学 位 論 文 審 査 の 要 旨

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学 位 論 文 題 名

Crystal size, photoluminescence and electroluminescence optimization of $MAPbBr_3$ perovskite microcrystals
（$MAPbBr_3$ペロブスカイト微結晶の結晶サイズ、フォトルミネッセンスおよびエレクトロルミネッセンスの最適化）

The candidate focused his doctoral research on lead halide perovskites (LHPs), emerging semiconductor materials for next-generation light-harvesting and light-emitting applications. The excellent properties of LHPs, such as high photoluminescence (PL) quantum yield, large absorption cross-section, low heat of formation, and tunable bandgap, make them promising for widespread photovoltaic and electro-optical applications. The straightforward synthesis, tunable bandgap, and blinking luminescence of LHPs attracted the candidate to address certain limitations of LHP microcrystals (MCs), such as size and shape variations, fluctuations of electroluminescence (EL) intensity, and bromide ion-vacancy-assisted nonradiative losses of charge carriers. The thesis includes size- and shape-controlled synthesis of methylammonium lead bromide ($MAPbBr_3$) LHP microcrystals (MCs), evaluation of the effect of light-soaking on bromide vacancy filling in $MAPbBr_3$ MCs, and evaluation of time-resolved EL properties of the MCs as a function of bromide vacancy filling. The thesis is classified into five chapters.

In Chapter 1, the candidate outlined and explained the general properties of LHPs. First, the candidate introduced the unit cell structure, chemical compositions, and stability factors of LHPs. Next, he discussed literature methods for LHP synthesis, including MCs, nanocrystals, and quantum dots. This was followed by explaining the optical properties, bandgap characteristics, charge carrier dynamics, and PL and EL blinking of LHPs. Finally, in Chapter 1, the candidate introduced selected applications of LHPs, especially to solar cells and light-emitting diodes. Also, the candidate summarized his motivation to undertake the research embodied in his doctoral thesis. Chapter 2 provides details of the materials and methods in the research. The candidate provided a detailed explanation of chemicals, materials, spectroscopic methods, and microscopic methods. Initially, details about the synthesis of $MAPbBr_3$ MCs by various methods, such as room temperature crystallization (RTC), anti-solvent vapor-assisted crystallization (AVC), inverse temperature crystallization (ITC), modified-ITC and blade-coating methods are given. In the synthesis section, the candidate used *N*-cyclohexyl-2-pyrrolidone (CHP) as an additive to control the $MAPbBr_3$ MC size and shape. The role of CHP in LHP crystallization is discussed in this chapter. Next, the EL device fabrication is explained. Also, the candidate included theoretical and technical aspects of steady-state and time-resolved spectroscopic methods employed for analyzing the PL and EL properties of $MAPbBr_3$ MCs. In Chapter 3, he demonstrated the synthesis of cuboid $MAPbBr_3$ MCs and investigated the role of reaction temperature and CHP concentration in MCs' size, shape, and luminescence quality. He discussed the $MAPbBr_3$ crystal nucleation mechanism and crystal growth kinetics by estimating the concentrations of the precursors during crystalization at different temperatures and CHP concentrations. Chapter 4 is about the light-soaking effect on the PL lifetime and EL blinking of $MAPbBr_3$ MCs. PL lifetime and EL ON time increases were detected by light-soaking, which was attributed to bromide ion redistribution from the interstitial sites to bromide vacancies. The mechanism of light-soaking-induced halide ion migration and trap healing is correlated with the EL intensities and PL lifetimes of single MCs. In Chapter 5, the candidate investigated the time-resolved EL properties of $MAPbBr_3$ MCs before and after bromide vacancy filling using MABr solutions. Real-time bromide-vacancy-filling-induced PL lifetime and intensity increases helped identify the role of bromide vacancies on nonradiative losses. Successively, the candidate examined the EL lifetime for MCs before and after bromide vacancy filling. Increases in EL intensities and lifetimes helped the candidate improve the quality of MC EL devices. Finally, general conclusions and prospects of the doctoral research are provided.

The committee highly evaluated these achievements and judged that the applicant was sincere and dedicated as a researcher, and that the applicant was sufficiently qualified to receive the degree of Doctor of Philosophy (Environmental Science), together with his studies in the graduate school doctoral course and the credits he had earned.