学 位 論 文 審 査 の 要 旨

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A microspectroscopic investigation of photoluminescence and electroluminescence in lead halide perovskites
(ハロゲン化鉛ペロブスカイトにおける光および電気励起発光の顕微分光学的研究)

Lead halide perovskites are gaining rapid attention in solar cells, LEDs, lasers, etc. on account of their attractive properties like easy synthesis, tunable bandgap, and excellent charge carrier dynamics. However, their commercialization is still hindered by certain factors, mainly being the stability concern. In this thesis, the candidate carried out a microspectroscopic investigation of photoluminescence (PL) and electroluminescence (EL) in lead halide perovskites microcrystals for understanding the factors that decrease photoluminescence and electroluminescence efficiencies. This thesis has five chapters. In chapter 1, the candidate presented an introduction of lead halide perovskite by giving focus to the chemical structure, optoelectronic properties, various synthesis methods, and applications of halide perovskites. PL and EL blinking affect the efficiencies of perovskite-based electrooptical and photovoltaic devices, which is discussed in chapter 1. Various methods like the pressure-induced solid-state synthesis, antisolvent vapor-assisted crystallization, and inverse-temperature crystallization to synthesize perovskites crystals are summarized in chapter 2. Also, the candidate presented various characterization methods such as absorption spectroscopy, steady-state and time-resolved fluorescence spectroscopy, single-particle microspectroscopy, X-ray diffraction, scanning electron microscopy (SEM), etc. used in this thesis, for understanding the properties. In chapter 3, results of photoluminescence studies on perovskite pellets synthesized by a solid-state, pressure-induced method are presented. The synthesized perovskite pellet showed very good optical properties, which matched the samples synthesized by wet chemical routes. Due to the large thickness of the pellets, EL studies were not carried out on the pellets. Instead of that, the candidate focused on PL stuties and disclosed photon recycling by analyzing energy transfer using steady-state and time-resolved fluorescence microspectroscopy. In chapter 4, EL and PL studies were conducted on perovskite microcrystals using single-particle microscopy and EL spectroscopy. EL blinking was observed from the microcrystals, which was characterized by high-intensity and low-intensity levels in the EL trajectories. The nature of EL blinking in perovskites was clarified with the help of statistical analysis. In a microcrystal showing multiple-emitting sites, truncated power-law behaviors for ON- and OFF-time

probability densities were observed. Such a truncated behavior is common to type-A blinking by the charging-discharging processes. However, in an ensemble of crystals, a linear power-law behavior was extracted as the signature of type-B blinking, which is due to the charge carrier trapping-de-trapping processes. The main factor responsible for EL blinking was characterized as the migrating halide vacancies in the microcrystals, which act as EL quenchers. These vacancies randomly shifted their locations. Type-B blinking mechanism dominated the whole microcrystals. In chapter 5, the candidate focused on understanding role of halide vacancies in EL blinking. For this purpose, perovskite microcrystals of varying bromide compositions were prepared by varying the molar ratio of precursors. An under-stoichiometric sample, which was expected to carry many halide vacancies, showed a linear power-law behavior in the ON- and OFF-time probability densities. This behavior is typical of type-B blinking due to the trapping and de-trapping of charge carriers involving halide vacancies. However, a stoichiometric and an over-stoichiometric perovskite sample showed type-A blinking, as suggested by the truncated ON and OFF time distributions, showing trion formation and Auger-assisted nonradiative recombination. The role of halide vacancies in EL blinking was verified by analyzing $MAPbBr_3$ microcrystals treated with MABr solutions, for post-synthesis vacancy filling. Enhancements in the PL and EL intensities of the MABr treated $MAPbBr_3$ microcrystals were verified by correlating single-particle microspectroscopic studies with elemental analyses. The PL and EL experiments on lead halide perovskites helped the candidate understand the low efficiencies of perovskite-based EL devices. The research results and discussions in this thesis can be helpful for improving the efficiencies of perovskite-based optoelectronic, photovoltaic, and electroluminescent 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。