学 位 論 文 内 容 の 要 旨/Dissertation Abstract

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学 位 論 文 題 名/Title of Dissertation

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)

Zero-dimensional (0D) organic-inorganic hybrid copper halides (OIHCHs) are considered a promising lead-free alternative to lead halide perovskites, which are well known as excellent semiconductor materials for optoelectronic applications. OIHCHs exhibit unique optical properties such as efficient UV light absorption, broad and tunable photoluminescence (PL) band with large Stokes shift, high exciton binding energy, and long-lived emission. These features are attributed to the formation of self-trapped excitons (STEs) arising from the strong exciton-phonon coupling. Various combinations of organic ligands and inorganic copper clusters have been demonstrated for the STE emission modulation. External stimuli such as heat and pressure, can also modulate the STE emission by phase transitions or fine lattice distortions, thereby enabling controlled exciton-phonon coupling. However, the influence of structural features on STE formation and the detailed mechanisms governing STE emission remain insufficiently understood.

In this dissertation, I investigate how lattice distortions induced by external stimuli affect the STE states in 0D OIHCH, namely, 1-butyl 1-methyl piperidinium copper bromide [$(Bmpip)_2Cu_2Br_4$] microcrystals (MCs). I developed new strategies to modulate PL color, exciton recombination dynamics, and the energy barriers between these states through interactions with conductive materials, as well as by applying heat, pressure, laser irradiation, and heterometal ion doping. I synthesized $(Bmpip)_2Cu_2Br_4$ MCs using a simple wet-chemistry method. Additionally, Sb^{3+}-doped $(Bmpip)_2Cu_2Br_4$ MCs were prepared to elucidate the effects of heterometal ion doping on the photophysical properties of the MCs. I characterized these MCs using powder and single-crystal X-ray diffraction as well as scanning-electron microscope (SEM) equipped with the energy-dispersive X-ray spectroscopy (EDX). I conducted steady-state, time-resolved, and temperature-dependent PL spectroscopy to investigate the STE-based emission modulations in both the $(Bmpip)_2Cu_2Br_4$ MCs and Sb^{3+}-doped $(Bmpip)_2Cu_2Br_4$ MCs.

First, I demonstrated STE-based emission modulation of the 0D $(Bmpip)_2Cu_2Br_4$ MCs by applying

the interaction with the conductive material surface, mechanical force, and heating. The MCs prepared on borosilicate glass plates show green-red dual-emission. The MCs powdered using insulating materials show no significant emission modulation. In contrast, the MCs interacted with conductive material surface exhibit intense green emission. Temperature-dependent emission color modulation of the MCs indicates the presence of green and red emission states originating from the surface phonons (STE_S) and lattice phonons (STE_L), respectively. Additionally, heating activates the STE_L-associated red-emission state and facilitates the STE trapping and de-trapping between those states.

Second, I demonstrate a laser-induced PL intensity enhancement in $(Bmpip)_2Cu_2Br_4$ MCs under intense continuous-wave (CW) laser irradiation (405 nm, >66 kW cm^{-2}). The PL intensity increases by up to tenfold, accompanied by a spectral change from the initial green–red dual emission to a broad yellow emission. The PL lifetime decreases from 12 ns to 2 ns, indicating suppression of the STE trapping and de-trapping process. SCXRD analysis shows no detectable phase transitions, although slight variations in the lattice parameters are observed. Such PL intensity enhancement with spectral change driven by subtle lattice distortions without phase transitions has not been previously reported in OIHCHs.

Third, I explore the effects of Sb^{3+}-doping on the optical properties of the 0D $(Bmpip)_2Cu_2Br_4$ MC using $SbBr_3$ as the dopant precursor. The Sb^{3+}-doped MCs exhibit a broad orange–red emission with longer PL lifetime compared with undoped MCs. SEM-EDX analysis confirms the presence of Sb^{3+} within the host lattice. The degree of Sb^{3+}-doping-induced optical modulation depends on the Sb^{3+} concentration. I also investigated the effect of Br vacancy filling by varying the Br/Cu ratio during MC synthesis, ruling out the possibility that the observed spectral changes originate from bromide vacancy filling caused by $SbBr_3$ addition.

This research provides new insights into previously unexplored aspects of the photophysics of 0D OIHCHs. The findings not only advance the fundamental understanding of STE-based emission in these materials but also offer practical strategies for the design and application of next-generation optoelectronic devices.