

# ABSTRACT

In today's world, the demand for energy continues to rise alongside population growth and industrialization. Our reliance on traditional fossil fuels like coal, petroleum, and natural gas has sustained global energy needs but comes at a cost. These finite resources are not only depleting but also contribute significantly to environmental degradation and pose challenges to biodiversity and human health. To ensure a sustainable future, it is imperative to explore renewable energy sources that provide cleaner and more efficient alternatives. Renewable energy, such as solar, wind, tidal waves, geothermal, and biomass, presents viable solutions. These sources harness natural processes that are continuously replenished and have minimal environmental impact compared to fossil fuels. Solar energy, in particular, stands out for its abundant availability and versatility in various applications, from residential rooftops to large-scale solar farms.

While conventional silicon-based photovoltaic technologies show promise, their high costs hinder competitiveness with current energy production methods. In contrast, perovskite solar cells represent a novel photovoltaic technology that has attracted significant attention due to promising efficiencies, cost-effectiveness, recyclability, and versatility for diverse applications. Despite the exploration of various PSCs, issues like lead toxicity, stability, and durability have impeded widespread commercial adoption. This thesis aims to advance lead-free perovskite solar cell (PSC) technologies to improve their environmental sustainability, cost-effectiveness, stability, and power conversion efficiency. Organized into eight chapters, this study aims to yield significant advancements in the field, contributing to practical applications and sustainable energy solutions.

**Chapter 1** explores the current global energy landscape and highlights the urgent need for renewable energy sources. It provides an overview of various types of photovoltaic devices, with a focus on Perovskite Solar Cells. A detailed analysis of the various components of PSCs is presented, including the perovskite absorber layer, electron and hole transport layers, and electrodes. The intricate working mechanisms of PSCs are explained, elucidating how these components interact to convert sunlight into electricity. Additionally, the chapter explores recent advancements and challenges

in PSC research. The insights provided in this chapter lay the groundwork for further exploration of PSCs as a promising renewable energy technology.

**Chapter 2** provides a comprehensive overview of the fundamental theory and detailed descriptions of various experimental techniques used to characterize the materials of the different components of PSCs. These techniques include X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), UV-VIS spectroscopy, Fourier-transform infrared spectroscopy (FTIR), Kelvin probe force microscopy (KPFM), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and photoluminescence (PL) spectroscopy. Additionally, this chapter discusses the principles of current-voltage (I-V) measurement, quantum efficiency (QE) calculations, and electrochemical impedance spectroscopy (EIS), along with a detailed explanation of the critical parameters that determine device performance.

In **Chapter 3**, we provide a comprehensive discussion of the fundamentals of Density Functional Theory (DFT), including the Kohn-Sham theorem. We also address the necessity of using the exchange-correlation functional in the DFT approach. In this work, we employed the WIEN2K software for DFT computations, providing an in-depth discussion of its fundamental operational principles and the various material properties it can accurately calculate. Additionally, we analyze the basic working techniques of the SCAPS-1D simulation tool used to theoretically estimate the performance of PSC devices.

**Chapter 4** presents a study on improving the photovoltaic performance of lead-free  $\text{MASnI}_3$ -based perovskite solar cells, which uses a mixture of the polar solvent DMSO and activated carbon powder as the counter electrode. The solar cells are fabricated using three different counter-electrode preparation techniques. The device with the DMSO-mixed carbon powder as a counter electrode exhibited the best photovoltaic performance. DMSO was found to improve the carrier production rate at the perovskite surface and strengthen the bonding between perovskite and carbon, leading to enhanced device performance. Finally, the DFT-calculated electronic and optical properties are compared with the experimentally obtained results to validate the key findings.

**Chapter 5** evaluates the structural, electronic, and optical properties of the lead-free perovskite  $\text{CsGeI}_x\text{Br}_{3-x}$  utilizing density functional theory (DFT) calculations. The electronic band gap increased significantly from 1.363 eV to 1.885 eV as the number of Br atoms substituted for I atoms increased. Analysis of the total density of states (TDOS) showed the total electron density in the valence band region increased significantly with Br substitution, reaching a maximum in  $\text{CsGeBr}_3$ . SCAPS-1D device simulations were performed to optimize the performance of perovskite solar cells by adjusting parameters like absorber layer thickness and defect density. The DFT-calculated band gaps and effective density of state values were used to obtain the simulated outcomes.

**Chapter 6** presents a theoretical investigation of the effect of metal (Cr, Sr, Ag, Cu) doping on the performance of lead-free  $\text{RbSnI}_3$ -based perovskite solar cells. Using density functional theory calculations, the structural and opto-electronic properties of the doped perovskites were measured. The results show that Cu-doped  $\text{RbSnI}_3$  exhibits the most favorable properties for solar cell applications, including a reduced bandgap, increased dielectric constant, and enhanced charge carrier transport. In addition, SCAPS-1D simulations of the devices based on these doped perovskite materials indicate that the Cu-doped perovskite achieves the highest power conversion efficiency, significantly outperforming the undoped  $\text{RbSnI}_3$  and other metal-doped counterparts.

**Chapter 7** focuses on evaluating the performance of lead-free  $\text{CsSnI}_3/\text{CsSnBr}_3$  heterostructure-based perovskite solar cells. The surface morphology of the deposited perovskite heterostructure layer was analyzed using SEM and AFM, while EDS and XRD experiments verified sample purity. The optical properties of the heterostructures were characterized using UV-Vis, FTIR, and PL spectroscopy analysis. These analyses revealed the superior suitability of heterostructure perovskites compared to single perovskites for solar cell applications. The current-voltage and EIS results confirm these findings. The analysis of the External Quantum Efficiency (EQE) and Internal Quantum Efficiency (IQE) indicates a significant improvement in the performance of heterostructure-based perovskite solar cells. The surface potential of both the single and heterostructure layers was investigated using KPFM experiments. UPS study was performed to estimate the work function of the perovskite layer. In addition, the study employed both GGA(PBE) and mBJ-LSDA exchange-correlation functionals for DFT

computations: GGA for computational efficiency and mBJ-LSDA for accurate band gap and density of states calculation, aligning well with experimental data. The theoretically calculated electronic properties, including the band structure, DOS, and optical characteristics, were thoroughly compared with the experimental outcomes. XPS study was performed to understand the physics behind carrier transport between the absorber layer of the heterostructure perovskite. The results revealed the potential of these lead-free perovskite heterostructures for optoelectronic and photovoltaic applications. The insights gained from this comprehensive study contribute to the understanding of the fundamental properties of these materials and their potential for practical applications in the field of renewable energy.

**Chapter 8** summarizes the essential findings and conclusions arising from the present work.