学 位 論 文 審 査 の 要 旨

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学 位 論 文 題 名

Investigation of optical modulation of organic-inorganic hybrid copper halide microcrystals
（有機–無機ハイブリッド銅ハライド微結晶における光学的制御の研究）

The candidate's doctoral research focuses on elucidating and controlling the photophysical properties of zero-dimensional (0D) organic–inorganic hybrid copper halides (OIHCHs), which are emerging as promising lead-free alternatives to lead halide perovskites for optoelectronic applications. Owing to their strong exciton–phonon coupling, these materials exhibit unique optical features such as broadband and tunable photoluminescence (PL), large Stokes shifts, high exciton binding energies, and delayed emission arising from self-trapped excitons (STEs). Despite their potential, the structural origins and detailed mechanisms governing STE formation and emission remain insufficiently understood. The candidate addresses these challenges by systematically tuning exciton recombination dynamics and emission color via substrate interactions, external stimuli, and heterometal-ion doping.

The dissertation is organized into five logically structured chapters. In the first chapter, the candidate provides background on 0D materials, covering methods of synthesis, crystal structures, methods of structural characterization, electronic structures, optical properties, and emerging applications. Particularly, the structures of such materials and their STE properties are discussed in detail. Also, structural modifications and external-stimulus-induced changes in the optical properties are thoroughly discussed in this chapter before he provides motivation and specific objectives of the thesis. In chapter two, the candidate discusses materials and methods, including the synthesis of 1-butyl-1-methyl piperidinium copper bromide [$(Bmpip)_2Cu_2Br_4$] microcrystals and their structural characterization by powder and single-crystal X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy with energy-dispersive X-ray analysis, and Inductively Coupled Plasma Mass Spectrometry. Also, he provides methods about steady-state, time-resolved, and temperature-dependent PL spectroscopy. The third chapter makes a key contribution to the thesis by showing substrate-dependent modulation of STE emission from Bmpip)$_2$Cu$_2$Br$_4$ microcrystals. The candidate shows that these microcrystals grown on insulating substrates exhibit dominant red emission, whereas interaction with conductive metal substrates induces strong green emission. Through steady-state and time-resolved PL analyses, these effects are attributed to metal–semiconductor interactions and the formation of hybrid interfacial states, which selectively deactivate static charge on the crystals and promote excitonic green emission. Another notable achievement is the observation of laser-induced increases in the emission intensity of (Bmpip)$_2$Cu$_2$Br$_4$ microcrystals, which he studied in detail under Chapter Four. He covers enhancement and spectral transformation under intense continuous-wave irradiation. The candidate reports a tenfold increase in emission intensity, accompanied by a transition to broad yellow emission, without detectable phase transitions or major lattice distortions. This previously unreported phenomenon in OIHCHs provides new insight into STE dynamics and excited-state deactivation pathways. Finally, chapter five presents a systematic study of the effects of antimony (Sb^{3+}) doping on the optical properties of Bmpip)$_2$Cu$_2$Br$_4$ microcrystals, revealing concentration-dependent changes in emission color and prolonged excited state lifetimes. By carefully ruling out alternative explanations such as halide vacancy filling, the candidate convincingly demonstrates that heterometal ion incorporation plays a decisive role in modifying STE-related emission pathways. Overall, the candidate's research provides significant and original contributions to the fundamental understanding of STE-based photophysics in 0D hybrid copper halides. The work is experimentally rigorous, conceptually sound, and clearly articulated. The findings offer practical strategies for tuning and optimizing emission properties and exciton dynamics in lead-free metal halides. The candidate demonstrates a high level of scientific competence and independence.

The committee highly evaluated the above achievements. Based on his research accomplishments and doctoral coursework, the committee determined that the applicant fully meets the requirements for the Doctor of Philosophy (Environmental Science).