INVESTIGATIONS ON HYSTERESIS IN PEROVSKITE HALIDES FOR PHOTOVOLATIC APPLICATIONS

THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE AWARD OF DEGREE

Doctor of Philosophy

In

Physics

By

PREM CHANDRA BHARTI

UNDER THE SUPERVISON OF

PROF. PRABHAKAR SINGH

DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY

(BANARAS HINDU UNIVERSITY)

VARANASI – 221005

17171504 **2024**

Chapter-6

Conclusions and Future Scopes

CHAPTER 6: Conclusions and Future Scopes

6.1 Conclusion of the Present Investigation

This thesis focused on employing cost-effective materials and simple synthesis techniques to produce perovskite halides for application in perovskite solar cells (PSCs). The synthesis process was carried out under ambient conditions and at room temperature. As discussed in Chapter 1, perovskite halides have some well-known challenges, including photo-instability, structural instability, and current-voltage hysteresis.The primary objective of this thesis was to investigate the current-voltage hysteresis in perovskite halides in detail. Therefore, it was proposed to synthesise copper lead iodide ($CuPbI_3$), copper tin iodide ($CuSnI_3$), and Cesium tin Iodide ($CsSnI_3$),via solid state rection route method. Considering the research carried out, the outcomes obtained, and the conclusions offered in previous chapters, the overall conclusion of the thesis work can be concisely summarized as follows:

We observed the alteration in polarisation characteristics at the surface/interface by utilising the Havriliak-Negami equation to analyse the relatively unfamiliar $CuPbI_3$ compound before and after exposure to light. We have successfully synthesised $CuPbI_3$ using the cold sintering approach. Additionally, we have observed that the polarisation mechanisms have been modified.Raising the temperature for sintering, specifically in a cold environment. The crystal structure of $CuPbI_3$ was previously unknown, and our prediction suggests that it has a hexagonal ($R\bar{3}m$) structure with a 21R prototype representation. The hysteresis is said to be influenced by ferroelectricity, which involves reorientable dipoles with non-centrosymmetry. To investigate this, a centrosymmetric $CuPbI_3$ material is used. Despite the presence of centrosymmetry, we have observed a significant shift in the hysteresis area and form of the I-

V curve under AM 1.5G sunlight, as the polarisation behaviour changes. Our experimental findings indicate that the presence of apolar dielectric behaviour is responsible for the observed I-V hysteresis, rather than the existence of strong ferroelectric polarisation (which was not observed in this particular example).

Lead-based perovskites have exhibited exceptional power conversion efficiency in solar cells. Nevertheless, the environmental concerns and toxicity of lead have generated substantial interest in the development of lead-free alternatives. To tackle these issues, researchers have looked into lead-free perovskite halides, like tin-based (Sn) perovskites. As a replacement to lead, tin halide perovskites ($CsSnI_3$ and $CuSnI_3$ etc.) show promise because they share lead's electrical characteristics while being less hazardous. However, these materials often suffer from stability issues .Here, we conducted a study on the less well-known compound $CuSnI_3$ to investigate the photo hysteresis behaviour in its non-centrosymmetric phase. It is important to understand the impact of phase transitions on photoelectric hysteresis in perovskite halides in order to enhance the durability and efficacy of perovskite-based devices. Researchers can create techniques to manage and limit the impacts of phase transitions on hysteresis by understanding the factors that influence them, resulting in more stable and efficient devices. This understanding is crucial for developing next-generation solar cells to avoid hysteresis, which can degrade performance over time. Our investigation of $CuSnI_3$ provides valuable insights into the influence of phase transitions on the photoelectric hysteresis observed in perovskite halides. The compound $CuSnI_3$ has a triclinic $P3m1$ structure at a temperature of 300 K. Phase transitions are seen at around 320 K and 408 K. These transitions alter the photoelectric response of the material by influencing its electrical characteristics, defect states, and ion migration routes. Phase transitions play a crucial role in modifying hysteresis behaviour, as evidenced by the dramatic reduction in hysteresis area surrounding the first phase transition that is shown by I-V measurements. These results are further supported by AC conductivity investigations, which demonstrate clear variations in dc conductivity, hopping frequency, and frequency exponent during the phase transitions. Raman spectroscopy confirms the structural alterations seen, with shifts in E and A modes showing symmetry and molecular deformation. In order to address the issues of performance instability and degradation, a better understanding of the impacts of phase transitions on photoelectric hysteresis can be used to build devices based on perovskites that are more stable and efficient.

Again we investigated on the lead free perovskite halide to explore the hysteresis property in $CsSnI_3$ .The green polymorph of $CsSnI_3$, which was obtained via the cold-sintering process, exhibits a cubic phase at a temperature of 295(±1) K.The structural refinement reveals the presence of the cubic T_h phase.The $CsSnI_3$ compound exhibits a (m-3)-Pa$\overline{3}$ crystal phase with paramorphic hemihedry, namely diacisdodecahedry. The lattice constants have been determined with standard uncertainty values. The value for lattice constant an is 12.2771(1) Å, and the cell volume is 1850.49(4) Å3. The iodine atoms are not located in equivalent places, and there are 8 molecules per unit cell. In contrast to other colour variations, this green $CsSnI_3$ has exhibited consecutive isomorphic phase transitions in accordance with the group-subgroup theory.

Further we examined the impact of phase transitions on hysteresis and discovered pyroelectricity in the G-$CsSnI_3$ sample, similar to ferroelectric materials. Despite the sample's centrosymmetric nature (as suggested by its overall behaviour), we used various techniques such as PFM, temperature-dependent dielectric measurements, impedance spectroscopy, and Raman spectroscopy (details provided below). Our findings indicate that local changes in vibrational modes have a significant effect on the current-voltage hysteresis and conduction properties of perovskite halides, revealing the presence of local non-centrosymmetry within the globally centrosymmetric $CsSnI_3$. In summary, this study suggests that the local alteration in vibration modes greatly influences the current-voltage hysteresis and conduction behaviour of perovskite halides, indicating the existence of local non-centrosymmetry within the globally centrosymmetric $CsSnI_3$.

All compounds ($CuPbI_3$, $CuSnI_3$, and $CsSnI_3$) were prepared by Cold sintering (CS)–Solid-state reaction (SSR) route.

Table 6.1 Distribution of relaxtion time in defferent samples after poling and after light fall

Sample Name	Relaxation Time of grain (S)		
	Pristine	AL	AP
$CuPbI_3$	2×10^{-6}	2×10^{-6}	----
$CuSnI_3$	2.7×10^{-2}	2.52×10^{-12}	8.34×10^{-11}
$CsSnI_3$	2.18×10^{-7}	2.5×10^{-14}	1.7×10^{-5}

Overall, conclusion of this work is listed as-

- The hysteresis is reported to be affected by the change in polarization behaviour.
- Hysteresis being a slow process is observed here to be affected by relaxation time depending on the type of defect centres leading to the alteration in relaxation time of grain
- In centrosymmetric $CuPbI_3$, relaxation time has not altered with light fall

- In centrosymmetric $CsSnI_3$, relaxation time has reduced with light fall and poling suggesting its ionic behaviour and minimal hysteresis.
- In $CuSnI_3$, faster response is seen after poling and photo exposure assisting in reducing the hysteresis and proving the suitability of material not only for photovoltaic applications but also in photo/pyroelectric devices.

6.2 Outlook for Future Work

Some of the following points should be considered for future opportunities in this field of work.

- Develop the material to facilitate the development of faster optoelectronic switching devices, photodetectors, and solar cells.
- With the thickness alteration in $CuSnI_3$, photo/pyroelectric devices can be fabricated
- The influence of poling field, duration, and temperature variation on the hysteresis behavior of perovskite halides on single crystals for photo/pyroelectric