Video Article

Low Pressure Vapor-assisted Solution Process for Tunable Band Gap Pinhole-free Methylammonium Lead Halide Perovskite Films

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Abstract

Organo-lead halide perovskites have recently attracted great interest for potential applications in thin-film photovoltaics and optoelectronics. Herein, we present a protocol for the fabrication of this material via the low-pressure vapor assisted solution process (LP-VASP) method, which yields ~19% power conversion efficiency in planar heterojunction perovskite solar cells. First, we report the synthesis of methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) and methylammonium bromide ($\text{CH}_3\text{NH}_3\text{Br}$) from methylamine and the corresponding halide acid (HI or HBr). Then, we describe the fabrication of pinhole-free, continuous methylammonium-lead halide perovskite ($\text{CH}_3\text{NH}_3\text{PbX}_3$ with $\text{X} = \text{I}, \text{Br}, \text{Cl}$ and their mixture) films with the LP-VASP. This process is based on two steps: i) spin-coating of a homogenous layer of lead halide precursor onto a substrate, and ii) conversion of this layer to $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ by exposing the substrate to vapors of a mixture of $\text{CH}_3\text{NH}_3\text{I}$ and $\text{CH}_3\text{NH}_3\text{Br}$ at reduced pressure and 120 °C. Through slow diffusion of the methylammonium halide vapor into the lead halide precursor, we achieve slow and controlled growth of a continuous, pinhole-free perovskite film. The LP-VASP allows synthetic access to the full halide composition space in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ with $0 \leq x \leq 3$. Depending on the composition of the vapor phase, the bandgap can be tuned between 1.6 eV $\leq E_g \leq$ 2.3 eV. In addition, by varying the composition of the halide precursor and of the vapor phase, we can also obtain $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$. Films obtained from the LP-VASP are reproducible, phase pure as confirmed by X-ray diffraction measurements, and show high photoluminescence quantum yield. The process does not require the use of a glovebox.

Video Link

The video component of this article can be found at <https://www.jove.com/video/55404/>

Introduction

Hybrid organic-inorganic lead halide perovskites ($\text{CH}_3\text{NH}_3\text{PbX}_3$, $\text{X} = \text{I}, \text{Br}, \text{Cl}$) are a new class of semiconductors that has emerged rapidly within the last few years. This material class shows excellent semiconductor properties, such as high absorption coefficient¹, tunable bandgap², long charge carrier diffusion length³, high defect tolerance⁴, and high photoluminescence quantum yield^{5,6}. The unique combination of these characteristics makes lead halide perovskites very attractive for application in optoelectronic devices, such as single junction^{7,8} and multijunction photovoltaics^{9,10}, lasers^{11,12}, and LEDs¹³.

$\text{CH}_3\text{NH}_3\text{PbX}_3$ films can be fabricated by a variety of synthetic methods¹⁴, which aim at improving the efficiency of this semiconducting material for energy applications¹⁵. However, optimization of photovoltaic devices relies on the quality of the halide perovskite active layer, as well as its interfaces with charge selective contacts (i.e. electron and hole transport layers), which facilitate photocarrier collection in these devices. Specifically, continuous, pinhole-free active layers are necessary to minimize shunt resistance, thereby improving device performance.

Among the most widespread methods for fabricating organo-lead halide perovskite thin films are solution-based and vacuum-based processes. The most common solution process uses equimolar ratios of lead halide and methylammonium halide dissolved in dimethylformamide (DMF), dimethylsulfoxide (DMSO), or γ -butyrolactone (GBL), or mixtures of these solvents.^{2,16,17} Precursor molarity and solvent type, as well as

annealing temperature, time and atmosphere, must be precisely controlled to obtain continuous and pinhole-free films.¹⁶ For example, to improve surface coverage, a solvent-engineering technique was demonstrated to yield dense and extremely uniform films.¹⁷ In this technique, a non-solvent (toluene) is dripped onto the perovskite layer during the spinning of the perovskite solution.¹⁷ These approaches are usually well suited for mesoscopic heterojunctions, which employ mesoporous TiO_2 as an electron selective contact with increased contact area and reduced carrier transport length.

However, planar heterojunctions, which use selective contacts based on thin (usually TiO_2) films, are more desirable because they provide a simple and scalable configuration that can be more easily adopted in solar cell technology. Therefore, the development of organo-lead halide perovskite active layers that show high efficiency and stability under operation for planar heterojunctions may lead to technological advancements in this field. However, one of the main challenges to fabricate planar heterojunctions is still represented by the homogeneity of the active layer. A few attempts, based on vacuum processes, have been made to prepare uniform layers on thin TiO_2 films. For example, Snaith and collaborators have demonstrated a dual evaporation process, which yield highly homogenous perovskite layers with high power conversion efficiencies for photovoltaic applications.¹⁸ While this work represents a significant advancement in the field, the use of high vacuum systems and the lack of tunability of the composition of the active layer limit the applicability of this method. Interestingly, extremely high uniformity has been achieved with the vapor-assisted solution process (VASP)¹⁹ and modified low pressure VASP (LP-VASP)^{6,20}. While the VASP, proposed by Yang and collaborators¹⁹, requires higher temperatures and the use of a glove box, the LP-VASP is based on the annealing of a lead halide precursor layer in the presence of methylammonium halide vapor, at reduced pressure and relatively low temperature in a fumehood. These specific conditions enable access mixed perovskite compositions, and fabrication of pure $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$, and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ can be easily achieved. Specifically, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films over the full composition space can be synthesized with high optoelectronic quality and reproducibility^{6,20}.

Herein, we provide a detailed description of the protocol for the synthesis of organic-inorganic lead halide perovskite layers via LP-VASP, including the procedure for synthesizing the methylammonium halide precursors. Once the precursors are synthesized, formation of $\text{CH}_3\text{NH}_3\text{PbX}_3$ films consists of a two-step procedure that comprises i) the spin-coating of the $\text{PbI}_2/\text{PbBr}_2$ (PbI_2 , or $\text{PbI}_2/\text{PbCl}_2$) precursor on glass substrate or fluorine-doped tin oxide (FTO) coated glass substrate with planar TiO_2 , as electron transport layer, and ii) the low pressure vapor-assisted annealing in mixtures of $\text{CH}_3\text{NH}_3\text{I}$ and $\text{CH}_3\text{NH}_3\text{Br}$ that can be finely adjusted depending on the desired optical bandgap ($1.6 \text{ eV} \leq E_g \leq 2.3 \text{ eV}$). Under these conditions, the methylammonium halide molecules present in the vapor phase slowly diffuse into the lead halide thin film yielding continuous, pinhole-free halide perovskite films. This process yields a two-fold volume expansion from the starting lead halide precursor layer to the completed organic-inorganic lead halide perovskite. The standard thickness of the perovskite film is about 400 nm. It is possible to vary this thickness between 100-500 nm by changing the speed of the second spin coating step. The presented technique results in films of high optoelectronic quality, which translates to photovoltaic devices with power conversion efficiencies of up to 19% using a Au/spiro-OMeTAD / $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ /compact TiO_2 /FTO/glass solar cell architecture.²¹

Protocol

Caution: Please consult all relevant material safety data sheets (MSDS) before use. Several of the chemicals used in these syntheses are acutely toxic, carcinogenic, and toxic to reproduction. Implosion and explosion risks are associated with the use of a Schlenk line. Please make sure to check the integrity of the glass apparatus before performing the procedure. Incorrect use of the Schlenk line in association with a liquid nitrogen cold trap may result in condensation of liquid oxygen (pale blue) that can become explosive. Please ensure to receive appropriate on the job training by experts before using vacuum-systems, Schlenk lines, and cryogenic liquids. Please use all appropriate safety practices when performing the synthesis including the use of engineering controls (fume hood) and personal protective equipment (safety glasses, gloves, lab coat, full length pants, closed-toe shoes). All of the following procedures described below are performed in a fume hood in air, unless stated differently.

1. Preparation of Methylammonium Halide

1. To a 250 mL round bottom flask equipped with a stir bar, add ethanol (100 mL) and methylamine (190 mmol, 16.5 mL, 40%_{w/v} in H_2O), and cool the flask to 0 °C with an ice bath.
2. While the methylamine solution is stirring (for about 5 min at 600 revolution per min (rpm)), add HI (76 mmol, 10 mL, 57%_{w/v} in H_2O) or HBr (76 mmol, 8.6 mL, 48%_{w/v} in H_2O) dropwise, and seal the flask with a septum.
3. Allow the reaction to stir for 2 h at 0 °C.
4. Remove the reaction flask from the ice bath and evaporate the solvent and unreacted volatile components at reduced pressure (~50 Torr) with a rotary evaporator equipped with a water bath at 60 °C for 4 h or until the volatiles are removed.
5. To recrystallize the resulting solid, add warm (~50 °C) ethanol (100 mL) and dissolve the residual material.
6. Slowly add diethyl ether (200 mL) to induce crystallization of a white solid.
7. Vacuum filter the mixture over a coarse 50 mm glass frit filter.
8. Recover the supernatant and add diethyl ether (200 mL) to induce additional crystallization of white solid. Vacuum filter the mixture over a second coarse 50 mm glass frit filter.
9. Combine the white solids on a coarse 50 mm glass frit filter and, while vacuum filtering, wash the resulting powder with diethyl ether three times (~30 mL each time).
10. Dry the white solid under vacuum. This procedure yields (58.9 mmol, 9.360 g, 77%) of methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) and (55.5 mmol, 6.229 g, 73%) of methylammonium bromide ($\text{CH}_3\text{NH}_3\text{Br}$).
11. Store in the dark and in a desiccator at room temperature in order to minimize decomposition over time.

2. Preparation of Methylammonium Lead Halide ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$) Thin Films^{6,20}

1. **Pre-conditioning of the Schlenk tube**

1. Load a 50 mL Schlenk tube (diameter 2.5 cm) with 0.1 g of methylammonium halide. To prevent the chemicals sticking to the walls of the test tube, use a weighing paper cylinder to transfer the methylammonium halide into the tube.
NOTE: The final ratio of I/(I+Br) in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ is determined by the methylammonium halide composition in the test tube. For example, to achieve 30% I content, the Schlenk tube is loaded with 0.03 g $\text{CH}_3\text{NH}_3\text{I}$ and 0.07 g $\text{CH}_3\text{NH}_3\text{Br}$. Actual obtained compositions may vary with experimental setup, so calibration of the synthesis conditions to yield specific target compositions is necessary. In the present case, this was accomplished by measuring halide content in the synthesized films via energy dispersive X-ray spectroscopy (EDX).
 2. Use a Schlenk line equipped with a rotary pump to connect and evacuate the tube. Adjust the pressure to 0.185 Torr. Then, immerse the test tube in a silicone oil bath pre-heated to 120 °C, with a magnetic stirrer (600 rpm) for 2 h (pre-conditioning of the Schlenk tube).
NOTE: This step allows for sublimation of the methylammonium precursor along the sides of the Schlenk tube. It is important to ensure the sublimation of the methylammonium precursor during the two hours of pre-conditioning. A thin layer of methylammonium precursor will condense along the sides of the Schlenk tube to cover the lower half of the tube. If sublimation of the methylammonium precursor is not observed or is happening too fast, check if the pressure of the Schlenk line and the temperature of the oil bath are correct, or try to use fresh methylammonium halide precursor.
 3. Remove Schlenk tube from the oil bath and leave methylammonium halide under an overpressure of flowing N_2 to avoid moisture intake.
- 2. Substrate preparation**
1. Sonicate one substrate (glass or FTO coated glass, 14 x 16 mm²) with water (~3 mL) containing detergent for 15 min in a test tube (diameter 1.5 cm and height 15 cm) at 35 KHz.
 2. Discard the detergent/water by rinsing with ultrapure water (~10 mL) 5 times.
 3. Discard the ultrapure water, add acetone (~3 mL), and sonicate for 15 min at 35 KHz.
 4. Discard the acetone, add isopropanol (~3 mL), and sonicate for 15 min at 35 KHz.
 5. Discard the isopropanol, recover the substrate from the test tube with tweezers, and dry it with a N_2 gun for 15 s.
 6. Deposit TiO_2 compact layer (100 nm) on FTO glass substrates by electron beam evaporation at a substrate temperature of 350 °C, and a deposition rate of 0.5 Å/s using substrate rotation.²¹
- 3. Preparation of the lead halide precursor solution**
1. For the preparation of $\text{MAPbI}_{3-x}\text{Br}_x$ ($0 < x < 3$), dissolve PbI_2 (0.8 mmol, 0.369 g) and PbBr_2 (0.2 mmol, 0.073 g) in 1 mL DMF to achieve a final concentration of 0.8 M of PbI_2 and 0.2 M of PbBr_2 . Sonicate for 5 min at 35 KHz to fully dissolve the precursor.
 1. For the preparation of pure iodine or bromine films, dissolve PbI_2 (1 mmol, 0.461 g) or PbBr_2 (0.8 mmol, 0.294 g) in 1 mL DMF, to achieve a final concentration of 1 M and 0.8 M, respectively. Sonicate for 5 min at 35 KHz to fully dissolve the precursor.
 2. For the preparation of chlorine-doped methylammonium lead iodide perovskite films, dissolve PbI_2 (0.369 g) and PbCl_2 (0.056 g) in 1 mL DMF, to achieve a final concentration of 0.8 M of PbI_2 and 0.2 M of PbCl_2 . Sonicate for 5 min at 35 KHz to fully dissolve the precursor.
 2. Filter the precursor solution with a 0.2 µm polytetrafluorethylene (PTFE) filter.
- 4. Lead halide deposition**
1. Pre-heat the precursor solution on a hot plate set to 110 °C for 5 min.
 2. With a micropipette, drop 80 µL of the pre-heated lead halide precursor solution onto the non-rotating substrate (glass or TiO_2 deposited on FTO coated glass; 14 x 16 mm² size). Spin at 500 rpm for 5 s with an acceleration rate of 500 rpm s⁻¹, and 1500 rpm for 3 min with an acceleration rate of 1,500 rpm s⁻¹.
 3. In a fumehood, dry precursor film for 15 min at 110 °C on a hot plate under flowing N_2 .
NOTE: A crystallizing dish is used and placed over the substrate to allow the precursor to dry in a N_2 atmosphere. To vary the thickness of the resulting perovskite film, the speed of the second spin-coating step can be varied from 1,200 to 12,000 rpm to achieve film thickness in the range of 500 to 100 nm. To further decrease the film thickness, diluted precursor solution can be used.
- 5. Vapor-assisted annealing**
1. Load sample into the Schlenk tube (prepared according to instructions in section 2.1.2). Adjust the pressure to 0.185 Torr.
NOTE: The sample sits in the test tube above the methylammonium halide without being in direct contact with it. To slow down incorporation of methylammonium, the lead halide surface is oriented to face away from the methylammonium halide.
 2. Immerse the Schlenk tube loaded with the sample in silicone oil bath heated to 120 °C for 2 h.
 3. Take out the sample and quickly rinse it by dipping it in a beaker containing isopropyl alcohol. Immediately dry the rinsed sample with a N_2 gun.
NOTE: To prepare pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ use PbI_2 as the halide precursor and pure methylammonium iodide in the vapor-assisted annealing step. To prepare $\text{CH}_3\text{NH}_3\text{PbBr}_3$ use PbBr_2 as the halide precursor and pure methylammonium bromide in the vapor-assisted annealing step.

Representative Results

Proton nuclear magnetic resonance (NMR) spectra were taken after the methylammonium halide synthesis to verify the molecule purity (**Figure 1**). Scanning electron microscopy (SEM) images were acquired before and after vapor annealing (**Figure 2**) to characterize the morphology and the homogeneity of both the mixed lead halide precursor and the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films. X-ray diffraction (XRD) patterns were collected to confirm phase purity and conversion of lead halide to $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ (**Figure 3**).

Figure 1: Nuclear magnetic resonance spectra. (a) ¹H NMR of CH₃NH₃Br in DMSO-d₆. Peaks at δ 7.65 (br s, 3H) and 2.35 (s, 3H) ppm confirm the identity of the molecule.²² (b) ¹H NMR of CH₃NH₃I in DMSO-d₆. Peaks at δ 7.45 (br s, 3H) and 2.37 (s, 3H) ppm confirm the identity of the molecule.²³ The peaks at 2.50 and 3.33 ppm are due to residual DMSO and water. [Please click here to view a larger version of this figure.](#)

Methylammonium bromide and methylammonium iodide may be readily characterized by ¹H NMR (**Figure 1**). The chemical shift of the methyl group is a sharp singlet centered at δ 2.35 ppm (3H) for the CH₃NH₃Br, and δ 2.37 ppm (3H) for CH₃NH₃I. The ammonium shift is a broad singlet centered at δ 7.65 ppm (3H), and δ 7.45 ppm (3H) for CH₃NH₃Br and CH₃NH₃I respectively. The difference in chemical shift of the two methylammonium halides is due to the different halide electronegativities, which affect (de)shielding of the protons present in the molecules. These chemical shifts are consistent with previously reported spectra^{22,23}.

Figure 2: Conversion of lead halide precursor to CH₃NH₃PbI_{3-x}Br_x. SEM images of the mixed lead halide precursor (a and b). Representative SEM images of CH₃NH₃PbI_{3-x}Br_x films annealed in 100% (c, d), 50% (e, f), and 30% (g, h) methylammonium iodide. The faceted films are pinhole free, and show grain sizes up to 700 nm. Scale bar = 5 μm (a, c, e, g), and 1 μm (b, d, f, h). [Please click here to view a larger version of this figure.](#)

Figures 2a and 2b show the homogeneous morphology of the lead halide precursor that is subsequently converted to $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ in mixtures of methylammonium iodide and bromide (c-h). The resulting perovskite films are continuous, pinhole-free with grain sizes up to 700 nm. The standard thickness of the perovskite film is about 400 nm, which is obtained by spin coating 1 M lead halide precursor solution at a speed of 1,500 rpm. The thickness can be changed by varying the rotational speed, with higher speeds yielding thinner films and *vice versa*. Interestingly, the conversion from the lead halide precursor layer to the resulting lead halide perovskite results in an approximate two-fold volume expansion.

The temperature of 120 °C for the vapor phase anneal is chosen such that methylammonium halide sublims, diffuses into the lead halide film, and the equilibrium between methylammonium halide vapor and solid $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ is in favor of the perovskite phase. In a previous study, we showed that annealing at 100 °C resulted in largely incomplete conversion to the perovskite phase and that device performance was best when synthesis was performed at 120 °C instead of 150 °C.²⁰ The phase characterization of precursor and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films on FTO glass substrates by XRD is presented in **Figure 3a**. The lead halide precursor (0.8 M PbI_2 and 0.2 M PbBr_2) shows PbI_2 phase with its main peak at approximately 12.7°. $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films are phase pure and do not contain residual PbI_2 phase. The $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ XRD peaks exhibit a systematic shift to higher angles due to gradual replacement of the larger I atoms by smaller Br atoms leading to a decrease in lattice constant from ~6.29 Å ($x = 0$) to ~5.93 Å ($x = 3$)².

Figure 3: Phase analysis and full composition spectrum $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films. (a) XRD patterns of lead halide precursor showing PbI_2 phase, and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films with decreasing iodine content. The magnified pattern clearly depicts the shift of the (110) peak position towards larger diffraction angles upon Br incorporation. (b) Picture of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films with gradual incorporation of Br (left to right: pure $\text{CH}_3\text{NH}_3\text{PbI}_3$, 90%, 80%, 70%, 50%, 40%, 30%, 20%, 10%, and pure $\text{CH}_3\text{NH}_3\text{PbBr}_3$). [Please click here to view a larger version of this figure.](#)

The picture of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films (**Figure 3b**) illustrates the gradual incorporation of Br, resulting in a band gap increase from 1.6 eV to 2.3 eV, and thus the change in visible appearance (left, pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ to right, pure $\text{CH}_3\text{NH}_3\text{PbBr}_3$). The gradual increase of bandgap has been shown by photoluminescence measurements, which were previously reported on $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ films with high optoelectronic quality over the full composition space.⁶

Discussion

In order to fabricate highly efficient organo-lead planar perovskite heterojunctions, the homogeneity of the active layer is a key requirement. With respect to existing solution^{2,16,17} and vacuum-based^{18,19} methodologies, our process is remarkably amenable to composition tunability of the active layer that can be synthesized over the full $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ composition space with high optoelectronic quality and reproducibility.^{6,20} In addition, this process allows for the use of reduced pressure and relatively low temperature in a fume hood without requiring the use of a glove box or high vacuum deposition.

While LP-VASP is highly reproducible and no modification to the protocol should be necessary, it is noted that the actual Br/(Br+I) composition in the film may be slightly lower than the initial composition of the Schlenk tube. To address this issue, it is critical to measure the halide content via EDX in the final film as well as to confirm the perovskite structure via XRD, in order to perform a calibration of the synthetic conditions yielding specific target compositions with respect to the utilized experimental setup.

In addition, there are a few useful recommendations that can ensure the correct reliability of our process. The quality of the starting materials is particularly important. Storing of both the organic ($\text{CH}_3\text{NH}_3\text{X}$) and inorganic (PbX_2) precursors in a desiccator under nitrogen atmosphere and

controlled humidity is instrumental to ensure reproducibility in the synthesis. In addition, the organic precursors need to be very clean and all the traces of starting materials should be removed with careful washing.

We have demonstrated the synthesis of methylammonium halide and the subsequent transformation of lead halide precursors to $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ in mixtures thereof, resulting in smooth, pinhole free films that exhibit good optoelectronic quality. With respect to previous methods,^{2,16,17,18,19} this synthetic protocol is versatile and amenable to be adapted in different laboratories because it is easily carried out in a fumehood. In addition, LP-VASP allows for facile accessibility of different organo-lead halide perovskite composition and tuning of the band gap.

The presented film fabrication method provides superior morphology control as compared to pure solution coating methods, yielding highly efficient planar perovskite heterojunction solar cells. Because of the low processing temperature and of the use of standard equipment available in most laboratories (i.e. fumehoods and Schlenk lines), this methodology is especially suitable to fabricate single as well as multijunction solar cells, light emitting diodes, and lasers. We are currently developing a process that allows to deposit large ($>2\text{ cm}^2$) area continuous perovskite thin films.

Disclosures

The authors have nothing to disclose.

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