$Cu_2HgSn(Se_xS_{1-x})_4$ based Quaternary Chalcogenides for Photovoltaic and Thermoelectric Applications

A Thesis submitted by

Sumit Kukreti

in partial fulfillment of the requirements for the award of the degree of

Doctor of Philosophy

॥ त्वं ज्ञानमयो विज्ञानमयोऽसि ॥

Indian Institute of Technology Jodhpur
Department of Physics

March 2024

7
Conclusion and Future scope of work

The emerging chalcogenide family of Cu-based quaternary diamond-like semiconductors showed tremendous potential for energy applications. Unlike the extensively studied Cu_2ZnSnS_4, our study primarily focuses on the Zn cation substituted Cu_2HgSnS_4 and its effectiveness in energy applications. We theoretically demonstrated that while varying S and Se composition in $Cu_2HgSn(Se_xS_{1-x})_4$ compound with x= 0, 0.25, 0.50, and 1, the band gap varies in a range of 1.33-0.811 eV along with almost nearly identical absorption coefficient of ~ 10^4 cm^{-1}. We observed the ductile nature of this alloy composition, as the estimated Pugh's ratio is larger than 1.75 and is found to be even greater than the parent compound Cu_2ZnSnS_4, which signifies its suitability for flexible optoelectronic devices.

Further considering the optimized material parameters, our device modelling for single/tandem and graded bandgap absorber-based solar cells emphasized essential factors for optimal photovoltaic response. We found limited efficiency for the tandem junction device due to a lower bottom cell current with a lower bandgap $Cu_2HgSnSe_4$ bottom absorber. Interestingly, motivation from the less complex and largely explored graded bandgap absorber-based CZTSSe solar cells, examining $Cu_2HgSn(Se_xS_{1-x})_4$ alloy-based absorber, has demonstrated its potential.

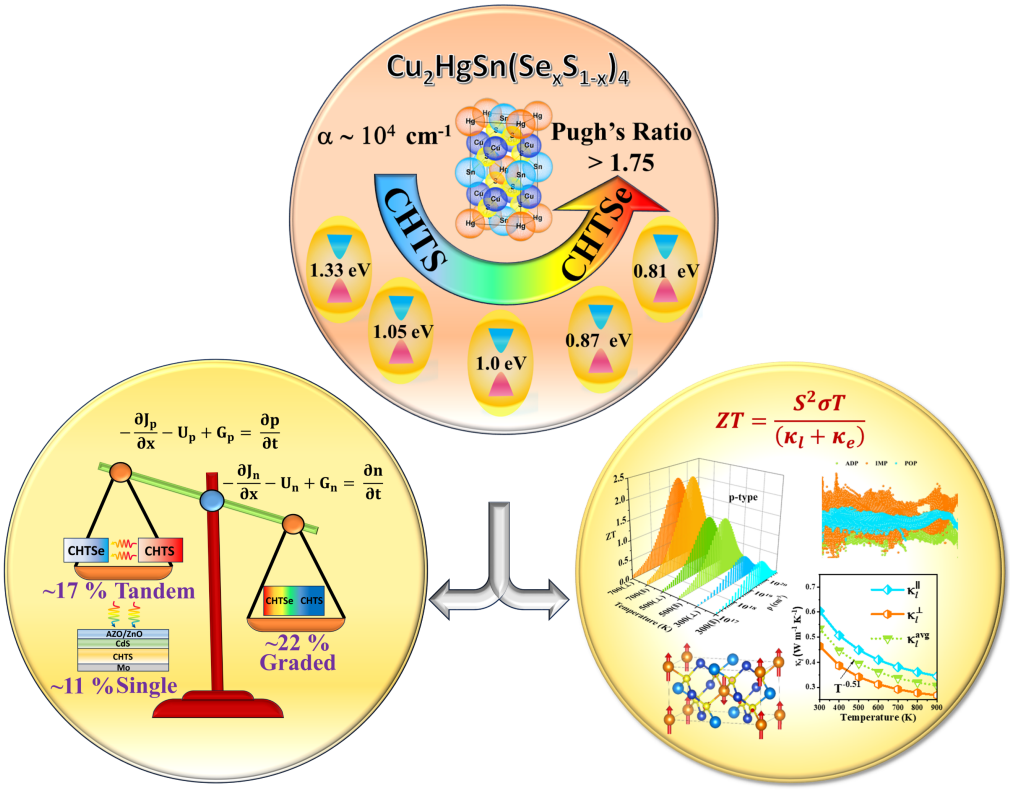


Figure 7.1 Schematic highlighting the $Cu_2HgSn(Se_xS_{1-x})_4$ material prospects and its potential for photovoltaics and Cu_2HgSnS_4 as p-type thermoelectric applications.

The positive bandgap grading with the optimized CL of ~ 200 nm provides the best performance that could surpass the estimated tandem cell efficiency of ~ 17%. The sharp increasing Se concentration on the back contact enables the device to perform more efficiently with a total absorber thickness of 2 μm. Our studies suggest the device can perform efficiently until 10^{15} cm^{-3} bulk defect density. However, it is highly susceptible to interface defects, which downgrade the performance even after 10^{12} cm^{-2} interface defect concentration. A positive conduction band offset of ~0.3 eV is favorable for large efficiency, which inherently provides a large built-in field at the junction, assisting the device in extracting the photocarrier effectively with efficiency >20%. This study highlights the possibility of the graded bandgap absorber in the chalcogenide family as a practical approach to achieve the best efficiency with little thickness.

Furthermore, considering the ultralow thermal conductivity reported in similar diamond-like structures such as Cu-based tellurides and selenides, the phonon dynamics in the Cu_2HgSnS_4 is probed for the intermediate temperature range. Our examination via single mode relaxation time approximation (SRTA) with particle-like and wave-like phonon consideration gives 0.53 $Wm^{-1}K^{-1}$ (0.33 $Wm^{-1}K^{-1}$) lattice thermal conductivity at 300 K (700 K) in Cu_2HgSnS_4. The heavy element Hg contributes a modest amount of anharmonicity to the system. The relatively weak binding of the Hg atom is causing significant vibrations, similar to the rattling mode in cage-like compounds. Therefore, due to ultralow thermal conduction, the maximum estimated ZT value for the p-type (n-type) system is found to be 2.28 (0.77), indicating a potential for intermediate-temperature thermoelectric application. A further possibility of alloying S/Se compositions on thermal conduction needs to be explored towards enhanced ZT value(s) via the possible reduction in κ_l values due to the heavy Se element and its alloy compositions with S.

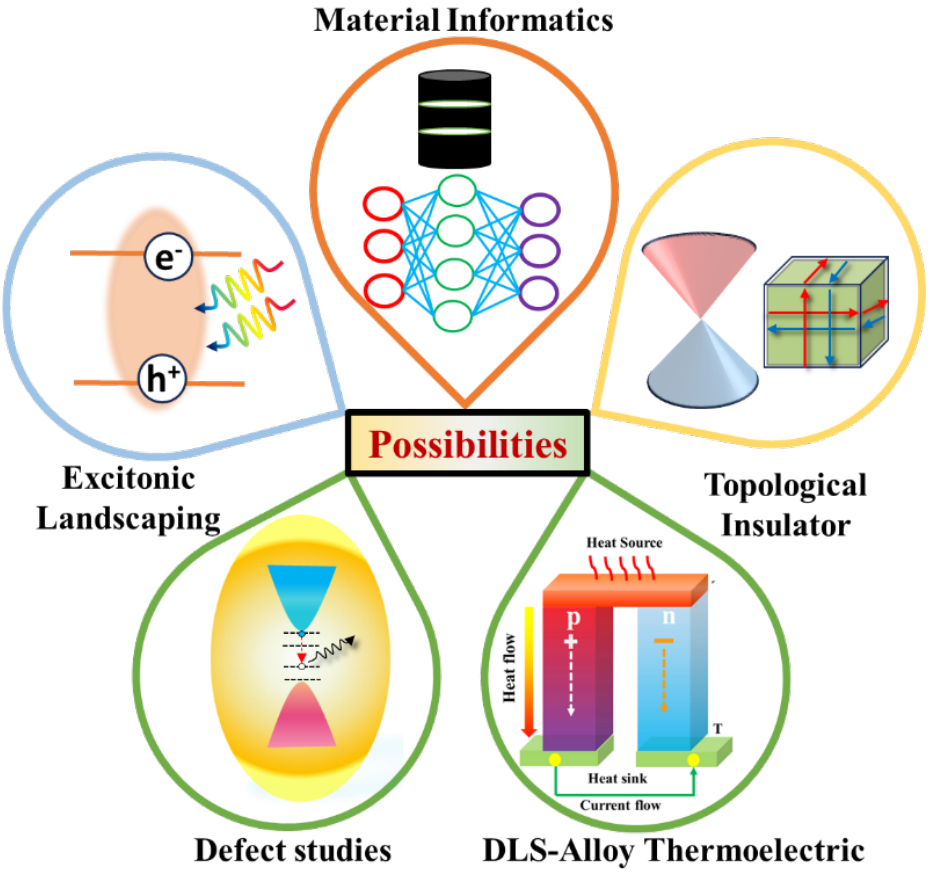


Figure 7.2 Schematics highlighting the potential aspects that need to be explored for a better understanding of their potential in next-generation optoelectronic devices.

Cu-based Diamond-like structure family offers a vast range of applications. While understanding these systems for optimal photovoltaic and thermoelectric responses together with other energy applications, it is essential to understand the defect and their impact on electron dynamics within this family. For Cu_2ZnSnS_4, the multiple point defects, such as antisite defect, vacancy defect, and their transition level information, are available in the literature. In contrast, these relevant pieces of information are still missing for the rest of the possible quaternary chalcogenide, especially when discussing avoiding the Cu_{Zn} antisite defect via substituting Zn with another element. Furthermore, understanding the effect of intrinsic and extrinsic point defects on thermoelectric properties is vital because V_{Cu} can reduce mobility by increasing carrier scattering. However, this effect can be mitigated by substituting Sn with other elements by introducing antisite defects in Cu-rich configurations.

To further investigate this entire family for photovoltaics and detector applications, exciton binding energy and polaronic mobility-related information could be precious for screening materials for device applications. In addition, investigating the topological surface states in low bandgap Diamond-like semiconductors is another area of research that is promising for fundamental aspects as well as for future electronic device applications. Additionally, a proper database of Cu-based quaternary chalcogenides for designing new materials for multiple energy devices would be highly beneficial. Further cost-effective realization of numerous quaternary chalcogenide thin films is still under exploration, which, in the future, could come up with some effective methodologies for thin film to optoelectronic and thermoelectric device technology.

In conclusion, our current study opens the door for experimentalists to investigate graded bandgap absorber-based photovoltaics and intermediate temperature thermoelectrics using Cu-based quaternary chalcogenide materials, in addition to the aforementioned opportunities for further exploration of quaternary chalcogenides.