

http://pubs.acs.org/journal/aelccp

Domain Size, Temperature, and Time Dependence of Photodegradation in MAPbl₃ Probed by Raman Spectroscopy

Jose F. Castaneda, Jeong-Hyeok Im, Yucheng Liu, Shengzhong Liu, Nam-Gyu Park,* and Yong Zhang*



polycrystalline films, proceeding one-dimensionally inward from the surface. These results suggest that the surface acts as a location for photogenerated carrier accumulation, leading to degradation and PbI₂ formation.

nderstanding the photodegradation process and mechanisms is pivotal for halide perovskites to be practical, high-efficiency, and low-cost photovoltaic materials. A material's vibrational properties are sensitive to subtle structural changes, such as strain, temperature, and light illumination. Raman spectroscopy is widely used to probe the effects of such perturbations, often with a well-defined baseline spectrum established first to serve as the intrinsic reference. However, Raman scattering efficiency or cross-section¹ and photodegradation threshold² from one material to another can vary many orders in magnitude, making this first step not trivial for some materials. This was the case for $MAPbI_3$ (MA = methylammonium) a few years ago_1^2 after it gathered attention for its extraordinary potential in photovoltaics.³ Early attempts to measure its Raman spectrum at room temperature showed multiple Raman active vibrations in approximately 50-120 cm⁻¹ with varying degrees of resolvability.⁴⁻⁹ This spectral range coincides with well-known PbI₂ signatures,¹⁰⁻¹⁴ raising the question of if the observed Raman signals were expected from the inorganic backbone structure consisting of lead and iodine or simply from remnants of a secondary phase of PbI₂ present or forming from degradation.

In 2015, it had become evident that the material could change rapidly, often with PbI_2 remaining under external stimuli such as light excitation and heating.^{2,6–8} It was first pointed out in 2016 that a pristine MAPbI₃ Raman spectrum in its room temperature tetragonal phase exhibited practically no

resolvable Raman features within the above-mentioned spectral range.² However, the Raman spectra of these pristine samples were partially obscured by broad emission from photoluminescence (PL) stray light,¹⁵ because of the much stronger PL signal of MAPbI₃ that can surpass even the best conventional semiconductors such as CdTe and GaAs under low-excitation conditions.¹⁶ Conflicting results for the intrinsic Raman spectrum of MAPbI3 in the low-frequency region (below 300 cm^{-1}) persist in the literature, ranging from a few barely resolved broad bands to multiple well-resolved peaks.¹⁷⁻²² Except for the cases where the observed Raman modes are close to those well-known for PbI₂, typically, the reported spectra exhibit poor repeatability in the literature,^{2,17} especially in the resonance regime with above bandgap excitation, including the effects of both photocarrier generation and potential laser-induced heating. However, calculated Raman spectra for MAPbI₃ seem to exhibit well-resolved spectral features.^{22–24}

The surface chemistry of grain boundaries in $MAPbI_3$ polycrystalline films was found to play an essential role in

Received: July 18, 2022 Accepted: August 26, 2022





Figure 1. (a) 0.8 kW/cm² spectra of polycrystalline films. (b) 95 cm⁻¹ intensity change with excitation power with slopes indicated (inset: expanded low power region). (c) High-power spectra of 1.4 μ m and (d) 0.4 μ m films.

device characteristics (e.g., hysteresis).²⁵ "Impurity phases" located more frequently at grain boundaries are initiators of photodegradation.²⁶ However, the physical parameters of these materials, such as domain size, are often not given adequate attention for their role in photostability. Photo and thermal instability coupled with the low thermal conductivity²⁷ for the material has made it challenging to obtain the intrinsic Raman spectrum of MAPbI₃ without rapid degradation under photoexcitation. Lack of control in the physical parameters likely also contributes to the uncertainty arising from various reported synthesis techniques and methods. Accurate information is pertinent for understanding the degradation mechanism and providing a benchmark for theoretically modeling this highly unusual disordered system. This work attempts to first determine the intrinsic Raman spectrum of pristine tetragonal MAPbI₃ at room temperature and then monitor the degradation process. We compare polycrystalline films of varying domain sizes with a single crystal and monitor the structural changes with variable illumination time, excitation power, and temperature of the material. It is seen that under the same excitation level, the domain size directly affects the obtained spectrum. Surface defects or their formation are seen, and increased PbI₂ transformation with decreasing physical dimension occurs. In the case of the single crystal, an additional temperature change by heating into the cubic phase is needed to induce photodegradation under a similar excitation level, showing the role of defects related to the surface or grain boundaries in the Raman spectra of the polycrystalline films.

Averaged Raman spectra for polycrystalline films were obtained from a 10 s 532 nm illumination on 121 locations with a $\sim 1 \ \mu m$ excitation spot to minimize the long-term exposure to a single site and inhomogeneity effects. These averaged spectra are further normalized at the smallest wavenumber to emphasize the relative intensity variations at the spectral features of interest. Figure 1a shows averaged Raman spectra obtained under relatively low excitation power

(0.8 kW/cm²) for a set of films with average domain sizes of 0.4, 0.9, and 1.4 μ m as determined by SEM (Figure S1). Seen are two broad bands, as reported in other work, under resonance²⁸ and nonresonance excitation,¹⁹ where one is thought to involve the Pb–I stretching modes (~100 cm⁻¹) and the other the torsion mode (~250 cm⁻¹) of the MA ion.⁴ It is seen that these spectra appear almost identical at this low excitation power density and overlap throughout the observed spectral range, except for a feeble difference about the ~100 cm⁻¹ broad band. The 1.4 μ m domain film measured here has a slightly reduced intensity in this region. Different spectra between different domain sizes have been reported in the literature, but their variations were far more significant, with several additional Raman peaks at 119 cm⁻¹ and one ranging from 150 to 160 cm^{-1.5}

The main degradation product PbI₂ has spectral features that can occur at 95 and 110 cm⁻¹, and through their monitoring, insight can be gained into the transformation process of the structure under photoexcitation. Figure 1b shows the signal changes at 95 cm⁻¹ with increased excitation power density between the three domain sizes. There are two regimes of signal intensity change. A slow increase in the lowpower regime from 0.8 to 8 kW/cm² occurs before it approaches a saturated value with slightly higher values for the smaller domain films, as seen in the inset of Figure 1b. In the high-power regime above 8 kW/cm², a stability threshold seems to have been surpassed as the 95 cm⁻¹ region grows again and appears linear with increasing excitation power. The two smaller domain films demonstrate $\sim 3 \times (0.4 \,\mu\text{m}, \text{triangles})$ and $\sim 2 \times (0.9 \ \mu \text{m}, \text{squares})$ the growth rate of the 1.4 μm film (circles). The appearance of the 95 and 110 cm^{-1} peaks of PbI₂ is shown in Figure 1c,d for the 1.4 and 0.4 μ m films, respectively. Along with the growth of these prominent PbI₂ peaks, other vibrational modes also arise in the smaller domain films at 70, 160, and 220 cm⁻¹ (Figure 1d, Figure S2), the approximate positions of additional Raman modes of PbI₂,



Figure 2. (a) Continuous illumination on single crystal and comparison with polycrystalline thin films. (b) Temperature-dependent Raman spectra of a single crystal. (c) Power-dependent spectral changes of single crystal and (d) 95 cm⁻¹ intensity change with excitation power (inset: expanded lower power region).

indicating increased overall change and extensive PbI_2 formation with increased excitation power.

Differences between the domain sizes arise primarily near the $\sim 100 \text{ cm}^{-1}$ broad band throughout the 0.8–21 kW/cm² power range. Despite the different influence of the domain size within the low and high-power regions, the 95 cm^{-1} signal increases as the domain size decreases. Films measured here are synthesized by the same method,²⁹ with their main difference being the final domain size, resulting in different concentrations of domains probed within the $\sim 1 \ \mu m$ excitation beam (0.90 NA 100× objective lens). The excitation spot size is smaller than the average domain size of the 1.4 μ m film, but several domains may be illuminated in the case of the smaller sizes. Due to these smaller sizes, more domains will be measured. Thus, a more surface-like environment results in an increased number of grain boundaries and more photoreactive defects than the bulk of the material. Increased surface defects and grain boundaries also imply more sites for the intercalation of H_2O^{28} and O_2^{30} and known locations for charge carrier trapping and accumulation under photoexcitation. $\tilde{3}^{1-34}$ All could lead to increased degradation rates in the smaller domain films. Alternatively, smaller domains could reduce thermal conductivity, leading to less-efficient heat dissipation from laser illumination. However, it has been suggested that the ultralow thermal conductivities²⁷ of these materials do not differ much from the intrinsic bulk value until below 100 nm.³⁵ If thermal conductivity differences dominated the photodegradation variations, the shared threshold between the low and highpower regions would likely not arise. The fact that the 95 cm⁻¹ signal scales linearly with excitation power in the high-power region further suggests that photoexcitation plays a more significant role, with the differences in linear rates between the domain sizes arising from the different contributions of the surface being probed that are likely trapping and accumulating photoexcited charge carriers. PL lineshapes in MAPbI₃ demonstrate that photoexcited carriers do not follow typical

carrier thermalization as they tend to be more symmetric due to disorder and contributions from inhomogeneous independent regions.¹⁶ Increased contributions from the more defective surface can further affect obtained PL properties with blueshifts,²⁸ as seen with obtained PL spectra under 0.8 kW/ cm² excitation (Figure S3) and reported to reduce lifetimes,^{28,32} suggesting increased contributions from photoexcited carriers on or near the surface as the domain size decreases.

Further inspecting the effects of the surface, a large single crystal was measured at a slightly reduced temperature of 20 °C under nitrogen. This crystal was cleaved to expose a region of the bulk as the new surface to probe, which could be considered pristine. The Raman spectrum on the same site of this cleaved surface was monitored under continuous 2.5 s integration at 10.5 kW/cm². Figure 2a shows averaged spectra from this continuous monitoring within three periods (0-300)s, 500-800 s, and 1100-1400 s). In the first 300 s (dark blue), compared with spectra from the largest (blue) and smallest (red) domain films collected at a lower excitation density of 5.0 kW/cm², it is seen that the features were reduced in intensity within this spectral range with the ~ 100 and ~ 250 cm⁻¹ broad bands suppressed. A similar trend was reported when the Raman spectrum of a crystal face center was compared to the same crystal's more defective edge.²⁸ Nevertheless, prolonged exposure to the excitation beam progressively enhances the signal near ~ 110 cm⁻¹, accompanied by a ~ 160 cm⁻¹ band (green and orange traces in Figure 2a). Peaks within this $100-200 \text{ cm}^{-1}$ region have been suggested to be related to the libration modes of the MA ion.^{4,17} However, they have also been reported to be related to defects with the possibility of oxygen incorporation, which was found in films deposited on substrates with varying properties.³⁰ In another study involving long-term excitation of polycrystalline films, it was also seen that these peaks arise later under illumination and were attributed to an I_x phase.¹⁷



Figure 3. (a) Early spectral changes under continuous illumination at 8 kW/cm² for 0.9 μ m domain size film; (b) 95 cm⁻¹ intensity over time for all domain sizes.

Exposure to high excitation also resulted in similar peaks for $MAPbI_3$ and other structures within the inorganic–organic perovskite family.³⁶ Also, polyiodides used to synthesize hybrid perovskites reported similar peaks.³⁷ These peaks only appear after a longer illumination time (Figure 2a), indicating that we may attribute them to defect formation resulting in an iodine-related species, most likely I₂ or I₃. An accumulation of iodine-related species on the surface under photoexcitation is thought to occur, leading to additional defect formation with eventual saturation and PbI₂ formation.³² A similar conclusion was made recently where two types of iodine-related defects were found in metal halide perovskite solar cells under bias and illumination.³³ We may consider this stage as a mild form of structural degradation.²

The formation of PbI₂, however, is not seen until higher temperatures or longer heating times are applied. In Figure 2b, spectra collected from 24 to 50 °C, each over 600 s, are identical, suggesting that heating is not the direct cause for PbI₂ formation under these excitation conditions. However, once 60 °C is reached, features of PbI₂ become very prominent, producing a spectrum like that seen in the small domain film (0.4 μ m) at 21 kW/cm² in Figure 1d. This temperature is above the tetragonal to cubic phase transition, around 54 °C.³⁸ In this phase, it is suggested that the MA ion is less tightly bound due to the weakening of the hydrogen bonds that keep the molecule within the cavity of the inorganic backbone structure. These results suggest that above the cubic phase transition, even the relatively more stable single crystal structure becomes less stable under photoexcitation, possibly facilitating ion migration and eventual structural collapse. Such combined heating and photoexcitation effects have also affected degradation in solar cell devices.³⁹ Power-dependent spectra under ambient conditions demonstrate that the 95 cm⁻¹ signal is relatively constant until 11.7 kW/cm² (inset of Figure 2d) due to increasing signal at \sim 110 and \sim 160 cm⁻¹ (green curve in Figure 2c) and at the higher excitation power of 13.9 kW/cm² PbI₂ readily occurs as shown in spectra from Figure 2c and the dramatic increase in the 95 cm⁻¹ intensity (Figure 2d). Along with peaks for PbI_2 , an increased ~165 cm⁻¹ intensity is present, suggesting the increasing formation of iodine-related species as this peak is shared along with the \sim 110 cm⁻¹ region with varying excitation power. This finding is consistent with the understanding that MAPbI₃, despite having negative formation energy of the order of 0.1 eV (i.e., thermodynamically unstable),⁴⁰ a small kinetic barrier helps stabilize the structure in a relatively low-temperature range, which has led to developments in compositional engineering toward more stable materials.⁴¹ Such barrier may arise from the energy required for ion and defect migration that is also on

the order of 0.1 eV for MAPbI₃.⁴² Therefore, a composition resulting in more considerable formation energy is desirable as seen for an II–VI based organic–inorganic hybrid, ZnTe- $(en)_{0.5}$, demonstrating a much higher temperature and longer-term stability due to its sizable formation energy and kinetic barrier.^{42,43}

In the low-power regime, spectra among the polycrystalline films vary to a small degree, mainly about the $\sim 100 \text{ cm}^{-1}$ broad band. However, PbI₂ forms linearly with excitation power in the high-power regime but at different rates. The smallest domain (0.4 μ m) film showed the highest PbI₂ formation rate, while the largest domain (1.4 μ m) film was the lowest in Figure 1b. To gather more insight into these domain size-related differences, the transformation process was monitored over time at 8 kW/cm², the excitation power close to the stability threshold seen in Figure 1b. Spectral changes are taken from the average of 9 locations for each domain size, with the 95 $\rm cm^{-1}$ signal intensity used as the marker for PbI₂. Figure 3a shows several spectra collected initially within the transformation for the 0.9 μ m film, clearly showing the growth of 70, 95, 110, 160, and 220 cm⁻¹ peaks. These features indicate PbI₂ formation and agree with the power-dependent results in Figure 1. Figure 3b also shows that the 95 cm⁻¹ intensity again differs between the three domain sizes with a similar trend: as the domain size decreases, PbI₂ forms more rapidly. The growth begins slowly before increasing, then falling again and plateauing as the reaction ends, producing a sigmoidal shape. This sigmoidal shape, increasing transformation rate that reaches a maximum followed by slowing as the reaction comes to completion (Figure S4), resembles Avrami kinetics.44-48

The Avrami model is used to describe the nucleation and growth of a new phase by

$$\alpha = 1 - \exp^{-kt^n} \tag{1}$$

where α is the transformed fraction, k is the effective reaction rate, and n is a parameter reflecting the new phase's variable nucleation rate and growth dimensions under isothermal conditions. Avrami kinetics have already been used to describe several processes for inorganic—organic halide perovskites, such as the formation and crystallization of the perovskite phase^{45,46} and its degradation in constructed solar cells,⁴⁷ exposure to the ambient environment,⁴⁸ as well as to X-ray irradiation.⁴⁹ It is first customary to transform the signal (95 cm⁻¹ intensity) into an α value determined by the starting initial value (S_0), value at time t (S_t), and the final value (S_f) at the end of the process as shown in (2).



Figure 4. (a) Transformation fraction over time. (b) Avrami Plot for all three domains. (c) Reduced-Time Plot. (d) Local n changes over time.

$$\alpha = \frac{S_0 - S_t}{S_0 - S_f} \tag{2}$$

Equation 1 can also be rearranged to produce

$$\ln(-\ln(1-\alpha)) = n\ln(t) + \ln(k) \tag{3}$$

allowing determination of k and n by plotting the relationship between $\ln(-\ln(1-\alpha))$ and $\ln(t)$.⁵⁰ Figure 4a and 4b use eqs 1 and 3 to determine k and n_i , where long times have been removed due to increased noise after the reaction completion. In Figure 4a, α increases more rapidly over time as the domain size decreases, and from fitting to eq 1, two trends are seen where the reaction rate k increases (blue) and n decreases (red) with decreasing domain size. In the Avrami plot, Figure 4b, formed by $\ln(-\ln(1-\alpha))$ vs $\ln(t)$, the *k* and *n* parameters are determined from the slope of this relationship. It can be seen the relationship is not ideally linear, indicating that the nparameters are not constant throughout the transformation process. Linear fits, however, have been applied to determine kand n for comparison with those in Figure 4a. Their values are somewhat different, but the trends as the domain size decreases are qualitatively similar.

The Avrami parameter *n* alludes to mechanistic information such as whether the nucleation rate is constant or already saturated when the transformation occurs, and embedded within this parameter is also how the new phase nuclei grow in spatial dimensions such as in 1D, 2D, or 3D.⁵¹ The fluctuation and decrease of *n* indicate that the transformation mechanism is not constant over time. The new phase growth is further restricted in spatial dimension with a decreasing domain size. In Figure 4c, the transformation curves from Figure 4a are normalized in time to produce reduced-time (t/t_{α}) plots, where time is scaled by the time where α is ~0.99, for comparison along with theoretical curves calculated using the methods of Różycki and Maciejewski.⁵² Such plots remove the differences between reaction rates and allow for comparison on the same time scale, confirming that the transformation mechanism is different among the three domains and appears to lie between the theoretical n = 2 (blue) and n = 2.5 (red) curves. If the mechanism were the same, these curves would have overlapped.

Fluctuating *n* values have been a discussion within the literature. Several reports indicate that they arise due to the breakdown of assumptions within the Avrami model when applied to thin films or finite domains.^{53,54} Pang et al. have shown computationally how *n* is affected as a function of the film thickness over time, monitoring what is called the local *n* throughout the transformation by eq 4.⁵³

$$\operatorname{local} n = \frac{d\ln[-\ln(1-\alpha)]}{d\ln(t)}$$
(4)

Surface nucleation beginning on one side of the film showed local n reduction as nuclei growth approached the opposite interface at small dimensions. The local n would decrease at larger dimensions as well, however, before eventually following 1D growth. This can be visualized as growing nuclei exhausting all available space laterally to each other before reaching the opposite interface and would form a plane that can only grow in one direction. This 1D plane growth was realized as a sharp increase in the local n at higher transformation fractions or later times. Figure 4d shows the local n for the three domain sizes versus ln(t). What is apparent is the decrease in the local n over time for all three domains before it increases dramatically, suggesting 1D growth is eventually reached during the reaction, and this process occurs earlier with smaller dimensions. Conceptually, this can be described by PbI₂ nuclei forming from the surface and growing in various dimensions before meeting each other and extending in the only available space in one direction. As for the exact interpretation of these local n values, it is not easy to provide a detailed picture as additional measurements would be needed. However, qualitative trends could be alluded to by this analysis, such as the difference in the local *n* at early times in Figure 4d. Initially, the larger 1.4 μ m domain has a local *n* above 4, while the smaller

domains are closer to 3. An increased local *n* could indicate more nonuniform nucleation as nuclei are more sparsely distributed over the surface. As a result, the local *n* is inflated as it grows faster than predicted.⁵³ This interpretation is qualitatively in agreement as less of the surface is measured in the largest 1.4 μ m domain film.

Even though moisture can induce degradation, more slowly,⁵⁵ polycrystalline films measured under ambient conditions did not form PbI2 until an excitation power threshold was surpassed, regardless of its domain size. Below this threshold, the Raman signal at 95 cm⁻¹ increased following a negative exponential function due to a more defective or disrupted structure forming at the surface. In the single crystal, instead of changes at 95 cm⁻¹, defect-related iodide species resulted in Raman peaks at \sim 110 and \sim 160 cm⁻¹ from longterm illumination at somewhat higher excitation density. These results indicate how the synthesis method affects the material structure and photodegradation process. Such variations in synthesis methods have already been shown to affect the trap properties in solar cell devices.³⁴ Udalova et al. also witnessed PbI₂ appearing readily within thin films under photoexcitation, but in the case of powder samples, iodine and polyiodide species had increased generation along with PbI₂.³⁶ However, thin films have also displayed these similar peaks,^{5,56} perhaps further indicating that different thin-film fabrication methods may result in different spectra from differences in surface and grain structures that lead to different relative concentrations of photodegradation products. One such possibility could be the precursor molar ratio used during synthesis. Son et al. showed that an MAI layer formed at the grain boundaries even with a 6% mole excess of MAI precursor.⁵⁷ This layer could provide the conditions for increased iodine and polyiodide-generated species in thin films. Ni et al. have also shown that I_i^+ defects are more prevalent with increasing MAI precursors during synthesis, which upon electron capture (I_i^0) , can participate toward $2I_1^0 \rightarrow I_2$ and irreversible degradation.³³ Polycrystalline films in this study were synthesized by the two-step method and were unlikely to result in MAI excess conditions. For this reason, iodine-related species were not seen or are not as abundant to be detected readily.

The polycrystalline films and the single crystal formed PbI₂ only once a threshold was surpassed. In the thin films above 8 kW/cm^2 , PbI₂ growth scaled linearly with excitation power. At the same time, initially, iodine-related species form under illumination in the large single crystal. Still, higher excitation was needed to induce PbI₂ formation, or a combination of additional heating into the cubic phase was required when the excitation density was below the threshold. Both results suggest that photocarrier generation and heating can affect the degradation process. Charge carriers have been reported to induce photostriction effects, which are proportional to illumination intensity, that expand the lattice due to the reduction of the hydrogen bonding strength of MA with the inorganic backbone structure⁵⁸ and have also been reported to reduce the activation energy of ion migration, further accelerating degradation.⁵⁹ The linear growth of PbI₂ with high-power excitation likely arises from increased charge carrier concentrations. Considering the presented results, we suggest that the role of the domain size and ultimately the surface acts as a method of escape for MA and iodine-related species and acts as a boundary that increases the effective concentration of charges as localization and trapping can occur.³¹ The increased charge carrier concentration at the

surface facilitates ion migration, ultimately creating a more defective and distorted structure. As defective regions grow, they eventually pass a threshold where they begin interacting with each other, resembling a percolation process, forming PbI₂. This is one reason why, even at the comparable threshold power used for the single crystal, PbI₂ is only seen after an intentional cubic phase transition as a higher threshold occurs due to the reduced surface and defective regions. MA is less tightly bound in the cubic phase due to reduced hydrogen bonding and is more mobile, thus facilitating the creation of defects. Degradation of the MAPbI3 domain surface was monitored under ambient conditions in an air-conditioned lab with relatively low humidity, without any surface protection or encapsulation. Other studies under different environments (e.g., N_{2} , varying levels of moisture), with or without surface encapsulation, and with partial or complete substitution of MA with other options that are commonly used (e.g., formamidinium (FA) and cesium (Cs)) would be of great interest. Also, the role photogenerated charge carriers have on the MAPbI₃ domain surface further suggests that other perturbations like the electric field from an applied voltage should also be considered in completed devices.

EXPERIMENTAL METHODS

MAPbI₃ polycrystalline films and single crystals were received under a vacuum, stored in a vacuum desiccator to reduce humidity-induced effects, and kept in the dark. Briefly, films were synthesized by a previously reported method²⁹ where the MAPbI₃ layer was formed by two-step deposition with a varying CH₃NH₃I concentration solution deposited onto a dried PbI₂ film. The variable CH₃NH₃I concentration resulted in polycrystalline films with different domain sizes after 100 °C annealing with average domain sizes determined by micrographs obtained with a JEOL SEM w/EDAX. Single crystals of millimeter size were grown by a seed-induced method that has also been reported previously.⁶⁰

Optical characterization involving Raman and photoluminescence measurements were conducted on a Horiba LabRAM HR800 confocal Raman microscope with a 1200 g/ mm grating and hole sizes of 100 and 70 μ m, respectively. An additional 650 nm shortpass filter was placed before the confocal hole to eliminate stray photoluminescence light for Raman spectra collection. A 532 nm laser source was focused on polycrystalline films and single crystals by $100 \times (NA = 0.9)$ or long-working distance $50 \times (NA = 0.5)$ lenses. The source operation current controlled the laser power with excitation densities estimated as D = P/A, where P is the laser power and A the area of the diffraction-limited spot size $1.22(\lambda_{ex}/NA)$. Under ambient or flowing nitrogen conditions, characterization under applied heating was conducted within a Linkam Model TS1500 heating chamber. This heating chamber incorporates a quartz window for simple coupling of laser excitation, and the power measured is that after passing through this quartz window; however, the effective power density may be slightly lower than reported due to possible distortions of the focused laser spot. Flowing water cools this chamber during measurements, and the applied temperature was held for 2 min before measurement.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.2c01640.

SEM micrographs, additional high-power Raman spectra, PL spectra, and transformation rate changes for polycrystalline films (PDF)

AUTHOR INFORMATION

Corresponding Authors

Yong Zhang – Nanoscale Science, The University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States; Department of Electrical and Computer Engineering, The University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States;
orcid.org/0000-0003-4781-1583; Email: yong.zhang@ uncc.edu

Nam-Gyu Park – School of Chemical Engineering and Center for Antibonding Regulated Crystals, Sungkyunkwan University, Suwon 16419, Republic of Korea; SKKU Institute of Energy Science & Technology (SIEST), Sungkyunkwan University, Suwon 16419, Republic of Korea; orcid.org/ 0000-0003-2368-6300; Email: npark@skku.edu

Authors

- Jose F. Castaneda Nanoscale Science, The University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States
- Jeong-Hyeok Im School of Chemical Engineering and Center for Antibonding Regulated Crystals, Sungkyunkwan University, Suwon 16419, Republic of Korea
- Yucheng Liu Key Laboratory of Applied Surface and Colloid Chemistry, National Ministry of Education, Institute for Advanced Energy Materials, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710062, China
- Shengzhong Liu Key Laboratory of Applied Surface and Colloid Chemistry, National Ministry of Education, Institute for Advanced Energy Materials, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710062, China; ◎ orcid.org/0000-0002-6338-852X

Complete contact information is available at:

https://pubs.acs.org/10.1021/acsenergylett.2c01640

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work at UNCC was supported by the University of North Carolina's Research Opportunities Initiative (UNC ROI) through the Center of Hybrid Materials Enabled Electronic Technology; at SKKU by the National Research Foundation of Korea (NRF) grants funded by the Korean government (MSIT) under contract NRF-2021R1A3B1076723 (Research Leader Program); and at SNU by National Key Research and Development Program of China (2017YFA0204800), the National Natural Science Foundation of China (91733301).

REFERENCES

(1) Cardona, M. Resonance phenomena. In *Light Scattering in Solids II*; Cardona, M., Güntherodt, G., Eds.; Springer Berlin Heidelberg, 1982; p 19.

(2) Chen, Q.; Liu, H.; Kim, H.-S.; Liu, Y.; Yang, M.; Yue, N.; Ren, G.; Zhu, K.; Liu, S.; Park, N.-G.; et al. Multiple-Stage Structure Transformation of Organic-Inorganic Hybrid Perovskite CH3NH3PbI3. *Phys. Rev. X* 2016, 6 (3), 031042.

(3) Kim, H. S.; Lee, C. R.; Im, J. H.; Lee, K. B.; Moehl, T.; Marchioro, A.; Moon, S. J.; Humphry-Baker, R.; Yum, J. H.; Moser, J. E.; et al. Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. *Sci. Rep.* **2012**, *2* (1), 591.

(4) Quarti, C.; Grancini, G.; Mosconi, E.; Bruno, P.; Ball, J. M.; Lee, M. M.; Snaith, H. J.; Petrozza, A.; De Angelis, F. The Raman Spectrum of the CH3NH3PbI3 Hybrid Perovskite: Interplay of Theory and Experiment. J. Phys. Chem. Lett. **2014**, 5 (2), 279–284.

(5) Grancini, G.; Marras, S.; Prato, M.; Giannini, C.; Quarti, C.; De Angelis, F.; De Bastiani, M.; Eperon, G. E.; Snaith, H. J.; Manna, L.; et al. The Impact of the Crystallization Processes on the Structural and Optical Properties of Hybrid Perovskite Films for Photovoltaics. *J. Phys. Chem. Lett.* **2014**, 5 (21), 3836–3842.

(6) Ledinsky, M.; Loper, P.; Niesen, B.; Holovsky, J.; Moon, S. J.; Yum, J. H.; De Wolf, S.; Fejfar, A.; Ballif, C. Raman Spectroscopy of Organic-Inorganic Halide Perovskites. *J. Phys. Chem. Lett.* **2015**, *6* (3), 401–406.

(7) Gottesman, R.; Gouda, L.; Kalanoor, B. S.; Haltzi, E.; Tirosh, S.; Rosh-Hodesh, E.; Tischler, Y.; Zaban, A.; Quarti, C.; Mosconi, E.; et al. Photoinduced Reversible Structural Transformations in Free-Standing CH3NH3PbI3 Perovskite Films. *J. Phys. Chem. Lett.* **2015**, 6 (12), 2332–2338.

(8) Park, B. W.; Jain, S. M.; Zhang, X.; Hagfeldt, A.; Boschloo, G.; Edvinsson, T. Resonance Raman and Excitation Energy Dependent Charge Transfer Mechanism in Halide-Substituted Hybrid Perovskite Solar Cells. *ACS Nano* **2015**, *9* (2), 2088–2101.

(9) Ha, S. T.; Liu, X.; Zhang, Q.; Giovanni, D.; Sum, T. C.; Xiong, Q. Synthesis of Organic-Inorganic Lead Halide Perovskite Nanoplatelets: Towards High-Performance Perovskite Solar Cells and Optoelectronic Devices. *Adv. Opt. Mater.* **2014**, *2* (9), 838–844.

(10) Zallen, R.; Slade, M. L. Inter-Polytype Conversion and Layer-Layer Coupling in PbI2. *Solid State Commun.* **1975**, *17* (12), 1561–1566.

(11) Capozzi, V.; Fontana, A.; Fontana, M. P.; Mariotto, G.; Montagna, M.; Viliani, G. Raman Scattering in PbI2. *Nuovo Cimento B* **1977**, 39 (2), 556–560.

(12) Sears, W. M.; Klein, M. L.; Morrison, J. A. Polytypism and the Vibrational Properties of Pb12. *Phys. Rev. B* **1979**, *19* (4), 2305–2313. (13) Grisel, A.; Schmid, P. Polytypism and Lattice Vibrations of Pb12. *Phys. Status Solidi B* **1976**, *73* (2), 587–591.

(14) Preda, N.; Mihut, L.; Baibarac, M.; Baltog, I.; Lefrant, S. A Distinctive Signature in the Raman and Photoluminescence Spectra of Intercalated PbI2. *J. Phys.: Condens. Matter* **2006**, *18* (39), 8899.

(15) Chen, Q.; Liu, H.; Kim, H.-S.; Liu, Y.; Yang, M.; Yue, N.; Ren, G.; Zhu, K.; Liu, S.; Park, N.-G.; et al. Erratum: Multiple-Stage Structure Transformation of Organic-Inorganic Hybrid Perovskite CH3NH3PbI3. *Phys. Rev. X* 2017, 7 (1), 019902.

(16) Zhang, F.; Castaneda, J. F.; Chen, S.; Wu, W.; DiNezza, M. J.; Lassise, M.; Nie, W.; Mohite, A.; Liu, Y.; Liu, S.; et al. Comparative Studies of Optoelectrical Properties of Prominent PV Materials: Halide Perovskite, CdTe, and GaAs. *Mater. Today* **2020**, *36*, 18–29. (17) Pistor, P.; Ruiz, A.; Cabot, A.; Izquierdo-Roca, V. Advanced Raman Spectroscopy of Methylammonium Lead Iodide: Development of a Non-destructive Characterisation Methodology. *Sci. Rep.*

2016, 6, 35973. (18) Luan, M.; Song, J.; Wei, X.; Chen, F.; Liu, J. Controllable Growth of Bulk Cubic-Phase CH3NH3Pb13 Single Crystal with Exciting Room-Temperature Stability. *CrystEngComm* 2016, *18* (28), 5257–5261.

(19) Nakada, K.; Matsumoto, Y.; Shimoi, Y.; Yamada, K.; Furukawa, Y. Temperature-Dependent Evolution of Raman Spectra of Methylammonium Lead Halide Perovskites, CH(3)NH(3)PbX(3) (X = I, Br). *Molecules* **2019**, *24* (3), 626.

(20) Qiu, J.; McDowell, L. L.; Shi, Z. Room-Temperature Cubic Perovskite Thin Films by Three-Step All-Vapor Conversion from PbSe to MAPb13. *Cryst. Growth Des.* **2019**, *19* (3), 2001–2009.

(21) Jin, F.; Ji, J.-T.; Xie, C.; Wang, Y.-M.; He, S.-N.; Zhang, L.; Yang, Z.-R.; Yan, F.; Zhang, Q.-M. Characterization of Structural Transitions and Lattice Dynamics of Hybrid Organic–Inorganic Perovskite CH3NH3Pb13. *Chin. Phys. B* **2019**, 28 (7), 076102.

(22) Sharma, R.; Dai, Z.; Gao, L.; Brenner, T. M.; Yadgarov, L.; Zhang, J.; Rakita, Y.; Korobko, R.; Rappe, A. M.; Yaffe, O. Elucidating the Atomistic Origin of Anharmonicity in Tetragonal CH3NH3PbI3 with Raman Scattering. *Phys. Rev. Mater.* **2020**, *4* (9), 092401.

(23) Brivio, F.; Frost, J. M.; Skelton, J. M.; Jackson, A. J.; Weber, O. J.; Weller, M. T.; Goñi, A. R.; Leguy, A. M. A.; Barnes, P. R. F.; Walsh, A. Lattice Dynamics and Vibrational Spectra of the Orthorhombic, Tetragonal, and Cubic Phases of Methylammonium Lead Iodide. *Phys. Rev. B* **2015**, *92* (14), 144308.

(24) Talit, K.; Strubbe, D. A. Stress Effects on Vibrational Spectra of a Cubic Hybrid Perovskite: A Probe of Local Strain. *J. Phys. Chem. C* **2020**, *124* (50), 27287–27299.

(25) Lee, J. W.; Kim, S. G.; Bae, S. H.; Lee, D. K.; Lin, O.; Yang, Y.; Park, N. G. The Interplay between Trap Density and Hysteresis in Planar Heterojunction Perovskite Solar Cells. *Nano Lett.* **2017**, *17* (7), 4270–4276.

(26) Macpherson, S.; Doherty, T. A. S.; Winchester, A. J.; Kosar, S.; Johnstone, D. N.; Chiang, Y. H.; Galkowski, K.; Anaya, M.; Frohna, K.; Iqbal, A. N.; et al. Local Nanoscale Phase Impurities are Degradation Sites in Halide Perovskites. *Nature* **2022**, *607* (7918), 294–300.

(27) Pisoni, A.; Jacimovic, J.; Barisic, O. S.; Spina, M.; Gaal, R.; Forro, L.; Horvath, E. Ultra-Low Thermal Conductivity in Organic-Inorganic Hybrid Perovskite CH3NH3PbI3. *J. Phys. Chem. Lett.* **2014**, *5* (14), 2488–2492.

(28) Grancini, G.; D'Innocenzo, V.; Dohner, E. R.; Martino, N.; Srimath Kandada, A. R.; Mosconi, E.; De Angelis, F.; Karunadasa, H. I.; Hoke, E. T.; Petrozza, A. CH3NH3PbI3 Perovskite Single Crystals: Surface Photophysics and Their Interaction with the Environment. *Chem. Sci.* **2015**, *6* (12), 7305–7310.

(29) Im, J. H.; Jang, I. H.; Pellet, N.; Gratzel, M.; Park, N. G. Growth of CH3NH3PbI3 Cuboids with Controlled Size for High-Efficiency Perovskite Solar Cells. *Nat. Nanotechnol.* **2014**, *9* (11), 927–932.

(30) Climent-Pascual, E.; Hames, B. C.; Moreno-Ramírez, J. S.; Álvarez, A. L.; Juarez-Perez, E. J.; Mas-Marza, E.; Mora-Seró, I.; de Andrés, A.; Coya, C. Influence of the Substrate on the Bulk Properties of Hybrid Lead Halide Perovskite Films. *J. Mater. Chem. A* **2016**, 4 (46), 18153–18163.

(31) Ahn, N.; Kwak, K.; Jang, M. S.; Yoon, H.; Lee, B. Y.; Lee, J. K.; Pikhitsa, P. V.; Byun, J.; Choi, M. Trapped Charge-Driven Degradation of Perovskite Solar Cells. *Nat. Commun.* **2016**, 7 (1), 13422.

(32) Motti, S. G.; Meggiolaro, D.; Barker, A. J.; Mosconi, E.; Perini, C. A. R.; Ball, J. M.; Gandini, M.; Kim, M.; De Angelis, F.; Petrozza, A. Controlling Competing Photochemical Reactions Stabilizes Perovskite Solar Cells. *Nat. Photonics* **2019**, *13* (8), 532–539.

(33) Ni, Z.; Jiao, H.; Fei, C.; Gu, H.; Xu, S.; Yu, Z.; Yang, G.; Deng, Y.; Jiang, Q.; Liu, Y.; et al. Evolution of Defects during the Degradation of Metal Halide Perovskite Solar Cells under Reverse Bias and Illumination. *Nat. Energy* **2022**, *7* (1), 65–73.

(34) Sherkar, T. S.; Momblona, C.; Gil-Escrig, L.; Avila, J.; Sessolo, M.; Bolink, H. J.; Koster, L. J. A. Recombination in Perovskite Solar Cells: Significance of Grain Boundaries, Interface Traps, and Defect Ions. *ACS Energy Lett.* **2017**, *2* (5), 1214–1222.

(35) Liu, T.; Yue, S. Y.; Ratnasingham, S.; Degousee, T.; Varsini, P.; Briscoe, J.; McLachlan, M. A.; Hu, M.; Fenwick, O. Unusual Thermal Boundary Resistance in Halide Perovskites: A Way To Tune Ultralow Thermal Conductivity for Thermoelectrics. *ACS Appl. Mater. Interfaces* **2019**, *11* (50), 47507–47515.

(36) Udalova, N. N.; Tutantsev, A. S.; Chen, Q.; Kraskov, A.; Goodilin, E. A.; Tarasov, A. B. New Features of Photochemical Decomposition of Hybrid Lead Halide Perovskites by Laser Irradiation. ACS Appl. Mater. Interfaces 2020, 12 (11), 12755–12762.
(37) Petrov, A. A.; Belich, N. A.; Grishko, A. Y.; Stepanov, N. M.; Dorofeev, S. G.; Maksimov, E. G.; Shevelkov, A. V.; Zakeeruddin, S. M.; Graetzel, M.; Tarasov, A. B.; et al. A New Formation Strategy of

Hybrid Perovskites via Room Temperature Reactive Polyiodide Melts. *Mater. Horiz.* 2017, 4 (4), 625–632.

(38) Weller, M. T.; Weber, O. J.; Henry, P. F.; Di Pumpo, A. M.; Hansen, T. C. Complete Structure and Cation Orientation in the Perovskite Photovoltaic Methylammonium Lead Iodide Between 100 and 352 K. *Chem. Commun.* **2015**, *51* (20), 4180–4183.

(39) Chen, B.; Song, J.; Dai, X.; Liu, Y.; Rudd, P. N.; Hong, X.; Huang, J. Synergistic Effect of Elevated Device Temperature and Excess Charge Carriers on the Rapid Light-Induced Degradation of Perovskite Solar Cells. *Adv. Mater.* **2019**, *31* (35), e1902413.

(40) Zhang, Y.-Y.; Chen, S.; Xu, P.; Xiang, H.; Gong, X.-G.; Walsh, A.; Wei, S.-H. Intrinsic Instability of the Hybrid Halide Perovskite Semiconductor CH3NH3PbI3. *Chin. Phys. Lett.* **2018**, *35* (3), 036104.

(41) Jena, A. K.; Kulkarni, A.; Miyasaka, T. Halide Perovskite Photovoltaics: Background, Status, and Future Prospects. *Chem. Rev.* **2019**, *119* (5), 3036–3103.

(42) Meggiolaro, D.; Mosconi, E.; De Angelis, F. Modeling the Interaction of Molecular Iodine with MAPbI3: A Probe of Lead-Halide Perovskites Defect Chemistry. *ACS Energy Lett.* **2018**, 3 (2), 447–451.

(43) Ye, T.; Kocherga, M.; Sun, Y. Y.; Nesmelov, A.; Zhang, F.; Oh, W.; Huang, X. Y.; Li, J.; Beasock, D.; Jones, D. S.; et al. II-VI Organic-Inorganic Hybrid Nanostructures with Greatly Enhanced Optoelectronic Properties, Perfectly Ordered Structures, and Shelf Stability of Over 15 Years. ACS Nano **2021**, *15* (6), 10565–10576.

(44) Khawam, A.; Flanagan, D. R. Solid-State Kinetic Models: Basics and Mathematical Fundamentals. *J. Phys. Chem. B* **2006**, *110* (35), 17315–17328.

(45) Ummadisingu, A.; Gratzel, M. Revealing the Detailed Path of Sequential Deposition for Metal Halide Perovskite Formation. *Sci. Adv.* **2018**, *4* (2), e1701402.

(46) Park, S. J.; Kim, A. R.; Hong, J. T.; Park, J. Y.; Lee, S.; Ahn, Y. H. Crystallization Kinetics of Lead Halide Perovskite Film Monitored by In Situ Terahertz Spectroscopy. *J. Phys. Chem. Lett.* **2017**, *8* (2), 401–406.

(47) Bastos, J. P.; Uytterhoeven, G.; Qiu, W.; Paetzold, U. W.; Cheyns, D.; Surana, S.; Rivas, J.; Jaysankar, M.; Song, W.; Aernouts, T.; et al. Model for the Prediction of the Lifetime and Energy Yield of Methyl Ammonium Lead Iodide Perovskite Solar Cells at Elevated Temperatures. ACS Appl. Mater. Interfaces **2019**, *11* (18), 16517– 16526.

(48) Tran, C. D. T.; Liu, Y.; Thibau, E. S.; Llanos, A.; Lu, Z.-H. Stability of Organometal Perovskites with Organic Overlayers. *AIP Adv.* **2015**, *5* (8), 087185.

(49) Steirer, K. X.; Schulz, P.; Teeter, G.; Stevanovic, V.; Yang, M.; Zhu, K.; Berry, J. J. Defect Tolerance in Methylammonium Lead Triiodide Perovskite. *ACS Energy Lett.* **2016**, *1* (2), 360–366.

(50) Sun, N. X.; Liu, X. D.; Lu, K. An Explanation to the Anomalous Avrami Exponent. *Scr. Mater.* **1996**, *34* (8), 1201–1207.

(51) Haye, E.; Capon, F.; Barrat, S.; Boulet, P.; Andre, E.; Carteret, C.; Bruyere, S. Properties of Rare-Earth Orthoferrites Perovskite Driven by Steric Hindrance. *J. Alloys Compd.* **2016**, *657*, 631–638.

(52) Różycki, C.; Maciejewski, M. Method of the Selection of the $g(\alpha)$ Function Based on the Reduced-Time Plot. *Thermochim. Acta* **1987**, 122 (2), 339–354.

(53) Pang, E. L.; Vo, N. Q.; Philippe, T.; Voorhees, P. W. Modeling Interface-Controlled Phase Transformation Kinetics in Thin Films. J. Appl. Phys. **2015**, 117 (17), 175304.

(54) Očenášek, J.; Novák, P.; Agbo, S. Finite-Thickness Effect on Crystallization Kinetics in Thin Films and its Adaptation in the Johnson–Mehl–Avrami–Kolmogorov Model. J. Appl. Phys. 2014, 115 (4), 043505.

(55) Wang, Q.; Chen, B.; Liu, Y.; Deng, Y.; Bai, Y.; Dong, Q.; Huang, J. Scaling Behavior of Moisture-Induced Grain Degradation in Polycrystalline Hybrid Perovskite Thin Films. *Energy Environ. Sci.* **2017**, *10* (2), 516–522.

(56) Park, M.; Kornienko, N.; Reyes-Lillo, S. E.; Lai, M.; Neaton, J. B.; Yang, P.; Mathies, R. A. Critical Role of Methylammonium

Librational Motion in Methylammonium Lead Iodide (CH3NH3PbI3) Perovskite Photochemistry. *Nano Lett.* **2017**, *17* (7), 4151–4157.

(57) Son, D.-Y.; Lee, J.-W.; Choi, Y. J.; Jang, I.-H.; Lee, S.; Yoo, P. J.; Shin, H.; Ahn, N.; Choi, M.; Kim, D.; et al. Self-Formed Grain Boundary Healing Layer for Highly Efficient CH3NH3PbI3 Perovskite Solar Cells. *Nat. Energy* **2016**, *1* (7), 16081.

(58) Zhou, Y.; You, L.; Wang, S.; Ku, Z.; Fan, H.; Schmidt, D.; Rusydi, A.; Chang, L.; Wang, L.; Ren, P.; et al. Giant Photostriction in Organic-Inorganic Lead Halide Perovskites. *Nat. Commun.* **2016**, 7 (1), 11193.

(59) Lin, Y.; Chen, B.; Fang, Y.; Zhao, J.; Bao, C.; Yu, Z.; Deng, Y.; Rudd, P. N.; Yan, Y.; Yuan, Y.; et al. Excess Charge-Carrier Induced Instability of Hybrid Perovskites. *Nat. Commun.* **2018**, *9* (1), 4981.

(60) Liu, Y.; Yang, Z.; Cui, D.; Ren, X.; Sun, J.; Liu, X.; Zhang, J.; Wei, Q.; Fan, H.; Yu, F.; et al. Two-Inch-Sized Perovskite CH3NH3PbX3 (X = Cl, Br, I) Crystals: Growth and Characterization. *Adv. Mater.* **2015**, 27 (35), 5176–5183.