Abstract

The research presented in this dissertation provides a comprehensive investigation into the structural and electronic landscapes of Pb-free, two-dimensional (2D) hybrid organic-inorganic perovskites (HOIPs) under various temperatures and hydrostatic pressures. By replacing previously studied toxic Pb-based systems with Sn^{2+} and Cu^{2+} alternatives, this work demonstrates how the inherent lattice softness of these materials can be exploited to achieve unprecedented control over their optoelectronic properties. The primary objective is to understand the interplay between lattice dynamics, electronic bandwidth, and exciton localization when subjected to hydrostatic pressures up to $\sim$11 GPa and temperatures ranging from 20 to 320 K.

Chapter 1 establishes the conceptual and theoretical framework of the dissertation, including hypothesis. It introduces the structural fundamentals of HOIPs, emphasizing the consequences of octahedral flexibility and orbital hybridization for band structure formation. Particular attention is given to the scientific hypothesis that lattice softness governs the competition between electronic bandwidth broadening and lattice relaxation energy. This chapter identifies key unresolved questions in the field, such as contradictory pressure-dependent band gap trends and the stability of self-trapped excitons (STEs) under extreme compression, providing the theoretical foundation necessary to interpret the experimental results.

Chapter 2 details the experimental methodologies developed to prove these materials. It describes the integration of a membrane-driven diamond anvil cell (DAC) with closed-cycle helium cryostat, enabling precise thermodynamic control. A significant portion of this chapter is devoted to the systematic characterization of the Daphne 7575 pressure-transmitting medium, establishing its hydrostatic limits down to 40 K. The chapter also outlines the rigorous calibration protocols used, including temperature-corrected ruby fluorescence and the cross-validation of reflectance (R), transmission, and photoluminescence (PL) spectroscopy to ensure the extraction of intrinsic material parameters.

Chapter 3 comprises four peer-reviewed research articles that detail the primary findings of this work.

In the studies presented in Sections 3.1 and 3.2 the electronic tunability of tin-based iodide perovskites, specifically $(4FP)_2SnI_4$ and TMA_2SnI_4, is investigated. These works establish that Sn-based systems possess record-breaking pressure coefficients (up to -187 meV/GPa), significantly surpassing their Pb-based counterparts. The results demonstrate a linear band gap narrowing across structural phase transitions, positioning these materials as ideal candidates for high-sensitivity optical pressure sensors.

The work described in Section 3.3 explores the complex excitonic energy landscape in $(4FPEA)_2SnBr_4$. This study uncovers a striking excitonic dichotomy: while the near-band-edge emission redshifts under compression, the self-trapped exciton emission exhibits an

anomalous blueshift. This research provides a microscopic framework for understanding small polaron formation, demonstrating how halide-specific lattice rigidity and dielectric screening dictate the stabilization of localized versus delocalized excitonic states.

Section 3.4 transitions the investigation to Cu-based systems, specifically $(PMA)_2CuX_4$ (X= Cl, Br). This study addresses the critical challenge of thermodynamic stability and provides a comparative analysis of thermochromism versus piezochromism. It is demonstrated that while both temperature and pressure induce significant redshifts, the underlying mechanisms, thermal expansion versus mechanical compression, interact with the electron-phonon landscape in fundamentally different ways, influencing the structural resilience of the material up to 11 GPa.

Finally, the dissertation provides a summary of the findings and formulates overall conclusions regarding the future of stimuli-responsive optoelectronics.

In summary, this dissertation provides a coherent description of the relationships between mechanical perturbations, electronic structure, and excitonic behavior in selected Pb-free 2D perovskites. The results constitute a significant contribution to the development of semiconductor physics, proving that lattice softness, often viewed as a limitation, can function as a tunable degree of freedom for quantum-state engineering and the design of next-generation adaptive optoelectronic devices.