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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

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Chapter 1

Introduction

1-1: Lead halide perovskites

1-1-1: The structure and fundamental optical and electronic properties

In recent years, metal halide perovskite compounds have emerged as a new class of versatile semiconductor materials for next-generation optoelectronic devices such as solar cells (1), light emitting diodes (2), displays (3), photodetectors (4), and lasers (5). Perovskite is one big category of compounds that have the pristine crystal structure the same as the conventional CaTiO_3 . This crystal structure was first discovered in a skarn sample by Prussian mineralogist Gustav Rose in 1839 and named in the honor of Count Lev A. Perovski (1792–1856) (6). Metal halide perovskite compounds are expressed as ABX_3 , where A is a cation like methylammonium (CH_3NH_3^+), formamidinium ($\text{NH}=\text{CHNH}_2^+$), or cesium (Cs^+), B is a metal cation (Pb^{2+} , Sn^{2+} , Ge^{2+}), and X is a halide ion (Cl^- , Br^- , I^-) (7). As shown in Figure 1.01, their structure is a three-dimensional network of corner-sharing BX_6 octahedron with A cation fitting into the 12-fold coordinated holes.

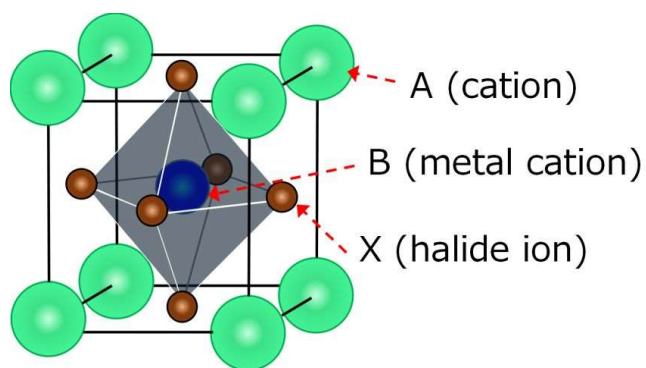


Figure 1.01: Crystal structure of metal halide perovskite compounds.

Detailed studies of optical and electronic properties of metal halide perovskite compounds were initiated in the 1990s by D. Mitzi *et al.* (8). Nowadays, it is widely recognized that their properties have the superiority for photovoltaic and luminescence applications. Metal halide perovskite compounds behave similarly as typical inorganic semiconductors from the respect of charge transport characteristics. They possess long charge carrier diffusion lengths and moderate charge carrier mobilities (9). These charge transport characteristics originate intrinsically from their electronic band structure, of which the valence band maximum and the conduction band minimum consist of mainly the electronic states of a metal cation in the B site and halogen anions in the X sites (10). Furthermore, the dielectric environment of the inorganic framework results in a small exciton binding energy for a photo-generated electron and hole pair (several to tens of meV) (11). As a result, the majority of photo-generated excitons spontaneously dissociate into free carriers even at room temperature. This nature of photo-generated charge carriers is one of the origins of their relatively long carrier lifetimes (ca 8 μ s) in the thin film or bulk crystal state (12).

Another important feature of metal halide perovskite compounds is their strong light absorption over a broad wavelength range (13). Interestingly, the absorption edge or the bandgap strongly depends on halide ions. In the case of the most widely-studied methylammonium lead halide perovskites [MAPbX₃, X = Cl, Br, or I, (MA = CH₃NH₃)], the absorption onset locates at 410 nm for MAPbCl₃, 550 nm for MAPbBr₃, and 790 nm for MAPbI₃ (14). Light with the wavelength shorter than this onset is efficiently absorbed with an absorption coefficient of 10⁴–10⁵ cm⁻¹ (15). This high absorption coefficient means that more than 90% of the incident light is absorbed with the thickness of submicrometer, enabling one to design very thin and flexible optoelectronic devices.

1-1-2: Preparation of nanocrystal, thin film, and bulk crystal

Metal halide perovskite compounds of different dimensions can be synthesized from two precursors. Here, the preparation methods of methylammonium lead halide perovskites [MAPbX₃, X = Cl, Br, or I] are introduced since they are widely studied among metal halide perovskite compounds. Nanocrystals are prepared by so-called “re-precipitation technique” (Fig. 1.02a). Two precursors, MAX and PbX₂, are dissolved in a good solvent like *N, N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). Then the nanocrystals of MAPbX₃ are prepared by injecting the precursor solution to a poor solvent, such as toluene, containing capping ligands (16). The precursors in a poor solvent are gathered to form MAPbX₃. The ligands attach to the surface of growing MAPbX₃, and its growth is stopped, giving nanocrystals. Two-dimensional MAPbX₃ thin film is prepared by simply drop-casting the precursor solution and the subsequent spin coating (Fig. 1.02b) (17).

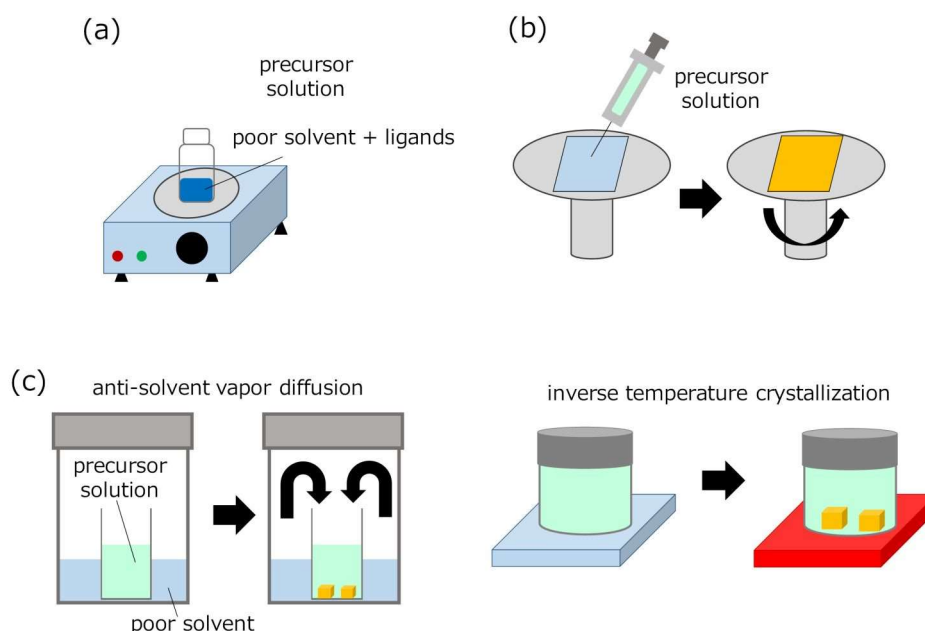


Figure 1.02: Schematic illustration of the preparation methods of metal halide perovskite compounds of different dimensions; (a) nanocrystals, (b) a thin film and (c) bulk crystals.

Bulk crystals are prepared by gradually increasing the saturation degree of the precursor solutions (Fig. 1.02c). For example, the vapor of a poor solvent like chloroform is introduced to a precursor solution where MAX and PbX₂ are dissolved in a good solvent. Due to the poor solvent, the solubility of precursors is gradually decreased, and the saturation degree is slowly increased, leading to nucleation and growth of MAPbX₃ (Fig. 1.02c). This is known as “anti-solvent vapor diffusion method” (18).

Another approach is based on temperature-dependent solubility of MAPbX₃ (Fig. 1.02c). It was reported that the solubility of MAPbX₃ in a specific solvent is decreased with temperature elevation. This tendency is called “retrograde solubility”, which is completely opposite to solubility trend of organic molecules. For example, MAPbBr₃ and MAPbCl₃ show retrograde solubility in DMF and a mixture of DMSO and DMF (1:1, v:v), respectively (19, 20). Based on this characteristic solubility, MAPbBr₃ or MAPbCl₃ bulk crystals can be synthesized by increasing the temperature of a mixture of MABr and PbBr₂ in DMF or MACl and PbCl₂ in a mixture (1:1, v:v) of DMSO and DMF. Different from these two, MAPbI₃ shows unique solubility trend in gamma-butyrolactone (19). Below 60 °C, the solubility is increased with temperature elevation. On the other hand, the solubility is decreased with the temperature above 60 °C. Due to this retrograde solubility, bulk crystals of MAPbI₃ can be synthesized by heating the precursor solution over 60 °C. This technique is known as “inverse temperature crystallization”, which enables one to prepare high-quality, large perovskite single crystals (millimeter to centimeter scale) with a much faster growth rate (within one day) (20, 21).

1-1-3: Bandgap tuning by halide mixing and halide exchange

Conduction band of lead halide perovskite compounds mainly consists of the p orbital of lead ion. On the other hand, their valence band results from the mixing of the s orbital of lead ion and the p orbital of halide ions (22). Therefore, the halogen substitution

in perovskite crystals leads to the variation of octahedron size consisting of lead and halogen ions, which is due to the difference in the ionic radius of each halogen ion such as Cl^- (0.181 nm), Br^- (0.196 nm), and I^- (0.220 nm). Due to this character, mixed halide composition in metal halide perovskite compounds enables one to tune optical and electronic properties from pure halide ones. Actually, the bandgap of $\text{MAPbX}_n\text{Y}_{3-n}$ ($\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{or I}, n = 0 \text{ to } 3$) can be changed from 1.6 to 3.1 eV by incorporating two different halides at an appropriate composition in the crystal (13).

Mixed halide perovskite compounds are synthesized by mixing more than three kinds of precursors in an organic solvent (23–25). For example, $\text{MAPbX}_n\text{Y}_{3-n}$ are prepared from the precursor solution by dissolving methylammonium halides (MAX, MAY) and lead halides (PbX_2 , PbY_2). The methods summarized above (Fig. 1.02) leads to the formation of nanocrystals, thin films, and bulk crystals of mixed halide perovskite compounds (Fig. 1.03a).

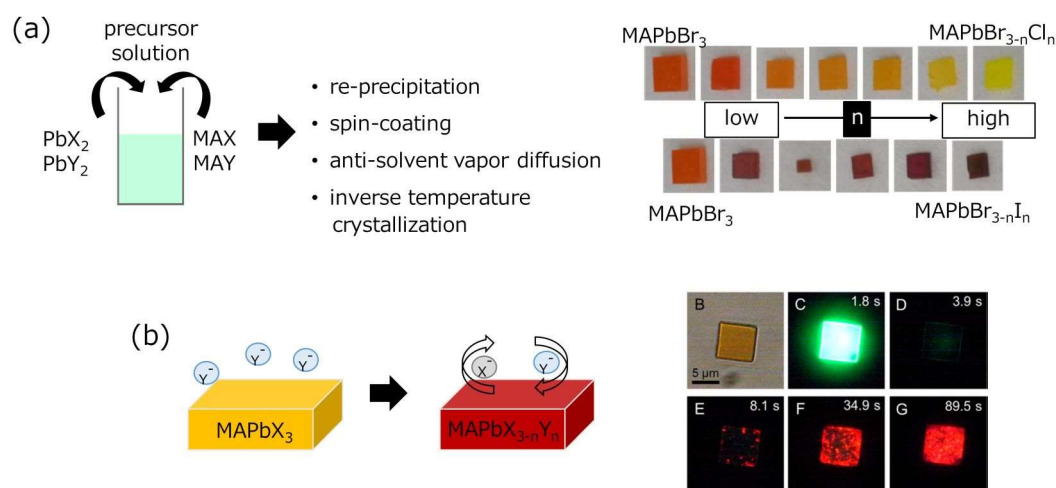


Figure 1.03: Schematic illustration and experimental results on the formation of mixed halide methylammonium lead perovskite compounds ($\text{MAPbX}_n\text{Y}_{3-n}$) with the approach of (a) precursor mixing and (b) halide exchange reaction. Reprinted with permissions from *AIP Adv.* **2016**, 6, 045115 (ref. 23) & *J. Phys. Chem. Lett.* **2017**, 8, 1724–1728 (ref. 26). Copyright (2017) American Chemical Society.

Another approach to prepare mixed halide perovskite compounds is halogen exchange reaction. It is well known that metal halide perovskite compounds undergo fast anion exchange reactions when they encounter different halide ions (26–28). This reaction proceeds at the solid-liquid (26), solid-gas (27), or solid-solid interface (28). This rapid anion exchange reaction is based on the high mobility of halogen ions in the crystal lattice, which is ascribed to many halogen vacancies (0.4%) formed with the low defect formation energy (0.1 eV) (29). It was demonstrated that, with this post-synthesis approach, mixed halide perovskite compounds of different forms, like nanocrystals (30–32) and bulk crystals (33) are prepared by changing the halogen composition from the pure halide ones (Fig. 1.03b).

The advantage of the halide exchange reaction is that the reaction can be induced locally at particular positions. Namely, we can conduct the spatially-selective bandgap tuning. Spatially-resolved halide exchange reaction is reported by Son *et al.* (34). They demonstrated photoinduced halide exchange reaction, in which electron transfer from photoexcited perovskite nanocrystals to solvent produces halide ions. They also showed patterning of CsPbBr₃ in a thin film of CsPbCl₃ with this method. However, photoexcitation of perovskites has potentials for causing photo-degradation or phase segregation, and undesired intermediates and products are generated upon reductive dissociation of the solvent. Yang *et al.* developed a spatially resolved halide exchange reaction with a nanofabrication technique (35, 36). A target perovskite crystal was masked with poly (methyl methacrylate) resist designed by e-beam lithography, and the exchange reaction was induced in a specific area of the crystal. Although e-beam nanofabrication is a well-sophisticated technique, its process is costly and lengthy. Thus, a new facile and flexible tool to manipulate perovskite precursors in solution is considered to be useful to control halide exchange reaction which is in addition to the synthesis of metal halide perovskite compounds. One potential tool is laser trapping described below.

1-2: Laser trapping

1-2-1: History of laser trapping study

It is well known that physical force arises from light due to the momentum of the light itself. However, the magnitude of optical force generated with incoherent light sources is too small to be utilized in terrestrial applications. It was believed that, only in astronomy, the force plays a significant role in moving objects because of less interactions between objects and surroundings as well as strong light intensities from the sun.

In 1960, the laser was invented by Theodore H. Maiman. The laser is an acronym of "Light Amplification by Stimulated Emission of Radiation", enabling the generation of special electromagnetic wave with high coherence, directionality, and monochromatic character. Due to these unique properties, a laser beam led to dramatic advances in the experimental study of optical force. In 1970, Arthur Ashkin in Bell Telephone Laboratories demonstrated acceleration and trapping of micron-sized dielectric particles upon laser irradiation (37). When a micron-sized particle was irradiated by the laser from one side, the particle was pushed toward the direction of the light propagation (Fig. 1.04a). In the case that a micron-sized particle was exposed to counter-propagating two laser beams, the particle was pushed from two sides and trapped at the position where the force is balanced (Fig. 1.04b). This is the first experimental demonstration of optical manipulation with the use of laser beams.

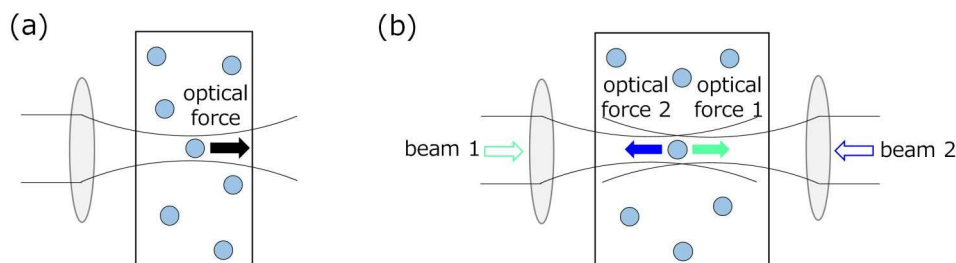


Figure 1.04: Schematic illustration of (a) acceleration and (b) trapping of a dielectric particle by laser beams.

In 1986, Arthur Ashkin and co-workers reported that a small particle with a size of 10 μm to 25 nm was trapped at the focal spot of a tightly focused single laser beam (Fig. 1.05) (38). Nowadays, this innovative optical approach is well known as “optical tweezers”, enabling us to trap and manipulate various small objects in solution but without any mechanical contact. The paper also proposed, as perspectives, that the single beam optical trap could be applied to other colloidal systems, macromolecules, polymers, and biological objects as well as light-absorbing particles that have resonantly large values of the polarizability. Among them, Arthur Ashkin extended optical tweezers to the biological system and demonstrated optical manipulation of viruses, living cells, and organelles (39–41). For the invention of optical tweezers and its application to the biological system, Arthur Ashkin was awarded the Nobel Prize in Physics in 2018.

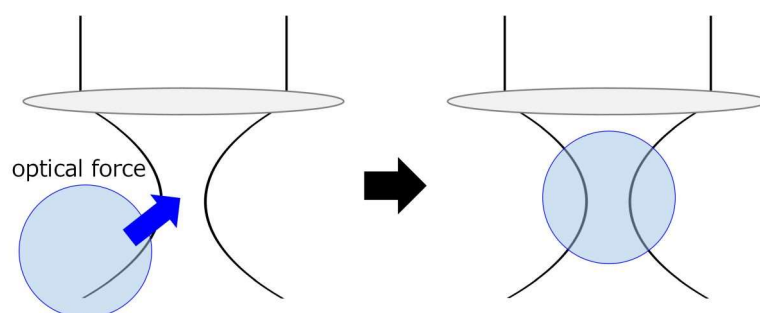


Figure 1.05: Schematic illustration of single beam optical trapping, in other word, optical tweezers.

In the paper published in 1970, Arthur Ashkin proposed that the acceleration and trapping are possible for atoms with the use of laser tuned to specific optical transitions (37). Based on this hypothesis, Steven Chu, one of the co-authors of the paper on single beam optical trap reported in 1986 (38), extended the study of optical force to precise manipulation and control of atoms in a vacuum. This phenomenon is well known as “atom cooling” (42). For this work, he was awarded the Nobel Prize in Physics in 1997.

1-2-2: Fundamental principle of laser trapping

Here, how optical force is generated is summarized. When light is irradiated to a mirror, it is reflected as shown in Figure 1.06. Light has momentum in the direction of its propagation. The magnitude of momentum (p) is expressed as $p = h/\lambda$, where h is the Planck constant and λ is the wavelength of the light. Upon reflection of light at the mirror surface, the magnitude of momentum is kept. On the other hand, the light propagation direction becomes opposite. Accordingly, the momentum of light is changed. On the basis of Newton's second law, the rate of change of the momentum of light is proportional to the force applied ($F = dp/dt$). Namely, it can be interpreted that the incident light received the force toward the direction opposite to its propagation. In accordance with Newton's third law, the force applied to light gives the mirror the reaction force with equal magnitude but of the opposite direction. As a result, the mirror is pushed along the propagation direction of the incident light.

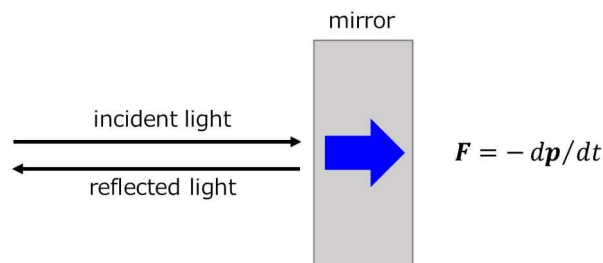


Figure 1.06: Schematic illustration of the generation of optical force upon light reflection at a mirror surface.

As the next step, light refraction at the interface of two different dielectric materials is considered. Here, light is irradiated from air to a water thin film with a certain angle (Fig. 1.07). Light is refracted at the interface in accordance with the Snell's law. To simplify, the reflection of light at the interface and the change in the wavelength of light in water are ignored. The momentum of light is changed, which corresponds to the force

applied to the light. Its reaction force with an equal magnitude but of opposite direction is given to the air/water interface. Consequently, the interface is pulled up to the air side by the light.

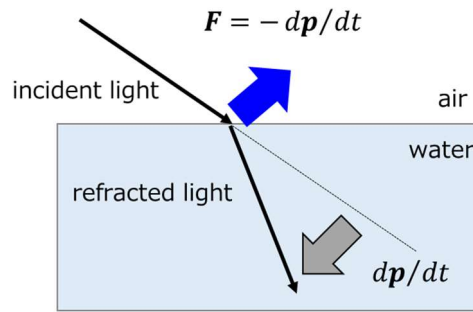


Figure 1.07: Schematic illustration of the generation of optical force upon light refraction at the air/water interface.

In the case that a spherical dielectric microparticle is irradiated with a tightly focused laser beam, the generation of optical force is similarly explained from the viewpoint of light refraction (Fig. 1.08). The outermost beam rays pass through the particle, with refraction at interfaces in accordance with the Snell's law. The light reflection at the interface and change in wavelength of the light in the particle are ignored. Due to change in the light propagation direction, optical force is generated at the interface, however, its magnitude and direction are different depending on the position. In general, a laser beam has a Gaussian profile of intensity. In this case, the total optical force directs to the focal spot of the laser beam. As a result, the particle is attracted to the focal spot and finally trapped through the balance with gravity. A metal microparticle is not trapped because of strong light reflection at the surface. The light reflection generates optical force toward the propagation direction of the incident light, and the particle is pushed away.

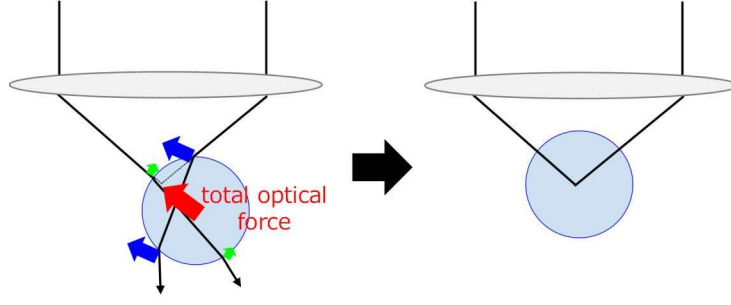


Figure 1.08: Schematic illustration of the generation of optical force upon the focused laser irradiation into a spherical dielectric microparticle.

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 (43).

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

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 of 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. It should be noted that the polarizability is proportional to the volume of the nanoparticle (43). That is, the force becomes weak proportionally with the decrease in the volume of the nanoparticle.

1-2-3: Application of laser trapping to chemistry

At the early stage after the invention of optical tweezers by Arthur Ashkin, the technique was mostly used in biological research, involving non-contact and non-invasive manipulation of viruses, living cells, and organelles. In chemistry, laser trapping study has progressed with a diversification of trapping targets. Representative targets are nanoparticles (44), quantum dots (45), polymers (46), proteins (47), and amino acids (48). Their size is much smaller compared to the focal volume that is usually a similar extent to the wavelength of the laser beam. Therefore, a large number of such targets are simultaneously confined in the focal volume, and their assemblies are formed (Fig. 1.09).

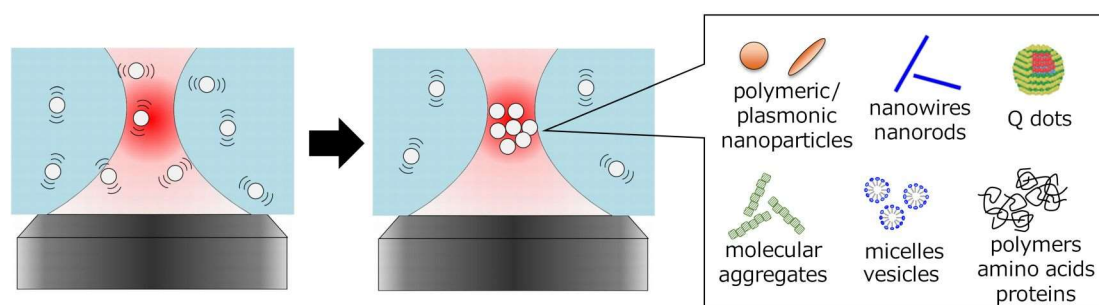


Figure 1.09: Assembly formation by laser trapping of various nanometer-size objects.

The mechanistic study on laser trapping and assembling phenomena is reported for dye-doped polystyrene nanoparticles (49) and plasmonic nanoparticles (50). In the former case, the experiments were designed to excite nanoparticles only at the focal spot, which was through two-photon absorption. That is, the number of particles in the focal volume can be estimated from the fluorescence intensity. During laser trapping, the fluorescence intensity was increased and saturated at a certain time. The result gave a clear picture that the nanoparticles are sequentially gathered and gradually occupied the focal volume. In the case of laser trapping of plasmonic nanoparticles, the change in optical property due

to plasmonic coupling was observed as the result of the shortening of the interparticle distance. Such laser trapping assembling phenomena are also reported for polymers, proteins, and amino acids, of which the size is much smaller when compared to that of nanoparticles (46–48).

The above experiments were performed inside the solution. On the other hand, an ordered structure is formed when laser trapping is carried out at an air/solution interface. It was demonstrated that the crystallization of amino acids could be induced from the focal spot by irradiating a continuous-wave laser beam at an air/solution interface of their aqueous solutions (51). The crystallization mechanism was explained from the viewpoints of local concentration increase by laser trapping and spontaneous molecular rearrangement characteristic to the solution surface. Due to local concentration increase, crystallization can be induced even in an unsaturated solution where spontaneous crystallization does not take place (52, 53). Furthermore, polymorph control was demonstrated by changing the polarization of the trapping laser (54, 55). Selective crystallization of α - or γ -forms of glycine was achieved with circularly- or linearly-polarized laser beams (54). Optical force is useful to control not only crystal nucleation but also crystal growth. A single plate-like L-phenylalanine crystal was prepared by a focused laser beam, and its two-dimensional crystal growth rate was precisely controlled by changing the laser power (56). The laser trapping-induced crystallization was extended from amino acids to an inorganic compound, and spatio-temporal crystallization of NaClO_3 was demonstrated in a microdroplet (57).

1-3: Motivation of this research

Laser trapping is an innovative optical approach to trap, manipulate, and concentrate on various nanometer-sized objects in solution but without any mechanical contact. While spatio-temporal preparation of assemblies or crystals was achieved with

this technique, the potentials of laser trapping for chemical reactions remain unexplored. The current work aims to explore such potentials through the control of synthesis and modification of perovskite crystals with the use of a focused laser beam in the perovskite precursor solutions. The obtained results will be an important milestone for the new application of laser trapping. Besides, the new approach based on laser trapping will offer new methodologies for engineering perovskite crystals.

This thesis consists of 6 chapters. In chapter 1, fundamental properties of metal halide perovskites and their preparation methods are introduced. In addition, the history and principle of laser trapping are summarized. In chapter 2, experimental setup and procedures are described.

In chapters 3 & 4, laser trapping behavior was investigated at air/solution interfaces of perovskite precursor solutions which is with the use of a continuous-wave laser beam of 1064 or 800 nm. A formed perovskite crystal was characterized by microspectroscopic analysis and X-ray diffraction (XRD) measurements. Crystallization mechanism was discussed from the viewpoints of local concentration increase in precursors' complexes and their de-solvation which are in addition to laser heating.

In chapter 5, laser trapping is carried out at a surface of MAPbX_3 crystal. Bandgap tuning and photoluminescence (PL) color change are observed in the crystal exposed to the laser. The mechanism is discussed by considering the halogen exchange reaction through local concentration increase.

In chapter 6, the results obtained in this study are summarized and future perspectives on perovskite research and laser trapping study are discussed.

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Chapter 2

Experiments

2-1: Optical setup

2-1-1: Laser trapping

Figure 2.01a shows a schematic illustration of an optical system used in this study. The optical system consists of lasers, an inverted microscope, a charged coupled device (CCD) camera, and a spectrometer. A near-infrared (NIR) continuous-wave (CW) laser (Spectron Laser System, $\lambda = 1064 \text{ nm}$) was used as a light source for laser trapping. A half-wave plate and a polarizing beam splitter were placed in the optical path. The former is an optical item to rotate the polarization direction of a linearly polarized laser beam. The latter is an optical item to split light into beams of differing polarization, namely, horizontally polarized light transmits while vertically polarized one reflects. Their combination enables tuning of the NIR laser power.

The NIR laser was introduced to the inverted microscope (Olympus, IX71) and reflected with a dichromatic mirror. The mirror has high reflectance at 1064 nm for laser trapping and high transmittance in the visible light region (Fig. 2.01b). The reflected NIR laser was focused with an objective lens of 60-time magnification (Olympus, UPlanFLN, numerical aperture (NA); 0.90). The high numerical aperture objective lens is necessary for laser trapping since optical force is proportional to the gradient of the light intensity (1). In addition, the spatial resolution in imaging is increased in inverse proportion to the numerical aperture, so that the high numerical aperture objective lens enables us to observe small objects with high resolution. The power of the NIR laser passing through

the objective lens was tuned between 0.2–1.0 W by rotating a half-wave plate placed in front of a polarizing beam splitter. The trapping laser was replaced to an 800-nm CW laser (Coherent, Mira9000) as necessary. The sample chamber was heated from the upper side with a thermoplate (TOKAI HIT, TP-110R-100) in certain experiments.

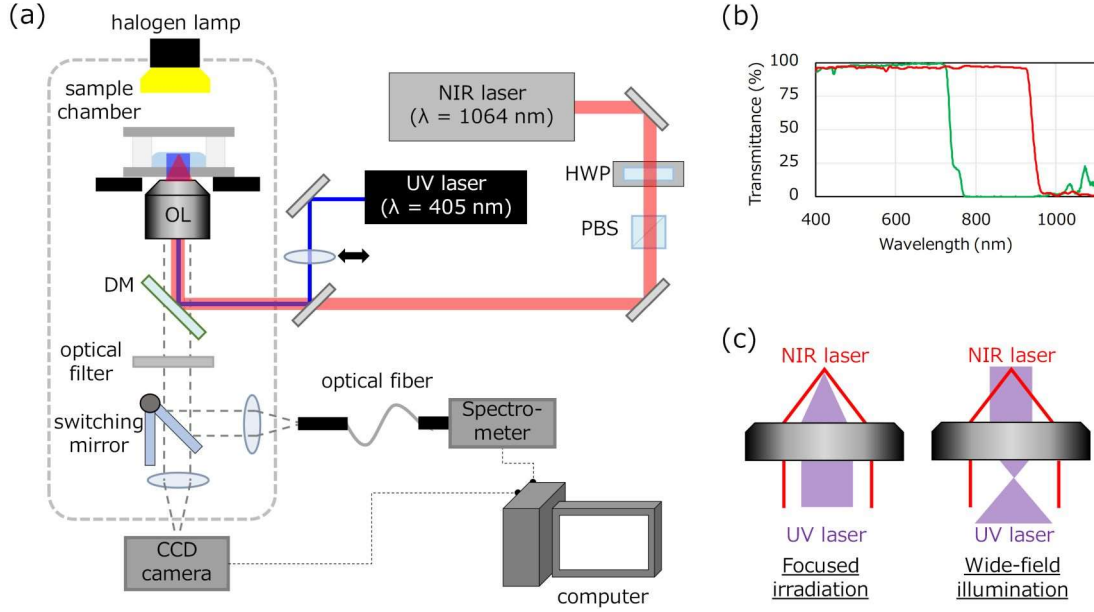


Figure 2.01: (a) Schematic illustration of the optical system used. OL, DM, HWP, and PBS denote objective lens, dichromatic mirror, half-wave plate, and polarizing beam splitter, respectively. (b) Transmission spectra of dichromatic mirrors used. (c) Two illumination modes of the UV laser.

The ultraviolet (UV) laser (Thorlabs, CPS405, $\lambda = 405$ nm) was also introduced to the microscope in the optical path same as that of the NIR laser and focused with an objective lens. The output power of the UV laser was 4.5 mW at the source but after objective lens, it is less than 0.045 mW due to high transmittance at the dichroic mirror (Fig. 2.01b). Transmittance of the objective lens for the UV laser is 80 %. The laser power was tuned with a variable reflective neutral density filter. In the case of wide-field illumination, the UV laser was focused in front of the microscope in order to be parallel

with the axis of the objective lens. This beam illuminated $100 \times 80 \mu\text{m}^2$ area of the samples (Fig. 2.01c).

I used a CCD camera (Watec, WAT250D) for imaging. The microspectroscopic analysis was carried out with a spectrometer (Ocean Optics, Flame) combined with an optical fiber with core diameter of $200 \mu\text{m}$. The detection area size for the spectroscopic analysis was about $3 \mu\text{m}$ in diameter around the focal spot of the NIR laser, which was calculated on the basis of magnification of the objective lens and a core diameter of the optical fiber. During imaging and spectroscopy, the NIR laser and the UV laser were blocked with an optical filter placed below the dichromatic mirror.

2-1-2: Spectroscopy and imaging under microscope

In the microspectroscopic analysis, the transmitted light or generated PL was detected with the spectrometer. The transmission spectroscopy of a perovskite crystal was carried out in the following procedure (Fig. 2.02). Firstly, the white light passing through a sample solution was measured as a reference spectrum (I_{ref}). Crystallization of perovskites was induced by laser trapping. Then, a spectrum of white light was detected through the crystal as a sample spectrum (I_{cryst}). A transmission spectrum was calculated by dividing I_{cryst} by I_{ref} , by which the effect of transmission of a dichromatic mirror is canceled.

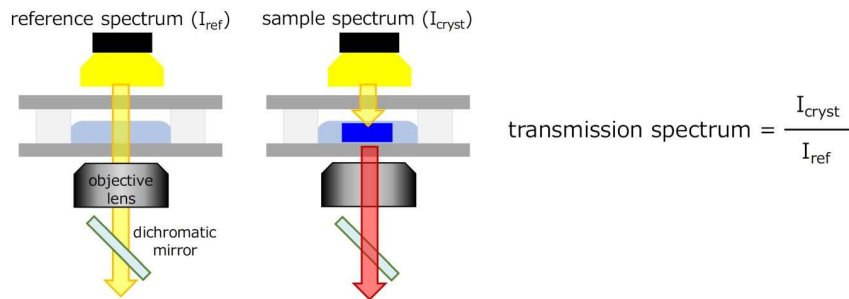


Figure 2.02: Schematic illustration for transmission microspectroscopy of a perovskite crystal in a sample chamber.

The PL of a perovskite crystal was generated through one-photon excitation of the UV laser or two-photon excitation of the NIR laser. Generally, two-photon excitation is induced with laser pulses having a very high peak power. In the current experiments, I used a tightly focused CW laser beam, but two-photon excitation is possible due to the high photon density at the focal spot comparable to the case of pulsed laser irradiation. The PL was detected through a dichromatic mirror, therefore the detected signal was modified by the transmittance of the mirror. I calibrated its effect by dividing the obtained PL spectrum with the transmission curve of the mirror.

The sample on the microscope stage was observed with transmission imaging or PL imaging. In the former case, the sample was illuminated with a white light of a halogen lamp from above. In the latter case, the sample was excited with a widely illuminating UV laser from the bottom. The transmitted light or generated PL was detected with the CCD camera connected to a computer. The transmission and PL images were recorded at the video rate of one photo per 30 ms. I used an objective lens of low magnification ($\times 4$, NA; 0.1 or $\times 10$, NA; 0.3) in order to observe a larger area as necessary.

2-2: Experimental procedure

2-2-1: Chemicals and materials

I used the following chemicals without any further purification; methylammonium chloride, MA₂Cl, (TCI, >98.0%); methylammonium bromide, MA₂Br, (TCI, >98.0%); methylammonium iodide, MAI, (TCI, >98.0%); lead (II) chloride, PbCl₂, (Aldrich, 98.0%); lead (II) bromide, PbBr₂, (Aldrich, $\geq$ 98.0%); lead (II) iodide, PbI₂, (Aldrich, 99.0%); dimethyl sulfoxide, DMSO, (Wako); *N, N*-dimethylformamide, DMF, (Wako); γ -butyrolactone, GBL, (TCI, >99.0%); isopropyl alcohol, IPA, (Wako); and Hexadecene (Wako). Fundamental properties of these solvents are shown in the table 2.01 (2–22).

Table 2.01: Properties of solvents used and water as a reference.

Solvent	Boiling point (°C)	Refractive index	Dielectric constant	Dipole moment (D)	Thermal conductivity (W/m·K)
Water	100	1.33	80.0	1.85	0.608
DMSO	152	1.47	46.7	3.96	0.183
DMF	189	1.43	38.3	3.82	0.186
GBL	204	1.44	42.8	3.40	0.100
Isopropanol	82	1.38	19.92	1.65	0.158
Hexadecene	278	1.44	2.01	0.39	0.080

All trapping experiments were performed in a hand-made chamber prepared in the following procedure (Fig. 2.03). A silicone rubber sheet with a thickness of 3 mm was cut to a size of 20 mm × 20 mm, and a hole with a diameter of 4 mm was created in the center part. The fabricated silicone rubber was glued to cover glass (Matsunami, 25 mm × 25 mm, thickness 0.13–0.17 mm) using silicone glue (Shin-Etsu, KE42RTV).

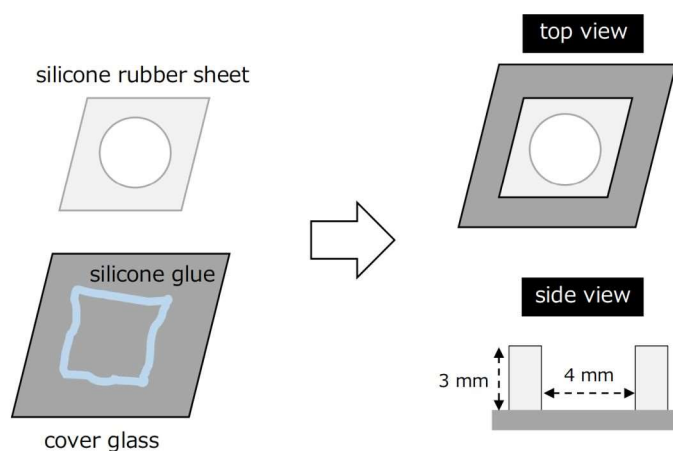


Figure 2.03: Schematic illustration for procedure to prepare a sample chamber.

2-2-2: Sample preparation for laser trapping crystallization of MAPbX₃

I used the following three solutions for the experiments on MAPbX₃ synthesis and crystallization in chapter 3 (table 2.02) (23). The saturation degrees at room temperature (18 °C) were estimated from the reported solubility curves (Fig. 2.04) (24, 25). The

MABr:PbBr₂ precursor solution with lower concentrations were also prepared to investigate concentration dependence of the synthesis and crystallization of MAPbBr₃.

Table 2.02: Precursor solutions for synthesis and crystallization of MAPbX₃ (23).

MAPbX ₃	Solvent	Precursors (M)	Saturation degree at room temperature
MAPbBr ₃	DMF	MABr:PbBr ₂ (1.3)	0.83
MAPbCl ₃	DMF:DMSO (1:1, v:v)	MACl:PbCl ₂ (1.0)	0.85
MAPbI ₃	GBL	MAI:PbI ₂ (1.0)	1.2

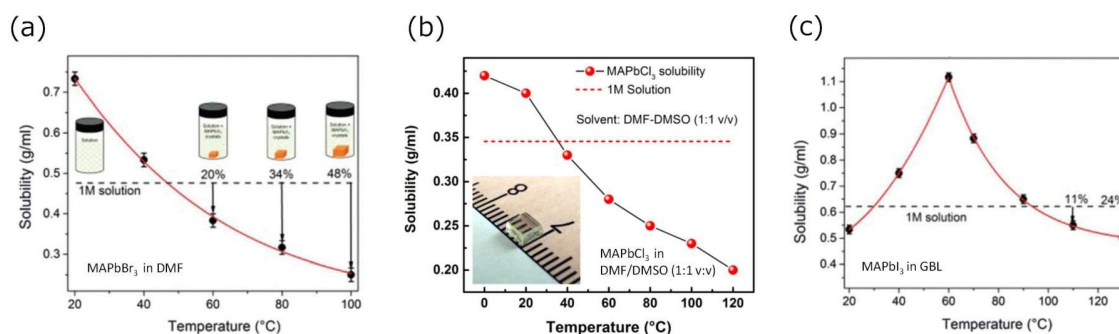


Figure 2.04: Retrograde solubility curves of (a) MAPbBr₃, (b) MAPbCl₃, and (c) MAPbI₃ crystals in specific solvents. Reprinted with permissions from *Chem. Commun.* **2015**, 51, 17658–17658 & *J. Phys. Chem. Lett.* **2015**, 6, 3781–3786. Copyright (2015) The Royal Society of Chemistry. Copyright (2015) American Chemical Society.

Equimolar amounts of MABr and PbBr₂ powder samples were added into DMF, and the mixture was stirred at 1000 rpm. After one hour, a colorless solution (MABr:PbBr₂ in DMF) was obtained. A precursor solution of MACl:PbCl₂ was prepared in two steps. Firstly, equimolar amounts of MACl and PbCl₂ were mixed in DMSO. This mixture was shaken at 1000 rpm for one hour with a shaker (HCM100-Pro, DLAB) until it was converted into a white suspension. This suspension was kept without stirring on a hotplate, where the solution temperature was set at 140 °C. After one hour, a colorless

solution ($\text{MAI}:\text{PbCl}_2$ in DMSO) was obtained. This solution was mixed with the required amount of DMF, and the precursor solution of $\text{MAI}:\text{PbCl}_2$ in a DMSO:DMF mixture was prepared. Equimolar of MAI and PbI_2 were put into γ -butyrolactone (GBL), and the mixture was stirred at 1000 rpm on a hotplate, where the solution temperature was set at 50 °C. After 30 min, a yellow transparent solution ($\text{MAI}:\text{PbI}_2$ in GBL) was obtained.

The precursor solutions were centrifuged at 10,000 rpm for 5 minutes or filtered through a 0.22 μm pore sized syringe filter, and their supernatants were used in laser trapping experiments. The solution of ca 10 μL was placed in a chamber and its thin film with a thickness of 100–200 μm was prepared. The NIR laser beam was focused at an air/solution interface of the precursor solution.

I measured the size of precursors in the DMF solution of $\text{MABr}:\text{PbBr}_2$ using dynamic light scattering (DLS) technique (Malvern Instruments). The measurement was carried out for the 200 μL DMF solution of $\text{MABr}:\text{PbBr}_2$ (1.3 M), which was prepared in the procedure same as the sample preparation for laser trapping described above. The result is shown in chapter 3-4.

2-2-3: Sample preparation for laser trapping crystallization of $\text{MAPbBr}_n\text{Cl}_{3-n}$

For synthesis and crystallization of $\text{MAPbBr}_n\text{Cl}_{3-n}$ in chapter 4, I used precursor solutions summarized in table 2.03 (26). The precursor solutions same as above were used in the preparation of $\text{MAPbBr}_{3.0}$ and $\text{MAPbCl}_{3.0}$. For the preparation of $\text{MAPbBr}_{2.5}\text{Cl}_{0.5}$ precursor solution, $\text{MABr}:\text{PbBr}_2:\text{MAI}$ (1.0 M) was dissolved in DMF. Although MAI can be dissolved well in DMF, it lowers the solubility of precursors, so that the concentration of the precursor solution was adjusted to be 1.0 M.

Table 2.03: Precursor solutions for the crystallization of $\text{MAPbBr}_n\text{Cl}_{3-n}$ (26).

MAPbX_3	Solvent (DMF:DMSO, v/v)	Precursors mole ratio (Conc.) $\text{MABr:PbBr}_2:\text{MACl:PbCl}_2$ (M)	Saturation degree
$\text{MAPbBr}_{3.0}$	1:0	1:1:0:0 (1.3)	0.83
$\text{MAPbBr}_{2.5}\text{Cl}_{0.5}$	1:0	1:2:1:0 (1.0)	-
$\text{MAPbBr}_{2.0}\text{Cl}_{1.0}$	4:1	2:2:1:1 (1.56)	-
$\text{MAPbBr}_{1.5}\text{Cl}_{1.5}$	2.5:1	1:1:1:1 (1.5)	-
$\text{MAPbBr}_{1.0}\text{Cl}_{2.0}$	2:1	1:1:2:2 (1.3)	-
$\text{MAPbBr}_{0.5}\text{Cl}_{2.5}$	1.5:1	1:1:5:5 (1.25)	-
$\text{MAPbCl}_{3.0}$	1:1	0:0:1:1 (1.0)	0.85

The precursor solutions of $\text{MAPbBr}_n\text{Cl}_{3-n}$ ($n = 0.5, 1.0, 1.5, 2.0$) were prepared by adding appropriate amounts of MABr:PbBr_2 to MACl:PbCl_2 in a DMSO:DMF mixed solvent. These precursors (MABr:PbBr_2) were well dissolved in DMSO but without showing any retrograde solubility. Furthermore, these all improve the solubility of the precursors. Considering these characteristics, I increased the content of DMF in a DMSO:DMF solvent mixture of the precursor solutions along with an increase in the PbBr_2 concentration.

Impurities in the precursor solutions were removed by centrifugation or filtration, and the NIR laser beam was focused at an air/solution interface of a thin film of the precursor solution in a chamber. The saturation degree of the precursor solutions of $\text{MAPbBr}_n\text{Cl}_{3-n}$ ($n = 0.5, 1.0, 1.5, 2.0$, and 2.5) is unclear. However, I confirmed that they are unsaturated at room temperature and show retrograde solubility curves.

2-2-4: Sample preparation for halide exchange reactions

The preparation of initial perovskite crystals and halide exchange reaction were carried out in a sample chamber shown in Figure 2.03. Micrometer-size MAPbBr_3 crystals were directly synthesized by solvent evaporation on a clean cover glass of the chamber. Firstly, a micro-droplet (around 1 μL) of 1.3 M MABr:PbBr_2 solution in DMF with the

diameter of several hundred micrometers was prepared on the glass substrate of the chamber. Then, spontaneous crystallization started through natural solvent evaporation, and the crystals appeared in the droplet. By this way five micrometer dimensional square shape crystal formed within 2-3 minutes. After the confirmation of the crystallization, the remaining solution was wiped out with a filter paper. Similarly, MAPbCl₃ microcrystals were prepared from 1.0 M solution of MACl:PbCl₂ in a DMSO:DMF mixture. The reaction solution containing MAI or MABr was added to the chamber, which was followed by the laser irradiation.

Like the size measurement of the MABr:PbBr₂ precursor solution by DLS, I also measured the size of precursors in the reaction solution of MAI for halogen exchange. For the measurement, I used 200 μ L MAI solution (110 μ M) in a mixture of hexadecene and isopropyl alcohol (100:1, v:v). The obtained result is shown in chapter 5-2-3.

2-3: X-ray diffraction (XRD) measurement

I characterized perovskite crystals formed by laser trapping through single crystal X-ray diffraction (XRD) method. After the single crystal was grown up to $400 \times 400 \mu\text{m}^2$, I picked up the crystal from the sample chamber and analyzed the structure of the crystal. The crystal was mounted on a glass capillary tube and fixed with epoxy resin. Crystallographic data were collected using a Rigaku RAXIS-RAPID diffractometer with Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation from a graphite monochromator. Structural refinements were performed using the full-matrix least-squares method on F². The calculations were carried out with the Yadokari-XG software package. Powder XRD patterns were constructed with Mercury software, based on the resultant CIF files from the analyses.

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Chapter 3

Crystallization of pure halide lead perovskites by laser trapping

In this chapter, laser trapping behavior was examined by focusing a CW laser beam of 1064 or 800 nm at an air/solution interface of MAX:PbX₂ (X = Cl, Br, or I) precursor solutions. In all solutions, whatever unsaturated, crystallization was induced from the focal spot. The resultant crystal was characterized by microspectroscopic analysis and XRD measurement and identified as MAPbX₃. This means that the synthesis (crystallization) of MAPbX₃ results from chemical reactions through local concentration increase induced by laser trapping of perovskite precursors.

3-1: Crystallization of methylammonium lead bromide (MAPbBr₃)

Laser trapping was conducted at an air/solution interface of a precursor solution of MABr:PbBr₂ (1.3 M) dissolved in DMF (Fig. 3.01a) (1). It is reported that MAPbBr₃ shows retrograde solubility in DMF at temperatures up to 100 °C (Fig. 2.04a) (2). Based on this solubility, the saturation degree of the precursor was estimated at 0.83, which is at 18 °C in the experimental room. Figure 3.01b shows optical transmission micrographs during laser trapping. At the beginning of the irradiation, an optical micrograph showed only the faint trapping laser reflected at the air/solution interface [panel (i) of Fig. 3.01b]. A small crystal of a few micrometers was identified in a camera image at 103 s [panel (ii) of Fig. 3.01b]. The nucleated crystal continuously grew large while being trapped at the focal spot and attained the size of 11 × 13 μm² at 120 s [panels (iii)–(iv) of Fig. 3.01b].

The formed crystal moved away from the focal spot and dissolved soon after the laser was turned off [panels (v)–(vi) of Fig. 3.01b], which is due to the unsaturation 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 precursor solutions of 1.2 M are required for consistent crystallization.

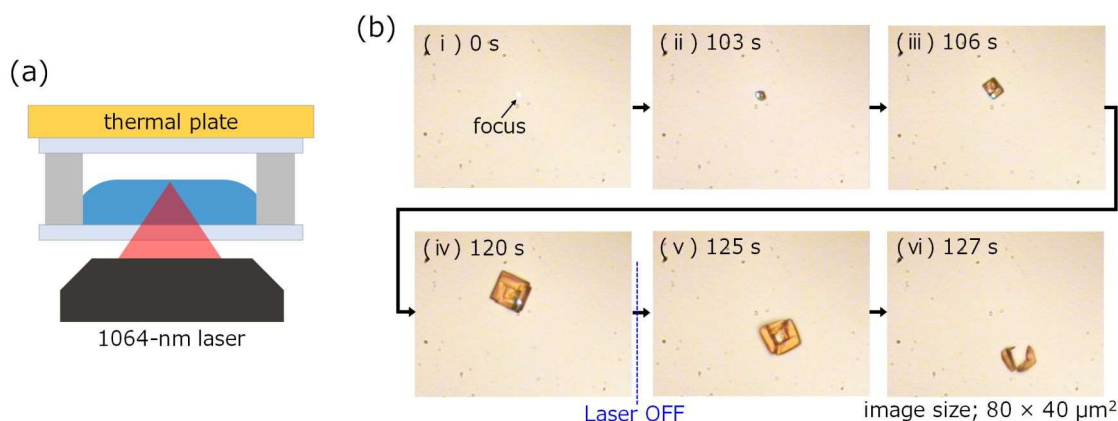


Figure 3.01: (a) Schematic illustration for the experimental procedure of laser trapping at an air/solution interface of a MABr:PbBr₂ solution in DMF. (b) Optical micrographs of the solution under 1064-nm laser irradiation. The power of the laser after passing through the objective lens was 0.6 W (1).

The measurements of a PL spectrum and an XRD pattern in addition to observation of dissolution/growth behavior revealed that the crystal formed in the MABr:PbBr₂ solution is MAPbBr₃. The formed crystal showed green emission during the trapping, and its peak was observed at 550 nm (Fig. 3.02a). This PL is the result of two-photon absorption of the trapping laser. The obtained spectral profile was like that reported for MAPbBr₃ (3). For observing dissolution/growth behavior of the crystal, I heated the sample chamber with a thermal plate, which was after the crystal nucleation [panel (i) of Fig. 3.02b]. The nucleated single crystal grew continuously under the combined trapping and heating condition. After the crystal size became ca $60 \times 60 \mu\text{m}^2$, the trapping laser

was turned off, and the crystal continued to grow under heating, which was observed through a low magnification objective lens [panels (ii)–(iii) of Fig. 3.02b]. The growth under the heating condition and the dissolution upon de-trapping at room temperature suggest the retrograde solubility of the formed crystal, indicating the formation of MAPbBr₃ in an unsaturated solution. The XRD data (Fig. 3.02c) obtained for the single crystal perfectly matched with the characteristic Miller indices of cubic MAPbBr₃.

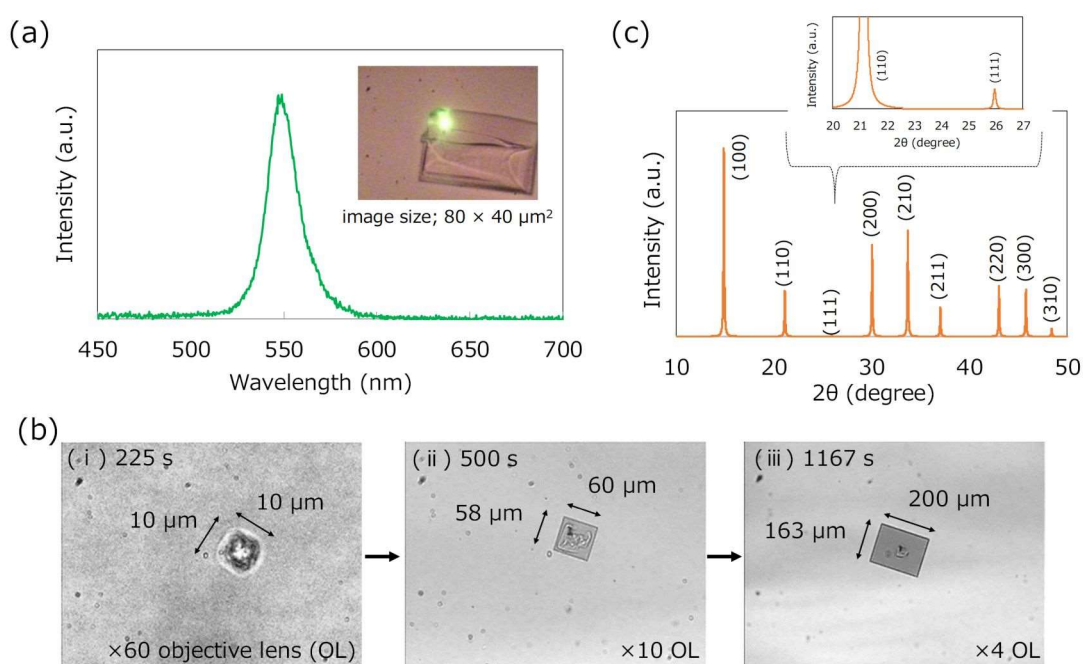


Figure 3.02: (a) A PL spectrum obtained during the trapping of the formed crystal. The inset shows the optical micrograph of the PL generated at the focal spot of the trapping laser. (b) Optical micrographs of the crystal that was incubated in the chamber heated with a thermal plate. The temperature of the thermal plate was set at 70 °C. The dark spots in the crystal are due to an inhomogeneous thickness of the crystal. (c) The powder XRD pattern of the large crystal formed by laser trapping (1).

Despite the growth of single crystal by the focused laser irradiation, retrograde solubility of MAPbBr₃ encouraged us to consider the role of laser-induced heating on crystal nucleation. It is reported that the local temperature under laser trapping condition

elevates as a function of the absorption coefficient at the wavelength of the trapping laser and the thermal conductivity of the solvent (4). Here, the absorption coefficient of DMF at 1064 nm was estimated by measuring transmittance with cuvettes of different optical path lengths. The data were analyzed in the following way (Fig. 3.03a).

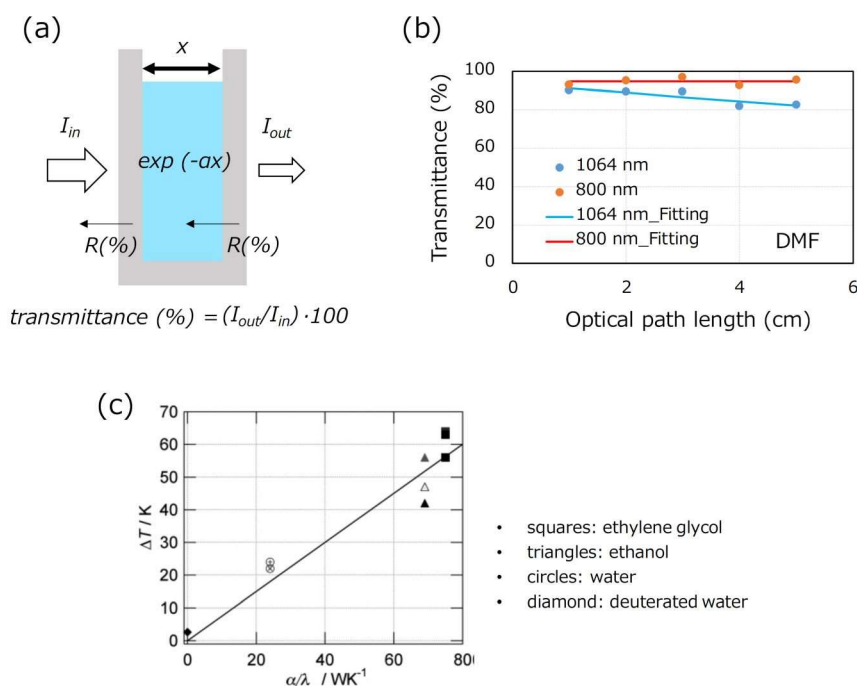


Figure 3.03: (a) Schematic illustration for analysis of the transmittance. (b) The transmittance of the 1064- and 800- nm light passing through DMF as a function of optical path length. (c) A plot of the temperature elevation coefficients, $\Delta T/\Delta P$, as a function of the ratio of the extinction coefficient of the solvents, α , to the thermal conductivity of the solvents, λ . Reprinted with permission from *J. Phys. Chem. B* **2007**, *111*, 2365–2371 (ref. 4). Copyright (2007) American Chemical Society.

Transmittance (%) is defined as $(I_{out}/I_{in}) \cdot 100$, where I_{in} is the intensity of light input to a cuvette and I_{out} is the intensity of light passed through the cuvette. The input light is reflected at the air/cuvette interface and the cuvette/solvent interface. The intensity of the light incident to DMF is expressed as $I_{in} \cdot [1 - (R/100)]$, where R is the total reflectance (%) at the front face of the cuvette, including contributions at air/cuvette and

cuvette/solvent interfaces. This light is absorbed by DMF in accordance with the Lambert-Beer's law, depending on absorption coefficient; α (cm^{-1}) and optical path length; L (cm). After the light passes through DMF, its intensity is decreased to $I_{in} \cdot [1 - (R/100)] \cdot \exp(-\alpha L)$. At the back face of the cuvette, light reflection occurs again with the reflectance of R (%). Namely, I_{out} is expressed as $I_{in} \cdot [1 - (R/100)] \cdot \exp(-\alpha L) \cdot [1 - (R/100)]$. As the result of light reflection at interfaces and light absorption in DMF, the relation; transmittance (%) = $100 \cdot [1 - (R/100)]^2 \cdot \exp(-\alpha L)$; is obtained. This function was used to fit the measured transmittance (Fig. 3.03b), and absorption coefficient of DMF at 1064 nm was estimated at 2.62 m^{-1} (1). This absorption is due to the overtone of vibrational modes. Thermal conductivity of DMF is reported to be $0.183 \text{ W/m}\cdot\text{K}$ (5).

Local temperature elevation per 1.0 W under laser trapping condition is linearly increased with the slope of 0.75 against the value calculated by dividing the absorption coefficient with thermal conductivity (Fig. 3.03c). In the current experiment, this value is 14.3, meaning that the local temperature elevation is 10.7 K for 1.0 W laser irradiation. Assuming the linear relation between temperature elevation and input laser power, the laser irradiation at 0.6 W leads to temperature elevation of 6.4 K. This laser heating lowers the solubility and increases the saturation degree by 0.1. However, the solution is still below saturation. It can be concluded that the local temperature elevation is not the main driving force for synthesis and crystallization of MAPbBr_3 (1).

In order to rule out the possibility of laser heating in another approach, the same experiment was conducted with 800-nm laser (1). Light absorption at this wavelength is negligibly small (Fig. 3.03b). In the case of the MABr:PbBr_2 precursor solution under the 800-nm laser irradiation, the crystallization occurred at the focal spot (Fig. 3.04a). The size and the number of crystals were increased all at a sudden. Followed by the formation, the crystals were detached from the focal spot and moved away to the surrounding

solution. This explosive crystal growth behavior can be explained from the viewpoint of efficient two-photon induced heating of the resultant crystal and the subsequent increase in saturation degree in the surrounding solution. During the nucleation and growth of the crystals, green emission was observed at the focal spot, which is the result of two-photon absorption of the trapping laser by the MAPbBr₃ crystal. The peak position of emission spectra dynamically shifted around 540 nm (Fig. 3.04b). I assume that this fluctuation occurs due to factors such as rotation and breakage of crystals and the crystal angle-dependent difference in the degree of reabsorption emission. Although the crystal growth was complicated, the fact that the 800-nm laser-induced crystallization from the focal spot clearly indicates that laser heating is not the main driving force for crystal nucleation and local concentration increase contributes to the nucleation. Subsequent crystal growth is due to two-photon induced heating of the formed crystal.

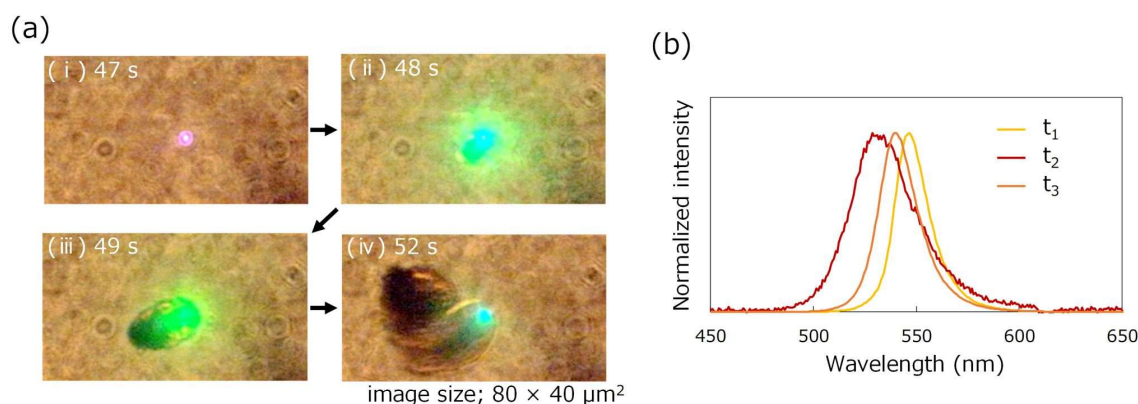


Figure 3.04: (a) Optical micrographs in the DMF solution of MABr:PbBr₂ under the 800-nm laser irradiation at the air/solution interface. The power of the laser passing through the objective lens is 0.4 W. (b) Emission spectra of the crystals formed in the precursor solution under the irradiation. In the graph, t₁, t₂, and t₃ represent sequential spectra during trapping, showing spectral fluctuations (1).

3-2: Crystallization of methylammonium lead chloride (MAPbCl₃)

Crystallization using focused laser irradiation was extended to MAPbCl₃. As the initial precursor solution, I prepared MACl:PbCl₂ (1.0 M) dissolved in a DMSO:DMF solvent mixture (1:1, v:v). MAPbCl₃ shows retrograde solubility in a DMSO:DMF (1:1, v:v) mixture at temperatures up to 120 °C (Fig. 2.04b). Based on the reported solubility (6), saturation degree of the MACl:PbCl₂ precursor solution was estimated at 0.85. The experiment was carried out with the procedure similar to that of MAPbBr₃. Figure 3.05a shows laser trapping behavior upon the 1064-nm laser irradiation at the air/solution interface of the MACl:PbCl₂ precursor solution. A small crystal of a few micrometers was identified in a camera image at 93 s. The nucleated crystal grew large while being trapped at the focal spot. The growth was saturated with the crystal size of ca 5 × 5 μm², which was different from the continuous growth behavior of MAPbBr₃. I confirmed that the formed crystal completely dissolved after switching off the trapping laser.

For further growth of the crystal, I heated the sample chamber with a thermal plate, which was after the nucleation [panel (i) of Fig. 3.05b]. The nucleated single crystal grew continuously under the combined trapping and heating condition. After the crystal size became ca 60 × 60 μm², the trapping laser was turned off, and the crystal continued to grow under heating, which was observed through a low magnification objective lens [panels (ii)–(iii) of Fig. 3.05b]. The growth under the heating condition and dissolution upon de-trapping at room temperature suggest the retrograde solubility of the formed crystal, indicating the formation of MAPbCl₃. The grown large crystal was picked out from the chamber, and the XRD pattern was measured. The XRD data (Fig. 3.05c) obtained for the grown single crystal perfectly matched with the characteristic pattern of the cubic form of MAPbCl₃ (6). Thus, the focused laser irradiation enabled the crystallization of MAPbCl₃ and MAPbBr₃ in a spatially- and temporally- controlled manner.

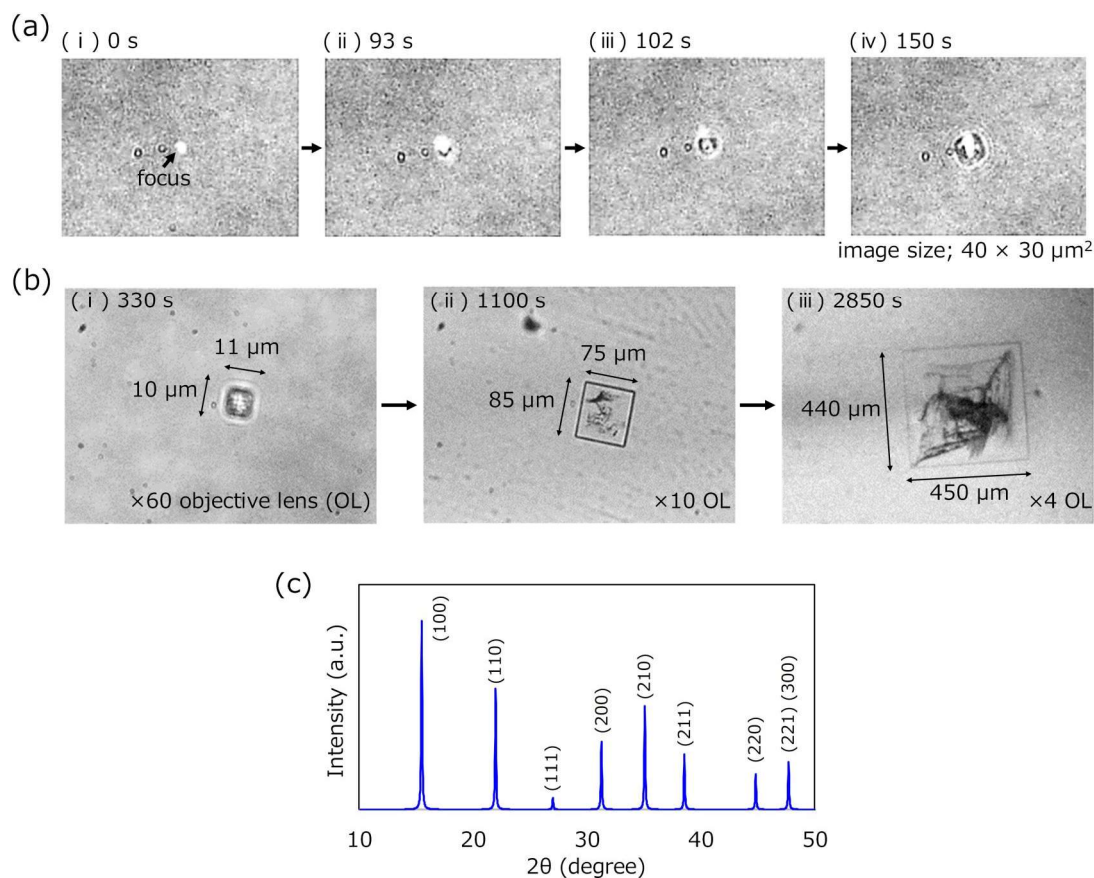


Figure 3.05: (a) Optical micrographs in the solution of MACl:PbCl_2 under the 1064-nm laser irradiation at the air/solution interface. The power of the laser after the objective lens was 0.6 W. (b) Optical micrographs of the crystal that was incubated in the chamber heated with a thermal plate set at 90 °C. The dark spots outside the crystal are from dust in the microscope optics, whereas those in the crystal are due to the inhomogeneous thickness of the crystal. (c) The powder XRD pattern of the large crystal formed by optical trapping (1).

The laser irradiation induces local temperature elevation through light absorption and overtone vibrations. The local temperature elevation was estimated in the procedure the same as that of the experiment for MAPbBr_3 . Figure 3.06 shows transmittance of DMSO measured in cuvettes of different optical path lengths as well as the fitted curve. The absorption coefficient of DMSO at 1064 nm was estimated at 3.22 m^{-1} . This

absorption is due to the overtone of vibrational modes. Thermal conductivity of DMSO is reported to be $0.186 \text{ W/m}\cdot\text{K}$ (7). The value calculated by dividing the absorption coefficient with thermal conductivity is 17.3, meaning that the local temperature elevation is 13.0 K per 1.0 W. The laser irradiation at 0.6 W into neat DMSO increases temperature by 7.8 K. Considering the absorption coefficient of DMF which is lower than that of DMSO, the local temperature elevation in a DMSO:DMF solvent mixture (1:1, v:v) should be less than 7.8 K. Thus, I consider that MAPbCl₃ crystallization under the focused laser irradiation accompanies local temperature elevation of several K.

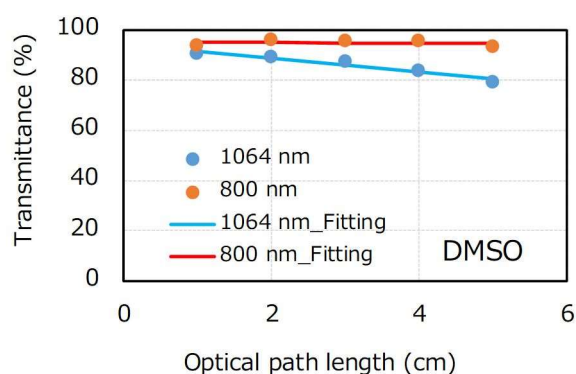


Figure 3.06: Transmittance of the 1064- and 800- nm light passing through DMSO as a function of optical path length.

To suppress temperature elevation during the focused 1064-nm laser irradiation, I carried out the trapping experiment using 800-nm laser with the power of 0.4 W (1). As shown in Figure 3.06, temperature elevation under the 800-nm laser irradiation is negligibly small due to poor absorption of the laser. Figure 3.07a shows optical micrographs around the focal spot upon the 800-nm laser irradiation at the air/solution interface of the MACl:PbCl₂ precursor solution. The crystallization was induced from the focal spot at 210 s [panel (ii) of Fig. 3.07a]. The crystal grew slowly while being stably trapped at the focal spot, and the growth was saturated with the crystal size of 15×15

μm^2 [panels (iii)–(iv) of Fig. 3.07a]. Although the precursor solution doesn't absorb the 800-nm trapping laser, the trapped crystal showed blue emission through two-photon absorption of the laser. From the spectral profile (Fig. 3.07b), I consider the trapping-induced formation of a MAPbCl_3 crystal. Through the two-photon absorption, heating is induced by non-radiative relaxation, and the temperature of the surrounding solution is increased. Since a MAPbCl_3 crystal shows retrograde solubility in the DMSO:DMF mixed solvent, the resultant crystal grew continuously under the laser irradiation.

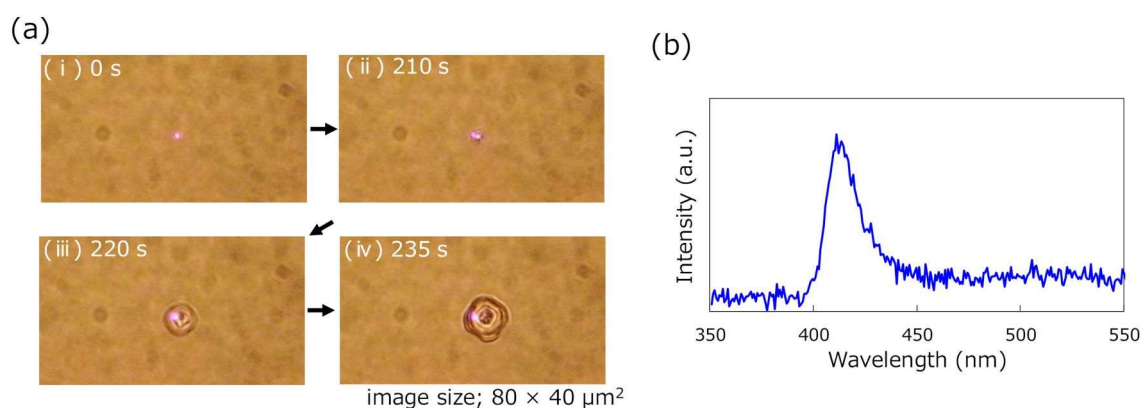


Figure 3.07: (a) Optical micrographs in a solution of MACl:PbCl_2 in DMSO:DMF under the 800-nm laser irradiation at the air/solution interface. The power of the laser after the objective lens was 0.4 W. (b) Emission spectrum of the crystal formed in the precursor solution under the irradiation (1).

3-3: Crystallization of methylammonium lead iodide (MAPbI_3)

As the sample for crystallization of MAPbI_3 , I used MAI:PbI_2 (1.0 M) dissolved in GBL. The solubility of MAPbI_3 in GBL increases with temperatures up to 60°C , but retrograde solubility is observed in the $60\text{--}120^\circ\text{C}$ range (Fig. 2.04c) (2). Based on the reported solubility curve, the saturation degree of the precursor solution at room temperature was estimated at 1.2. Apart from the solutions of MACl:PbCl_2 and MABr:PbBr_2 , I didn't observe any crystallization in the MAI:PbI_2 solution exposed to the

trapping laser of 1.0 W for 30 minutes at room temperature.

In order to estimate local temperature elevation, I measured the transmittance of GBL in cuvettes of different optical path lengths (Fig. 3.08). The absorption coefficient of GBL at 1064 nm was estimated at 1.42 m^{-1} . Thermal conductivity of GBL is reported to be $0.100 \text{ W/m}\cdot\text{K}$ (8). The value calculated by dividing the absorption coefficient with thermal conductivity is 14.2, meaning that the local temperature elevation is 10.6 K per 1.0 W. Absorption coefficient at 800 nm is negligibly small. I did not conduct the trapping experiment with the 800-nm laser because the MAI:PbI₂ solution has strong absorption at the wavelength below 450 nm and two-photon absorption of the solution is induced under the 800-nm laser irradiation.

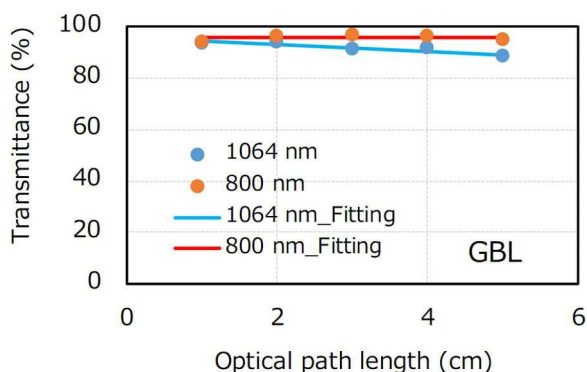


Figure 3.08: The transmittance of the 1064- and 800- nm light passing through GBL as a function of optical path length.

Interestingly, crystallization was induced under laser trapping in the MAI:PbI₂ solution set at 100 °C with a thermal plate. Suddenly, many black crystallites were formed at the focal spot [panels (i)–(ii), Fig. 3.09a], and the number of crystals was increased within 1 to 2 seconds [panel (iii), Fig. 3.09a]. Followed by the formation, the crystals were detached from the focal spot [panel (iv), Fig. 3.09a] and dissolved while moved away to the surrounding solution.

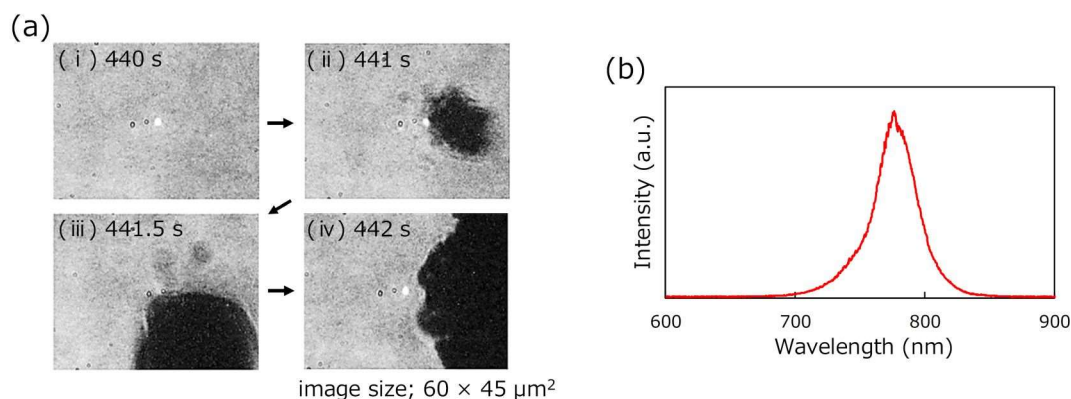


Figure 3.09: (a) Optical micrographs in the solution of MAI:PbI₂ under the 1064-nm laser irradiation at the air/solution interface. The laser power after the objective lens was 1.0 W (b) A PL spectrum of the black crystals under the 1064-nm laser irradiation (1).

I characterized the formed crystals by measuring the PL spectrum through two-photon excitation with the trapping laser (Fig. 3.09b), although the crystal was dissolved soon after the detachment from the focal spot or the trapping laser was turned off. By considering the red emission with a peak at 790 nm, I suggest that the microcrystals formed in a MAI:PbI₂ solution under laser trapping is MAPbI₃ perovskite. At room temperature, the solubility of MAPbI₃ is increased with temperature elevation. Therefore, immediately after the formation of a MAPbI₃ crystallite at the focal spot, it might have dissolved through the efficient two-photon induced heating. On the other hand, MAPbI₃ has retrograde solubility, leading to explosive crystal growth through the rapid elevation of saturation degree.

3-4: Crystallization dynamics of pure halide lead perovskites

Here, I suggest a possible mechanism for laser trapping-induced crystallization of MAPbX₃ (Fig. 3.10). Under the irradiation at 0.6 W, the power density at the focal spot (a circle of 1 μm diameter) is calculated to be 76 MW/cm². It is proposed that perovskite

precursors form complexes including solvent molecules (3, 9). Precursor complexes should have a larger size compared to that of individual ions. Since the trapping force is proportional to the target volume (10), a precursor complex of large size generates strong trapping force, resulting in its trapping at the focal spot (Fig. 3.10a). Once precursor complexes begin to assemble in the focal volume, their effective size and polarizability become large, and their local concentrations increase nonlinearly with irradiation time, realizing supersaturated condition at the focal spot.

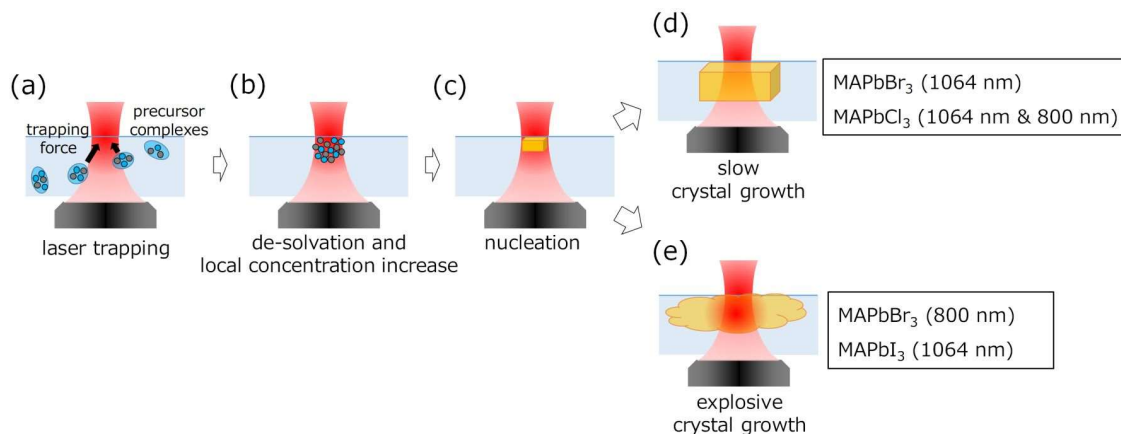


Figure 3.10: The mechanism for crystal nucleation and growth. Nucleation is initiated through local concentration increase, de-solvation, and molecular and ionic reordering at the solution surface, and the crystal growth rate depends on whether the perovskite absorbs the trapping laser or not (1).

However, the DLS measurement of the MABr:PbBr₂ precursor solution showed the distribution of solutes only at the size less than 3 nm (Fig. 3.11). I consider that, at an air/solution interface, precursor complexes can be easily formed due to the two-dimensionally suppressed diffusion. In addition, the electromagnetic energy of the trapping laser modifies the free energy of the focal volume to be lower, as discussed by Walton and Wynne (11). Due to such an optical potential, individual precursors are attracted to the focal spot, accelerating the formation of the precursor complexes.

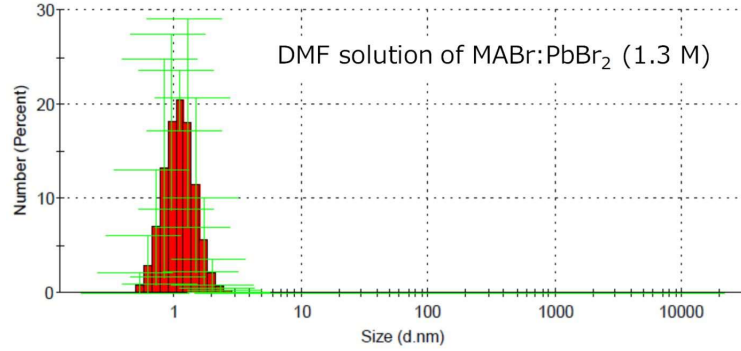


Figure 3.11: The size distribution with standard deviation in the DMF solution of MABr:PbBr₂ (1.3 M) estimated by the DLS measurement.

One of the key processes in the nucleation of perovskites is de-solvation of their precursor complexes. One possible reason for de-solvation is the optical force. It is noteworthy that dehydration occurs for polymers assembled in the optical potential. Tsuboi *et al.* spectroscopically validated that poly(*N*-isopropylacrylamide), a well-known thermo-responsive polymer, forms anhydrous microparticles in the aqueous solution, which is by dehydration under optical trapping (12). Similarly, I assume that the solvent molecules are partially or completely removed from the gathered precursor complexes during their trapping (Fig. 3.10b). The local temperature elevation during laser trapping is negligibly small to account for any de-solvation by laser-induced heating. Overall, the nucleation is initiated through local concentration increase, de-solvation, and molecular re-ordering at the solution surface (Fig. 3.10c).

The minimum size at which the crystal can survive in solution is known as critical nucleus size (r_{crit}). It is reported that r_{crit} is given with the following equation,

$$r_{crit} = \frac{2\gamma v}{k_B T \cdot \ln(S)}$$

, where notations of γ , v , k_B , T , and S are surface energy, molar volume, Boltzmann's constant, temperature, and saturation degree of the solution, respectively (13). For instance, it is reported that γ and v for sodium chloride are 87 mJ/cm² and 27 cm³/mol,

respectively (14). Based on these values, the critical nucleus size (r_{crit}) of sodium chloride at 300 K and 1.5 saturation degree can be calculated to be 4.6 nm. For calculating r_{crit} in the current experimental system, surface energy of perovskite crystals and saturation degree at the focal spot are necessary. Due to the lack of these information, the calculation is difficult at the present stage.

The rate at which the nucleated crystal grows depends upon whether the perovskite absorbs the trapping laser (1064 nm) or not. Since a MAPbBr₃ crystal absorbs light below 550 nm, two-photon absorption is induced by the focused trapping laser. Excess energy is dissipated through intra-band non-radiative relaxation, and the temperature of the crystal, as well as the surrounding solution, is slightly increased. As a result, the solubility of the precursors is decreased, and the local saturation degree is elevated, leading to continuous crystal growth (Fig. 3.10d). On the other hand, a MAPbCl₃ crystal does not absorb the 1064-nm trapping laser, and its growth is saturated at the size of several micrometers. MAPbI₃ perovskite absorbs light below 820 nm. Thus, the trapping laser is efficiently absorbed through two-photon absorption process, leading to explosive crystal growth through the rapid elevation of saturation degree in accordance with retrograde solubility of MAPbI₃ (Fig. 3.10e). Similarly, the MAPbBr₃ crystallization shows explosive growth under the 800-nm laser irradiation. The controlled crystallization and growth of MAPbI₃, without any explosive crystal growth, can be realized with trapping lasers of a wavelength longer than 1640 nm.

3-5: Summary

I demonstrated nucleation and growth of MAPbX₃ perovskite single crystals through chemical reactions of their precursor solutions by laser trapping at the air/solution interface in a spatially- and temporally- controlled manner. The crystallization process and mechanism should be general for various perovskite compounds. Thus, the current

work on the preparation of perovskite single crystals by laser trapping would develop new methodologies to engineer perovskite bulk crystals and advance the studies on light-induced crystallization.

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Chapter 4

Crystallization of mixed halide perovskites by laser trapping

In this chapter, laser trapping-induced crystallization was extended to mixed bromide/chloride methylammonium lead perovskite ($\text{MAPbBr}_n\text{Cl}_{3-n}$; $n = 0-3$). Laser trapping behavior was examined by focusing a CW laser beam of 1064 nm at the air/solution interface of $\text{MABr:PbBr}_2\text{:MACl:PbCl}_2$ precursor solutions. In all solutions, crystallization was induced from the focal spot even in unsaturated solution. I demonstrated that the resultant crystal has higher chloride composition than the initial precursor solution. The crystallization dynamics is discussed from the viewpoints of laser trapping of perovskite precursors and de-solvation of gathered precursors.

4-1: Crystallization of mixed bromide and chloride perovskites ($\text{MAPbBr}_n\text{Cl}_{3-n}$)

For crystallization of $\text{MAPbBr}_n\text{Cl}_{3-n}$ crystals, I prepared precursor solutions by dissolving $\text{MABr:PbBr}_2\text{:MACl:PbCl}_2$ in DMSO/DMF mixtures. The details of these solutions are described in chapter 2-2-3 (Table 2.02). Before starting laser trapping experiments, firstly I examined spontaneous crystallization by heating the prepared precursor solutions in the sample bottle to be 55 °C with a hotplate. Although no crystallization was observed at room temperature, many crystals were formed under the heating conditions. The formed crystals were completely dissolved after the hotplate was switched off. This result indicates that the precursor solutions at room temperature were

unsaturated and have characteristic retrograde solubility.

Figures 4.01a and 4.01b present optical micrographs around the focal spot under the focused laser irradiation at the air/solution interface of $\text{MAPbBr}_{3.0}$ and $\text{MAPbBr}_{2.5}\text{Cl}_{0.5}$ precursor solutions, respectively (1). The power of the laser passed through the objective lens was 1.0 W. The top of the chamber was closed with a cover glass to suppress solvent evaporation as shown in (Fig. 3.01a). At the beginning of the irradiation, an optical micrograph showed only the faint trapping laser reflected at the air/solution interface [panel (i) of Fig. 4.01a]. At several ten seconds to a few minutes, a small crystal of a few micrometers was identified in a camera image [panel (ii) of Fig. 4.01a and panel (i) of Fig. 4.01b]. The nucleated crystal continuously grew large while being trapped at the focal spot [panels (iii)–(v) of Fig. 4.01a and panels (ii)–(v) of Fig. 4.01b].

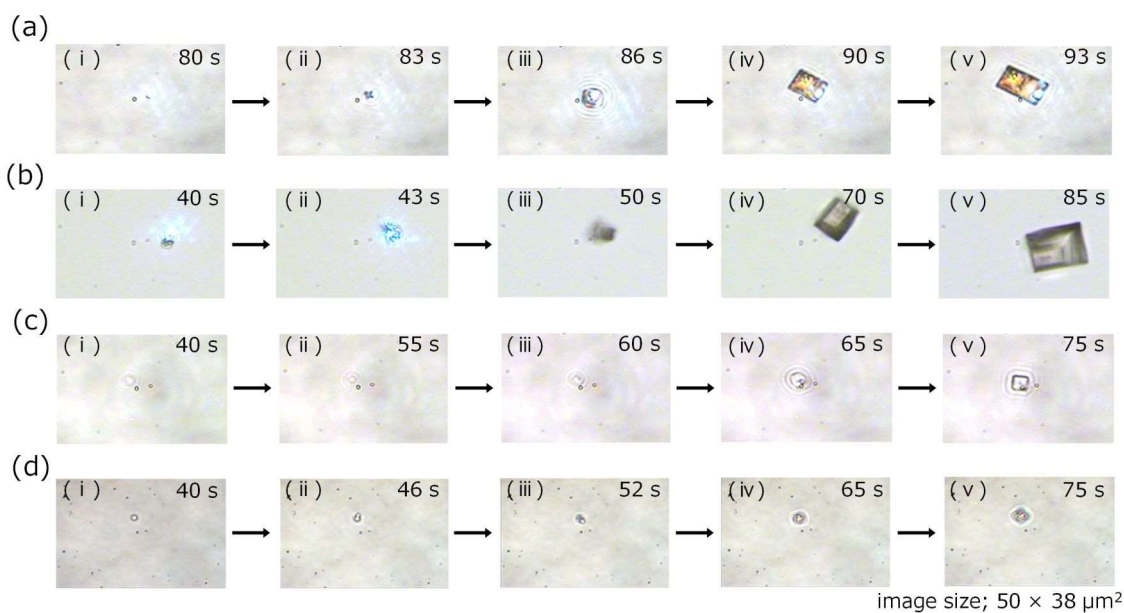


Figure 4.01: Optical micrographs of precursor solutions of (a) $\text{MAPbBr}_{3.0}$ (b) $\text{MAPbBr}_{2.5}\text{Cl}_{0.5}$ (c) $\text{MAPbBr}_{1.5}\text{Cl}_{1.5}$, and (d) $\text{MAPbBr}_{0.5}\text{Cl}_{2.5}$ under the 1064-nm laser irradiation at the air/solution interface in the closed chamber. The irradiation time in second is shown in each image.

In both cases, the crystals grew continuously under the laser irradiation and became the size larger than the field of view ($50 \times 38 \mu\text{m}^2$). The crystal formed in the $\text{MAPbBr}_{3.0}$ precursor solution showed green emission resulting from two-photon absorption of the trapping laser, whereas no emission was observed in the other crystal formed in the $\text{MAPbBr}_{2.5}\text{Cl}_{0.5}$ precursor solution. That is, the crystal formed in the $\text{MAPbBr}_{3.0}$ precursor solution is heated through two-photon absorption. The local temperature in the surrounding solution is increased, and the solubility is decreased. As a result, saturation degree is slightly elevated, leading to continuous growth. On the other hand, the crystal formed in the $\text{MAPbBr}_{2.5}\text{Cl}_{0.5}$ precursor solution is hardly heated through the two-photon absorption process. The growth mechanism is discussed later in chapter 4-4.

Figures 4.01c and 4.01d show crystallization behavior under laser trapping conditions in the $\text{MAPbBr}_{1.5}\text{Cl}_{1.5}$ and $\text{MAPbBr}_{0.5}\text{Cl}_{2.5}$ precursor solutions, respectively. A small crystal was formed from the focal spot [panels (i) of Fig. 4.01c and 4.01d]. Subsequently, the nucleated crystal grew slightly during its trapping, however, the growth was saturated with the crystal size $\text{ca } 5 \times 5 \mu\text{m}^2$ [panels (ii)–(v) of Fig. 4.01c and 4.01d]. The other precursor solutions ($\text{MAPbCl}_{3.0}$, $\text{MAPbBr}_{1.0}\text{Cl}_{2.0}$, and $\text{MAPbBr}_{2.0}\text{Cl}_{1.0}$) showed similar crystallization behavior (Fig. 4.02). No emission was observed during the laser irradiation. 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 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 shown in panels (iv) of Figure 4.02. This result implies that the crystals are formed through a local increase in saturation degree by laser irradiation in unsaturated solution, not by homogeneous condensation through solvent evaporation (2). The possible mechanism for the crystallization is discussed later in chapter 4-4.

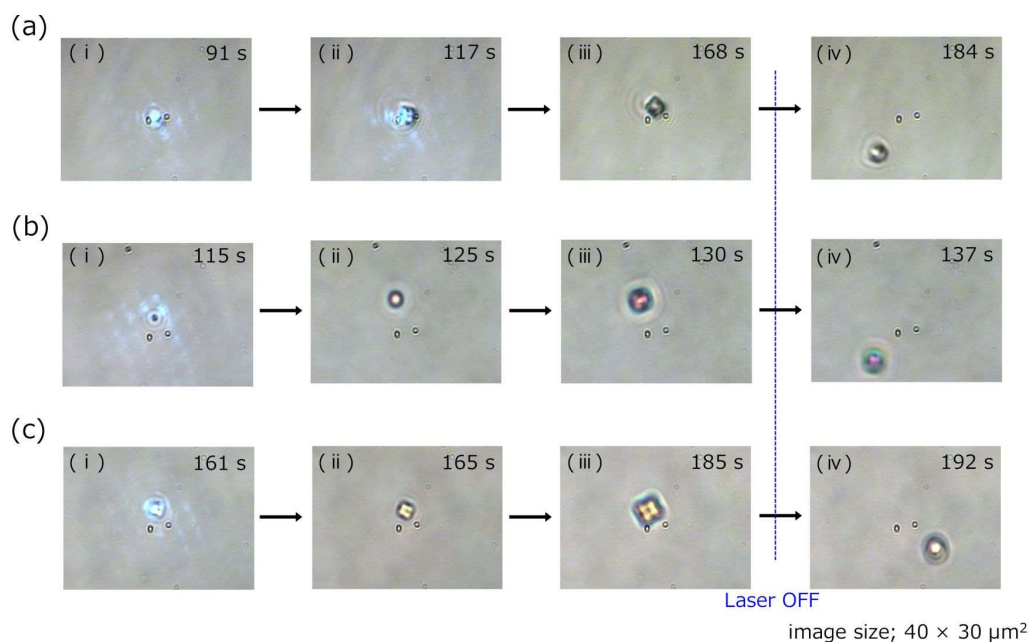


Figure 4.02: Optical micrographs of precursor solutions of (a) $\text{MAPbCl}_{3.0}$ (b) $\text{MAPbBr}_{1.0}\text{Cl}_{2.0}$, and (c) $\text{MAPbBr}_{2.0}\text{Cl}_{1.0}$ under the 1064-nm laser irradiation at the air/solution interface in the closed chamber.

4-2: Characterization of $\text{MAPbBr}_n\text{Cl}_{3-n}$ perovskite crystals

I characterized the formed crystals by measuring their transmission spectra under the microscope. Thick crystals are necessary for the microspectroscopy, so that laser trapping experiments were carried out in the chamber without an upper cover glass in order to prepare a large crystal (Fig. 4.03a). DMSO and DMF have low values of vapor pressure at room temperature, but they are slowly evaporated, and the formed crystal was allowed to grow continuously (1). As representatives, Figures 4.03b, 4.03c, 4.03d, and 4.03e present laser trapping behavior under the laser irradiation at the air/solution interface of the $\text{MAPbCl}_{3.0}$, $\text{MAPbBr}_{1.0}\text{Cl}_{2.0}$, $\text{MAPbBr}_{1.5}\text{Cl}_{1.5}$, and $\text{MAPbBr}_{2.0}\text{Cl}_{1.0}$ precursor solutions, respectively, in an open chamber. Different from the above crystallization in the closed chamber where crystal growth was saturated at the size of few micrometers ($\sim 5 \mu\text{m}$), the formed crystal grew continuously while being stably trapped at the focal spot.

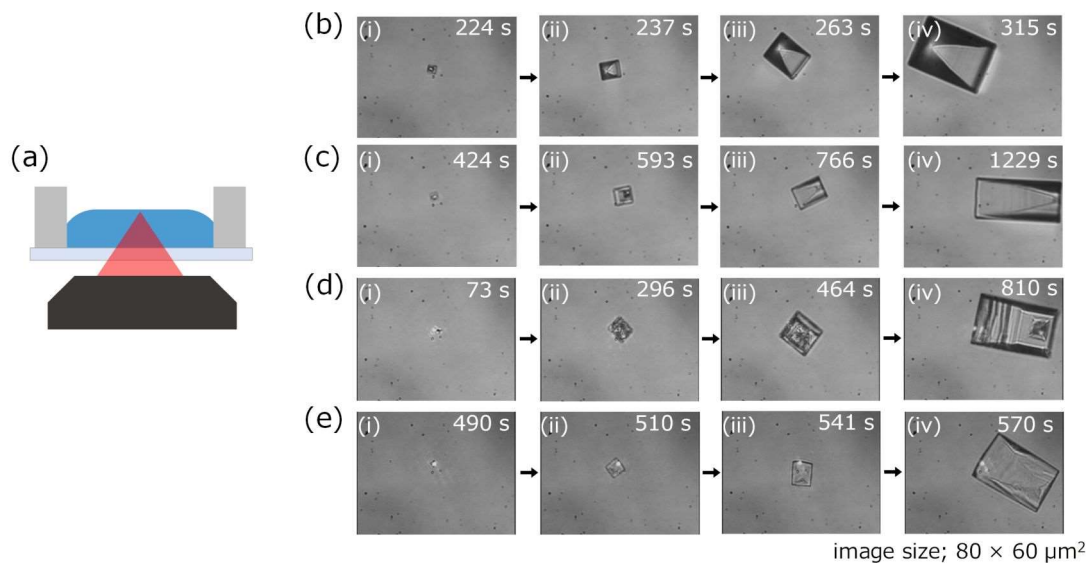


Figure 4.03: (a) Schematic illustration for the laser trapping experiments in an open chamber. Optical micrographs of precursor solutions of (b) $\text{MAPbCl}_{3.0}$ (c) $\text{MAPbBr}_{1.0}\text{Cl}_{2.0}$ (d) $\text{MAPbBr}_{1.5}\text{Cl}_{1.5}$, and (e) $\text{MAPbBr}_{2.0}\text{Cl}_{1.0}$ under the 1064-nm laser irradiation at the air/solution interface in the open chamber.

After the single crystal was grown up to the size in the scale of a few tens micrometers, the switching mirror in the microscope was rotated, and a transmission spectrum was acquired. Figure 4.04 shows representative transmission spectra of the crystals formed in respective precursor solutions (1). In the solution of $\text{MAPbBr}_{3.0}$, an absorption edge of the resultant crystal was observed around 550 nm. The transmittance at longer wavelength was about 70%, which is possibly ascribed to the loss of the incident light through scattering or reflection at the crystal surface. On the other hand, the transmittance at a shorter wavelength was 10%. I infer that the crystal is not thick enough to absorb incident light perfectly and the light partially passes through the crystal. It is reported that an absorption coefficient (α) of a $\text{MAPbBr}_{3.0}$ crystal is approximately 54000 cm^{-1} at 500 nm (3). By considering this absorption coefficient (α), the crystal thickness

(L) giving 10% transmittance of light with the wavelength of 500 nm was estimated at 430 nm based on the relation of $T(\%) = 100 \cdot \exp(-\alpha L)$. Actual crystal thickness is unknown at the present stage but can be measured by applying an optical interference technique (4). A transmission edge shifted to shorter wavelength with the increase in the chloride composition in the precursor solutions.

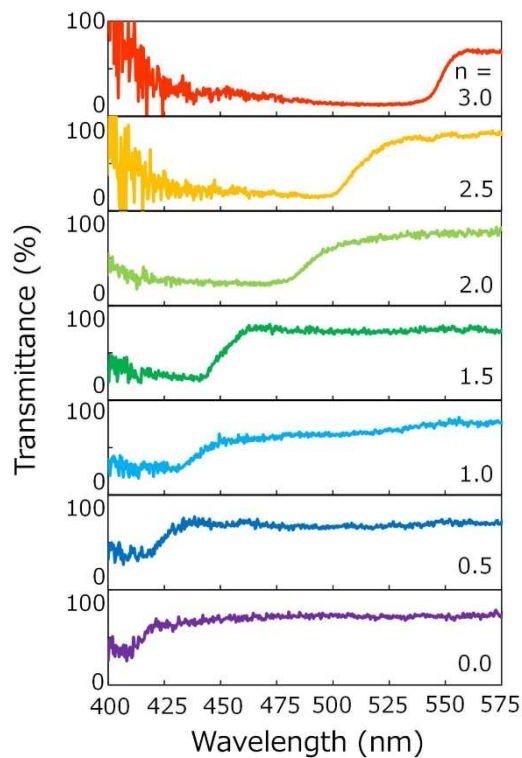


Figure 4.04: Transmission spectra of the crystals formed in the precursor solutions of $\text{MAPbBr}_n\text{Cl}_{3-n}$.

For determining the energy gaps of the crystals, the transmission spectra were converted to Tauc Plots. The horizontal axis was converted from wavelength to energy. On the other hand, the vertical axis was changed from transmittance to $(\alpha h\nu)^2$, where α , h , ν are absorption coefficient, Planck's constant, and photon's frequency, respectively. Transmittance is expressed as $\exp(-\alpha L)$ with the use of sample thickness (L). Based on this relation, the absorption coefficient was calculated. The thickness of the crystal (L) is

unknown so that the arbitrary unit was used for the vertical axis. As shown in Figure 4.05a, the energy gap was calculated for three samples at respective compositions by fitting the spectrum near an absorption edge with a linear function. In Figure 4.05b, blue circle symbols show the calculated energy gaps of the formed crystals against the composition of the initial precursor solutions. The energy gaps of MAPbCl_{3.0} and MAPbBr_{3.0} crystals were estimated at 2.86–2.94 and 2.24–2.26 eV, respectively, which are similar to the reported values (5, 6).

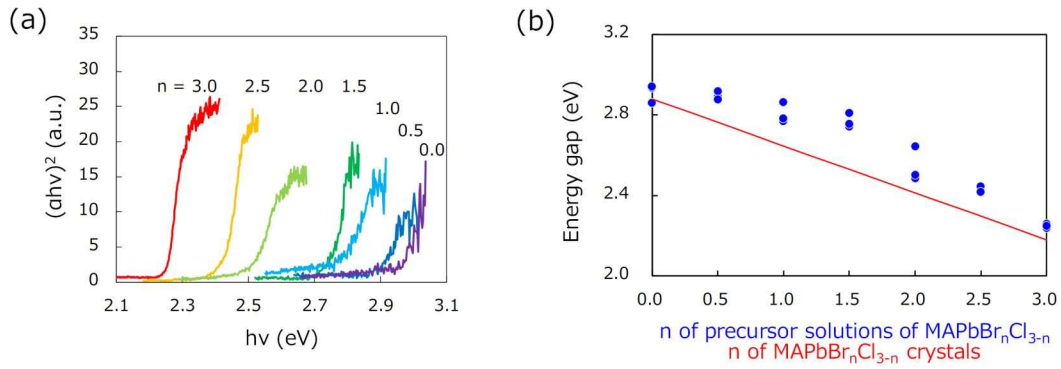


Figure 4.05: (a) Tauc Plots of the crystals formed in the precursor solutions of MAPbBr_nCl_{3-n} (b) The relation between the energy gaps of the prepared perovskite crystals and the bromide composition (n) of precursor solutions of MAPbBr_nCl_{3-n}. Three samples were measured at each composition. A solid line shows the energy gap of a MAPbBr_nCl_{3-n} crystal estimated in accordance with the Vegard's law.

The energy gap of mixed perovskites, MAPbBr_nCl_{3-n}, can be calculated according to the Vegard's law because both MAPbBr_{3.0} and MAPbCl_{3.0} crystals are the cubic forms in common. The solid line is the tendency of the energy gap of a MAPbBr_nCl_{3-n} crystal estimated in accordance with the relation of $E_g[\text{MAPb}(\text{Br}_x\text{Cl}_{1-x})_3] = E_g[\text{MAPbBr}_3]_x + E_g[\text{MAPbCl}_3]_{(1-x)}$, ($n = 3x$, $x = 0-1$). I used 2.24 and 2.88 eV as $E_g[\text{MAPbBr}_3]$ and $E_g[\text{MAPbCl}_3]$, respectively. It should be noteworthy that the crystals formed by the laser have a higher energy gap when compared with the crystals of the composition same as

the corresponding initial precursor solutions. This result indicates that the crystals prepared by the laser have the chloride concentration higher than that of the precursor solutions.

The PL spectra showed a similar tendency. After a crystal is grown to a large size in an opened chamber during optical trapping, the 1064-nm laser was switched off, and the PL spectrum was obtained under the UV laser irradiation. Figures 4.06a and 4.06b show the normalized PL spectra of the crystals prepared in the precursor solutions of $\text{MAPbBr}_n\text{Cl}_{3-n}$ ($n = 1.5\text{--}3.0$) and the corresponding PL images. Due to the optical property of the filter used, I could not measure PL spectra of the crystals with other precursor solutions.

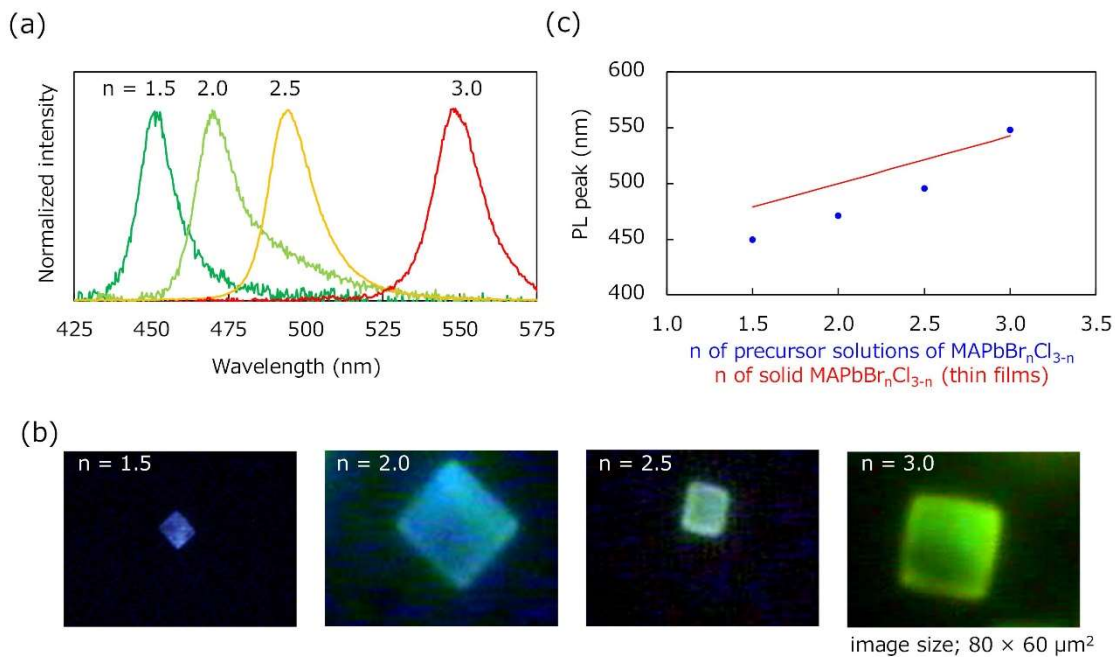


Figure 4.06: (a) PL spectra of the crystals formed by laser trapping in the precursor solutions of $\text{MAPbBr}_n\text{Cl}_{3-n}$ and (b) the corresponding PL images. (c) The relation between the peak positions of PL spectra of the prepared perovskite crystals and n of precursor solutions of $\text{MAPbBr}_n\text{Cl}_{3-n}$. A solid line shows the PL peaks of solid $\text{MAPbBr}_n\text{Cl}_{3-n}$, which was constructed on the basis of the results reported for $\text{MAPbBr}_n\text{Cl}_{3-n}$ thin films (7).

The peak wavelength of Figure 4.06a was plotted as the function of n of the precursor solutions, as shown in Figure 4.06c. The PL peak was blue-shifted with a decrease in n . A solid line shows the PL peak position of $\text{MAPbBr}_n\text{Cl}_{3-n}$ against n of the solid thin film, which was constructed on the basis of the reported results; PL peak (eV) = $-0.238n + 2.9624$ (7). It should be noted that the formed crystals have a peak at shorter wavelengths compared to the relation of solid $\text{MAPbBr}_n\text{Cl}_{3-n}$. This result also supports that the crystals formed by the laser have higher chloride concentration compared to the initial composition 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 $\text{MAPbBr}_n\text{Cl}_{3-n}$ ($n = 0, 1, 2$, and 3) precursor solutions and carried out the XRD measurement. The powder XRD patterns were calculated on the basis of the result obtained for the single crystals (Fig. 4.07a). Figure 4.07b shows the powder XRD peaks of (100) planes of the crystals. The peak position shifted to the large angle with decrease in n of the precursor solutions. This shifting is consistent with the Bragg's law. The lattice constants of respective crystals were estimated and plotted in Figure 4.07c. The lattice constant of mixed perovskites, $\text{MAPbBr}_n\text{Cl}_{3-n}$, can be calculated according to the Vegard's law in the procedure similar to that of the case of the energy gap. The solid line is the estimated tendency of the lattice constant of a $\text{MAPbBr}_n\text{Cl}_{3-n}$ crystal. I used 5.714 and 5.940 Å as the values for $\text{MAPbCl}_{3.0}$ and $\text{MAPbBr}_{3.0}$ based on our measurement, respectively (2). It is notable that the crystals formed by the laser tend to have a smaller lattice constant than that of the crystals with the composition same as the corresponding initial precursor solutions. This result clearly indicates that the chloride-rich crystal is formed by laser trapping (1). The reason is discussed in chapter 4-4.

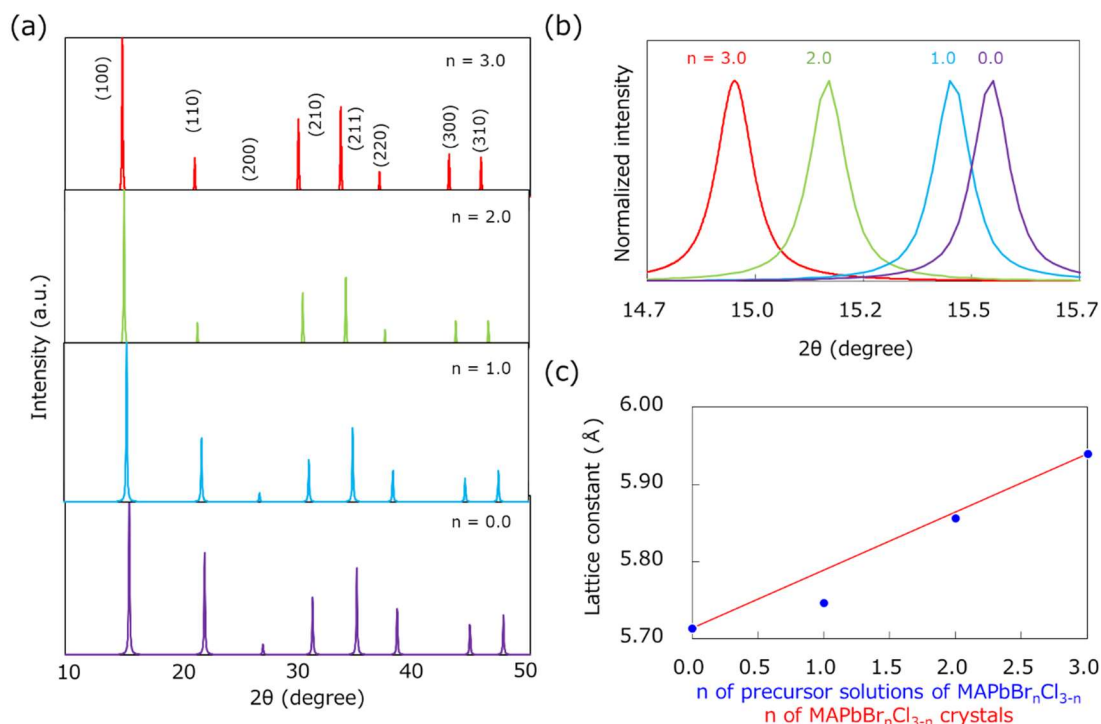


Figure 4.07: (a) The powder XRD patterns calculated from the results of the crystallographic analysis of perovskite crystals prepared in corresponding $\text{MAPbBr}_n\text{Cl}_{3-n}$ precursor solutions. (b) Enlarged peaks of (100) planes. (c) The relation between the lattice constant of the prepared perovskite crystals and n of precursor solutions of $\text{MAPbBr}_n\text{Cl}_{3-n}$. A solid line shows the lattice constant of a $\text{MAPbBr}_n\text{Cl}_{3-n}$ crystal estimated in accordance with the Vegard's law.

4-3: Comparison of perovskite crystals formed under heating and optical trapping conditions

Despite the crystallization of mixed halide perovskites under the focused laser irradiation, retrograde solubility of their precursor solutions encouraged me to consider the role of laser-induced heating on crystallization. In order to obtain the information on the influence of laser heating during laser trapping, spontaneous crystallization under heating conditions were investigated for the precursor solution of $\text{MAPbBr}_{2.5}\text{Cl}_{0.5}$ as one of the representative composition among all samples used. I heated the solution to be 55,

70, and 80 °C with a hotplate and took out resultant crystals from the solution, and subsequently, their transmission spectra were measured under the microscope at 18 °C (Fig. 4.08a). No crystal was formed at temperatures below 50 °C even with the incubation over 6 hours.

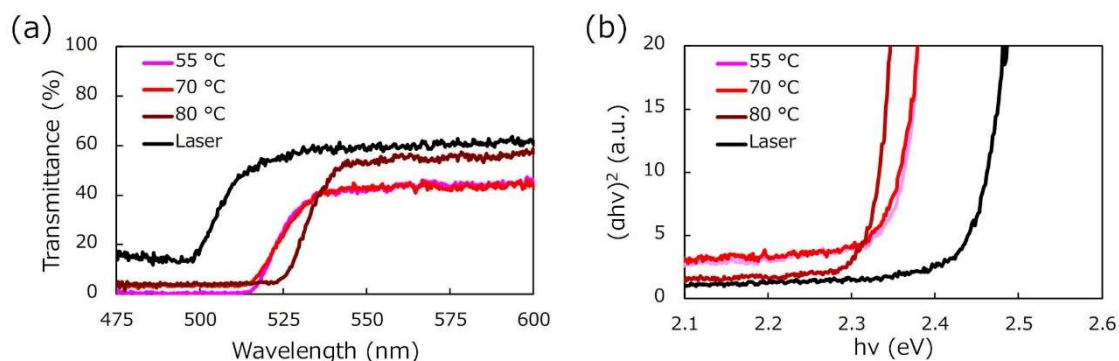


Figure 4.08: (a) Transmission spectra and (b) Tauc Plots of the crystals formed by heating at different temperatures or by laser trapping in the precursor solution of $\text{MAPbBr}_{2.5}\text{Cl}_{0.5}$.

The transmission edge of thermally formed crystals was observed at the similar positions independent of heating temperature but located at the wavelength longer than that of the crystal prepared by the laser. The energy gaps estimated from Tauc Plots (Fig. 4.08b) were 2.44 eV for the crystal formed by laser and 2.32–2.35 eV for the crystals formed under heating conditions. These differences indicate that the crystallization by the laser cannot be explained just from the viewpoint of laser heating. Actually, local temperature elevation in the present precursor solutions was estimated <13 K (2) as discussed in chapter 3. This estimation is based on the absorption coefficient and thermal conductivity of solvents and laser power. As described above on the heating-induced crystallization, this temperature elevation is not enough to trigger the nucleation of perovskite crystals.

4-4: Crystallization dynamics of $\text{MAPbBr}_n\text{Cl}_{3-n}$

I consider that de-solvation is critical to determine the composition of the finally obtained crystal (Fig. 4.09). In the case of $\text{MAPbBr}_n\text{Cl}_{3-n}$ ($n = 0.5\text{--}2.0$), I dissolved $\text{MABr}:\text{PbBr}_2$ and $\text{MACl}:\text{PbCl}_2$ in a DMF:DMSO mixture. It is reported that MAPbBr_3 shows retrograde solubility in DMF but not in DMSO (6). This result means 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 (5). That is, $\text{MACl}:\text{PbCl}_2$ precursors are easily de-solvated compared to $\text{MABr}:\text{PbBr}_2$ if they are dissolved together in a DMF:DMSO mixture. As the result, upon laser trapping in the $\text{MAPbBr}_n\text{Cl}_{3-n}$ ($n = 0.5\text{--}2.0$) precursor solution, the gathered $\text{MACl}:\text{PbCl}_2$ precursors are preferentially de-solvated 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 hypothesized that MACl is de-solvated in DMF more easily than bromide precursors.

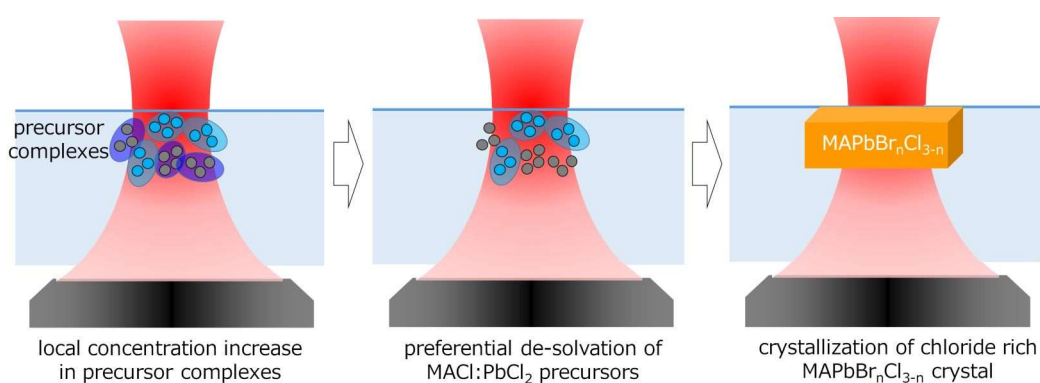


Figure 4.09: Schematic illustration of laser trapping induced $\text{MAPbBr}_n\text{Cl}_{3-n}$ crystallization, which proceeds through local concentration increase in precursor complexes and subsequent de-solvation of $\text{MACl}:\text{PbCl}_2$ precursors.

The rate at which the nucleated crystal grows depends upon whether the perovskite absorbs the trapping laser or not. Since a $\text{MAPbBr}_{3.0}$ crystal absorbs light below 550 nm, two-photon absorption is induced under the 1064-nm laser irradiation. Actually, PL through two-photon absorption was observed as described in chapter 4-3. Excess energy is dissipated through intra-band non-radiative relaxation, and the temperature of the crystal and surrounding solution is increased. As a result, the solubility of the precursors is decreased, and the local saturation degree is elevated, leading to continuous crystal growth. The crystal formed in a $\text{MAPbBr}_{2.5}\text{Cl}_{0.5}$ precursor solution showed no PL under the NIR laser irradiation, which implies that the two-photon energy is lower than the bandgap. Nevertheless, continuous crystal growth proceeded similarly to the case of $\text{MAPbBr}_{3.0}$. This result might be ascribed to light absorption at the trap site that locates between the valence and conduction bands and accompanying heating due to subsequent non-radiative relaxation.

4-5: Summary

Here I demonstrated spatially- and temporally- controlled synthesis and crystallization of mixed bromide-chloride methylammonium lead perovskites. The crystallization is induced at the focal spot under the irradiation of the NIR laser focused at the air/solution interface of the precursor solutions. The crystals prepared by the laser showed the tendency that the chloride is incorporated in the crystal more preferentially than the bromide. This tendency is different compared to the crystals prepared by heating the same precursor solutions. I explained the crystallization dynamics by considering the local concentration increase by laser trapping of precursor complexes and their desolvation during the trapping. This crystallization process should be general for various mixed perovskite compounds, not only for mixed halide perovskites but also for mixed-cation and mixed-metal perovskites.

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Chapter 5

Halide exchange reaction at a specific crystal controlled by laser trapping

In chapters 3 and 4, I demonstrated crystallization of $\text{MAPbX}_n\text{Y}_{3-n}$ ($\text{X}, \text{Y} = \text{Cl}, \text{Br}$, or I , $n = 0-3$) in perovskite precursor solutions by irradiating a focused NIR laser beam at the air/solution interface. The crystallization was induced from the focal spot in a spatially- and temporally- controlled manner. The initial precursor solutions were unsaturated, and the formed crystal was dissolved after the laser was switched off. This result means that the local concentration increase in perovskite precursors caused chemical reactions and accompanying crystallization. I concluded that the driving force of the concentration increase is the optical force that acts toward the laser focus. I consider that such laser trapping of perovskite precursors and accompanying concentration increase work at different interfaces. Here, I apply laser trapping to the surface of a perovskite crystal, aiming to achieve and control halide exchange reactions in a specific area around the focal spot. This new approach enables us to tune the bandgap and emission color of a perovskite bulk crystal through site-specific halide exchange reaction.

5-1: Concentration- and temperature- dependent spontaneous halide exchange reaction

I carried out experiments on spontaneous halide exchange reaction which was in order to determine experimental conditions for laser trapping. I used MAPbBr_3 as the initial crystal and induced the exchange reaction with MAI. The reaction resulted in the

formation of $\text{MAPbBr}_{3-n}\text{I}_n$. I investigated how this exchange reaction proceeds under different conditions of reactant concentration and temperature. Figure 5.01 shows the procedure for the experiment on the concentration dependence. Micrometer-sized MAPbBr_3 crystals were directly synthesized by solvent evaporation on a clean cover glass of the chamber. Firstly, a micro-droplet (ca 1 μL) of a $\text{MABr}:\text{PbBr}_2$ solution (1.3 M) with the diameter of several hundred micrometers was prepared on the cover glass (Fig. 5.01a). Spontaneous crystallization started through natural solvent evaporation, and the crystals grew in the droplet (Fig. 5.01b). After the growth of crystals with ca 5 μm size, the remaining solution was wiped out with a filter paper (Fig. 5.01c). As the reaction solution, I used MAI dissolved in a mixture of hexadecene and isopropyl alcohol (100:1, v:v). Firstly, MAI was dissolved in isopropyl alcohol, and then the solution was mixed with hexadecene just before experiments on halide exchange reaction. The reaction solution of 40 μL was added to the chamber, and the exchange reaction was initiated (Fig. 5.01d).

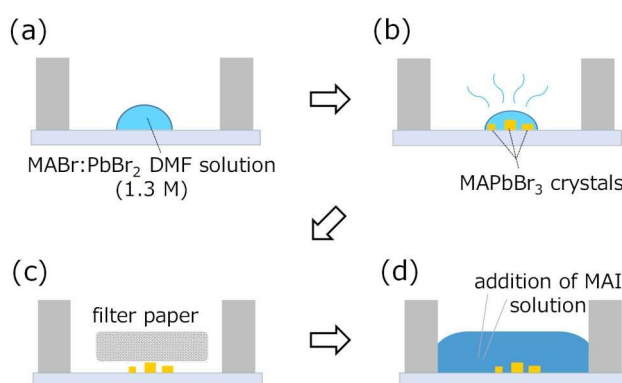


Figure 5.01: Schematic illustration for experimental procedure of spontaneous halide exchange reaction.

I used four different concentrations of MAI; 0, 45, 110, and 330 μM . PL images of the crystals were obtained at 5 minutes after adding the reaction solutions. A MAPbBr_3 crystal in a mixture of hexadecene and isopropyl alcohol without MAI showed green

emission in accordance with its intrinsic property (Fig. 5.02a). Similarly, green emission was observed at the concentrations of 45 and 110 μM , as shown in Figure 5.02b and 5.02c, respectively. On the other hand, PL color was changed to red at 330 μM MAI (Fig. 5.02d). Corresponding PL spectra are shown in Figure 5.02e. The PL color change at 330 μM is the result of the formation of $\text{MAPbBr}_{3-n}\text{I}_n$ through halide exchange reaction on MAPbBr_3 with MAI. In this way, the exchange reaction strongly depends on the concentration of MAI, and the reaction is much accelerated at the concentration between 110 and 330 μM .

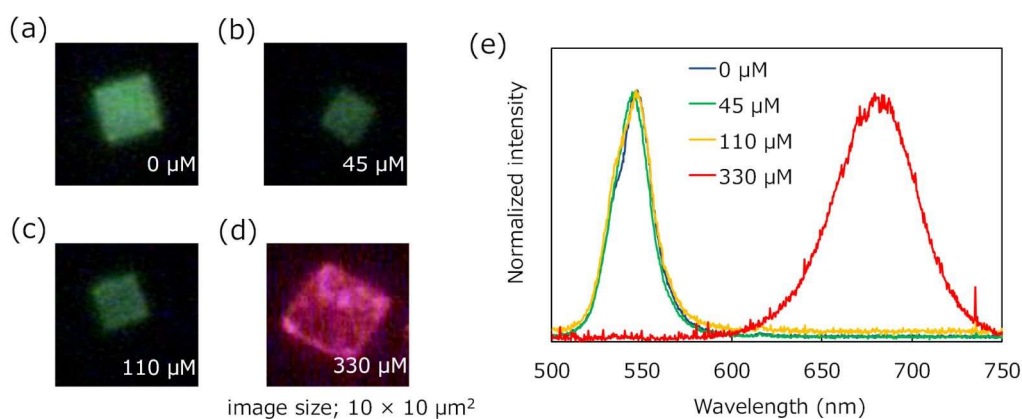


Figure 5.02: PL images of MAPbBr_3 crystals in the reaction solution of (a) 0, (b) 45, (c) 110, and (d) 330 μM MAI, respectively. The images were obtained at 5 min after adding MAI solutions. (e) PL spectra of the crystals in the respective reaction solutions.

As the next step, I carried out experiments on the influence of temperature to spontaneous halide exchange reaction. Here, I refer to the report on the exchange reaction induced by contacting two perovskite crystals containing different halogen ions (1). The reaction proceeds in a few days at room temperature, while the reaction is accelerated in several hours by heating. I investigated whether or not our samples show such acceleration of the reaction under heating conditions. Figure 5.03 shows the experimental procedure. The initial MAPbBr_3 crystals were similarly prepared as described above (Fig.

5.03a). I used the reaction solution with the MAI concentration of 330 μM , which corresponds to the highest concentration of the above experiment on the concentration dependence. The sample chamber was placed on a hotplate set at 18, 70, 100, or 150 $^{\circ}\text{C}$, then the reaction solution of 40 μL was added to the chamber (Fig. 5.03b). The chamber was kept for 5 minutes on the hotplate (Fig. 5.03c). After 5 minutes of heating, the sample was cooled down to room temperature (18 $^{\circ}\text{C}$) and observed under the microscope (Fig. 5.03d).

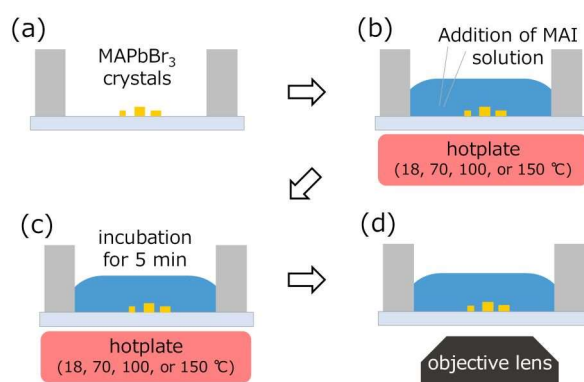


Figure 5.03: Schematic illustration for the experimental procedure of spontaneous halide exchange reaction under heating conditions.

Figure 5.04 shows obtained PL images after incubation of the crystal in the reaction solution at different temperatures. Green emissive crystals changed into red emissive ones at 18 $^{\circ}\text{C}$ (Fig. 5.04a). On the other hand, such color change was not observed at 70, 100, and 150 $^{\circ}\text{C}$. The crystals remained green emissive even after the heating in the reaction solutions (Fig. 5.04b, 5.04c, and 5.04d). Corresponding PL spectra are shown in Fig. 5.04e. Opposite to the above report, halide exchange reaction in the current sample is suppressed under heating conditions.

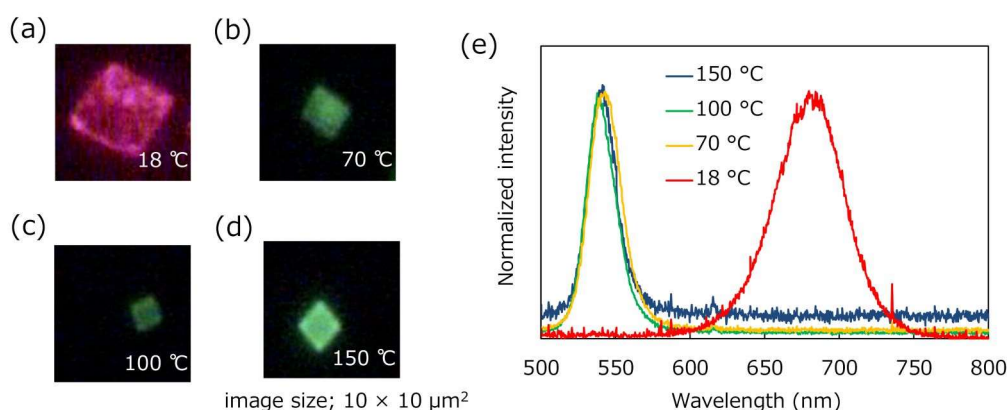
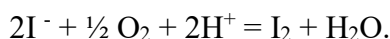


Figure 5.04: PL images of the MAPbBr₃ crystals in 330 μM MAI solution incubated for 5 min at (a) 18, (b) 70, (c) 100 and (d) 150 °C, respectively. (e) PL spectra of the crystals after the incubation.

In order to investigate the underlying mechanism of heating-induced suppression of the reaction, I measured the absorption spectra of the reaction solution with MAI concentration of 330 μM. I incubated the reaction solution at different temperatures for 30 min, which was followed by recording the absorption spectra (Fig. 5.05a). At 18 °C, a broad absorption was observed at 450–550 nm, meaning that the solution contains I₂ (2). I found that the broad absorption at 450–550 nm gradually disappeared upon heating. It is reported that I₂ dissolved in solution spontaneously evaporates (3). It is well known that I⁻ is oxidized to I₂ by the ambient O₂ in acidic medium (4) with the following equation;



CH₃NH₃I (MAI) is a salt of strong acid HI and weak base CH₃NH₂, so the reaction medium is acidic. I consider that heating of the reaction solution accelerates the evaporation of I₂ and lowers the concentration of iodide ions that are necessary for halide exchange reaction. As a result, the exchange reaction with iodide ions on a MAPbBr₃ crystal is suppressed at high temperatures.

In order to investigate the dynamics of thermal dissociation of MAI, the reaction

solution with MAI concentration of 330 μM was heated at 80 $^{\circ}\text{C}$ on a hotplate, and its absorption spectrum was measured at different incubation times. Figure 5.05b shows the temporal change in the absorption spectra of the reaction solution. The peak absorbance at 500 nm was decreased nonlinearly with time (Fig. 5.05c). The temporal change of the absorbance could be fitted with the first order rate equation (Fig. 5.05d) (5). The rate constant of the change in the absorbance was estimated at 0.186 (1/s). The absorbance is proportional to the concentration of I_2 , so that the concentration change in I_2 also proceeds in accordance with the first order rate equation.

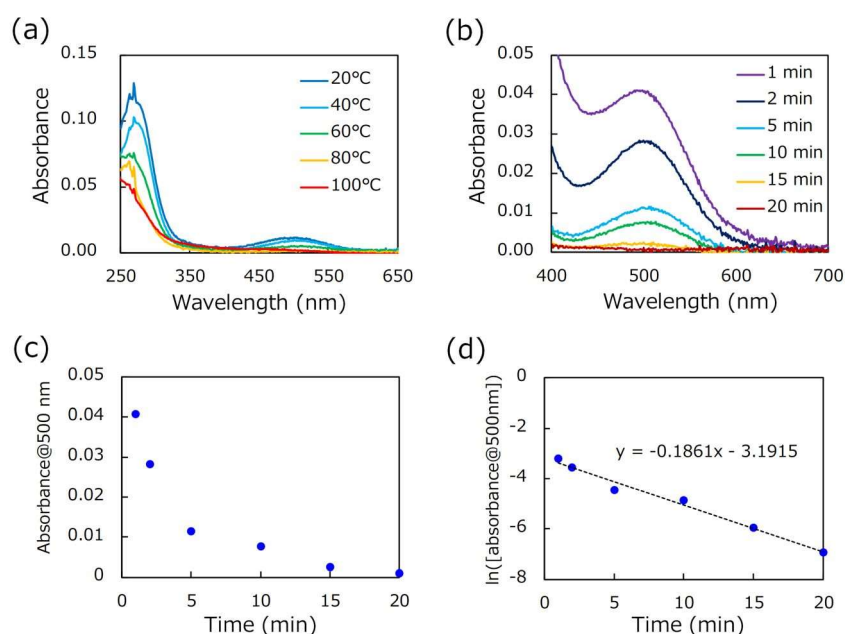


Figure 5.05: (a) Temperature-dependent absorption spectra of the reaction solution. The reaction solution was heated on a hotplate for 30 min, and the absorption spectra were measured in a conventional spectrometer. The temporal changes in (b) absorption spectra of the reaction solution MAI and (c) the peak absorbance at 500 nm under heating at 80 $^{\circ}\text{C}$ (d) Linear function fitting for determining the rate constant.

Thus, the halide exchange reaction depends on reactant concentration and temperature. In the former case, the threshold concentration was ca 110 and 330 μM . The

spontaneous exchange reaction at 110 μM proceeds at a negligibly small rate, but the 3 times higher concentration accelerates the reaction very much. Furthermore, the reaction is suppressed under heating conditions possibly due to thermal degradation of MAI. These fundamental information are helpful during the design of experiments on the exchange reaction with the use of laser trapping and the consideration of halide exchange reaction mechanism which is described in the next section.

5-2: Laser trapping-induced halide exchange reaction

5-2-1: Preparation of $\text{MAPbBr}_{3-n}\text{In}_n$ by halide exchange reaction in MAPbBr_3

Figure 5.06 shows the experimental procedure of laser trapping-induced halide exchange reaction of a MAPbBr_3 crystal with MAI. The initial MAPbBr_3 crystals were similarly prepared as described above. I used the reaction solution with MAI concentration of 110 μM . At this concentration, spontaneous halide exchange reaction proceeds at a negligibly small rate, but slight concentration increase is able to dramatically accelerate the reaction. The reaction solution of 40 μL was added to the chamber (Fig. 5.06a). I selected one target crystal among the prepared MAPbBr_3 crystals and focused a NIR laser beam onto the crystal surface (Fig. 5.06b). 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 (Fig. 5.06b) or one-photon excitation by the widely illuminated 405-nm laser (Fig. 5.06c).

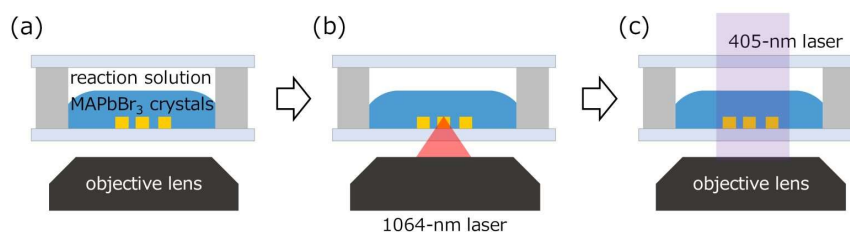


Figure 5.06: Schematic illustration of the laser irradiation process and the microspectroscopic analysis.

Figure 5.07a shows an optical transmission micrograph of initial MAPbBr₃ crystals in the chamber. Four crystals were located in the area of $25 \times 30 \mu\text{m}^2$. The crystals were observed as a square shape with the length of a side of $5 \mu\text{m}$. Figure 5.07b shows the temporal change in PL images of the crystal in the reaction solution during the irradiation of the focused NIR laser. At the beginning of the irradiation, the crystal showed green emission, which is the two-photon excited PL (panel (i) of Fig. 5.07b). The green PL was gradually changed into first yellow and finally red (panels (ii), (iii) of Fig. 5.07b). Subsequently, the PL intensity was increased during the irradiation, and the bright red PL was observed at 30 min (panel (iv) of Fig. 5.07b).

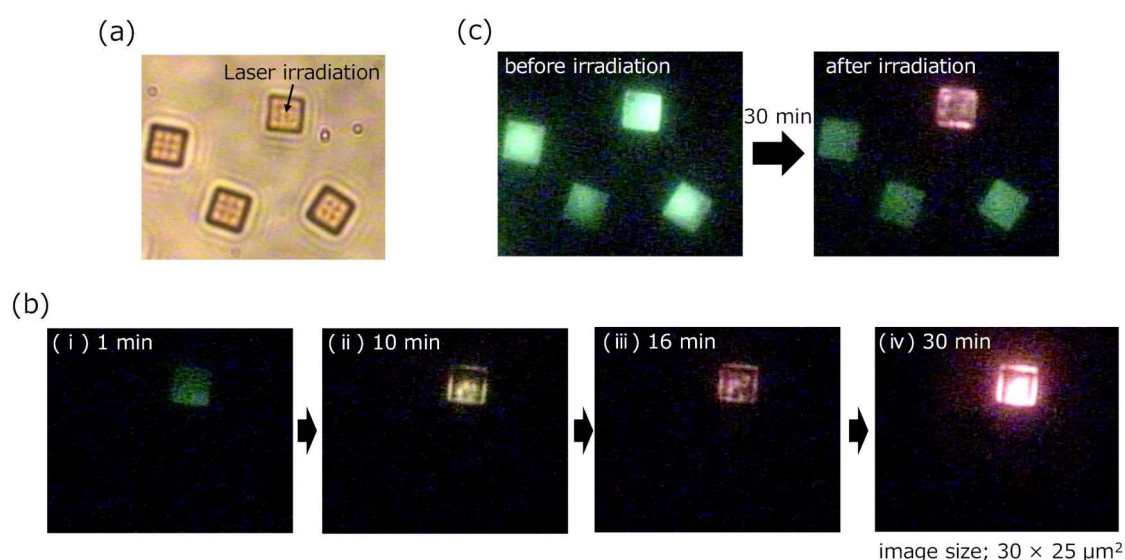


Figure 5.07: (a) An optical transmission micrograph of initial MAPbBr₃ crystals in the chamber. (b) Temporal changes in PL images under the NIR laser irradiation. The irradiation time is shown in each image. (c) PL images under the wide-field excitation (left) before and (right) after the 30-min NIR laser irradiation.

I confirmed that the PL change was induced only in the crystal irradiated with the NIR laser. Figure 5.07c shows PL images of perovskite single crystals under wide-field

illumination of the 405-nm laser, which were obtained before and after the 30-min irradiation of the NIR laser. In the former case, all four microcrystals showed bright green emission. In the latter, only the crystal exposed to the NIR laser showed red emission, and the neighboring crystals remained green emissive. This result indicates that the focused laser irradiation induces halide exchange reaction at a much higher rate compared to the spontaneous reaction, resulting in bandgap tuning in a spatially selective manner.

To understand the exchange reaction quantitatively, PL spectral measurements were carried out under the condition without and with the NIR laser irradiation. In the crystal without the NIR laser irradiation (Fig. 5.08a), the emission peak wavelength was kept constant while the peak intensity was decreased down to 70% of the original value after 30 min. No new emission peak was observed at a longer wavelength. These spectral changes indicate that MAPbBr_3 changes to $\text{MAPbBr}_{3-n}\text{I}_n$ of low iodide composition by 30%.

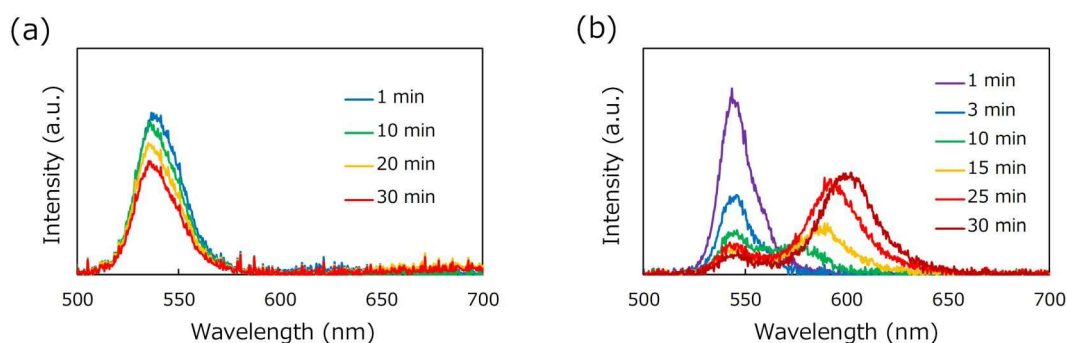


Figure 5.08: Temporal changes in PL spectra of a MAPbBr_3 crystal in the reaction solution (a) without and (b) with the NIR laser irradiation. The crystals in (a) and (b) were excited by the widely illuminated 405-nm laser and the focused NIR laser, respectively.

The energy difference in the conduction band levels between MAPbBr_3 and MAPbI_3 is approximately 0.1 eV (6). Therefore, the small energy difference in $\text{MAPbBr}_{3-n}\text{I}_n$ ($n = 0-0.75$), which is comparable with the thermal energy (0.025 eV) at room

temperature, enables thermal delocalization of photo-generated electrons. Conversely, holes are trapped in the iodide rich higher valence band levels of $\text{MAPbBr}_{3-n}\text{I}_n$. Consequently, radiative recombination is suppressed, and the PL intensity of MAPbBr_3 is decreased without emission from $\text{MAPbBr}_{3-n}\text{I}_n$ (Fig. 5.09a) (7).

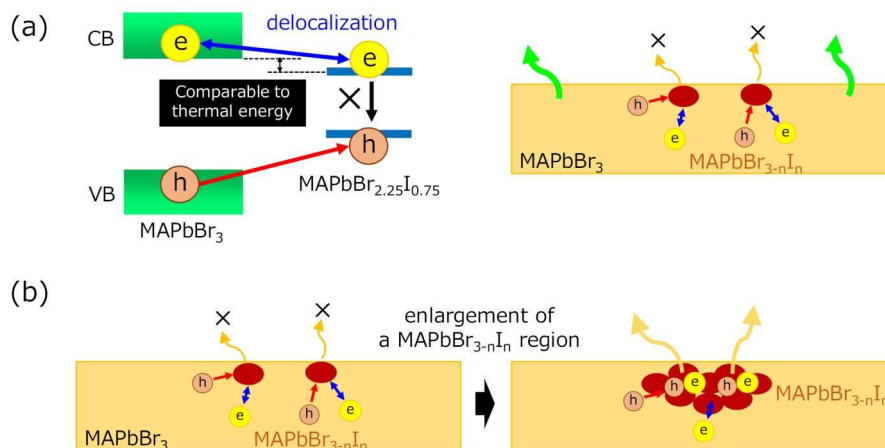


Figure 5.09: Schematic illustrations for the emission properties of the $\text{MAPbBr}_{3-n}\text{I}_n$ ($n = 0\text{--}0.75$) crystal (a) without and (b) with the NIR laser irradiation.

The NIR laser irradiation led to the decrease in the PL intensity around 540 nm, which was followed by the appearance of a new, low energy emission band at 10 min (Fig. 5.08b). This new band continuously red-shifted during the NIR laser irradiation, which was accompanied by an increase in PL intensity. At 30 min, the crystal showed the PL peak at 600 nm, and its intensity was increased by a factor of five when compared to that of the original band around 540 nm. This result indicates that a $\text{MAPbBr}_{3-n}\text{I}_n$ region is dominant compared to the original MAPbBr_3 crystal at the focal spot that is the spectral measurement point (Fig. 5.09b). The PL peak at 600 nm implies that the original MAPbBr_3 crystal was changed to $\text{MAPbBr}_{2.3}\text{I}_{0.7}$ (7).

In order to understand the PL spectral change under the NIR laser irradiation, I investigated the spontaneous exchange reaction with the use of the reaction solution of a

higher concentration (330 μM). The PL change was different depending of the crystal size. For the large crystals, green PL was quenched, and then red emission was observed from the dark crystal. Different from the large crystals, the small crystals showed yellow emission before red emission starts (Fig. 5.10a). These behaviors prior to red PL can be explained from viewpoint of the size of $\text{MAPbBr}_{3-n}\text{I}_n$ resulting from the exchange reaction. I assume that, in the large crystal, $\text{MAPbBr}_{3-n}\text{I}_n$ are distributed as small domains in the whole MAPbBr_3 crystal (Fig. 5.10b). Therefore, radiative recombination from $\text{MAPbBr}_{3-n}\text{I}_n$ is suppressed due to thermal delocalization of photo-generated electrons. On the other hand, in the small crystal, $\text{MAPbBr}_{3-n}\text{I}_n$ are formed closely due to the limited space of the crystal (Fig. 5.10c). In other word, the size of the $\text{MAPbBr}_{3-n}\text{I}_n$ region should be larger than the diffusion length of photo-generated electrons. As the result, thermal delocalization of photo-generated electrons is not dominant compared to Figure 5.10b, and yellow PL is generated from the large $\text{MAPbBr}_{3-n}\text{I}_n$ region.

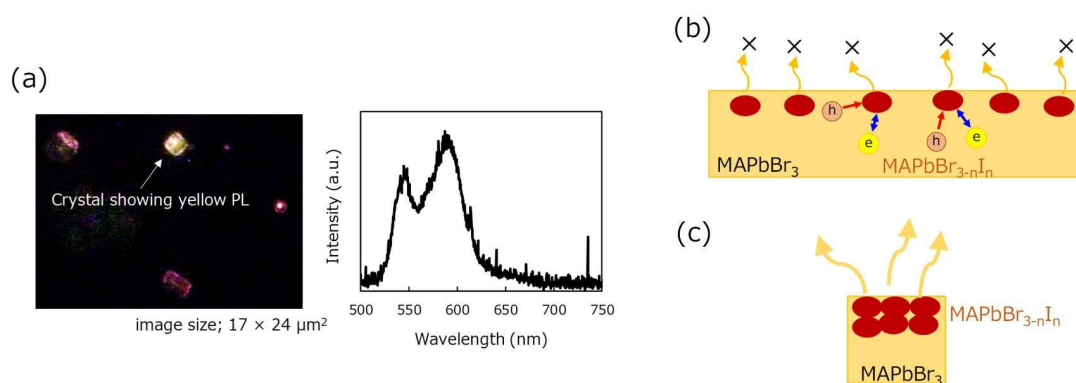


Figure 5.10: (a) PL image and spectrum of the crystal showing yellow PL during the exchange reaction of MAPbBr_3 to $\text{MAPbBr}_{3-n}\text{I}_n$ with 330 μM reaction solution. Schematic illustrations for the emission properties of the $\text{MAPbBr}_{3-n}\text{I}_n$ crystal of (b) large and (c) small size.

Kinetic analysis was performed to determine rate constants of halide exchange reaction with and without the NIR laser irradiation. I assume that the reaction proceeds

with the following equation;

$$-\frac{d[MAI]}{dt} = k[MAI]^x[MAPbBr_3]^y$$

, where x and y are the order of the reaction and k is the rate constant. It can be considered that the concentration of MAPbBr₃ is much high compared to that of MAI in the reaction solution. The above equation can be simplified as follows.

$$-\frac{d[MAI]}{dt} = k[MAI]^x$$

Since the reaction of MAI and MAPbBr₃ results in the formation of MAPbB_{3-n}I_n and subsequently leads to a decrease in the PL of MAPbBr₃ around 540 nm, the following relation can be assumed.

$$[(reacted) MAI] = [(reacted) MAPbBr_3] \propto [PL_{@540nm}] \propto [(I/I_o)_{@540nm}]$$

Here, I_o is the intensity of PL at 1 min and I is the intensity at different time with the progress of the reaction. For comparison between laser trapping induced halogen exchange reaction with spontaneous one, I use I/I_o rather than the absolute value of intensity in rate constant determination. Considering this proportional relation, the reaction can be expressed as follows.

$$-\frac{d[(I/I_o)_{@540nm}]}{dt} = k[(I/I_o)_{@540nm}]^x$$

I analyzed Figure 5.08b and plotted the peak PL intensity at 540 nm (Fig. 5.11a). The PL intensity could be fitted with the second order rate equation (Fig. 5.11b). Actually, the exchange reaction strongly depends on the reactant concentration as summarized in chapter 5-1, which is consistent with the property of the second order rate equation. The rate constant of the PL change was estimated at 0.363.

The same analysis was performed for the non-irradiated sample (Fig. 5.08a). I

plotted the peak PL intensity at 540 nm (Fig. 5.11c) and fitted with the second order rate equation (Fig. 5.11d). The rate constant was estimated at 0.015. It should be noted that the reaction under laser trapping is 24 times faster than that of the spontaneous case. The reaction accelerated by laser trapping enables us to conduct localized halide exchange reaction and the controlled tuning of the bandgap of a perovskite crystal.

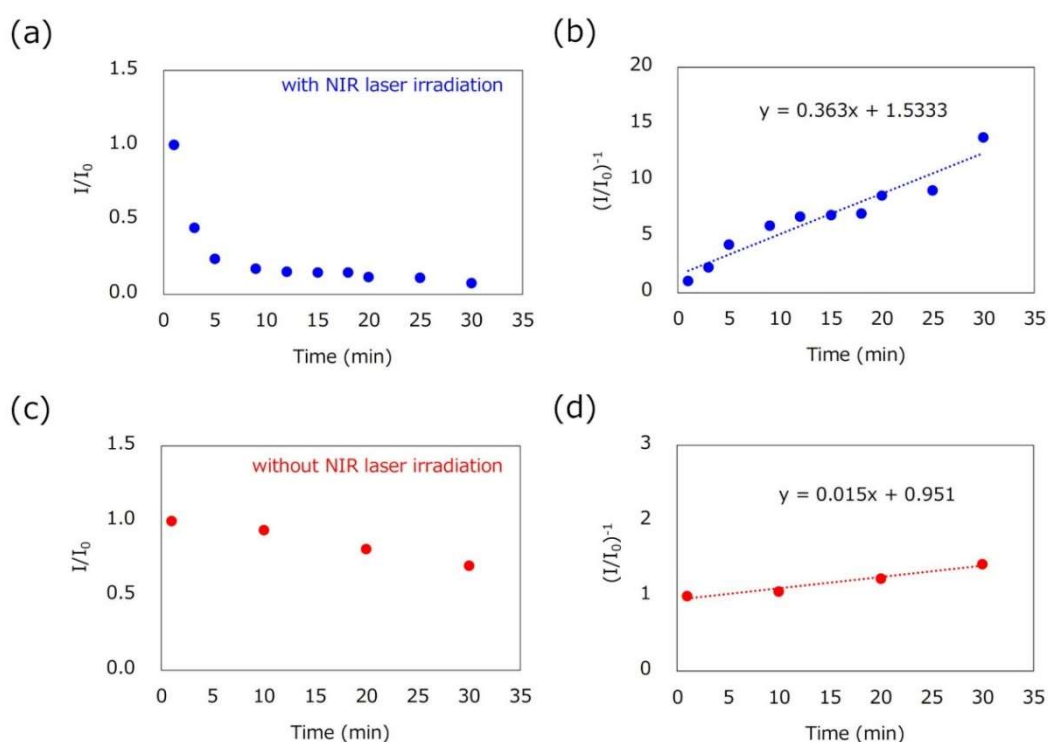


Figure 5.11: Temporal changes in the peak PL intensity at 540 nm. Panels (a), (b) and (c), (d) were obtained by analyzing Figure 5.08b and 5.08a, respectively.

5-2-2: The role of local temperature elevation on halide exchange under the laser irradiation

A MAPbBr₃ crystal absorbs the focused NIR laser through a two-photon absorption process, which is supported by emission under the laser irradiation. Following two-photon absorption, excess energy is dissipated through intra-band non-radiative relaxation, and

temperature at the focal spot is increased. In order to estimate local temperature elevation, I referred to the following paper of K. Metwally *et al.* (8). The paper describes that “*It has been established that bubble formation occurs around localized nano-absorbers when the temperature of the liquid reaches its spinodal temperature T_s , a temperature usually much higher than its boiling point T_b .*”. The general definition of spinodal temperature (T_s) is the limit of stability of the metastable liquid state, for example, overheated liquid, with respect to fluctuations toward a thermodynamically stable phase, such as the gas. Based on this report, I carried out the bubble formation experiment under the focused laser irradiation into a surface of a MAPbBr₃ crystal in isopropyl alcohol of which T_s is 200 °C (Fig. 5.12a) (9).

After MAPbBr₃ crystals were prepared on a cover glass of the chamber, isopropyl alcohol was added to the chamber. The 1064-nm laser was focused onto a MAPbBr₃ crystal surface. At the power of 1.1 W, the bubble generation was observed in addition to two-photon excited green PL (Fig. 5.12b). No bubble was observed below this laser power, while green emission was generated as the result of two-photon absorption (Fig. 5.12c). That is, the local temperature under the irradiation at 1.1 W is around 200 °C, which is the spinodal temperature of isopropyl alcohol. Room temperature is 18 °C, so that local temperature elevation is about 180 °C. Two-photon absorption is induced with proportional to the square of laser power. Therefore, the irradiation at 500 mW leads to about 20.6% of light absorption through two-photon absorption process compared to the case of 1.1 W. Assuming that light absorption and temperature elevation have a linear relation, I can calculate that the local temperature elevation in isopropyl alcohol is 37 K under the irradiation at 500 mW.

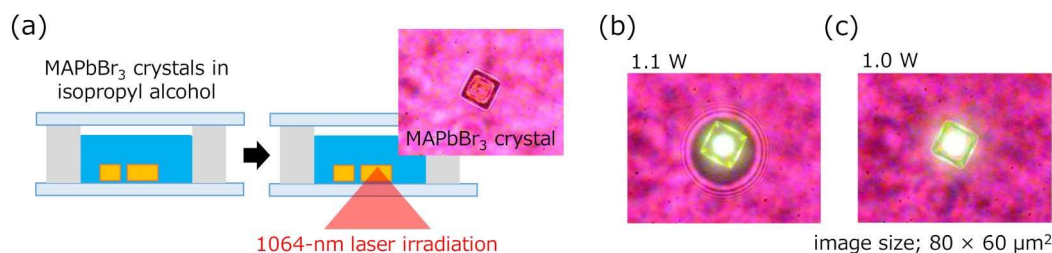


Figure 5.12: A schematic illustration of the experimental procedure for bubble generation under the focused laser irradiation. Optical transmission images of a MAPbBr₃ crystal under the laser irradiation at (b) 1.1 and (c) 1.0 W.

The experiments on halide exchange reaction of a MAPbBr₃ crystal were carried out in hexadecene. Thermal conductivity of hexadecene is 0.085 W/m·K (10), and that of isopropyl alcohol is 0.14 W/m·K (11). Due to the small thermal conductivity of hexadecene, higher temperature elevation (61 K) is induced under our laser irradiation condition in hexadecene. I concluded that local temperature at the focal spot on a MAPbBr₃ crystal surface is around 80 °C during the experiments on halide exchange reaction. As described above in chapter 5-1, halide exchange reaction in our sample is suppressed by heating. The local heating through two-photon absorption should also have suppressed the reaction.

5-2-3: Possible mechanism of halide exchange reaction induced by laser

Here, I propose the possible mechanism for halide exchange reaction with MAI on a MAPbBr₃ crystal under the focused NIR laser irradiation (Fig. 5.13). The exchange reaction strongly depends on reactant concentration. Spontaneous reaction proceeds in the negligibly small extent with the reactant of 110 μM. On the other hand, at a higher concentration (330 μM), PL of the crystal changes from green to red within 5 minutes. Based on this concentration dependence, I consider that the exchange reaction under the

focused NIR laser irradiation should be due to local concentration increase of iodide ions through laser trapping.

Hexadecene and isopropyl alcohol are poor and good solvents for methylammonium iodide, respectively. Therefore, it is likely that the mixed solvent is highly hydrophobic and methylammonium iodide tends to exist as clusters rather than isolated. Since optical force is proportional to the target volume (12), the aggregates or clusters with large size generate strong trapping force (Fig. 5.13a), resulting in the local concentration increase (Fig. 5.13b).

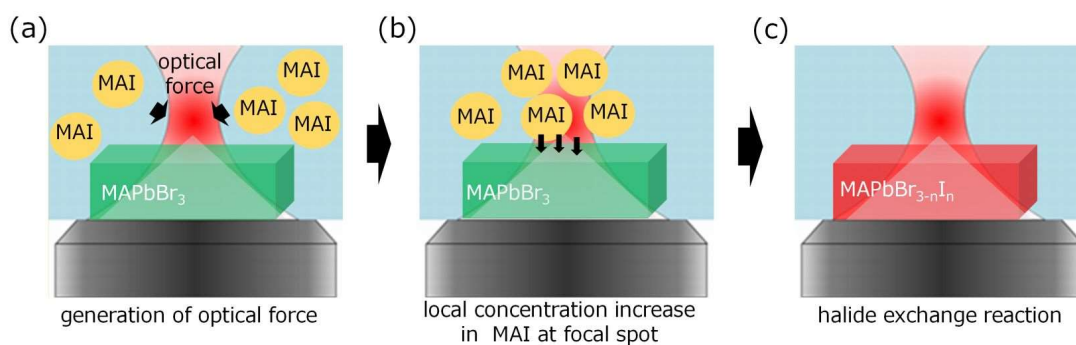


Figure 5.13: Schematic illustration of possible mechanism of local halide exchange reaction by a focused laser beam.

However, the DLS measurement of the reaction solution (110 μM) showed the distribution of solutes at the size less than 2 nm (Fig. 5.14). It is reported that optical force can work even on small molecules like amino acids and their diffusion is suppressed slightly in the focal volume of the trapping laser (13). Such “optically biased diffusion” might be induced even to isolated iodide ions. In addition, the electromagnetic energy of the trapping laser modifies the free energy of the focal volume to be lower, as discussed by Walton and Wynne (14). Due to such an optical potential, iodide ions are attracted to the focal spot. Consequently, their staying time at the focal spot becomes long, and local concentration increase leads to halide exchange reaction. This local concentration

increase by optical force overcomes the suppression of the reaction induced by heating through two-photon absorption at the focal spot. As the result, the reaction during laser trapping is accelerated 24 times compared to the non-irradiated positions. The exchanged iodide ions possibly migrate inside the crystal due to a relatively high concentration of halide vacancies (15), which may result in the PL change at the outside of the focal spot (Fig. 5.13c).

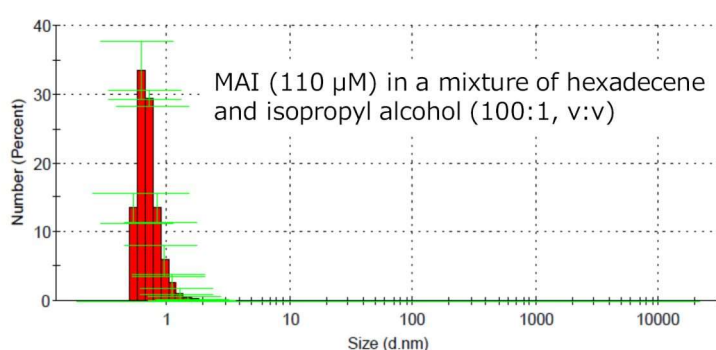


Figure 5.14: The size distribution with standard deviation in a mixture of hexadecene and isopropyl alcohol (100:1, v:v) of MAI (110 μM) estimated by the DLS measurement.

5-3: Preparation of $\text{MAPbCl}_{3-n}\text{Br}_n$ by halide exchange in MAPbCl_3 and MAPbBr_3

I carried out exchange reaction experiments for MAPbCl_3 . Microcrystals of MAPbCl_3 were prepared on the glass substrate of the chamber (Fig. 5.15a). In order to increase the concentration of the reaction solution, I used isopropyl alcohol as the solvent. Isopropyl alcohol with methylammonium bromide (0.1 M) was added to the chamber as the reaction solution, then the NIR laser was focused. After the 30-min NIR laser irradiation, the irradiated crystal showed green emission under the wide-field illumination of the 405- nm laser (Fig. 5.15b). But such green emission was not observed for the non-irradiated crystal in the surrounding.

I consider that halide exchange reaction with bromide ions on a MAPbCl_3 was

induced by the focused NIR laser irradiation and the irradiated crystal was changed to a bromide-rich mixed halide perovskite crystal having relatively high quantum yield. On the other hand, the non-irradiated crystal has low quantum yield due to a high concentration of chloride ions, resulting in a dark PL image (16). It should be noted that the two photons excited PL was not observed during the NIR laser irradiation. This is due to a large bandgap of an initial MAPbCl_3 crystal and $\text{MAPbCl}_{3-n}\text{Br}_n$ crystal that are prepared through the exchange reaction under the laser irradiation. In other words, local temperature elevation is negligibly small with less possibility of two-photon absorption of the NIR laser. Therefore, it is reasonable to consider that this exchange reaction is realized mainly through local concentration increase induced by laser trapping.

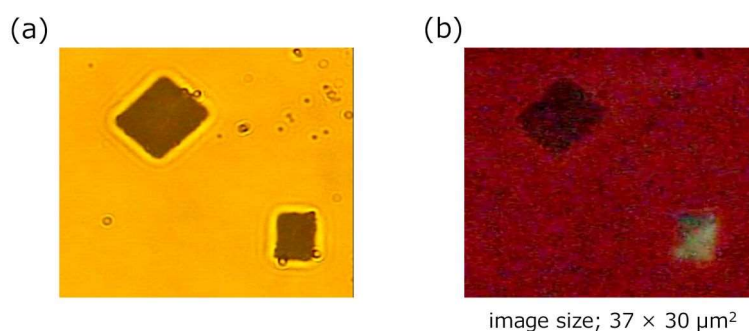


Figure 5.15: (a) Optical transmission image of MAPbCl_3 crystals. (b) PL image of the crystals after the 30-min NIR laser irradiation to the crystal located at the lower right. The crystals were excited under wide-field illumination of the 405-nm laser.

I tried laser trapping-induced halide exchange reaction of MAPbBr_3 with MAI . I prepared the reaction solution (0.1 M) by dissolving MAI in isopropyl alcohol. The reaction solution was added into a chamber where MAPbBr_3 microcrystals were prepared on the cover glass. After that, PL of all crystals was changed from green to cyanine through spontaneous halide exchange reaction (Fig. 5.16a). The non-irradiated crystals remained cyanine emissive, while the crystal exposed to the focused NIR laser showed

blue PL (Fig. 5.16b & 5.16c). That is, the exchange reaction is accelerated by focused laser irradiation, leading to the formation of chloride-rich $\text{MAPbCl}_{3-n}\text{Br}_n$ with the higher bandgap. Thus, laser trapping is useful for the control of halide exchange reaction giving not only $\text{MAPbBr}_{3-n}\text{I}_n$ but also $\text{MAPbCl}_{3-n}\text{Br}_n$.

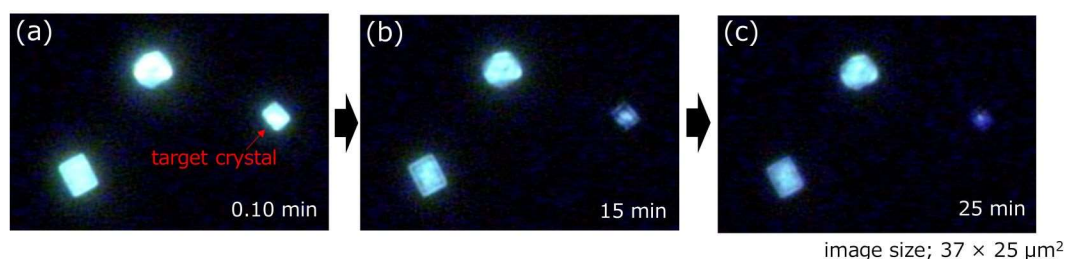


Figure 5.16: Temporal changes in PL images under the NIR laser irradiation in addition to wide-field illumination of the 405- nm laser. The irradiation time is shown in each image.

5-4: Summary

I demonstrated the site-selective halide exchange reactions of lead halide perovskite single crystals under the focused NIR laser irradiation. The exchange reaction proceeds through local concentration increase induced by optical force. The halogen exchange reaction under laser trapping is more than one order of magnitude faster than the spontaneous exchange. In the near future, a spatial resolution will be increased with the use of near-field optics as well as beam shaping, which will enable us to prepare multi-quantum well perovskite structures by laser scanning.

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Chapter 6

Summary and perspective

Laser trapping with the use of optical force of a tightly focused laser beam has played innovative roles in many research fields by trapping and manipulating small objects of nano- and micro-scale in solutions. Representative trapping targets were nanoparticles, quantum dots, polymers, proteins, and amino acids, and spatio-temporal preparation of their assemblies and crystals was achieved with this technique. However, the potential of laser trapping for chemical reactions remains unexplored. In the study described in this thesis, I demonstrated the potential application of optical trapping to conduct and control chemical reactions by exerting optical force on perovskite precursors at interfaces. Experimental results and discussions summarized in each chapter are as follows.

In chapter 3, synthesis and crystallization of MAPbX_3 ($X = \text{Cl, Br, or I}$) were demonstrated by focusing a NIR laser beam at the air/solution interface of the MAX:PbX_2 precursor solutions. One crystal of MAPbX_3 was formed from the laser focus even in an unsaturated solution where no spontaneous crystallization took place. Therefore, it was considered that the crystallization was induced through a local increase in saturation degree. Two possibilities were considered since the samples used had retrograde solubility. One is laser heating, and the other is laser trapping. The former decreases the solubility of perovskites, and the latter increases precursor concentration. Local temperature elevation was estimated on the basis of 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 was proposed from the viewpoint of laser trapping of precursor complexes that generate strong optical force. Once precursor complexes begin to assemble in the focal volume, their effective size and polarizability become large, and their local concentration increases nonlinearly with irradiation time, realizing supersaturated condition at the focal spot. Consequently, a chemical reaction between MAX and PbX₂ is initiated at the air/solution interface through de-solvation and molecular/atomic re-ordering of gathered precursor complexes which produced the MAPbX₃ single crystal.

In chapter 4, laser trapping-induced synthesis was extended to mixed halide perovskite compounds. The synthesis of MAPbBr_nCl_{3-n} (n = 0–3) was demonstrated by focusing a NIR laser beam at the air/solution interface of the MABr:PbBr₂:MACl:PbCl₂ precursor solutions. The crystallization of MAPbBr_nCl_{3-n} was induced from the focal spot, and the formed crystal was characterized by transmission and PL microspectroscopic techniques and XRD analysis. The characterization revealed that MAPbBr_nCl_{3-n} crystals formed under the laser irradiation have chloride composition higher than that of the initial precursor solutions. Furthermore, it was found that the crystal formed by the laser had chloride composition different from that prepared by the conventional temperature control method. The difference in the chloride composition was explained from the viewpoint of de-solvation of precursors of MACl:PbCl₂ which preferentially proceeds compared to those of MABr:PbBr₂.

In chapter 5, laser trapping of perovskite precursors was applied to a surface of a perovskite crystal for inducing halide exchange reaction site-specifically. The exchange reaction of a MAPbBr₃ crystal with MAI was demonstrated by focusing a NIR laser beam at the crystal surface. The PL of the irradiated crystal was changed from green to red due to the formation of MAPbBr_{3-n}I_n, while the non-irradiated crystals remained green emissive. Kinetic analysis of the PL change revealed that the exchange rate was

accelerated 24 times by the laser irradiation. The underlying mechanism was discussed by considering two laser-induced phenomena. One is a laser trapping that increases the concentration of the reactant precursors 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 the 24 times accelerated exchange reaction.

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 be an important milestone for such new applications of laser trapping.

Laser trapping-controlled chemical reaction can be also applied to the research field of perovskite compounds. Laser trapping under various chemical conditions will be helpful to develop various functional materials, such as mixed cation- or mixed metal-halide perovskite, new classes of perovskites with two-dimensional layered structures, as well as perovskite-related luminescent compounds. Another application is the fabrication of heterostructures of perovskite crystals. Semiconductor heterostructures are key components of optoelectronic devices. Site-specific halide exchange reaction based on laser trapping is a new approach for the fabrication of heterostructures of perovskite compounds. The spatial resolution will be increased with the use of near-field optics as well as beam shaping. The prepared multi-quantum well perovskite structures are expected to have unique optical and electronic properties.

List of Publication

1. Mixed-Halide Perovskite Synthesis by Chemical Reaction and Crystal Nucleation under an Optical Potential.
Md Jahidul Islam, Ken-ichi Yuyama, Kiyonori Takahashi, Takayoshi Nakamura, Katsuaki Konishi, Vasudevanpillai Biju.
NPG Asia Materials. **2019**, *11* (1), 31.
2. Crystallization of Methylammonium Lead Halide Perovskites by Optical Trapping.
Ken-ichi Yuyama, Md Jahidul Islam, Kiyonori Takahashi, Takayoshi Nakamura, Vasudevanpillai Biju.
Angewandte Chemie International Edition. **2018**, *57* (41), 13424–13428.
3. Remote tuning of bandgap and emission by spatially- controlled chemical reactions in lead perovskites.
Md Jahidul Islam, Md Shahjahan, Ken-ichi Yuyama, Vasudevanpillai Biju.
Submitted

List of Presentation

1. Crystallization of mixed chloride-bromide methylammonium lead perovskites by optical trapping at solution surface (poster)
Md Jahidul Islam, Ken-ichi Yuyama, Katsuaki Konishi, Vasudevanpillai Biju
Annual Meeting of Japanese Photochemistry Association, Sep. 5-7, 2018, Kwansei Gakuin University, Nishinomiya, Osaka, Japan.
2. Mixed halide lead perovskite single crystals prepared by optical trapping at solution surface (poster)
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