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Thesis Title: Optoelectronic Applications and Spintronic Aspects of Metal Halide Perovskites.

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The present thesis outlines the fabrication and characterization of a range of perovskite thin films and nanostructures to investigate their optoelectronic and spintronic properties. Primarily, the electronic bands, localized charge/spin transport, and photophysics in different perovskites were investigated through scanning probe microscopic techniques. In addition, a significant effort was devoted to device physics, in understanding their functionality for optoelectronic and spintronic applications.

Chapter 1. Introduction

This chapter deliberates the background of existing literature, which motivated the doctoral research work. Throughout the chapter, the overreaching goal is to provide a concise discussion on metal halide perovskites, from their basic composition and structure to the fundamental optoelectronic and spintronic properties followed by the progress and current status of different halide perovskite-based optoelectronic and spintronic devices.

Chapter 2. Experimental Methods

In this chapter, the procedures followed to form and characterize several perovskite compounds have been discussed, along with the fabrication of different photovoltaic and spintronic devices and their characterization.

Chapter 3. Ternary Halide Perovskites: Detrimental Role of Defects

In this chapter, the role of defects on band-edges of bismuth-based ternary halide perovskites ($A_3Bi_2I_9$) formed with cesium (Cs) and methylammonium (MA) ions at the A-site has been studied to investigate the charge transport towards photovoltaic applications. A range of precursor-stoichiometries are considered leading to different reaction environments. In $Cs_3Bi_2I_9$, the intrinsic defects formed during the perovskite formation affect the materials' band-energies as observed through scanning tunneling spectroscopy (STS). Upon a variation in the precursor stoichiometry in forming the perovskites, STS studies evidence a decrease in the band gap of the materials formed with BiI_3-rich precursors due to formation of deep defects above the VB-edge responsible for the poor photovoltaic performance of heterojunction solar cells. In contrast, the transport gap of $(CH_3NH_3)_3Bi_2I_9$ becomes independent of the precursor stoichiometry due to their defect-tolerant nature. As a result, the hybrid perovskite exhibits a superior charge transport and higher short circuit current compared to the inorganic one during photovoltaic performance.

Chapter 4. Double Perovskites: Introducing Cationic Order

In this chapter, the role of cation-ordering in double perovskite solar cells ($Cs_2AgBiBr_6$ to be specific) has been investigated towards efficient charge transport in photovoltaic devices. In spite of environmental stability and toxic-free merits, performance $Cs_2AgBiBr_6$ has not excelled due to their large indirect bandgap, low absorption of solar spectrum, and more importantly hurdles in carrier transport processes. A large number of intrinsic defects and self-trapped excitons (STE) appear in the double perovskite due to a disordered arrangement of Ag/Bi octahedra in the perovskite lattice. In this direction, a ligand-assisted film-fabrication method has been investigated through the use of phenethylammonium bromide (PEABr) to regulate the cation-ordering in the system towards an improved carrier conduction process.

Chapter 5. Quasi-2D Ruddlesden-Popper Lead Halide Perovskites: How edge Matters

In this work, a band-mapping technique is introduced to investigate the low energy edge states in quasi-2D Ruddlesden-Popper (RP) perovskites, $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ through a localized mode of measurement, namely

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scanning tunneling spectroscopy. The local intrinsic band structure reveals the formation of 3D $CH_3NH_3PbI_3$ ($MAPbI_3$) at the edges of the quasi-2D perovskites. The presence of $MAPbI_3$ at the edges of quasi-2D perovskites and thereby a self-forming type-II band-alignment in $BA_2MA_2Pb_3I_{10}$ ($n = 3$) has been the rationale behind achieving a high efficiency in solar cells based on the material, although it has a large exciton binding energy. Kelvin probe force microscopy under illumination conditions yields a higher surface photovoltage at the edges compared to the interior and supported the inference of internal exciton dissociation as a result of the in-situ type-II band-alignment in the quasi-2D RP perovskites.

Chapter 6: Rashba Band Splitting in Hybrid Halide Perovskite

This chapter reports an experimental observation of Rashba splitting in methylammonium lead iodide ($MAPbI_3$). Such non trivial Rashba split band-structure is unprecedentedly important for superior optoelectronic and spintronic applications of the compound. Because of a large spin-orbit coupling parameter in the non-centrosymmetric material, both of the bands were predicted to split having two different spin-textures leading to two different *Z*-components of total angular momentum (J_Z). Spin-polarized scanning tunneling spectroscopy is employed to probe only one-type of J_Z-matched bands throughout the film; dI/dV spectra recorded at many different points of a film however allow to monitor both the Rashba split-levels and also deliberate on their spin-textures and recombination mechanism thereby.

Chapter 7. Spin Photovoltaic Effect in Chiral Perovskites

In this chapter, a pair of lead-free chiral perovskites has been introduced towards the detection of circularly polarized light (CPL). Such organic-inorganic hybrid perovskites have an integration of a bismuth-based inorganic framework and a chiral organic sub-lattice (*R*/*S*-methylbenzylammonium). The chiroptical activities of the perovskites under CPL illumination evidence generation of spin-polarized carriers. Interestingly, due to the intrinsic chirality of the compounds, the perovskites exhibit chirality-induced spin-selectivity (CISS) allowing the transport of one type of spin-half state while blocking the other-type. Accordingly, a spin-dependent photovoltaic effect has been observed in the vertical heterojunction devices; the photocurrent response has been clearly different under left- and right-handed CPL illuminations resulting in photocurrent anisotropy. As a result, the polarization states of CPL photons could readily be detected by investigating the anisotropic current response of the photodetector devices.

Chapter 8. Concluding Remarks

This chapter contains the concluding remarks and the key findings of the doctoral research work as presented in the thesis. In addition, it also discusses about the development of new perovskite materials and future prospects of the research field.

Appendix A. Quantifying Anisotropic Thermal Transport in 2D Perovskite

In this additional work, the anisotropic thermal transport in two-dimensional (2D) perovskite has been investigated through a novel measurement technique called cross-sectional scanning thermal microscopy (xSThM).

Appendix B. Sulfur-Vacancy Passivation in Sb_2S_3 Thin Films

In this effort, a modified two-step sequential deposition method has been developed to form Sb_2S_3 thin film. In contrast to the conventional chemical bath deposition (CBD) route, this sequential deposition approach allowed passivation of sulfur-vacancies in Sb_2S_3 for better solar cell performance.

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