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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

Spatially- and temporally- controlled synthesis and modification of lead halide perovskites
by laser trapping

(レーザー捕捉によるハロゲン化鉛ペロブスカイトの合成と変換の時空間制御)

Metal halide perovskites show strong absorption of visible to near-infrared light, brilliant photo- and electro- luminescence, long-range diffusion of electrons and holes, which are in addition to low-temperature solution processing. Due to these properties, perovskites have emerged into a new class of semiconductor materials for next generation optoelectronic devices such as solar cells, light emitting diodes, displays, photodetectors, and lasers. Mixed halide perovskites enable one to tune optical and electronic properties from pure halide ones because the band gap is changed by two different halides at the appropriate compositions. Mixed halide perovskites are prepared in solution by direct synthesis from their precursors or post-synthesis halide exchange reaction. In conventional chemical approaches, such synthesis and exchange reaction proceed all over the precursor solution. Therefore, spatially- and temporally- controlled synthesis and halogen exchange remain challenging, demanding the development of new facile and flexible methods to synthesize and manipulate perovskites.

Laser trapping is an innovative optical approach to trap, manipulate, and concentrate various nanometer-size objects in solution but without any mechanical contact. With this technique, spatially- and temporally- controlled preparation of assemblies or crystals is demonstrated for nanoparticles, quantum dots, polymers, proteins, and amino acids. It is expected that laser trapping of perovskite precursors increases local concentration of the precursors, through which synthesis and halide exchange reaction of perovskite crystals is controlled spatially and temporally. With this motivation, laser trapping experiments are conducted in the perovskite precursor solutions by focusing a continuous-wave near-infrared (NIR) laser beam at the air/solution interface or the surface of perovskite crystals.

In chapter 1, fundamental properties and preparation methods of metal halide perovskites and principle of laser trapping are introduced. Then, the objectives and outline of the present thesis are described. In chapter 2, optical setup of laser trapping and microspectroscopy, sample preparation, and characterization methods are summarized.

In chapter 3, synthesis of MAPbX_3 ($\text{MA} = \text{CH}_3\text{NH}_3$, $\text{X} = \text{Cl}$, Br , or I) is demonstrated by focusing

a NIR laser beam at the air/solution interface of the $\text{MAX}:\text{PbX}_2$ precursor solutions. One crystal of MAPbX_3 is formed from the laser focus even in an unsaturated solution where no spontaneous crystallization takes place. Therefore, it is considered that the crystallization is induced through local increase in saturation degree. Two possibilities are proposed based on the retrograde solubility of samples. One is laser heating, and the other is laser trapping. The former decreases solubility, and the latter increases precursor concentration. Local temperature elevation is estimated based on absorption coefficient and thermal conductivity of solvents. It was concluded that laser heating is not the main driving force for the increase in saturation degree. The possible mechanism is proposed from the viewpoint of laser trapping of precursor complexes larger than the precursors, which generate strong optical force. Local concentration of the precursor complexes increases with irradiation time, realizing supersaturated condition at the focal spot. Consequently, MAPbX_3 is formed at the air/solution interface through de-solvation and re-ordering of gathered precursor complexes.

In chapter 4, laser trapping-induced synthesis is extended to mixed halide perovskites. The crystallization of $\text{MAPbBr}_n\text{Cl}_{3-n}$ ($n = 1-3$) is induced from the focal spot upon laser trapping at an air/solution interface of the $\text{MABr}:\text{PbBr}_2:\text{MACl}:\text{PbCl}_2$ precursor solution. The formed crystal is characterized by transmission and photoluminescence (PL) microspectroscopy and XRD analysis. The characterization revealed that $\text{MAPbBr}_n\text{Cl}_{3-n}$ crystals formed under the laser irradiation have chloride composition higher than that of the initial precursor solutions. The crystallization mechanism of the chloride rich perovskites is discussed by considering de-solvation of gathered precursor complexes that preferentially proceeds for precursors of $\text{MACl}:\text{PbCl}_2$ compared to $\text{MABr}:\text{PbBr}_2$.

In chapter 5, the NIR laser is focused at a surface of a perovskite crystal in a solution with reactant perovskite precursors. In the case of a MAPbBr_3 crystal in the MAI solution, the PL of the irradiated crystal is changed from green to red, which is due to the formation of $\text{MAPbBr}_n\text{I}_{3-n}$. On the other hand, the non-irradiated crystals remained green emissive. Kinetic analysis of the PL change reveals that the exchange rate is accelerated 24 times by the laser irradiation. The underlying mechanism is discussed from the viewpoints of two laser-induced phenomena. One is laser trapping that increases the concentration of the reactant precursor locally. The other is two-photon laser heating that decreases the precursor concentration through thermal decomposition. The laser trapping overcomes the negative effect of laser heating, which results in site-specific halide exchange reaction.

In chapter 6, the main results and the general conclusions of this thesis are summarized, and perspectives of perovskite research and laser trapping study are sketched.