# PREFACE

Our world needs replacement of conventional energy resources such as coal, and petroleum with renewable energy resources such as solar and wind. Solar energy is the most abundant source of renewable energy. Thus, solar energy can provide significant benefits to both the climate and the economy of developed and developing countries in times to come. Generation of electricity using photovoltaic (PV) solar cells appears to be a promising way of converting sunlight into electricity.

For the past few decades, there have been many changes in the development of PV technology, due to which cells have been classified into different generations, originally defined for inorganic materials as high cost/high efficiency (first generation), low cost/ low efficiency (second generation) and low cost/high efficiency (third generation). The first generation solar cell was a single-junction cell based on wafers fabricated from single crystals or polycrystals for PV technologies. The solar cell from its inception (PN junction) based on crystalline silicon solar cell that provided an efficiency of 4.5% at US Bell Laboratories in 1954 has begun to attract widespread attention. Starting in the 1970s, a-Si: H was developed in solar cells by Radio Corporation of America (RCA) by which steadily climbed in efficiency to about 13.6% in 2015. Mahmoud H. Elshorbagy et al. reported in Scientific Reports (2021), Low-cost hydrogenated amorphous silicon solar cells (a-Si: H) can perform better and be more competitive by including nanostructures. An optimized nano-dimer structure embedded in close contact with the back electrode of an a-Si: H ultra-thin solar cell can enhance the deliverable short-circuit current up to 27.5 %. It is the abilty to generate electricity at low cost that gives silicon. Silicon solar cells are the most recognized solar cell technology and are projected to dominate the market as more than 90% of the global PV market depends on c-Si-based solar cells. Compared to other PV existing materials, c-Si is among the most suitable candidates for solar cell construction due to its non-toxicity, good stability, natural abundance, and cost competitiveness. The first generation photovoltaic technology is considered to consist of PV technology based on thick crystalline films (mainly Si), leading to not only high efficiency but also high cost. The second-generation (thin films based such as CIGS and CdTe thin-film solar cells) have achieved a high power conversion efficiency (PCE), but industrial applications are hindered by environmental pollution, high production costs, and other problems. Third-generation PV technology includes DSSC, organic, quantum dot cells, polymer, and perovskite solar devices. The role of perovskite materials is gaining immense importance among researchers due to easy processing conditions, excellent PV performance, low-cost raw materials, their better photovoltaic, and promising optoelectronic properties.

In the present research work, perovskite active layer materials have been selected for investigation. The general formula for organic-inorganic halide perovskite is $AMX_3$ where A= $Cs^+$, MA ($CH_3NH_3^+$), FA (HC $(NH_2)_2^+$); M=$Pb^{2+}$, $Sn^{2+}$, $Ge^{2+}$; X= Cl, Br, I). The first application of perovskite ($CH_3NH_3PbI_3$)-based photocell was published in 2009 with a power conversion efficiency (PCE) of 3.8%. At present, the PCE of perovskite solar cells (PSCs) has been increased from 3.8% to above 25%. A research team, led by Professor Sang ll Seok at Ulsan National Institute of Science and Technology (UNIST) has set a new efficiency record for a perovskite solar cell (PSC) at 25.8% by forming an interlayer between electron-transporting and perovskite layers to minimize interfacial defects, contributing to the decrease in the power conversion efficiencies. This is the world's highest power conversion efficiency (PCE) reported so far. Besides, the record, certified by National Renewable Energy

Laboratory (NREL), is also the highest confirmed conversion efficiency of 25.5%. Within 13 years, perovskite has achieved excellent efficiency compared to other technologies. Astonishingly, in such a short time, the power conversion efficiency is approaching to that of the thin-film technology. There are several reasons why perovskite solar cells are highly efficient and are of great interest to the community. These materials are used as active material because of long charge carrier lifetime, high optical absorption, low exciton binding energy, long carrier diffusion lengths, high open-circuit voltage, adjustable band gap, charge carrier mobility, and low-cost fabrication. The bandgap tenability and high efficiency make it promising as a cost-effective next-generation photovoltaic device. However, these materials show a rapid degradation if exposed to external conditions such as oxygen, heat, humidity, and light.

Extrinsic and intrinsic factors are two issues that affect the loss of stability or degradation of the PSCs. Extrinsic factors can be prevented through the passivation of the perovskite layer or through encapsulation schemes. However, the intrinsic factors are cause more degradation. Defects such as ion interstitials and ion vacancies arise quickly in the perovskite lattice. It is reported that ion migration leads to the current hysteresis behavior in organic-inorganic halide perovskite solar cells, which is dominated by the grain boundary in perovskite films. The hysteresis problem in perovskite was first reported in 2014. It depends on several parameters such as scan direction, scan rate, preconditions, applied voltage, and architecture. Several reports are available regarding the mechanism of hysteresis. It has been claimed that the hysteresis behavior arises due to the trapping-detrapping process, slow transient capacitive current, band bending due to ferroelectric polarization, and band bending due to ion migration. For the perovskite halides, current-voltage hysteresis is the biggest puzzle to be solved before industrialization in spite of promising features for future photo-voltaic applications. All the possible causes, from the classical (viz., morphology, defects, slow transient capacitance, etc.) to quantum (viz., spin-orbit interaction) ones, are investigated. However, its origin is still under debate, as possibilities showed some ambiguity on the science known until now.

The stability and current-voltage hysteresis are two major problems for the perovskite halides. Therefore keeping this problem in mind, Ruddlesden-Popper (RP) material is also chosen as an active layer to understand the degradation issue. The Ruddlesden-Popper chemical formula is $A_{n+1}M_nX_{3n+1}$; here n denotes the distance between the 2D material. Rudelsden–Popper perovskites (2D) have gained widespread importance as candidates for next-generation optoelectronic devices, because of their more substantial quantum confinement effect, better stability to moisture, and higher critical exciton binding energy than 3D perovskite. Inorganic cation cesium (Cs) atoms doped in perovskite materials increased the stability of the material and the efficiency of the solar cells. Perovskite lead halides have shown utility as better optoelectronic devices with a band gap in the range of 1.5-2.3 eV due to high absorption co-efficient and removal of liquid hole transport layer, in case of dye-sensitized based solar cell materials.

On the basis of the above requirements, cesium lead halides, $CsPbX_3$ (where X = I and Br), have gained enormous interest in optoelectronics and photovoltaic applications. This material exhibits all necessary properties (as discussed above) except stability under exposure to ambient conditions (oxygen, heat, light, and humidity). Cesium lead halide compounds possess direct bandgap nature and high light-absorbing power in the UV and visible range prove their utility for solar cell applications. Maksym V. Kovalenkowe reported highly luminescent colloidal $CsPbX_3$ NCs (X = Cl, Br, I, and mixed Cl/Br and Br/I systems) with bright ( quantum yields = 50−90%), stable, spectrally narrow, and broadly tunable photoluminescence. These materials are also used in light-emitting diodes (LED), photodetector, and energy storage applications. Despite very significant optoelectronic features, the stability of these compounds becomes a vital issue to be resolved. To resolve the stability issues, there are various techniques employed to synthesize these materials in the air such as solvothermal synthesis, quantum dots, one-step microwave-assisted preparation, low-temperature synthesis, and solution phase synthesis, etc. Hence, it appears necessary to understand why these materials are unstable, and too hard to synthesize in ambient conditions. In this thesis, perovskite halides were synthesized using the cold sintered method via the solid-state route (SSR), a low-cost synthesis technique compared to other reported synthesis routes in an inert atmosphere.

$CsPbI_3$ is reported to have four phases: perovskite black phase (cubic (α), tetragonal (β), orthorhombic(γ)) and non-perovskite yellow orthorhombic (δ). With a band gap of ~ 1.73eV, $CsPbI_3$-α is the most suitable phase among all-inorganic lead halide Perovskites. However, in the ambient atmosphere (almost instantly) the perovskite black phase is converted into a non-perovskite yellow orthorhombic phase. At the same time, $CsPbBr_3$ remains in the orthorhombic phase at room temperature. Thus, in the present investigation, compositional variation of Br in Cesium lead iodide $CsPbBr_xI_{3-x}$ (x= 0.0 to 3.0 at the step of 0.5) samples synthesized by cold sintering technique has been studied. The thermodynamics of formation was explored by estimating ΔG and ΔS and stability of the cold sintered samples was studied. Further, a correlation between free energy and band gap energy of the studied samples has been established. We have also studied the time-dependent photo-conduction behavior of $CsPbBr_3$

in continuous illumination of AM 1.5 G Sun light for 3 h. We observed a negative differential resistance for a forward scanned current-voltage curve in AM 1.5 G Sun light.

A comparative study of perovskite and Rudlesden-Popper (RP) materials has been discussed. Current-voltage hysteresis for lead and lead-free halide materials is studied in detail. The conduction mechanism [forward scan (FS) as well as reverse scan (RS)] has been studied with continuous exposure to AM 1.5 G Sunlight for 3 h. All compounds ($CsPbBr_3$, $CsSnBr_3$, $Cs_2PbBr_4$, and $Cs_2SnBr_4$) were synthesized by cold sintering method via solid-state reaction route at room temperature.

Finally, in the last part of this research work, the thickness of the three layers ($TiO_2$, CuO, and $CsPb/SnBr_3$) has been optimized using the Finite Element Modelling technique. A device has been realized using the Pulsed Laser Deposition technique with the optimized thickness from FEM simulations.

The prime objective of the present thesis is to resolve the stability issues and investigate the current-voltage hysteresis problem for the perovskite halides. For this purpose, inorganic halide-based perovskites ($CsPbBr_xI_{3-x}$, in the step size of $x = 0.5$, $CsSnBr_3$ and Ruddlesden Popper of $Cs_2PbBr_4$ and $Cs_2SnBr_4$) have been selected as an active layer material. The stability and degradation mechanism of the perovskite halides have been studied. In addition, the *I-V* hysteresis of the samples has been investigated.

The thesis is divided into eight chapters and its brief description is given below:

**Chapter 1** introduces the topic of solar cells, including extensive literature surveys. This chapter shows the motivation of the research work, background, and fundamentals of solar cells, essential requirements for active materials for perovskite solar cells. Moreover, two major problems such as stability and current-voltage issues in perovskite halides (active materials) have been reviewed. This chapter also covers the main objectives of the present work.

**Chapter 2** discusses the various experimental techniques applied to the present investigation. It represents a description of the experimental equipment used, the analysis techniques, and the various synthesis routes adopted to synthesize the samples. Cold sintering methods via solid-state reaction routes, spin coater technique, and pulsed laser deposition (PLD) are also discussed. This section discusses important analysis techniques such as Rietveld refinement and Finite element method (FEM) analysis as well as a detailed description of tools such as XRD, SEM, XPS, DSC, UV-visible, PL, Raman, impedance spectroscopy and IV measurement, etc.

**Chapter 3** aims to study the compositional variation of Br- at X-site of Cesium lead halide $CsPbBr_xI_{3-x}$ (x= 0.0 - 3.0 at the step of 0.5), compounds were synthesized by cold sintering technique at room temperature. To understand the stability and degradation mechanism of the perovskite halides, structural, optical, thermodynamics, and electrical properties are analyzed. Moreover, the plausible mechanism for this compositional degradation has been investigated.

**Chapter 4** describes a comparative study of $CsPbI_3$ and $CsPbBr_3$ perovskite materials. This chapter has been divided into two parts. In part A, the cesium lead halides $CsPbX_3$ (where, X = I and Br) are synthesized by the cold sintering method. The thermodynamical stability using ΔS is also discussed. For the verification of the formation of these compounds, structural and optical properties are studied. A thermo-optical correlation between free energy and band gap is also established for the two Perovskites halides. Moreover, It was observed that the cesium lead bromide ($CsPbBr_3$) sample is a more stable compound than the $CsPbI_3$ sample. In part B, the $CsPbI_3$ sample was successfully synthesized by the cold sintering method via the solid-state reaction (SSR) route. In order to understand the charge transport mechanism, the hopping conduction and relaxation mechanisms are studied with temperature. For this, electrical properties are analysed by the real and imaginary part of the permittivity, modulus, and ac conductivity within the frequency range 10 to $10^6$ Hz at different temperatures between room temperature to 153 °C.

**Chapter 5** describes the time-dependent photo-conduction behavior of $CsPbBr_3$ under continuous illumination of AM 1.5 G sunlight for 3 h in order to understand the I–V hysteresis. It was observed a negative differential resistance for a forward scanned current-voltage curve in AM 1.5 G Sunlight. These investigations suggest that the photo-current voltage hysteresis is primarily affected by the thermionic-field emission, which slows down the drift velocity of hot charge carriers with field applications. This study will further lead the scientific community to investigate whether this slowdown in drift velocity is related to the Gunn effect or the Rashba effect.

In **Chapter 6**, A comparative study of Perovskite and Rudlesden-Popper for lead & lead-free halides has been carried out. XRD, UV-visible, and *I-V* characteristics were employed to understand the structural, optical, and electrical correlations, respectively. It was observed that the current-voltage is scan dependent and the value of 'n' ($J = kE^n$) varies in both forward scanning (FS) and reverse scanning (RS). Furthermore, the polarization is higher in FS than in RS for $CsPbBr_3$ and $Cs_2PbBr_4$ samples, but in lead-free materials ($CsSnBr_3$ and $Cs_2SnBr_4$), the polarization is higher in RS than in FS.

**Chapter 7,** describes the fabrication of thin-film and devices of $CsSnBr_3$ and $CsPbBr_3$ materials by pulsed laser deposition (PLD) technique. A comparative study found that cesium lead bromide ($CsPbBr_3$) thin film is more stable than cesium tin bromide ($CsSnBr_3$). Furthermore, it is observed that the $CsSnBr_3$ thin-film degrades faster than that of the $CsPbBr_3$ thin films. UV-visible and photoluminescence (PL) studies were used to calculate the bandgap. XRD was carried out to understand the studied structural properties. In addition, a theoretical simulation was studied by the finite element method (FEM). Through FEM simulation, $TiO_2/CsSnBr_3$ showed absorbance ~80% for 200 nm thickness. While $TiO_2/CsPbBr_3$ with 700 nm thickness has shown ~100% absorbance (This might be the reason for higher current). At $CuO/CsPbBr_3$ and $CuO/CsSnBr_3$ interface, both have the same absorbance but electric field distribution is different. ETL/perovskite plays a role in the $I_{sc}$ rather than HTL/perovskite interface. This theoretical study will help to understand the interfaces such as ETL/perovskite and HTL/perovskite problems.

In **Chapter 8,** the thesis concludes the results and future scope of the research work.