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Crystallization of Methylammonium Lead Halide Perovskites by Optical Trapping

Ken-ichi Yuyama,[a],* Md Jahidul Islam,[a] Kiyonori Takahashi,[a] Takayoshi Nakamura,[a] and Vasudevanpillai Biju[a],*

Abstract: Single crystals of organo-lead halide perovskites attract much attention to electrooptical and photovoltaic applications. They are usually prepared in precursor solutions incubated at controlled temperatures or under optimized vapor atmosphere conditions, nucleating multiple perovskite crystals all over the solution. Multiple nucleation of crystals prevents efficient use of precursors in the preferential growth of large single crystals, Here, we show an innovative approach for spatio-temporally controlled, selective nucleation and growth of single crystals of lead halide perovskites by optical trapping with a focused laser beam. Upon such a trapping in unsaturated precursor solutions, nucleation of $MAPbX_3$ (MA = $CH_3NH_3^+$, X = Cl^-, Br^-, or I^-) is induced at the focal spot through increase in the concentration of perovskite precursors in the focal volume. The rate at which the nucleated crystal grows depends upon whether the perovskite absorbs the trapping laser or not. These findings suggest that optical trapping would be useful to prepare various perovskite single crystals and modify their optical and electronic properties, offering new methodologies to engineer perovskite crystals.

Organo-lead halide perovskites receive much attention, owing to their advantages such as strong absorption of visible to near-infrared light, brilliant photo- and electro- luminescence, long-range diffusion of electrons and holes, and low trap-state densities, which are in addition to low-temperature solution-processiblity.[1] These advantages make perovskites one of the most promising classes of semiconductor materials for solar cells,[1a] LEDs,[2] lasers,[3] and photodetectors.[4] Nucleation and growth of perovskite bulk crystals in solution are the key processes in the advancement of perovskite-based devices as well as the understanding of fundamental properties of perovskite compounds. So far, perovskite bulk crystals are successfully prepared by vapor diffusion and temperature control methods.[1d,5] For example, Bark and coworkers successfully synthesized high-quality large single crystals of methylammonium lead trihalide in the solution phase by following the retrograde solubility of these perovskites.[5a] These methods have possibilities to form multiple nuclei all over the solution, resulting in an inhomogeneous distribution of crystal size.

Herein, we report an innovative approach based on optical trapping for preparing single perovskite crystal in a spatio-temporally controlled manner (Fig. 1a), which is accomplished by combining laser trapping crystallization with the retrograde solubility of perovskite crystals.[5a] Single beam optical trapping was reported by Ashkin in 1986[6] and, in chemistry, it has been applied to the preparation of assemblies in micro- and nano-scale, such as amino acid associates,[7] micelles,[8] polymer structures,[9] quantum dot clusters,[10] and nanoparticle assemblies.[11] Interestingly, assembled molecules or clusters evolve into a crystal nucleus when the trapping laser is focused onto a solution surface.[12] The local concentration increase through optical trapping of molecules or clusters is coupled with re-ordering of precursor molecules or ions at the solution surface, leading to crystallization.

For the crystallization of $MAPbBr_3$ by optical trapping, we used $MABr/PbBr_2$ (1.3 M) dissolved in DMF. $MAPbBr_3$ shows retrograde solubility in DMF at temperatures up to 100 ℃.[13] Based on the solubility of $MAPbBr_3$, the saturation degree of the sample solution was estimated at 0.83, which is at 18 ℃ in the experimental room. The details of sample preparation and optical setup are provided in Supporting Information (SI 1). Figure 1b shows optical trapping behavior upon the 1064 nm laser irradiation into the solution surface of $MABr/PbBr_2$. By varying the laser power between 100 to 600 mW and the concentrations of precursor solutions between 0.1 to 1.3 M, we estimated the threshold laser power at 200 mW and the threshold concertation of precursor solutions at 1.2 M for consistent crystallization. At the beginning of the irradiation, an optical micrograph showed only the faint trapping laser reflected at the air-solution interface [panel (i), Fig. 1b]. A small crystal of a few micrometers was identified in a camera image at 103 s [panel (ii), Fig. 1b]. The nucleated crystal continuously grew large while being trapped at the focal spot and attained the size of 11×13 μm^2 at 120 s [panels (iii)– (iv), Fig. 1b]. The formed crystal was moved away from the focal spot and dissolved soon after the laser was tuned off [panels (v)–(vi), Fig. 1b], which is due to unsaturation of the surrounding solution. The video movie of crystallization and crystal growth under optical trapping, and crystal dissolution upon switching off the laser is uploaded as supplementary video.

The measurements of photoluminescence (PL) and X-ray diffraction (XRD), and the solubility behavior revealed that the crystal formed in the solution of $MABr/PbBr_2$ is $MAPbBr_3$. The formed crystal showed green emission during the trapping, and its peak was observed at 550 nm (Fig. 2a). This PL is the result of two-photon absorption of the trapping laser. The formed crystals showed excellent photostability under one- or two-photon excitation. Also, the obtained spectral profile is similar to that reported for $MAPbBr_3$.[2,3,5a,c] For observing the solubility behavior of the crystal, we heated the sample chamber with a thermoplate, which was after the crystal nucleation [panel (i) of Fig. 2b]. The nucleated single crystal grew continuously under the combined trapping and heating condition. After the crystal size became ca 60 × 60 μm^2, the trapping laser was turned off, and the crystal continued to grow under heating, which was

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observed through a low magnification objective lens [panels (ii)–(iii) of Fig. 2b].

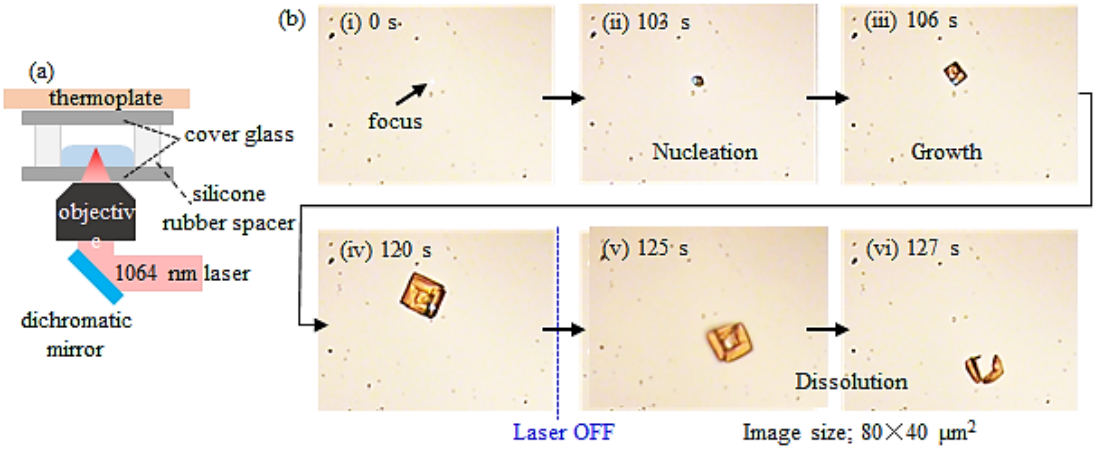


Figure 1. Nucleation and growth of a perovskite single crystal by optical trapping. a) A schematic illustration of the optical trapping setup. b) Optical micrographs of a solution of $MABr/PbBr_2$ under the 1064 nm laser irradiation. The laser power outside the objective lens is 0.6 W.

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 $MAPbBr_3$.[5a] The XRD data (Fig. 2c) obtained for the single crystal perfectly match with the characteristic Miller indices of cubic $MAPbBr_3$.[5a] Like $MAPbBr_3$, a cubic $MAPbCl_3$ crystal was formed from the focal spot in a $MACl/PbCl_2$ solution. XRD and PL data of $MAPbCl_3$ crystals are provided in SI (Fig. S1 and S5). In the case of $MAPbI_3$, stable single crystal formation was not observed. The crystallization started from the focal spot, however the formed crystals grew explosively and moved away to the surrounding solution. This crystallization behavior is summarized in SI 2. Overall, the focused laser irradiation at the surface of unsaturated solutions of perovskite precursors led to the formation of $MAPbX_3$ crystals in a spatio-temporally controlled manner.

Despite the growth of single crystal by the focused laser irradiation, the retrograde solubility of $MAPbBr_3$ encourages us to consider the role of laser-induced heating on crystallization. The local temperature elevation in the solution of $MABr/PbBr_2$ is estimated at <8 K under the present irradiation condition (Table S1). Although this temperature elevation increases the saturation degree by 0.1,[13] the concentration remains below saturation. Based on the above unsaturated condition of $MACl/PbCl_2$ or $MABr/PbBr_2$ and the negligibly small extinction coefficients of precursor solutions at 800 nm and 1064 nm (extinction spectra and transmittance values are provided in SI, Fig. S3), we hypothesize that the crystallization under the focused laser irradiation succeeds through local concentration increase by optical trapping of perovskite precursors. Indeed, the crystallization is induced from the focal spot of 800 nm trapping laser, under which local temperature elevation is negligibly small (SI 4, page 10).

Here, we suggest a possible mechanism for optical trapping-induced crystallization of $MAPbX_3$ (Fig. 3). It is proposed that perovskite precursors form complexes including solvent molecules.[5a,14] Optical trapping of precursor complexes leads to the formation of a high concentration region where precursors and solvent molecules are confined. Precursor complexes should have larger size compared to that of individual ions. Since the trapping force is proportional to the target volume (SI 5, page 11),[15] the precursor complexes of large size generate strong trapping force, resulting in their trapping at the focal spot (Fig. 3a). 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. In such a region, optical trapping force preferentially acts on precursors, which has refractive index higher than that of the surrounding. As the result, nucleation begins, excluding solvent molecules. One

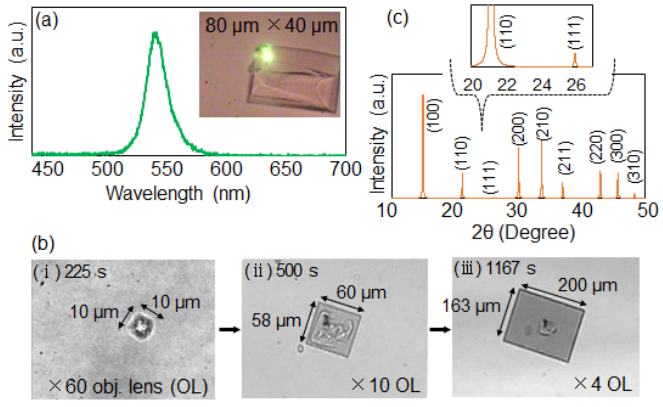


Figure 2. Characterization of perovskite single crystals. a) PL spectrum obtained during the trapping of the formed crystal. The inset shows the optical micrograph of the PL generated at the focal spot of the trapping laser. b) Optical micrographs of the crystal that was incubated in the chamber heated with a thermo-plate set at 70 °C. The dark spots in the crystal are due to inhomogeneous thickness of the crystal. c) The powder XRD patterns of the large crystal formed by optical trapping.

of key processes in 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

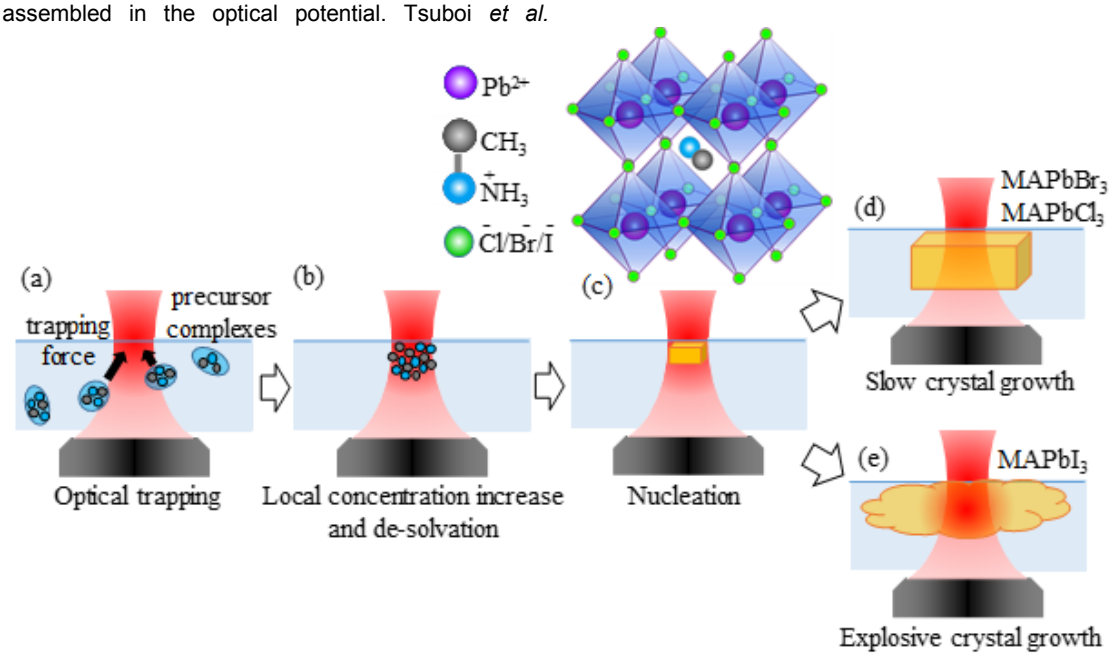


Figure 3. Mechanism for crystal nucleation and growth. The nucleation is initiated through local concentration increase, de-solvation, and molecular and ionic re-ordering at the solution surface, and the crystal growth rate depends on whether the perovskite absorbs the trapping laser or not.

aqueous solution, which is by dehydration under optical trapping.[16] Similarly, we assume that the solvent molecules are partially or completely removed from the gathered MAX/PbX_2 complexes during their trapping (Fig. 3b). The local temperature elevation during optical 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. 3c). It is noteworthy that the focal position of the trapping laser is critical in the crystallization. When the laser was focused onto the solution inside or the glass/solution interface, no crystallization was induced during the 30 min observation. This behaviour was same as optical trapping-induced crystallization of amino acids,[12] which always occurs at the solution surface.

The rate at which the nucleated crystal grows depends upon whether the perovskite absorbs the trapping laser of 1064 nm or not. Since a $MAPbBr_3$ crystal absorbs light below 570 nm,[5a] two-photon absorption is induced by the focused trapping laser. Different from the absorption coefficients, the complex refractive index ($n + ik$) is reported in the UV to NIR region.[17] The imaginary part (k) is associated with an absorption coefficient (α) in the equation, $\alpha = 4\pi k/\lambda$, where λ is wavelength of light. The k appears identical in the 600–1100 nm range in the reported graph. Thus, we assume that α is essentially constant. Following two-photon absorption, excess energy is dissipated through intra-band non-radiative relaxation, and the temperature of the surrounding solution is slightly increased. As the result, the solubility of the precursors is decreased, and the local saturation degree is elevated, leading to continuous crystal growth (Fig. 3d). On the other hand, a $MAPbCl_3$ crystal hardly absorbs the trapping laser, and its growth is saturated at the size of several micrometers. $MAPbI_3$ perovskite absorbs light below 820 nm.[5a] Thus, the trapping laser (1064 nm) 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 $MAPbI_3$ (Fig. 3e).[5a] The controlled crystallization and growth of $MAPbI_3$, without any explosive crystal growth, can be realized with trapping lasers of wavelength longer than 1640 nm.

In conclusion, we demonstrate nucleation and growth of $MAPbX_3$ perovskite single crystals by optical trapping at the surface of their precursor solutions in a spatio-temporally controlled manner. The crystallization process and mechanism should be general for various perovskite compounds. Furthermore, any elevation of precursor local concentration at the surface of a perovskite crystal leads to halide exchange reactions, which upon combination with optical trapping would allow one to modify optical and electronic properties of perovskite crystals in a spatially resolved manner. Like laser crystallization of perovskite films and solar cells,[18] the current work on preparation of perovskite single crystals by optical trapping would develop new methodologies to engineer perovskite bulk crystals with various compositions.

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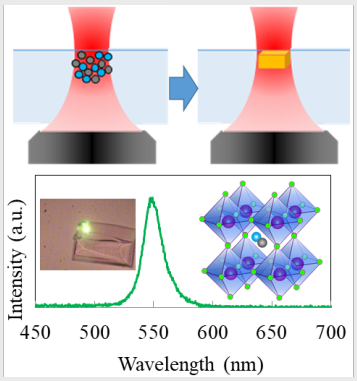
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Entry for the Table of Contents

Layout 1:

COMMUNICATION

Single crystals of methylammonium lead halide perovskites are selectively nucleated and grown by laser trapping in unsaturated precursor solutions. Laser trapping enables us to not only control the crystal nucleation and growth in a spatio-temporal manner but also prevent nucleation and growth of multiple small crystals. Laser trapping would be useful to prepare various perovskite single crystals and modify their optical and electronic properties, offering new methodologies to engineer perovskite crystals.



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