3Bi_2I_9$. Among these, $CH_3NH_3BiI_2Se$ exhibited a higher absorption coefficient, broader spectral absorption, and superior charge carrier mobilities compared to $CH_3NH_3BiI_2S$, with corresponding power conversion efficiencies (PCEs) of 24.06% and 21.85%, respectively. The bandgap tuning in $Sb_{1-x}Bi_xSeI$, achieved through increased Bi content, enhanced light absorption and carrier transport, making $Sb_{0.4}Bi_{0.6}SeI$ a promising absorber material for thin-film solar cells. Additionally, numerical simulations of $Cs_3Bi_2I_9$ and $CH_3NH_3Bi_2I_9$ based perovskite solar cells revealed the significant influence of defect densities on device efficiency, with optimized $Cs_3Bi_2I_9$ based PSCs achieving a PCE of 13.81%. Above findings from the compositional engineering of materials contribute to a deeper understanding of structure and property relationships in bismuth-based chalcohalides and provide valuable insights for the design of lead-free, non-toxic, and sustainable optoelectronic devices. This work paves the way for the development of environmentally friendly materials tailored for next-generation photovoltaic technologies.

Keywords

Density-functional theory (DFT), optical absorption, VASP, photovoltaic, perovskite, Bismuth Chalcogenides, Chalcohalides

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PSC	– Perovskite Solar Cell
PCE	– Power Conversion Efficiency
V_{oc}	– Open-Circuit Voltage
J_{sc}	– Short-Circuit Current Density
FF	– Fill Factor
ETL	– Electron Transport Layer
HTL	– Hole Transport Layer
SCAPS	– Solar Cell Capacitance Simulator
FTO	– Fluorine-Doped Tin Oxide
Au	– Gold (Back Contact)
DFT	– Density Functional Theory
SCAPS	– Solar Cell Capacitance Simulator
VBM	– Valence Band Maximum
CBM	– Conduction Band Minimum
DOS	– Density of States
PDOS	– Partial Density of States
TDOS	– Total Density of States
SOC	– Spin-Orbit Coupling
HTL	– Hole Transport Layer
ETL	– Electron Transport Layer
FTO	– Fluorine-Doped Tin Oxide
Au	– Gold (Back Contact)
VASP	– Vienna Ab Initio Simulation Package
m_0	– Rest Mass of Electron
$\mathcal{E}(\omega)$	– Dielectric Function
$\alpha(\omega)$	– Absorption Coefficient
$R(\omega)$	– Reflectivity