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学 位 論 文 内 容 の 要 旨

博士 (環境科学)

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学 位 論 文 題 名

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 the field of 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, I carry out a microspectroscopic investigation of photoluminescence and electroluminescence in lead halide perovskites for understanding the factors that lead to decreased photoluminescence and electroluminescence efficiencies. This thesis is made of five chapters. **In chapter 1**, I give an introduction of lead halide perovskite by giving focus to its chemical structure, optoelectronic properties, various synthesis methods, and their applications. I introduce perovskite blinking which is the main issue associated with perovskite leading to the loss of photoluminescence and electroluminescence efficiency. In this chapter, I also provide the motivation for my research in lead halide perovskites. **In chapter 2**, I discuss various methods like the pressure-induced solid-state method, antisolvent vapor assisted crystallization and, inverse temperature crystallization techniques that were adopted for synthesizing perovskites for my studies. Various characterization methods like absorption spectroscopy, fluorescence spectroscopy, single-particle microspectroscopy, X-ray diffraction, and SEM-EDS microscopy that was used to understand the photophysical properties are also discussed in detail. **In chapter 3**, I synthesize perovskite microcrystals by a solid-state pressure-induced method. The synthesized perovskite showed very good optoelectronic properties which match those synthesized using wet chemical routes involving toxic solvents like DMF, DCM, etc. Following this synthesis, I tried to fabricate an LED device with the synthesized perovskite pellets. Although I observed good photoluminescence features, electroluminescence properties were restricted due to the thickness of the pellet. However, I followed up the studies with the thick pellet. Photon recycling is a phenomenon seen in thick samples, in which emissions from the sample get reabsorbed and emitted multiple times. This phenomenon is known to improve solar cell efficiencies. The perovskite pellet synthesized by the pressure-induced method showed a distribution of energy states as confirmed by photoluminescence spectral and lifetime studies. I studied the rate of energy transfer occurring in such perovskites and found that energy transfer outweighs other radiative and nonradiative processes occurring in these pellets upon photo-excitation. I clarified this phenomenon by using mixed halide perovskite thus confirming the role of nonradiative energy transfer in the photon recycling mechanism. **In chapter 4**, I studied electroluminescence and photoluminescence from perovskite microcrystals using single-particle microspectroscopy and fluorescence spectroscopy. An interesting phenomenon of EL blinking was observed from these microcrystals. They were characterized by high-intensity and low-intensity EL spikes in their EL trajectory. I used statistical analysis to understand the nature of EL blinking in perovskites. In a microcrystal showing multiple-emitting sites, I observed a truncated power-law behavior for ON-

and OFF-time probability densities. Such a truncated behavior is commonly characterized as type-A blinking arising due to the charging-discharging processes. However, in the case of an ensemble of crystals, a linear power-law behavior was seen for ON- and OFF-time probability distributions. This is a signature of type-B blinking which arises due to the charge carrier trapping-de-trapping processes. From these studies, MAPbBr₃ microcrystals show both the type of blinking. The main factor responsible for EL blinking is thought to be the migrating halogen vacancies in these crystals which act as EL quenchers. They randomly shift their location. Such a mechanism dominates the whole microcrystal and is thus seen as the type-B blinking. The above studies made it possible to understand the origin and mechanism of EL blinking in perovskites. **In chapter 5**, I further study the role of halogen in EL blinking. I synthesize perovskite microcrystals of varying bromide composition by varying the precursor solution ratio used for perovskite microcrystal synthesis. An under-stoichiometric sample with a lot of halide vacancies shows a linear power-law behavior in the ON- and OFF-time probability densities. This behavior as said above is typical of type-B blinking which is due to trapping and de-trapping of charge carriers. The trapping of charge carriers occurs due to the excess halide vacancy traps. However, a stoichiometric and over-stoichiometric perovskite sample shows type-A blinking behavior as suggested by the truncated power-law behavior shown by ON- and OFF states. This is due to the charging-discharging mechanism due to the formation of trions and associated Auger-type nonradiative recombination. I also post-treat MAPbBr₃ microcrystals with MABr solution to fill these halide vacancies. I observed enhancement in the photo- and electroluminescence properties from the MABr treated MAPbBr₃ microcrystals as proved by single-particle microspectroscopic studies as well as SEM-EDS studies. The PL and EL experiments on lead halide perovskites helped in understanding fundamental issues associated with perovskite device efficiency losses such as that of EL blinking. These studies can be helpful in improving the efficiency of perovskite-based devices in the future.