INVESTIGATIONS ON HYSTERESIS IN PEROVSKITE HALIDES FOR PHOTOVOLATIC APPLICATIONS

THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE AWARD OF DEGREE

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In

Physics

By

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UNDER THE SUPERVISON OF

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2024

Dedicated

To

My

Great – Grandfather

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Date:

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LIST OF SYMBOLS AND ABBREVIATIONS

PH	Perovskite Halide
PV	Photovoltaics
VB	Valence Band
CB	Conduction band
I_{sc}	Short Circuit Current
J_{sc}	Current Density
V_{oc}	Open Circuit Voltage
P	Power
P_{max}	Maximum Power Output
P_{in}	Power Incident
FF	Fill Factor
PCE (η)	Power Conversion Efficiency
R_s	Series Resistance
R_{sh}	Shunt Resistance
I-V	Current – Voltage
I_0	Reverse Saturation Current
I_L	Photo-generated Current
I_m	Maximum Current
V_m	Maximum Voltage
AM	Air Mass
DSSC	Dye-Sensitized Solar Cell
PSC	Perovskite Solar Cell
MA	Methyl ammonium
FA	Formamidinium
ETL	Electron Transport Layer

EDAI	Ethylenediammonium Iodide
TFEA	Trifluoroethylamine
AVAI	Aminovaleric acid Iodide
MDMC	Mixed Dimensional and mixed Compositional
HTL	Hole Transport Layer
HTM	Hole Transport Material
SCLC	Space Charge Limited Current
EDX	Energy Dispersive X-Ray Analysis
E_g	Band Gap
hv	Photon Energy
E_u	Urbach Energy
eV	Electron volt
meV	Mili electron Volt
FWHM	Full width at half maximum
g	Gram
K	Kelvin
M.P.	Melting Point
JCPDS	Joint Committee on Powder Diffraction Standards
LED	Light Emitting Diode
ΔG	Gibbs Free Energy
ΔS	Entropy
ΔH	Enthalpy
RT	Room Temperature
Å	Angstrom
mg	milligram
N	Avogadro's number
cm	Centimeter

µm	Micro-meter
W/m^2	Watt per meter square
mV	mill volt
nm	nanometer
SSR	Solid State Reaction
SEM	Scanning Electron microscope
UV-Vis	Ultraviolet-Visible
DSC	Differential Scanning Calorimetric
XRD	X-ray Diffraction
DMF	Dimethylformamide
DI	Deionized

PREFACE

Renewable energy sources, such as solar and wind power, must supplant traditional energy supplies, such as coal and petroleum, in order to preserve our planet. Among renewable energy sources, solar power is likely the most common. Therefore, solar energy has the potential to greatly benefit both the climate and the economies of rich and developing nations in the future when paired with a clean and sustainable energy source. Solar cells that generate electricity through photovoltaic (PV) technology appear to be a promising method of converting sunlight into electricity.

Solar cell materials have been the subject of extensive research over the last few decades. Since the inception of the first solar cell concept (PN junction) using crystalline Silicon solar cells, which achieved efficiency at US Bell Laboratories in 1954, it gained significant interest. The efficiency of amorphous silicon-based solar cells with multiple-junction manufacturing cells has ranged from 4 . Polycrystalline/monocrystalline Si solar cells have attained a photovoltaic conversion efficiency of above twenty percent. Which is now commercially accessible. Due to their high efficiency, the PV market is now dominated by Si-based solar cells. As a result, the materials that are currently known for their practical applications in solar cell technology are still based on silicon technologies. There is a significant demand for alternative solar cell materials that are highly efficient in enhancing the efficiency of silicon technology. However, the downsides of Si-based solar cells include rigorous preparation conditions and high costs. Additionally, technologies such as CIGS and CdTe thin film solar cells have exhibited exceptional power conversion efficiency (η); however, their commercial applications are impeded by environmental contamination, high production costs, and other

complications. An essential criterion for selecting a material for solar cell application is its durability, which should be approximately 25 to 30 years. A more cost-effective method of producing tunable perovskite semiconductors is available, in contrast to the expensive procedure required to produce silicon. Perovskite exhibits numerous advantages compared to prevailing silicon panels. Nevertheless, Perovskites have attracted researchers because of their resilient optoelectronic properties and exceptional photovoltaic capabilities. ABX_3 is the general formula for organic-inorganic halide perovskite. Here, A = Cs^+, Cu^+, MA = $CH_3NH_2^+$, FA = HC $(NH_2)_2^+$, B = Pb^{2+}, Sn^{2+}, Ge^{2+}, and X = Cl, Br, or I. The first application of perovskite absorbers was documented in 2009. At that time, the efficiency rating of these cells was less than 4%, which was not particularly impressive. Furthermore, their durability was severely limited, making them unsuitable for practical applications. Because of these shortcomings, early perovskite solar cells failed to capture the attention or interest of researchers and scientists looking for more promising and efficient alternatives in photovoltaic technology. The scientific community consequently paid little attention to these early efforts using perovskite absorbers. Perovskite materials have drawn much attention because of their low cost and high potential in solar cell applications. Perovskite solar cells initially exhibited only modest power conversion efficiency (η). Nevertheless, scientists have made substantial progress in enhancing their performance through extensive research and technological advancements. Currently, the power conversion efficiency (η) of perovskite solar cells has surpassed 26%. Nevertheless, organic-inorganic halide perovskites are experiencing thermal instability as a result of the volatilization of organic cations that are present in the perovskite compositions. Perovskite lead halides have demonstrated their utility as outstanding optoelectronic devices, with band gaps between 1.3 and 2.3. This is attributed to their high absorption coefficient and the

elimination of the liquid hole transport layer, particularly in the context of dye-sensitized solar cell materials. Applications in optoelectronics and photovoltaics have shown significant interest in the cesium lead halides, denoted by the formula $CsPbX_3$(where X = I and Br). The direct bandgap nature of caesium lead halide compounds, along with their substantial light-absorbing capability in both the ultraviolet and visible spectrums, demonstrates their usefulness for solar cell applications. Additionally, these materials are utilized in applications, including light-emitting diodes (LED), photodetectors, and energy storage solutions. But, the major disadvantage of these materials is that they are too prone to moisture and degrade very fast. Hence, although these compounds possess notable optoelectronic characteristics, ensuring their stability is a crucial matter that must be addressed. Aside from compositional variation, several approaches are used to synthesize these materials in the air to address stability difficulties, such as solvothermal synthesis, quantum dots, one-step microwave-assisted, low-temperature synthesis, and solution phase synthesis. Therefore, it is imperative to comprehend the reasons for these materials' instability and their difficulty synthesizing them in ambient conditions. If it is intrinsic instability, it would not have been synthesized through the conventional solid-state route (SSR). But, in this thesis work, perovskite halides are nucleated at room temperature just by mixing the precursors, and that too in ambient conditions; thus, there is no need for calcination. The grain growth occurs after sintering the pellet in the vacuum at 80 for one hour (the synthesis details are provided in the experimental section). Therefore, this effortless cold sintering method was considered worthwhile for synthesizing the samples.

The main purpose of this thesis is to examine the current-voltage hysteresis issue in perovskite halides. Inorganic halide-based perovskite ($CuPbI_3$, $CuSnI_3$, and $CsSnI_3$) was chosen as the active material for this purpose. The I-V hysteresis of the samples has been

examined by altering the grain size by varying the sintering temperature and polarisation using DC poling.

The thesis has been divided into six chapters, each of which is described below:

Chapter 1: This chapter provides an overview of solar cells, including comprehensive reviews of existing literature. It analyzes the factors that drive work motivation, the historical context, and the basic principles of solar cells. It also highlights the necessary characteristics of active materials for perovskite solar cells. Furthermore, literature studies have identified significant perovskite halides (active materials) challenges. The chapter describes the current-voltage hysteresis problem in perovskite solar cells. This chapter also addresses the primary goals of the current study.

Chapter 2: This chapter explains the various experimental methods used in the current study. It describes the experimental equipment, analysis procedures, and synthesis routes used to produce the samples. The suggested system was synthesized using cold sintering procedures via a solid-state reaction process. It also provides a comprehensive overview of critical analytical techniques, including Rietveld refinement analysis. Additionally, it gives a detailed description of a variety of instruments, including XRD, SEM, TGA, DSC, UV-visible, AFM/PFM, DC Poling Unit, Electrometer for Pyro-current Measurement, Raman, impedance spectroscopy, and I-V measurement.

Chapter 3: this chapter aims to investigate the change in polarisation behaviour at the surface/interface of $CuPbI_3$ before and after light exposure. By altering the polarisation mechanism by varying the sintering temperature, compound $CuPbI_3$ was synthesized through the cold sintering technique. We also predicted the structure of $CuPbI_3$. Further, the chapter

will explore the effects of light exposure on $CuPbI_3$ hysteresis area and shape, impedance analysis, and conduction/hopping mechanisms**.**

Chapter 4: Due to environmental concerns and lead toxicity, there has been significant interest in developing lead-free alternatives such as Lead-free perovskite halides tin-based (Sn) perovskites. This chapter investigates the photo hysteresis behavior and the impact of phase transitions on the hysteresis of the lesser-known lead-free compound $CuSnI_3$. Lead-free halides perovskite $CuSnI_3$ was synthesized using the cold sintering method. Further, to investigate the impact of potential phase transitions on current-voltage hysteresis, we examined the temperature-dependent behavior of the current-voltage curve in both dark and light conditions, specifically in the presence of probable anomalies or phase transitions, such as AM 1.5 G. To observe the inherent characteristics of these irregularities, we subjected the sample to an electric field of 0.5 kV for a duration of 30 minutes. We then compared the current voltage behavior of the sample with its original state at a temperature of 300 K under normal environmental conditions.

Chapter 5: This chapter describes the isomorphic phase transition in the green polymorph of $CsSnI_3$ (G-$CsSnI_3$), which is cubic (Pa) at 295 K and persists in phase transitions at higher temperatures. We used PFM, temperature-dependent dielectric measurements, impedance spectroscopy, and Raman spectroscopy. To investigate the impact of the phase transition on current-voltage hysteresis, we examined the temperature-dependent behavior of the current-voltage curve under dark and light conditions (AM 1.5 G) around the phase transition. The poling impacts both domain size and grain number. Light and poling both appear to affect the relaxation time, which changes over transitions.

Chapter 6: This chapter concludes the findings of this research outcome and lists a few possibilities for future investigations.