

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

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

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Faculty of Engineering

University of Moratuwa  
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## DECLARATION

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Prof. G. A. Sewvandi

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Name of Supervisor:

11/08/2025

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Signature of the Supervisor:

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Date:

**Dedicated to**

*...to my loving husband and my son,*

*....to my parents and my parents-in-law*

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## 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 chalcogenides as Pb alternatives. A detailed theoretical and numerical analysis is conducted on materials including  $\text{CH}_3\text{NH}_3\text{BiI}_2\text{Se}$ ,  $\text{CH}_3\text{NH}_3\text{BiI}_2\text{S}$ ,  $\text{Sb}_{1-x}\text{Bi}_x\text{SeI}$ ,  $\text{Cs}_3\text{Bi}_2\text{I}_9$  and  $\text{CH}_3\text{NH}_3\text{Bi}_2\text{I}_9$ . Among these,  $\text{CH}_3\text{NH}_3\text{BiI}_2\text{Se}$  exhibited a higher absorption coefficient, broader spectral absorption, and superior charge carrier mobilities compared to  $\text{CH}_3\text{NH}_3\text{BiI}_2\text{S}$ , with corresponding power conversion efficiencies (PCEs) of 24.06% and 21.85%, respectively. The bandgap tuning in  $\text{Sb}_{1-x}\text{Bi}_x\text{SeI}$ , achieved through increased Bi content, enhanced light absorption and carrier transport, making  $\text{Sb}_{0.4}\text{Bi}_{0.6}\text{SeI}$  a promising absorber material for thin-film solar cells. Additionally, numerical simulations of  $\text{Cs}_3\text{Bi}_2\text{I}_9$  and  $\text{CH}_3\text{NH}_3\text{Bi}_2\text{I}_9$  based perovskite solar cells revealed the significant influence of defect densities on device efficiency, with optimized  $\text{Cs}_3\text{Bi}_2\text{I}_9$  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 chalcogenides 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, Chalcogenides

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## LIST OF ABBREVIATION

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
$\epsilon(\omega)$	– Dielectric Function
$\alpha(\omega)$	– Absorption Coefficient
$R(\omega)$	– Reflectivity