Pressure Effects on the Rate of Photoinduced Phase Separation of Methylammonium Lead (II) Bromide-Iodide Perovskite Thin Films

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Pressure Effects on the Rate of Photoinduced Phase Separation of Methylammonium Lead (II) Bromide-Iodide Perovskite Thin Films

by

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Abstract

There is currently a great deal of excitement surrounding perovskite materials for their potential applications in electro-optics and related fields of study. Here, we are specifically interested in methylammonium lead iodide-bromide mixed halide perovskite films. These have the unique and not fully understood property of reversibly phase separating into iodide- and bromide-rich regions upon exposure to light. The mechanism underlying this phenomenon is based on the mobility of iodide ions in the perovskite lattice. Here, we have attempted to better understand the role of the iodide ion in the phase separation mechanism by measuring the rate of photoinduced phase separation as a function of pressure. Our results suggest that the lattice compression resulting from pressure application ultimately limits ion mobility despite the prediction that vacancy-mediated ion diffusion would be facilitated under these conditions. The steps taken in this work toward a better understanding of ion mobility in perovskite films are highly relevant when it comes to the performance and longevity of electro-optic devices that utilize this material.
Acknowledgments

This project, like all scientific endeavors, was inherently a group effort. I would like to acknowledge the many people in my life that have helped me see this project through whether their support was technical, moral or both. First, I must thank my very knowledgeable and inspiring teacher, advisor and role model, Dr. J. Mathias Weber. His guidance over the years and unending enthusiasm for the sciences have profoundly impacted the trajectory of my career. He is truly a great teacher and I consider myself very lucky to have worked with and learned from him. Thanks also to my past and present co-workers in the Weber group: Leah Dodson, Wyatt Zagorec-Marks, Rebecca Hirsch, Madison Foreman, Luke Walther, Patrick Yehle and Curtis Beimborn. Working with such a supportive, genuine group of people has helped me grow both as a scientist and as a person. In particular, I would like to give thanks to Curtis Beimborn. His mentorship throughout my time in the Weber group has been beyond value. His patience and approachability were admirable to say the least and I consider myself lucky to call him both a mentor and a close friend. I must also thank my friends outside of the laboratory who were always there for me throughout the highs and lows of this project. I could never have completed this project without their unconditional support. Finally, I would like to express deepest gratitude to my parents, Julie and Heath as well as to my sister, Abby who have been surrounding me with love and support from the beginning. I cannot thank them enough.
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1.0 — **Introduction**

1.1 — *Background on Perovskites and Condensed Matter Physics*

In the most rudimentary terms, perovskites are a class of semiconductors whose structure is analogous to that of naturally occurring calcium titanium (IV) oxide (CaTiO$_3$). More generally, they correspond to ionic compounds with an octahedral ABX$_3$ framework where A and B are cations and X are anions. Figure 1.1 illustrates how the octahedra are centered on the B cation and their corners are composed of X anions. The large A cations reside in the spaces between the octahedra. The ability of the A, B and X ions to take nearly any form leads to a great deal of diversity in the composition and properties of perovskite materials.

![Octahedral Perovskite Framework](image1.png)

*Figure 1.1.1—Octahedral Perovskite Framework [1]*

While perovskites have potential applications in transistors [2], light-emitting diodes and even in memory storage [3], the bulk of recent perovskite research has been centered around electro-optics (i.e. interconversion between light and electricity). The tunability of their absorption and emission wavelengths [4] high charge carrier diffusion lengths [5] and facile synthesis are a
few of the characteristics that make perovskite materials so attractive for applications in electro-optics.

Since much of the relevant background information on perovskites originates from that of semiconductors and condensed matter physics, it will be important to address these topics before continuing on. In solids, the orbital overlap of many (~$10^{23}$) atoms or ions lead to continua of electronic states in which electrons reside. A continuum of many states is referred to as a \textit{band}. Characteristic of semiconductors is the \textit{band gap}; a region between two continuous bands, which contains no allowed electronic states [6]. In semiconductors, the highest energy, fully occupied band is known as the \textit{valence band} and lies directly below the band gap. The lowest unoccupied band, which is found directly above the band gap, is known as the \textit{conduction band}. It is useful to think of the band gap as analogous to the highest occupied-lowest unoccupied molecular orbital gap (i.e. the HOMO-LUMO gap) of single molecules or complex ions. During photoexcitation of a semiconductor, an electron is excited from the valence band, into the conduction band, leaving a positively charged quasiparticle in the valence band known as a \textit{hole} ($h^+$) (see Fig. 1.1.2). While still bound by Coulomb attraction, the electron-hole pair are collectively referred to as an \textit{exciton}. Like a hydrogen atom, the exciton has some binding energy due to this attractive force. However, due to dielectric screening of the ionic lattice, the binding energy of the exciton is significantly smaller than that of the hydrogen atom and the average size of the exciton (known as the \textit{exciton radius} or \textit{exciton Bohr radius}) is consequently much larger [7]. Emission of a photon from an excited material occurs upon recombination of an electron-hole pair. The energy of the emitted photon will be less than or equal to the energy of the absorbed photon\textsuperscript{1} since the excited electron will lose some amount of energy as it relaxes to the conduction band edge prior to recombination.

\textsuperscript{1} Except in the special case of up-conversion, which will not be addressed here.
(see Fig. 1.1.2 (b)). The lifetime or diffusion length\(^2\) of the exciton refers to the amount of time spent, or distance traveled by the exciton in the lattice prior to emission. As the charge carriers that make up the exciton travel through the dielectric medium that is the perovskite lattice, they cause lattice distortions due to Coulomb interactions with its composite ions\(^3\). In condensed matter physics, the photoinduced charge carriers, along with the lattice distortion they create as they move through the lattice, are collectively known as a *polaron*. The language outlined in this paragraph will prove important as we attempt to explain photoinduced phase separation in perovskites and how the phenomenon may be affected by pressure.

![Band gap diagram](image)

Figure 1.1.2—Band gap diagram

Figure 1.1.2: (a) Before excitation: incoming photon excites an electron in the valence band into the conduction band, creating a hole (b) Excited electron relaxes to conduction band edge (c) Excited electron relaxes back to valence band and recombines with the hole, resulting in a photoluminescence photon.

---

\(^2\) Also characterized by the terms diffusion volume and carrier mobility.

\(^3\) The interaction of lattice vibrations and a mobile electron is known as electron-phonon coupling. A phonon can be considered analogous to a bond vibration of a molecule in that it is orderly and has a defined energy.
1.2—*Methylammonium Lead Mixed Halide Perovskites*

This investigation will focus on methylammonium lead bromide-iodide mixed perovskite films where ion A is methylammonium, ion B is lead (II) and X are iodide or bromide. Such “mixed halide” perovskites are often denoted by the shorthand: $\text{MAPb(I}_{1-x}\text{Br}_x\text{)}_3$ where $0 \leq x \leq 1$. Note, however, that other halide combinations are also sometimes used. One reason mixed halide perovskites are of particular interest is that controlling $x$ (the relative composition of the material in each halide) allows one to easily tune its absorption and emission wavelengths throughout much of the visible spectrum [4].

At the heart of this investigation is this material’s unique response to light exposure of sufficient intensity: the films reversibly phase separate into iodide- and bromide-rich regions. Bischak et al. estimate the size of the iodide-rich regions to be 8-10 nm in diameter and show that they tend to localize along grain boundaries [3]. Upon discontinuation of light exposure, the material gradually (in the timespan of minutes to a few hours, depending on excitation intensity) regains its initial mixed composition. This phenomenon has been confirmed both spectroscopically and using X-ray diffraction [8]. As a result, charge carriers diffuse to and become trapped in iodide-rich phases, which amount to energetic wells. While undesirable for electro-optical applications, the phenomenon is an interesting avenue for observing halide migration in these materials.

Although a few different mechanisms have been proposed for phase separation in methylammonium lead bromide-iodide perovskites, none have been definitively proven. It is generally agreed upon, however, that facile halide ion mobility, electron-phonon coupling, long-lived charge carriers and crystal defects of the perovskite material are all important factors behind photoinduced phase separation [3].

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4 We will use “MA” to refer to the methylammonium ion, $\text{CH}_3\text{NH}_3^+$. 
The leading explanation for photoinduced phase separation in this material is thermodynamic: phase separation is favored under photoexcitation because an iodide phase has a smaller band gap than the un-mixed phase. While the energy of the conduction band edge is roughly equal in bromide and iodide phases, the energy valence band edge is dictated by the antibonding interactions between the halide $p$ and lead $5s$ orbitals. These antibonding interactions lead to more significant destabilization of the valence band edge in the iodide phase compared to the bromide phase. This can be explained by increased orbital overlap between the iodide $5p$ and the lead $6s$ orbitals than between the bromide $4p$ and lead $6s$ orbitals. It has been argued from multiple perspectives that lowering the band gap brings about a stabilizing effect. Draguta et al. approached this effect via photogenerated holes [9]. They argue that, since the band gap is appreciably smaller in an iodide region, photogenerated holes residing in these regions are stabilized relative to those residing in mixed regions. They also acknowledge the possibility of the diffusion of photogenerated carriers to regions of high iodide density, citing the characteristically large carrier diffusion lengths of the material [9]. Bischak et al. added to this picture by taking into account lattice distortions caused by photoexcitation [3]. Their argument is essentially the same but refers to the stabilization of the polaron rather than the photogenerated hole. They argue that, upon photoexcitation and formation of a polaron, the polaron can begin by migrating to a region of high iodide concentration where it becomes trapped. The stabilization achieved in doing so is equivalent regardless of whether the polaron moves to a region of high iodide concentration, or an iodide ion diffuses towards a trapped polaron. Consequently, nearby iodide ions begin to diffuse toward the trapped polaron, which soon leads to a distinct iodide-rich phase through a self-perpetuating cycle\(^5\) [3]. Fig. 1.2.1 below illustrates the roles of the iodide ion and polaron in the

\(^5\) Although the lifetime of a polaron is likely much shorter than the time required for iodide ion diffusion, the argument still holds since recombined polarons are constantly being replaced by newly photogenerated ones.
photoinduced phase-separation mechanism. Eventually, domain growth becomes limited by the size of the distorted region around the polaron.

![Key Diagram](image)

**Figure 1.2.1**—Polaron and Iodide Ion Diffusion During Photoinduced Phase Separation

Figure 1.2.1: Black lines indicate grain boundaries. Each grain is roughly 1 µm wide. (a) An excitation photon excites an electron into the conduction band, creating a polaron. (b) Iodide ions migrate toward the polaron so as to stabilize it. (c) The electron and hole of the polaron have recombined and an iodide-rich region has formed. (d) Another excitation photon strikes the film in a different location, creating another polaron. (e) This polaron migrates to the pre-existing iodide domain, leading to stabilization.
While polaron mobility is key in the phase separation mechanism, we believe the rate of phase separation is ultimately dependent on halide ion mobility. This mobility depends on the barriers for halide ions to diffuse between lattice sites, as well as on the distance between an occupied and an unoccupied site. Regarding halide mobility, Eames et al. have shown for MAPbI$_3$ that iodide ion diffusion primarily occurs between adjacent octahedral corners via octahedral vacancy sites [10]. On a much larger scale than individual octahedra, Xing et al. have additionally shown that iodide diffusion within MAPbI$_3$ thin films primarily occurs across grain boundaries [11]. Under pressures which are known to be sufficient to appreciably decrease interionic distances [1] (i.e. to cause lattice compression), we reason that iodide ion mobility could be facilitated in our MAPb(I$_{x}$Br$_{1-x}$)$_3$ seeing as the distances between ions and vacancy sites will be shortened. On the other hand, we could reason that compression of the lattice would cause a decrease in the amplitude of photoinduced lattice distortions, thus allowing ions less volume through which they could diffuse. We also predict, due to more intense Coulomb interactions between charge carriers and the perovskite lattice, that polaron mobility will be conversely limited by application of pressure. Additionally, it may also be important to consider the effects of pressure on the distance between individual grains, since iodide diffusion in the thin films primarily occurs between adjacent grains. A decrease in the distance between grains—which we suspect is possible under pressure—might facilitate iodide diffusion and increase the rate of phase separation. If these assumptions hold, the response of the rate of photoinduced phase separation to pressure application could help elucidate the role of iodide ion diffusion in the phase separation mechanism. An increase in the rate with pressure would underscore the importance of vacancy-mediated diffusion, while a decrease in rate would suggest that inter-ionic distances are ultimately more important.
2.0 – Methods

Due to the pre-existing infrastructure in our laboratory, deposition of perovskite films on the inner diameter of small quartz capillaries was the most convenient way of pressurizing them. After film deposition, the capillary was filled with pressure-transmitting fluid, sealed on one end, and adapted to a hydraulic pressure-generating apparatus (see section 2.2) [12]. The capillary was placed under a confocal fluorescence/Raman microscope (Horiba JY Xplora), allowing us to conveniently perform spectroscopic experiments. In brief, our experimental protocol consisted of a sixty-second laser irradiation period during which we recorded the films’ photoluminescence spectra, followed by ten minutes of “darkness” where the films were allowed to recover from photoinduced phase separation. Pressure was increased between successive runs in order to deduce whether phase separation kinetics were dependent upon pressure.

2.1 – Film and Capillary Preparation

The methods described below for the preparation of quartz capillaries were adapted from Tekmen et al. [12]. First, quartz capillaries (Polymicro Technologies, 50 µm inner diameter, 363 µm outer diameter, polyimide coated) were cut to 20 cm length before polyimide coating was removed from the last 5-7 cm of the capillary using a small propane torch. This afforded an optical window through which we could irradiate and observe the films during experimentation. Adaptation of capillaries to the pressure-generating apparatus (see section 2.2) was accomplished by threading the capillaries through small stainless steel “plugs” and fixing them with Armstrong epoxy⁶ (see Fig 2.1.1). These plugs were produced by modifying a plug (produced by High

⁶ Cured at 150°C for five minutes.
Pressure Equipment Co.) which was originally intended to seal the terminals of the HiP apparatus during pressurization. We modified the plugs by shortening them and drilling a 365 µm hole lengthwise through their center (see Fig. 2.1.1. (c)).

![Figure 2.1.1—Experiment-Ready Capillary and Plugs](image)

Figure 2.1.1: (a) Capillary cut to 20 cm with polyimide coating removed from one end before being glued to the plug. (b) A close-up photograph of the plug after a capillary has been glued into it. (c) (Rear) plug before modification, (front) plug after modification.

Once plugs were attached, capillaries were filled by capillary action with perovskite precursor solution to a height of 5-7 cm (from the window end upwards). This precursor solution consisted of a stochiometric mixture of ions in dimethylformamide (DMF) corresponding to MAPb(I\(_{0.5}\)Br\(_{0.5}\))\(_3\). Specifically, 500 µL of dry DMF were added to a vial containing the salts listed in table 1—these were in a 1:1:1:1 molar ratio\(^8\). Preparation of the precursor solution was carried out in ambient atmosphere.

---

\(^7\) The modified plug (front) is covered in an oxide layer. This layer formed when we heated the plugs to 400°C in order to burn away epoxy from previous experiments.

\(^8\) The dimethylformamide as well as all four salts listed in Table 1 were purchased from Sigma-Aldrich (now Millipore Sigma).
<table>
<thead>
<tr>
<th>Salt</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylammonium bromide (MABr)</td>
<td>8.8 mg</td>
</tr>
<tr>
<td>Methylammonium iodide (MAI)</td>
<td>12.2 mg</td>
</tr>
<tr>
<td>Lead (II) bromide (PbBr₂)</td>
<td>27.6 mg</td>
</tr>
<tr>
<td>Lead (II) iodide (PbI₂)</td>
<td>34.6 mg</td>
</tr>
</tbody>
</table>

Table 2.1.1 – Salt Masses Used to Prepare MAPb(I₀.₅Br₀.₅)₃ Precursor Solution

After filling capillaries with precursor solution, they were allowed to incubate overnight (16 – 20 hours) at elevated temperature (65°C) to encourage solvent evaporation⁹. At the conclusion of the incubation period, residual precursor solution was manually removed by applying pressure to the plug end of the capillary with a 1 mL syringe and specially machined adapter that allowed us to make an air-tight connection between syringe and capillary opening (see Fig. 2.1.2). In this step, a small amount of precursor solution evidently adhered to the inner capillary walls rather than being forced out. This small volume would form the perovskite thin film in the following step.

---

⁹ This step was originally intended to cause evaporation of all solvent from the capillaries; however, complete evaporation was found to be very time-consuming and ultimately unnecessary for successful film formation.
We then annealed the entire capillary at 100°C for five minutes in order to form the perovskite phase [2]. Within hours of annealing, capillaries were filled with paraffin oil as a pressure-transmitting fluid. This was accomplished by drawing ~0.2 mL of the oil into the same syringe used for solvent removal and forcing it through the capillary using the syringe adapter. Paraffin was chosen because it remains hydrostatic at and above the pressures reached in our experiment (~500 MPa) [13] and it does not dissolve our perovskite films. At each step, we verified that the capillaries were solvent-free, then completely filled with paraffin oil using a benchtop light microscope.

Finally, the window ends of the capillaries were sealed using a small propane-oxygen torch. This was accomplished by first holding the last ~2 cm of the capillary near the cooler part of the flame to allow a small amount of paraffin oil to burn away. The very tip of the capillary was then slowly brought into the hottest part of the flame and held there for 1-2 seconds. Burning away a small amount of paraffin oil beforehand prevented gas from expanding from inside the capillary.
into the melted quartz at the tip of the capillary and forming a bubble. Such bubbles significantly weakened the capillary, causing it to rupture at relatively low pressure. We verified capillaries were properly sealed using a benchtop light microscope.

Figure 2.1.3 – Capillary Tips Sealed Using a Propane-Oxygen Torch

2.2 – The High-Pressure (HiP) Generator

The pressure-generating apparatus was assembled from parts purchased from High Pressure Equipment Company. It is a relatively simple device consisting of a screw pump filled with pressure-transmitting fluid, which is manually compressed by a piston. Compressing the cylinder body transmits pressure throughout the apparatus and to the component to be pressurized
only when valve B is closed, and valve D is open. The pressure inside the system (and consequently, that being applied to component F) is read out on an analog pressure gauge.

Figure 2.2.1: High Pressure Generator

2.3 – Experimental Procedure

Prior to each experiment, any air bubbles were expelled from the HiP system by fully compressing the HiP cylinder body. During attachment of the capillary to the system via the plug, a small amount of ethanol leakage was allowed to ensure no air bubbles were trapped in the HiP system. We found that capillaries were prone to breakage if an air bubble remained inside the apparatus as pressure was increased. Since capillaries were usually pressurized to destruction, air bubbles would explosively decompress upon breakage; this presented a safety hazard. Proper personal protective equipment and a plexiglass barrier were used to counter this hazard.

The intensity of the 532 nm laser we used for all experiments (~35 mW / cm²) was calculated prior to each experiment after measuring its power output (Thorlabs power meter). After
alignment of the inner diameter of the capillary under the microscope objective, we chose a “spot” on the film by irradiating randomly chosen positions along the capillary with the 532 nm laser until one spot gave strong (or at least discernable) photoluminescence (PL) signal (~$10^2$ – $10^3$ counts per second) (commonly within 600 – 750 nm). Suitable spots were usually easy to find. Once a spot with strong PL intensity was found, that single spot would be observed through the duration of the experimental run. Experimental laser and microscope settings were as follows: 532 nm laser, 0.1 % filter, 500 µm confocal hole, 200 µm slit, spectrum centered at 680 – 720 nm, 600 lines/mm (0.3 nm spectral resolution, > 50 µm spatial resolution), using the 10x microscope objective.

Each pressure experiment consisted of 60 s of laser irradiation and spectrum acquisition, followed by ten-minute dark periods where the film could fully recover from reversible, photoinduced phase separation. During the 60 s of irradiation, PL spectra would be accumulated for 60 consecutive 1-s intervals. Each spectrum was saved automatically. During the dark period immediately following each minute of irradiation, the pressure on the film would be increased by some increment (20 MPa, 50 MPa or 100 MPa with consistent increments among runs of the same experiment). In a few experiments, the pressure was only increased after every other spectroscopic run in order to obtain two runs at each pressure on the same spot. This method allowed us to confirm the repeatability of our results as well as test whether the material completely recovered from phase separation during the ten-minute dark period. This process of collecting spectroscopic data, dark recovery and pressure ramping was repeated until the capillary ruptured (usually between 200 and 500 MPa).
2.4 – Numerical Methods

Our data collection and methods of analysis were based upon the photoluminescence intensity of the iodide-rich regions of our thin films. We reasoned that the total PL intensity of the iodide phase depends on the number of photons originating from iodide-rich domains. This intensity is dependent on both the number and size of these domains or, in short, the total combined volume of the domains. In brief, we calculated the intensity of the PL originating from the iodide phase and plotted this as a function of time for each time series. From each of these plots we extracted an exponential time constant and plotted these as a function of pressure.

Using a Python script, we fit each individual spectrum to the sum of two Gaussians by constraining the peak center of the mixed phase (i.e. peak 1) to a chosen wavelength and allowing the center of the peak corresponding to the iodide phase (i.e. peak 2) to vary. In our time series, peak 1 (~ 650 nm) usually dominated the PL spectrum in the first few seconds before its intensity would fall, and that of peak 2 (~ 740 nm) would quickly grow. Allowing peak 2 to vary was necessary to account for appreciable red shifting that occurred in peak 2 as it grew. A few spectra which demonstrate this fitting strategy are shown in Fig. 2.4.1 below.
Figure 2.4.1 – Peak-Fitting Snapshots

with Peak 1 Fixed at 665 nm (2019-07-01 capillary C at 100 MPa)
With each fit, we calculated normalized peak intensities for both peaks by dividing raw peak area of a given peak by the sum of the areas of the two peaks. This is shown mathematically in Eqn. 1 where \( I_{N,j} \) represents normalized peak intensity of peak \( j \). This technique allowed us to analyze film composition independent of overall PL intensity. These normalized peak areas were then plotted as a function of time for each pressure.

\[
I_{N,j} = \frac{I_{\text{Raw},j}}{I_{\text{Raw},1}+I_{\text{Raw},2}} \quad (j = 1,2)
\]

In addition to peak areas, we also recorded raw peak areas, spectral intensities at wavelengths attributed to the mixed (655 nm) and iodide-rich (755 nm) [14], and peak 2 center as a function of time.

After compiling normalized peak area data as a function of time for each pressure, we extracted mono-exponential time constants from each 60 s time series based on peak 2 area. This was accomplished by plotting \( I - I_{N,2} \) (i.e. one minus normalized peak 2 area) as a function of time, fitting the first 15 s to an exponential decay function and recording the time constant of the fit with its associated uncertainty. We chose to fit each time series as an exponential decay and fit only the first 15 s of each time series for a few reasons. For one, behavior up to this time was far more consistent: nearly every time series we recorded showed an increase in peak 2 area whose growth rate decayed to near zero by about 15 s. Once recorded, mono-exponential time constants were plotted against pressure and a separate plot was made for each experimental run (each experimental run (i.e. time series) representing a different capillary and a single spot on the film contained therein). Alternatively, we could have fit each time series to whatever duration most closely fit a mono-exponential function, but this would have introduced some avoidable bias. We also
attempted to fit some time series to bi-exponential models but found that fit qualities were very inconsistent and that it would be difficult to make meaningful interpretations as to what each term of the fit represented physically.

We checked for the repeatability of our results by comparing time constants of replicate time series (i.e. time series collected by measuring the same spot at the same pressure), and by comparing normalized peak areas point-by-point between replicate timeseries\textsuperscript{10}. The former strategy consisted of simply plotting the time constants of all “A” trials alongside all “B” trials for experiments in which replicate time series were collected. This allowed us to quickly decide whether trials A and B were in agreement for a given pressure and whether repeatability of time constants was at all dependent on pressure. In the latter method, we calculated the percent difference between normalized peak 2 areas of trials A and B at time $t$ by subtracting the trial B value from that of trial A and dividing by the value of trial A. We then computed the average of these percent differences for each time series and plotted them as a function of pressure, using the standard deviation of the percent differences in our error bars.

2.5 – Methylammonium Lead Triiodide Thin Film Controlled Experiment

We conducted a controlled experiment on methylammonium lead triiodide films at ambient pressure to determine the PL behavior of our films without the effects of phase separation. Due to time constraints, these films were prepared on a glass microscope slide rather than inside a capillary. As before, we prepared a 500 µL precursor solution in DMF. The masses of the salts used to prepare the precursor solution are listed in table 2.5.1 below.

\textsuperscript{10} Recall that a few experiments were conducted by taking two replicate, back-to-back trials (i.e. time series) at each pressure before incrementally increasing pressure.
<table>
<thead>
<tr>
<th>Methylammonium iodide (MAI)</th>
<th>23.8 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead (II) iodide (PbI$_2$)</td>
<td>69.1 mg</td>
</tr>
</tbody>
</table>

Table 2.5.1 – Salt Masses Used to Prepare MAPb$_3$ Precursor Solution

Films were prepared by drop-coating 20 mL of this precursor solution onto a 100°C pre-heated glass microscope slide and waiting for a combined total of five minutes for solvent evaporation and annealing.

Once prepared, we followed the same protocol as before, namely: 60 s of laser irradiation with a collection rate of one spectrum per second, followed by ten minutes of dark. All laser and microscope specification were exactly as before (see section 2.3). This procedure was repeated on three different spots on the surface of the film.

From here, we fit the single peak collected in each spectrum to a Gaussian distribution, extracted its center wavelength and converted these into units of electron volts. In order to approximate the band gap energy of the pure iodide phase, we simply calculated the average of these energies.
2.6 – Check for Fluctuations in Laser Intensity

We monitored the intensity of our laser indirectly by irradiating a piece of silicon and monitoring the intensity of the resultant Raman scattering. We followed normal experimental protocol, again, by collecting one spectrum per second during a 60 s laser irradiation period with each irradiation period being followed by ten minutes of darkness. Laser and microscope settings were slightly different than they are outlined in section 2.3. The setting in this experiment were as follows: 532 nm laser, 10 % filter, 500 μm confocal hole, 200 μm slit, spectrum centered at 547 nm, 600 lines/mm monochromator grating (0.3 nm spectral resolution, > 50 μm spatial resolution), using the 10x microscope objective. We repeated this experiment for a total of three trials, where we irradiated the same spot in each of the three trials.

We fit the Raman peak at 547 nm to a Gaussian distribution for each spectrum, then plotted the areas of these fits as a function of time. In order to correct for laser intensity fluctuations in our raw spectra (i.e. before the normalization method outlined in section 2.4) we wished to convert this plot of scattering intensity as a function of time into some factor which reflected any deviation from stable laser intensity. We noted that, after about 20 s in all three trials, the scattering intensity appeared to reach some stable value. Thus, we calculated the average scattering intensity in each time series from 20 s onward, then divided each raw scattering intensity in the time series by this average. This essentially left us with three plots showing the deviation of laser intensity from its long-term stable value, as a function of time. To correct for laser intensity fluctuations, we then simply divided the time series of raw peak intensity by the average of these three plots. Note that we did not correct all raw peak 2 intensity time series: we carried out this procedure on only a single time series in order to compare corrected and uncorrected plots.
3.0 — Results & Discussion

Although we can show that the repeatability of replicate trials—and, in some cases, the repeatability of results across different experiments—is good, much of our results do not suggest a clear relationship between pressure and the initial rate of phase separation. However, we will show and attempt to explain some consistent trends.

3.1 – Effects of Pressure on Initial Phase Separation Time Constants

We can ultimately categorize our experimental results into three groups. Of the eight experiments which produced viable results, three showed an increase in time constant with pressure, two showed a very interesting “V” pattern and the remaining three showed no distinct trend. Plots of the first two of these instances can be found in Fig. 3.1.

The data shown in Fig. 3.1 (a) suggest a linear increase in initial phase separation time constant with pressure, which would imply that external pressure application would slow, or hinder phase separation. From there, we might conclude that, although the average distance between iodide ions and adjacent vacancy sites is smaller under pressure, the decrease in volume available for iodide diffusion in the lattice ultimately outweighs this factor.
Figure 3.1 – Mono-Exponential Time Constants

for Initial Phase Separation Kinetics with Pressure
The distinct “V” pattern depicted in Fig. 3.1 (b), however, suggests there may be more factors at play. These results are especially intriguing in light of the strong agreement between the two experiments in that figure and the small error bars in the datapoints. One interpretation of this “V” pattern is that there are two opposing factors affecting the rate of phase separation and one overtakes the other at the turnaround point near 100 MPa. Although we cannot characterize the morphology of our films inside the capillaries, we argue that, if adjacent grains are not very tightly packed, application of pressure could bring neighboring grains as closely together as possible before beginning to actually decrease inter-atomic distances in the perovskite lattice. As iodide-rich regions tend to form at grain boundaries [3] and iodide diffusion occurs primarily between grain boundaries [11], it reasonably follows that decreasing the distance between grains would accelerate the rate of phase separation due to enhanced iodide ion mobility across grain boundaries. Meanwhile, if the lattice itself is not yet experiencing significant compression, we would expect iodide diffusion within individual grains to be unaffected.

This conceptual model is supported by the results displayed in Fig. 3.2. In this plot we have recorded the energy of the PL peak at the last second of each time series for two pressure experiments (i.e. each datapoint represents the PL peak at 58 s in a given time series). We chose to record PL peak information at the ends of time series because this is when we could expect iodide domains to have reached their maximum volume. Notice that, up until 100 – 150 MPa, the energy of the peak at long times remains more or less constant, and that it begins to sharply increase beyond this pressure window. In other words, the energy of the PL from iodide domains appears to be independent of pressure until we reach that pressure regime. Importantly, this 100 – 150 MPa range roughly agrees with the turnaround pressure observed in Fig. 3.1 (b). Thus, Fig. 3.2 supports our claim that we do not begin to cause lattice compression until we reach this pressure regime.
The conceptual model outlined above accounts for the behavior exhibited in Fig. 3.1. Once grains are forced as close together as possible and lattice compression begins, the increase in rate constant with pressure, again, suggests that the role of vacancy-mediated iodide diffusion is secondary to the hindering effects of the stiffening of the perovskite lattice.

It seems clear that small differences in film preparation are at the heart of the discrepancies between experimental runs. The data shown in Figure 3.1 (b) were taken from two different capillaries, but the films were prepared the same day.

In particular, average grain sizes throughout the films may vary significantly between different preparations. Xing et al. have shown that the barrier for ion diffusion in films is lower for films with smaller grains on average [11]. This is somewhat intuitive seeing as ion diffusion occurs
primarily through grain boundaries, because smaller grains would lead to more surface area across which iodide ions could diffuse. Due to inconsistencies in film preparation, the grain sizes of the films represented by Fig. 3.1 (a) may have been larger on average than those in Fig. 3.1 (b). This would naturally diminish the role of iodide diffusion in the phase separation mechanism under ambient conditions.

3.2 – Experimental Repeatability and Reliability of Results

The checks we made for the repeatability of our results gave us confidence that our results within one sample were reproducible, and that the ten-minute dark recovery time was sufficient for films to undergo complete recovery (i.e. to completely re-mix). Again, we checked for repeatability in two ways: by comparing initial time constants of replicate trials and by comparing replicate trials point-by-point by calculating average percent difference between points across entire time series.

Our comparison of initial time constants of replicate trials showed agreement between trials A and B for most time series (i.e. at each pressure) in all three experiments, and the qualitative observation that agreement between trials is more or less independent of pressure. This helps validate the results presented in Fig. 3.1 because it supports our assumption that the trends exhibited in Fig. 3.1 were the result of changes in the initial rate of phase separation due to pressure application.

Our other means of checking for repeatability lead to a similar conclusion. Fig. 3.4 shows the percent difference between individual data points between two consecutive runs, averaged across the entire time series (i.e. at each pressure). The calculation was based on the normalized peak 2 area of trial B subtracted from that of trial A. Thus, a data marker above zero on the y-axis
indicates that peak 2 area was, on average, greater in trial A than in B. Notice that, for all three experiments, the percent difference is generally positive, but that the absolute value of the average peak 2 area is consistently less than 15% different between trials A and B, and less than 10% for all but two out of the 27 data points. Based on these results, we ultimately do not consider repeatability to be a major concern.

Figure 3.4 – Mean Percent Difference Between Individual Datapoints of Trials A and B

Despite the good repeatability within a sample, there are a number of other important limitations on the reliability of the results as shown in this work. The first major concern among them has to do with capillary preparation. While we were consistently able to produce thin films inside capillaries, we had no way of characterizing them besides PL spectroscopy. For this reason, we must assume that the films we produced did not all possess the same properties (e.g. thickness, grain sizes, porousness, residual solvent content, etc.). Without physical characterization of film
morphology (e.g. using atomic force microscopy, scanning electron microscopy or x-ray diffraction) we ultimately cannot confirm either of the mechanisms proposed above since they rely on our knowledge of the distances between grains and average grain size. One relatively straightforward method for minimizing our uncertainty regarding film morphology would be to characterize the PL and, or absorption behavior of films at several different points along the lengths of multiple capillaries. While this would not provide detailed information on the macroscopic properties of the films, it would at least tell us whether they are consistent over large regions and between different capillaries.

Our tests for fluctuations in laser intensity during 60 s time series using Raman scattering of silicon revealed a consistent and appreciable fluctuation pattern before 20 s. Fig 3.5 depicts the intensity of silicon’s Raman scattering (or, indirectly, the intensity of the laser itself) relative to the value at which it appears to stabilize at 20 s onward.

![Average Correction Factor](image)

**Figure 3.5 – Average Correction Factor for Fluctuations in Laser Intensity with Time**
To correct for the appreciable fluctuations in laser intensity, we divided raw peak 2 intensity in a given time series by the corresponding correction factor as displayed in Fig. 3.5. A comparison of a raw peak 2 intensity time series with its corrected time series can be found in Fig. 3.6.

![Raw and Corrected Timeseries: 2019-07-01 capillary C at 0 MPa](image)

Figure 3.6 – Raw Peak 2 Intensity

Before and After Correcting for Fluctuations in Laser Intensity

The comparison in Fig. 3.6 shows that the PL behavior of the film naturally counteracted the effects of the fluctuations in laser intensity such that the resulting plot (black) appeared smoother. Our method of normalization completely smoothed out the feature at ~15 s shown in Fig. 3.6 because it reframed PL intensity of a given peak relative to the sum of the intensities of peaks 1 and 2. While this appeared to isolate the behavior of the laser from the films themselves, it weakens the reliability of our results overall because we cannot safely assume that even our normalized results were not unaffected by this appreciable fluctuation in laser intensity.
A third limitation we found in our experimental procedure was the fact that capillaries typically ruptured around 200 MPa, preventing us from collecting data beyond this pressure. We also found—especially at pressures less than ~ 100 MPa—that phase separation kinetics may not have been reliably captured by our one spectrum per second time resolution. Increasing the number of spectra collected per second—at least in the first 15 s of each time series—would boost the confidence we have in our initial time constants.

Finally, we have no certainty that pressure was being applied uniformly along the inner length of the capillaries. This could explain the starkly different trends illustrated in the different plots of Fig. 3.1: the films spots represented by these plots may not have been experiencing the pressure displayed on our pressure gauge. Non-uniform pressure application could be the result of capillaries becoming clogged with dislodged film, dust particles or perhaps small glass shards broken from the tip of the plug end of the capillary. Although not practical with our current experimental setup, one could check for non-uniform pressure application by conducting parallel spectroscopic experiments on different spots of the same capillary and check whether the results would be in agreement.

3.3 – Further Investigation

The results discussed here lead to several more avenues for further investigation. The most intuitive next step would be to attempt these experiments using a diamond anvil cell (DAC) as an alternate means of pressure application. The DAC would allow us to apply higher pressures while giving us more confidence that pressure is being applied uniformly. More importantly, however, it may be easier to both prepare and characterize our thin films with this approach. We could also conduct a similar investigation using a nanosecond-pulsed light source. This may allow us to
observe our films without causing photoinduced phase separation, which would afford the opportunity to capture the kinetics of re-mixing after termination of continuous wave excitation. Finally, as an interesting exercise, we could attempt to correlate the PL peak center of the iodide phase with the size of phase-separated iodide domains by modeling these as quantum dots (QDs). This study could help elucidate the physical meaning of the PL peak centers and could potentially offer us a convenient way of measuring the sizes of our iodide domains.

As an example, we will show how the PL energy of peak 2 as a function of time can be mapped onto the size of a QD. The band gap of a QD will depend on the band gap of the bulk material, as well as some confining potential which scales with the size of the QD. Buin et al. have found, for MAPbI$_3$ QDs that this energy can be approximated by [15]:

$$E_g = E_g^{bulk} + \frac{b}{r^2}$$  \hspace{1cm} (2)

Where $b \approx 100 \text{ eV} \cdot \text{Å}^2$ and $r$ is the radius of the QD. The constant $b$ approximates the confining potential for MAPbI$_3$ specifically. From our controlled experiment on drop coated MAPbI$_3$ films at ambient pressure, we determined the average PL energy of the pure iodide phase to be 1.621 eV. Using this value for $E_g^{bulk}$, we calculated a QD size from the experimental PL energy at every second for the July 1$^{st}$ capillary C time series at 0 MPa. The PL peak energy and mapped QD diameter for this time series are plotted in Fig. 3.7 below. Notice that the 8 – 10 nm iodide domain size proposed by Bischak et al. is in good agreement with our calculated results [2].
Fig. 3.7 – PL Peak Energy and PL Peak Energy Mapped onto Quantum Dot Size During Laser Irradiation (35 mW / cm^2, 532 nm)
Conclusion

The results shown in Fig 3.1 depict two distinct phenomena: one in which the initial rate of phase separation decreases with pressure and one in which it increases up to ~ 100 MPa before decreasing. From these observations, we postulate that there may be a pressure window in which individual grains are being forced closer together which precedes the pressure domain where the perovskite lattice itself experiences compression. Small differences in sample preparation that lead to variation in the distances between grains or the average grain size could explain these differing results. If our conceptual model is correct, it would suggest that the stiffening of the perovskite lattice as a result of pressure application ultimately leads to a decrease in the rate of photoinduced phase separation despite the prediction that vacancy-mediated iodide diffusion would be facilitated under these conditions. However, without accurate knowledge of the average distance between grains or grains sizes of our films, it is impossible to confirm this interpretation of the results shown in Figs. 3.1 (a) and (b). Our conclusions are also limited by the finding that the intensity of our excitation laser underwent appreciable fluctuations in the first ~ 15 s after being switched on. Although we cannot make definitive claims from these results, they pave the way for future high-pressure experiments on this material by suggesting the rate phase separation is affected by pressure and by providing starting points for further inquiry.
References


