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学 位 論 文 内 容 の 要 約

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 perovskite compounds are expressed as ABX_3 , where A is a cation [methylammonium ($CH_3NH_3^+$), formamidinium ($NH=CHNH_2^+$), or cesium (Cs^+)], B is a metal cation (Pb^{2+} , Sn^{2+} , or Ge^{2+}), and X is a halide ion (Cl^- , Br^- , or I^-). These compounds show strong absorption of visible to near-infrared light, brilliant photo- and electro- luminescence, and 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.

The photoluminescence color or band gap of metal halide perovskites is tunable in the whole visible light region by mixing two different halides at appropriate compositions. Mixed halide perovskites can be directly synthesized in organic solvents from more than three kinds of precursors. For example, $MAPb(X\cdot Y)_3$ ($MA = CH_3NH_3^+$) are prepared from precursor solutions by dissolving methylammonium halides (MAX , MAY) and lead halides (PbX_2 , PbY_2). Another approach to prepare mixed halide perovskites is halide exchange reaction. It is well known that metal halide perovskites undergo fast anion exchange reactions when they encounter different halide ions. In conventional chemical approaches, such synthesis and exchange reaction proceed all over the precursor solution. Therefore, spatial and temporal control of these processes remain challenging.

In order to develop a new facile and flexible method to synthesize and modify perovskites, I applied laser trapping to perovskite precursor solutions. Laser trapping is an innovative optical approach to trap, manipulate, and concentrate various nanometer-size objects in the solution but without any mechanical contact. In 1970, Arthur Ashkin in Bell Telephone Laboratories first demonstrated the acceleration and trapping of micrometer-sized dielectric particles upon laser irradiation. In the case that a particle is much smaller than the wavelength of the trapping light (nanometer size particle), it can be regarded as a point dipole (Rayleigh approximation). The optical force is approximately expressed as follows.

$$\mathbf{F} = \frac{1}{2} \epsilon_m \alpha \nabla \mathbf{E}^2$$

Here $\mathbf{E}$ denotes the electric field and ∇ represents a gradient with respect to the spatial coordinates. The parameter ϵ_m is the permittivity of the surrounding medium. The polarizability of the nanoparticle, α , under the dipole approximation is given by

$$\alpha = 4\pi r^3 \frac{(n_p/n_m)^2 - 1}{(n_p/n_m)^2 + 2}$$

Notations r , n_p , and n_m are the radius of the nanoparticle, and refractive indices of the nanoparticle and the surrounding medium, respectively. Optical force is generated when a particle is placed in a heterogeneous electric field of light. If the refractive index of the particle is higher than that of the surrounding medium, the force acts on the particle and pushes it toward the higher light intensity region of the beam. Consequently, the particle is trapped at the focal spot of the laser beam where the light intensity is the maximum. With this technique, spatially- and temporally- controlled preparation of assemblies or crystals was demonstrated for nanoparticles, quantum dots, polymers, proteins, and amino acids. It is expected that laser trapping in perovskite precursor solutions increases local concentration of the precursors, through which synthesis and halide exchange reaction of perovskite crystals can be controlled spatially and temporally. The above fundamental information on perovskites, the principle of laser trapping, and motivation of this research are summarized in chapter 1.

In chapter 2, optical setup of laser trapping and microspectroscopy are described. The setup was constructed by introducing a continuous-wave near-infrared (NIR) laser beam ($\lambda = 1064$ or 800 nm) into an inverted optical microscope. Laser trapping behavior was observed with transmission or photoluminescence (PL) imaging using a charge-coupled device (CCD) camera. Perovskite crystals under the microscope were characterized by measuring the transmission or PL spectra with a spectrometer. The procedures of sample preparation and X-ray diffraction (XRD) analysis are also described.

In chapter 3, synthesis of MAPbX_3 ($\text{MA} = \text{CH}_3\text{NH}_3$, $\text{X} = \text{Cl, Br, or I}$) is demonstrated, which is by focusing a NIR laser beam at the air/solution interface of the MAX:PbX_2 precursor solutions. For example, laser trapping was conducted at the air/solution interface of a precursor solution of MABr:PbBr_2 (1.3 M) dissolved in DMF. MAPbBr_3 shows retrograde solubility in DMF at temperatures up to 100 °C. Based on this solubility, saturation degree of the precursor was estimated at 0.83 , which is at 18 °C in the experimental room. At the beginning of the irradiation, an optical micrograph showed only the faint trapping laser reflected at the air/solution interface.

A small crystal of a few micrometers was identified in a camera image at 103 s. The nucleated crystal continuously grew large while being trapped at the focal spot and attained the size of $11 \times 13 \mu\text{m}^2$ at 120 s. The formed crystal moved away from the focal spot and dissolved soon after the laser was turned off, which is due to unsaturated condition of the surrounding solution. By varying the laser power between 100 to 600 mW and the concentrations of precursor solutions from 0.1 to 1.3 M, I confirmed that a threshold laser power of 200 mW and a threshold concentration of the precursor solution of 1.2 M are required for consistent crystallization. The measurements of a PL spectrum and an XRD pattern, which are in addition to observation of dissolution/growth behavior, revealed that the crystal formed in the $\text{MABr}:\text{PbBr}_2$ solution is MAPbBr_3 . The similar trapping experiments were carried out in the precursor solutions of MAPbCl_3 and MAPbI_3 . In both cases, crystallization was induced from the focal spot, but MAPbI_3 showed explosive crystal growth due to efficient heating through two-photon absorption of the trapping laser. One crystal of MAPbBr_3 or MAPbCl_3 was always formed from the laser focus even in an unsaturated solution where spontaneous crystallization was absent. 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 the sample. One is laser heating, and the other is laser trapping. The former decreases crystal solubility, and the latter increases precursor concentration. Local temperature elevation was estimated based on absorption coefficients and thermal conductivity of solvents. The estimated temperature elevation was insufficient to generate supersaturated condition through the decrease in the solubility. It is 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 with the size 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 crystallization is extended to mixed bromide/chloride methylammonium lead perovskites ($\text{MAPbBr}_n\text{Cl}_{3-n}$; $n = 0-3$). Laser trapping behavior was examined by focusing a 1064-nm laser beam at the air/solution interface of $\text{MABr}:\text{PbBr}_2:\text{MACl}:\text{PbCl}_2$ precursor solutions in DMSO/DMF mixtures. In all compositions of the precursors, crystallization was induced from the focal spot even in an unsaturated solution. The nucleated crystal continuously grew large while being trapped at the focal spot. Different from the solutions of $\text{MAPbBr}_{3.0}$ and $\text{MAPbBr}_{2.5}\text{Cl}_{0.5}$, the growth of the formed crystal was saturated in the $\text{MAPbBr}_n\text{Cl}_{3-n}$ ($n = 0-2$) solutions when it attained the size of a few micrometers. Although the crystallization was induced from the focal spot in all precursor solutions and the formed crystals were stably kept under the irradiation, they moved away from the focal spot and dissolved completely after switching off the laser. This result implies that the crystals are formed through a local increase in saturation degree by laser irradiation in an unsaturated solution, not by

homogeneous condensation through solvent evaporation. I characterized the formed crystals by measuring their transmission spectra under the microscope. Thick crystals are necessary for the microspectroscopy. In order to prepare a large crystal, the laser trapping experiments were carried out in a sample chamber without an upper cover glass. The transmission edge and PL peak shifted to shorter wavelength with the increase in the chloride composition in the precursor solutions. For determining the band gaps of the crystals, transmission spectra were converted to Tauc Plots. I found that the crystals formed by the laser trapping have a higher band gap than those with the crystals of the composition same as the corresponding initial precursor solutions, indicating that the crystals prepared by the laser have the chloride concentration higher than that of the precursor solutions. For further characterization, I prepared big crystals of a few hundred-micrometer dimension by the laser irradiation for a long time (around 30 minutes) after nucleation started. I picked up the large crystals prepared in $\text{MAPbBr}_n\text{Cl}_{3-n}$ ($n = 0-3$) precursor solutions and carried out the XRD measurement. The lattice constant of the crystals formed by the laser was smaller than that of the crystals of the composition same as the corresponding initial precursor solutions. This result also supports that chloride-rich crystal is formed by laser trapping. I considered that de-solvation is critical to determine the composition of the finally obtained crystal. In the case of $\text{MAPbBr}_n\text{Cl}_{3-n}$ ($n = 0.5-2.0$), I dissolved $\text{MABr}:\text{PbBr}_2$ and $\text{MACl}:\text{PbCl}_2$ in a DMF:DMSO mixture. MAPbBr_3 shows retrograde solubility in DMF but not in DMSO. This solubility tendency indicates that $\text{MABr}:\text{PbBr}_2$ precursor complexes are easily de-solvated in DMF compared to DMSO. In other word, $\text{MABr}:\text{PbBr}_2$ are expected to be dominantly solvated with DMSO in a DMF:DMSO mixture due to the higher polarity of the latter solvent. On the other hand, $\text{MACl}:\text{PbCl}_2$ precursor complexes are considered to be easily de-solvated in a DMF:DMSO mixture because MAPbCl_3 shows retrograde solubility in this mixed solvent. That is, $\text{MACl}:\text{PbCl}_2$ precursors are easily de-solvated when compared to $\text{MABr}:\text{PbBr}_2$ dissolved together in a DMF:DMSO mixture. As the result, upon laser trapping in the $\text{MAPbBr}_n\text{Cl}_{3-n}$ ($n = 0.5-2.0$) precursor solution, the gathered $\text{MACl}:\text{PbCl}_2$ precursors are preferentially de-solvated when compared to $\text{MABr}:\text{PbBr}_2$, and chloride rich crystal is formed. Similarly, in the case of $\text{MAPbBr}_{2.5}\text{Cl}_{0.5}$ in DMF, I hypothesize that MACl is de-solvated in DMF more efficiently than bromide precursors.

In chapter 5, laser trapping is applied at the surface of a perovskite crystal to achieve and control halide exchange reactions in a specific area around the focal spot. The NIR laser was focused at a surface of a MAPbBr_3 perovskite crystal placed in a solution containing MAI. I used a MAI solution with concentration of 110 μM , which was prepared in an isopropyl alcohol/hexadecene mixed solvent. At this concentration, spontaneous halide exchange reaction proceeds at a negligibly low rate, but with slight increase in concentration of MAI, I was able to dramatically accelerate the reaction. I selected one target crystal among the prepared MAPbBr_3 crystals and focused a NIR laser beam at the crystal surface. The power of the laser after passing through the objective lens was 500 mW. PL imaging and microspectroscopy were performed

through two-photon excitation by the focused NIR laser or one-photon excitation by the widely illuminated 405-nm laser.

At the beginning of the NIR laser irradiation, the crystal showed green emission. The green PL was gradually changed into first yellow and finally red. I confirmed that only the crystal exposed to the NIR laser showed red emission due to the formation of $\text{MAPbBr}_n\text{I}_{3-n}$ and the neighboring crystals remained green emissive. The PL spectra were measured under the conditions with and without the NIR laser irradiation. Kinetic analysis of the temporal changes in PL spectra revealed 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 of MAI. I concluded that laser trapping overcomes the negative effect of laser heating and 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. In the results summarized in this thesis, laser trapping of raw materials led to the formation of new materials through chemical reactions. This point is completely different from conventional laser trapping studies where the targets are trapped and manipulated as they are. It is expected that the various combinations of chemical conditions and laser irradiation parameters (power, wavelength, beam pattern, and so on) enable one to develop novel tools for the synthesis of new materials. The current work will not only offer a new approach to synthesize and modify perovskite crystals but also becomes an important milestone for the control of chemical reactions using laser trapping.