学 位 論 文 審 査 の 要 旨

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Spatially controlled bandgap engineering and charge carrier recombination in lead halide perovskites by optical trapping
(光トラッピングによるハロゲン化鉛ペロブスカイトにおけるバンドギャップ工学と電荷キャリア再結合の空間的制御)

Organic-inorganic lead halide perovskites are promising for next-generation energy-harvesting and light-emitting devices. Their strong visible (vis)-to-near-infrared (NIR) light absorption, brilliant photoluminescence (PL), long-range carrier diffusion, low-temperature solution processability attracted the candidate to this research subject. The candidate focused on tuning halide perovskites' optical properties and bandgap to develop high-quality bandgap-engineered materials by optical trapping using a NIR laser. One consideration was the principles and uses of laser-based optical trapping in various fields to manipulate microscopic objects. The research outcome was classified into five chapters.

In chapter 1, the candidate reviewed the chemical composition, structure, properties, and applications of perovskites. This chapter focuses on the common synthesis techniques of perovskites with different sizes and shapes. It discusses the characterization, optical properties, halide exchange reactions, and vacancy filling of perovskites. The candidate also reviewed the applications of perovskites to solar cells, LEDs, and lasers.

Experimental methods are collected and discussed in Chapter 2. This chapter includes detailed information about the chemicals and materials and the synthesis of perovskites in different shapes and sizes. The candidate used the solvent evaporation technique for preparing microcrystals and the ligand-assisted reprecipitation method for synthesizing nanocrystals. Thin films of the nanocrystals were prepared by the drop-casting method. The instrumentation section is focused on the basic working principle and instrumental setup for the laser trapping system using the 1064 nm near-infrared laser and spectroscopic analysis using 1064 nm and 405 nm continuous-wave lasers. The charge carrier dynamics in perovskites were studied using a time-correlated single-photon counting system. Perovskite samples were characterized using the techniques of steady-state fluorescence and UV-vis absorption spectroscopy, a scanning electron microscope, and the energydispersive X-ray spectroscopy.

In chapter 3, the candidate demonstrated a new laser trapping-based methodology for the site-specific halide exchange reaction in the halide perovskite crystals. In general, the halide exchange reaction proceeds homogeneously in the whole crystal, and the bandgap is varied in the entire region in reactant halide solutions. Here, with a focused near-infrared laser beam, halide exchange was accomplished site-specifically at the desired part of a large microplate or microrod crystals. Here, the candidate confirmed the site-specific halide exchange reaction from changes in the photoluminescence emission and spectra under near-infrared laser irradiation and wide-field ultraviolet laser irradiation. Then the possible mechanism of the exchange reaction was discussed from the viewpoint of local concentration increase of the halide ions at the focal volume under laser trapping.

Chapter 4 of the thesis collects results and discusses the suppression of halide exchange reaction by optically controlled site-specific halide vacancy filling of the perovskite microcrystals. The spontaneous halide exchange from bromide to iodide of as-prepared $MAPbBr_3$ crystals occurred homogeneously in a methylammonium iodide solution (MAI). However, such an exchange was absent for a crystal pre-incubated in a MABr solution. The candidate demonstrated such halide exchange suppression at specific sites of the microrod crystals through vacancy filling using a NIR laser beam. The NIR laser irradiation filled the halide vacancies exclusively at the irradiated part, while the characteristic features of the non-irradiated parts remained unchanged. The local halide vacancy filling was proved with steady-state and time-resolved fluorescence measurements.

Chapter 5 focuses on the preparation of halide perovskite heterojunctions at desired locations by laser trapping. Also, it discusses the control of the transport and accumulation of charge carriers across the heterojunctions. The site-specific halide exchange reaction fabricated microscopic heterojunctions with two distinct bandgap-gradient regions composed of iodide-rich and bromide-rich parts. Then, the candidate characterized the efficient accumulation of charge carriers in the narrow-bandgap iodide-rich region in the built-in halide gradient structures. The corresponding time-resolved spectroscopic analysis revealed the transportation of photogenerated excitons/charge carriers from the surrounding wide-bandgap bromide-rich areas to the narrow-bandgap iodide-rich region. In summary, this research develops the optical trapping methods for constructing perovskite heterostructures with distinct emission colors and bandgaps. Also, it demonstrated the controls of the intrinsic properties of halide perovskite. Such laser trapping-based structural modification can be promising for the fabrication of high-quality perovskite heterojunction optoelectronic devices.

審査員一同は，これらの成果を高く評価し，また研究者として誠実かつ熱心であり，大学院博士課程における研鑽や修得単位などもあわせ，申請者が博士（環境科学）の学位を受けるのに充分な資格を有するものと判定した。