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Lead Halide Perovskites: Challenges and Opportunities in Advanced Synthesis and Spectroscopy

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Supporting Information

ABSTRACT: Hybrid lead perovskites containing a mixture of organic and inorganic cations and anions have led to solar cell devices with performance and stability that are better than those of their single-halide analogs. ²⁰⁷Pb solid-state nuclear magnetic resonance and single-particle photoluminescence spectroscopies show that the structure and composition of mixed-halide and likely other hybrid lead perovskites are much more complex than previously thought and are highly dependent on their synthesis. While a majority of reports in the area focus on the construction of photovoltaic devices, this Perspective focuses instead on achieving a better understanding of the fundamental chemistry and photophysics of these materials, because this will aid not only in constructing improved devices but also in generating new uses for these unique materials.



ead halide perovskites with the general formula APbX₃, where A is an organic $(CH_3NH_3^+, CH(NH_2)_2^+)$ or inorganic cation (Cs^+) and X is a halide $(I^-, Br^-, or CI^-)$, have gained much attention as photovoltaic materials because of their high power conversion efficiency (PCE) of over 22%.^{1,2} These semiconducting materials exhibit many useful and interesting properties, including low cost and ease of synthesis (to an extent; see below), and have large absorption coefficients, intense photoluminescence, low exciton binding energies, long exciton diffusion lengths, high dielectric constants, and intrinsic ferroelectric polarization.^{3,4} In addition, the perovskite structure is highly tunable because of the variety of organic and inorganic cations (A), central elements (in lieu of Pb), and anions (X) that can be incorporated into a variety of "hybrid" structures, resulting in complete optical tunability over the entire visible spectrum.⁵

In this Perspective, we highlight our team's efforts in the spectroscopic-driven synthetic development of hybrid mixedhalide lead perovskites. ²⁰⁷Pb solid-state nuclear magnetic resonance (ssNMR) spectroscopy has allowed us to test the true chemical speciation of the lead nucleus, and optical spectroscopy has allowed us to correlate nanocrystal morphology and composition with single-particle luminescence. Hybrid mixed-halide perovskites and their devices display improved stability and performance in comparison to their single-halide analogs, and our results show that their structure and composition are much more complex than previously thought and are highly dependent on their synthesis. By providing a more ²⁰⁷Pb solid-state nuclear magnetic resonance (ssNMR) spectroscopy has allowed us to test the true chemical speciation of the lead nucleus, and optical spectroscopy has allowed us to correlate nanocrystal morphology and composition with single-particle luminescence.

detailed understanding of their fundamental chemistry and photophysics, further synthetic and advanced ssNMR, photoluminescence, and Raman spectroscopic experiments will help unlock the full potential of hybrid lead perovskites and related materials in solar cells and beyond.

Synthetic Development: Toward Structure–Property Relationships for Enhanced Stability and Performance. Lead halide perovskites are typically synthesized by spin-coating,^{1,6,7} vapor deposition,^{7,8} or precipitation from solution.^{5,9} Figure 1 illustrates these methods using methylammonium-based organolead halide perovskites, $CH_3NH_3PbX_3$ (X = I, Br, Cl), as an

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Figure 1. Films of $CH_3NH_3PbX_3$ (X = I, Br, Cl) are typically fabricated through (a) spin-coating by either a one-step (PbX₂ and CH_3NH_3X deposited at same time) or two-step (PbX₂ deposited first then dipped in CH_3NH_3X solution) process followed by annealing between 80 and 100 °C, or (b) vapor deposition by exposing a substrate to PbX₂ and CH_3NH_3X vapor. (c) Freestanding powders or nanoparticles of $CH_3NH_3PbX_3$ are formed by solution-phase synthesis when a mixture of PbX₂, CH_3NH_3X , and, in the case of particles, a surface terminating agent or ligand in a polar solvent is mixed with a nonpolar solvent. (d) Hybrid mixedhalide perovskites ($CH_3NH_3PbX_{3-a}X'_a$) are produced when two dry single-halide perovskites ($CH_3NH_3PbX_3 + CH_3NH_3PbX'_3$) are ground together and gradually annealed at 200 °C (see text below).²⁰

example. Spin coating from solution is widely used to fabricate perovskite devices because of its simplicity and low cost (Figure 1a). Spin-coating is also used in either a one-step method, which involves spin-coating a mixture of PbX₂ and CH₃NH₃X, typically dissolved in DMF, on a substrate, or by a two-step method in which a PbX₂ film is first spin-coated on a substrate followed by subsequent dipping in a CH₃NH₃X solution.^{7,8} Finally, the films produced by either of these methods undergo an annealing step at relatively mild temperatures, typically between 80 and 100 °C.7 Perovskite films prepared by spin-coating have led to some of the most efficient perovskite solar cells^{1,6} but tend to suffer from incomplete coverage, the presence of pinholes, and poor reproducibility.^{7,8} In contrast, vapor deposition typically involves depositing a film by sublimation of precursor powders or by exposing a PbX₂ film to CH₃NH₃X vapor at elevated temperatures (Figure 1b).⁸ Vapor deposition produces higher-quality (more uniform) films compared to spin coating, but the solar cell efficiencies of vapor-deposited perovskite films have not reached those obtained by spin coating.8 Precipitation from solution is more commonly used when freestanding perovskite powders or nanoparticles are desired (Figure 1c). Traditionally, a mixture of PbX₂, CH₃NH₃X, and a surface ligand (e.g., CH₃(CH₂)₇NH₃X, which is similar to CH₃NH₃X but too large to fit within the perovskite crystal structure) is dissolved in a polar organic solvent (DMF, acetonitrile, γ -butyrolactone) and then slowly added to a nonpolar solvent (toluene, acetone).^{5,9} This method is usually performed at room temperature or upon mild heating and can produce highly monodisperse nanoparticles of various

morphologies. Our team was among the first to demonstrate morphology control of perovskite nanocrystals by accessing dots, rods, plates, or sheets by varying the concentration of $CH_3(CH_2)_7NH_3X$, thus demonstrating control of aspect ratio by varying the rate of precursor injection into toluene.⁹ Among additional key developments, others have found that the thickness of perovskite nanoplatelets can be tuned by varying the ratio of ligand to cation,⁵ and the size of colloidal CsPbX₃ quantum dots made in organic solution can be controlled by varying the reaction temperature.¹⁰ Overall, these advances have led to better tunability of perovskite materials and their use in tandem solar cells⁶ and light-emitting displays (LEDs).^{11,12}

A fundamental problem with organolead halide perovskites is that they suffer from instability and decomposition under a variety of conditions including moisture, light, and heat.¹³ All-inorganic perovskites $(CsPbX_3, X = I, Br, Cl)^{14,15}$ and Cs-doped organolead halide perovskites^{1,6} are known to exhibit greater thermal stability compared to CH₂NH₃PbX₃. However, the black photoactive CsPbI₃ phase is thermodynamically stable only above 300 °C, with the photoinactive "yellow" δ -CsPbI₃ produced at room temperature.¹⁶ Moisture stability has been shown to improve in mixed-halide perovskites such as $CH_3NH_3Pb(I_{0.8}Br_{0.2})_3^{-1}$ Not surprisingly, much interest has been devoted to other "hybrid" perovskites made of multiple organic and inorganic cations and halides, including [HC(NH₂)₂]_{0.75}Cs_{0.25}Sn_{0.5}Pb_{0.5}I₃ and $[HC(NH_2)_2]_{0.83}Cs_{0.17}Pb(I_{0.5}Br_{0.5})_3$ for tandem solar cells⁶ and $Cs_x[(CH_3NH_3)_{0.17}(HC(NH_2)_2)_{0.83}]_{1-x}Pb(I_{0.83}Br_{0.17})_3 (1 \ge x \ge 0)$ for single-junction solar cells.¹ (See the Supporting Information.) Interestingly, little is known about the degree of alloying and phase segregation in these materials or how these may fundamentally affect their performance. This question is particularly interesting when one considers the high degree of halide ion mobility inherent to perovskites,^{18,4} in some cases induced by illumination,¹⁸ which is also responsible for complete halide exchange when a particular perovskite is exposed to an excess of a different or exogenous halide.¹⁹ These and similar observations long suggested that a certain degree of phase segregation was present in heavily mixed hybrid perovskites.

Hybrid mixed-halide perovskites and their devices display improved stability and performance in comparison to their single-halide analogs, and our results show that their structure and composition are much more complex than previously thought and are highly dependent on their synthesis.

We investigated this possibility by studying hybrid mixedhalide perovskites of the general formula " $CH_3NH_3PbX_{3-a}X'_a$ " (X, X' = I, Br, or Cl). We use quotation marks and italic script to differentiate hypothetical formulas from actual chemical compositions determined by ²⁰⁷Pb solid-state nuclear magnetic resonance (ssNMR) spectroscopy, which is highly sensitive to changes in the ²⁰⁷Pb electronic environment (Figure 2).²⁰ In particular, we studied heavily mixed, 50–50% (a = 1.5) mixedhalide perovskites made by three different methods: precipitation from solution at room temperature, thermally annealing of the solution-phase samples, and a novel solid-phase synthesis that consists of heating together a mixture of two single**ACS Energy Letters**



Figure 2. Representative static ²⁰⁷Pb ssNMR spectra of single- and mixed-halide perovskites $[CH_3NH_3Pb(X_{1,S}X'_{1,S})_3, X/X' = I (a),$ I/Br from solid-phase synthesis (b), I/Br from solution-phase synthesis (c), Br (d), Br/Cl (e), Cl (f)]. Single-halide perovskites were synthesized from solution. Initial experiment times ranged from few hours to >1 d. Pb(NO_3)₂ ($\delta = -3490$ ppm, 22 °C) was used as external calibration standard. Previously unknown phases observed in mixed-halide perovskites include amorphous (c) and nonstoichiometric phases (e) produced by halide miscibility gaps (synthesis depending) and spinodal decomposition (independent of synthesis), respectively.²⁰

halide perovskites in the absence of solvents (Figure 1d). In all three cases, we found that the samples consist of multiple stoichiometric and nonstoichiometric phases that survive and persist upon thermal annealing. While surprising, these results are not without precedent. They fully agree with a theoretical phase diagram for the $CH_3NH_3PbI_{3-a}Br_a$ system, which predicts the presence of a miscibility gap resulting in spinodal decomposition of heavily mixed perovskites.²¹ These results are also consistent with more recent work showing similar behavior in heavily mixed $CsPbI_{3-a}Br_a$ nanocrystals.²²

A key additional discovery made by ssNMR, exemplified here by solution-made " $CH_3NH_3PbI_{1.5}Br_{1.5}$ " is the presence of an amorphous $CH_3NH_3PbBr_3$ phase that is not observed by X-ray diffraction or optical measurements which persists upon thermal annealing up to 200 °C (Figure 2). Critically, our new solidphase synthesis, in which a stoichiometric ratio of $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ are mixed together followed by annealing at 200 °C, results in a sample without this amorphous $CH_3NH_3PbBr_3$ impurity (Figure 2). These results highlight the fact that the structure and composition of mixed-halide and likely other hybrid perovskites are much more complex than previously thought and can be highly synthesis-dependent. This underscores the need to account for phase segregation in hybrid perovskites and their devices, as the presence of Perspective



Figure 3. (a) Optical images, (b) diffuse-reflectance absorption spectra, and (c) final powder XRD data of two $CH_3NH_3PbI_3$ (I-side) and $CH_3NH_3PbBr_3$ (Br-side) films pressed together on Kapton polyimide tape upon annealing to 200 °C.²⁰ Spot size in panel a is ca. 7 mm across. Solid and dashed lines in panel b correspond to I- and Br-sides, respectively. Background noise in panels b and c is an artifact caused by Kapton tape.

multiple phases will likely have an impact in their performance and stability.

As further demonstration of the utility afforded by our new solid-phase synthesis, we find that solid-state halide diffusion easily occurs at the interface between two dry $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ films pressed together between two pieces of Kapton polyimide tape (Figure 3a, 20 °C). Kapton was selected to mimic a transparent, flexible substrate but also because of its thermal stability up to 260 °C and impermeability toward gases (CH_3NH_3X , HX, etc.). Upon annealing, the originally black $CH_3NH_3PbI_3$ and orange $CH_3NH_3PbBr_3$ films coalesce into one with a single absorption edge (Figure 3b). This agrees with the XRD of the final annealed sample, which shows a single set of peaks that is equidistant from the single $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ halides and corresponds to the $CH_3NH_3PbI_{1.5}Br_{1.5}$ mixed-halide phase (Figure 3c). No amorphous or semicrystalline perovskite phases are observed.²⁰

Characterization of Perovskite Materials by Solid-State NMR. Our research group and others have demonstrated that ²⁰⁷Pb ssNMR spectroscopy is a powerful probe of the local environment of the lead nucleus.^{20,23–25} For example, another group recently employed ²⁰⁷Pb ssNMR to study the formation and interconversion of hydrated and anhydrous $CH_3NH_3PbI_3$.²⁵ Other groups have also applied multinuclear magnetic resonance to study local structure, order, crystal quality, phase segregation, and cation dynamics. Multinuclear magnetic resonance is appealing because most elements found in perovskites are amenable to NMR (Table 1). ²H and ¹⁴N ssNMR spectra have been used to observe the dynamics of $CH_3NH_3^+$ cations.^{26–28} Understanding cation dynamics may be important because they

Table 1	. Properties	of NMR	Active	Nuclei	Found	in
Perovsk	kite Material	s ³³				

nucleus	nuclear spin (I)	Larmor frequency ratio (%)	natural isotopic abundance (%)	receptivity vs ¹³ C ^a
${}^{1}H^{b}$	1/2	100.00	99.99	5.87×10^{3}
${}^{2}\mathrm{H}^{c,d}$	1	15.35	0.01	6.52×10^{-3}
${}^{13}C^{e}$	1/2	25.18	1.07	1.00
${}^{14}N^{c}$	1	7.23	99.63	5.90
$^{15}N^{f}$	1/2	10.14	0.37	2.25×10^{-2}
³⁵ Cl ^g	3/2	9.80	75.78	21.00
⁷⁹ Br ^g	5/2	25.05	50.69	2.37×10^{2}
¹¹⁹ Sn ^h	1/2	37.29	8.59	26.60
$^{127}I^{g}$	5/2	20.01	100.00	5.60×10^{2}
$^{133}Cs^{i}$	7/2	13.12	100.00	2.84×10^{2}
${}^{207}\text{Pb}^{h}$	1/2	20.92	22.1	11.80

^{*a*}Expected NMR sensitivity versus natural abundance ¹³C.³³ ^{*b*}Best NMR sensitivity; small δ range; requires fast MAS or pulsed decoupling. ^{*c*}Useful for studying cation dynamics. ^{*d*}Isotopic enrichment required. ^{*e*}Can be used to fingerprint different CH₃NH₃PbX₃ perovskites. ^{*f*}Poor sensitivity from low natural abundance and frequency. ^{*g*}Gives rise to broad NMR signals; easier by NQR. ^{*h*}Broad δ range; highly sensitive.

can influence both optical and electronic properties of organolead halides. Different organolead halides possess slightly different ¹³CH chemical shifts,²⁹ and this can be used to assess the degree of alloying or phase segregation. All halide anions possess highly abundant NMR active nuclei, although these give rise to broad ssNMR spectra with limited resolution. Instead, ³⁵Cl, ⁸¹Br, and ¹²⁷I nuclear quadrupole resonance (NQR) spectroscopy has been applied to observe phase transitions and structural defects in lead halide perovskites.^{30,31} As mentioned above, hybrid Cs-formamidinium $(CH(NH_2)_2^+)$ lead halide perovskites have been found to possess high photo- and thermal stabilities and PCE.⁶ ¹³³Cs ssNMR will likely be a useful probe of structure and phase ordering in these materials. Finally, we note there is great interest in lead-free perovskites that contain instead Sn, Bi, or Ag.³² The strategies outlined here and in the literature could be applied to ¹¹⁹Sn ssNMR to understand the structure and halide ion speciation in Sn-based perovskites.

The previous ssNMR studies of lead halide perovskites described above have demonstrated the potential of this technique to probe dynamics, ordering, defects, and phase segregation. Conventional ²⁰⁷Pb ssNMR experiments on lead halide perovskites often suffer from low sensitivity due to signal broadening and short transverse ²⁰⁷Pb relaxation times. For these reasons, ²⁰⁷Pb ssNMR experiments are usually restricted to one-dimensional (1D) NMR experiments which provide limited resolution; two-dimensional (2D) NMR spectra could provide much more structural information. Conventional ssNMR is also restricted to pure powder samples. Lead halide perovskite thin films could potentially be probed by ssNMR to detect differences in the film quality for different synthetic procedures and treatments. However, perovskite thin films (of thickness ca. 500 nm) will likely have a perovskite content of less than 2 wt %, because the substrate is likely to make up most of the sample mass. For all of these reasons, we are currently exploring the application of state-of-the-art ssNMR technologies to dramatically improve sensitivity and reduce experiment times, and this will be presented in a forthcoming Lead halide perovskite thin films could potentially be probed by ssNMR to detect differences in the film quality for different synthetic procedures. We are currently exploring the application of state-of-the-art ssNMR technologies to dramatically improve sensitivity and reduce experiment times.

publication.³⁴ Here, we very briefly outline some key promising observations.

The most straightforward technique for improving the sensitivity of ssNMR is fast magic-angle spinning (MAS).^{35,36} To illustrate this concept, Figure 4a compares ²⁰⁷Pb ssNMR spectra of " $CH_3NH_3PbI_{1.5}Br_{1.5}$ " mixed-halide perovskites obtained with a stationary sample in a 4.0 mm probehead versus a sample undergoing 50 kHz MAS in a 1.3 mm probehead. To acquire a ²⁰⁷Pb NMR spectrum from the stationary sample, two individual subspectra were required because the 4.0 mm probe offered limited ²⁰⁷Pb RF fields. On the other hand, the 50 kHz MAS spectrum was acquired with a single transmitter offset because the high ²⁰⁷Pb RF fields (ca. 125 kHz) from the 1.3 mm probe enabled uniform excitation of the broad spectrum. The 50 kHz MAS spectrum was acquired in only 1.15 h, despite the small sample volume of ca. 10 uL. Note that the two ²⁰⁷Pb NMR spectra differ in appearance, likely because of different synthetic methods used to make the samples.²⁰ MAS also induces a beneficial longitudinal magnetization exchange between ²⁰⁷Pb and coupled ^{79/81}Br and ¹²⁷I quadrupolar nuclei in lead bromide and iodide systems,³⁷ which provides more than a 3-fold gain in sensitivity because it is possible to pulse more frequently.

Most importantly, fast MAS improves the sensitivity of ¹H ssNMR because it significantly narrows the ¹H NMR peak widths by averaging the ¹H–¹H homonuclear dipolar couplings. This enables efficient proton detection, which can theoretically improve sensitivity by more than 1 order of magnitude for ²⁰⁷Pb ssNMR experiments. Figure 4b compares the 50 kHz MAS ²⁰⁷Pb ssNMR spectra of the mixed-halide perovskite "*CH*₃*NH*₃*PbBr*_{1.5}*Cl*_{1.5}" obtained with direct detection of ²⁰⁷Pb (sensitivity 3.2 min^{-1/2}) versus 2D proton detected ¹H-²⁰⁷Pb HETCOR (sensitivity 23 min^{-1/2}). As expected, proton detection yields nearly an order of magnitude increase in sensitivity and provides more informative 2D ¹H-²⁰⁷Pb HETCOR NMR spectra in a similar time as was required to obtain the 1D ²⁰⁷Pb ssNMR spectrum.

While fast MAS is a promising technique to enhance sensitivity, it does not directly address the fundamental origins of low NMR sensitivity that occurs because of the very small polarization of the nuclear spin states at ambient temperatures. One method to address this problem is high field dynamic nuclear polarization (DNP).³⁸ In a DNP experiment, the high spin polarization of unpaired electrons in an exogenous molecular radical is transferred to NMR active nuclei by saturating the electron paramagnetic resonance (EPR) of the radical at cryogenic temperatures.³⁸ DNP can increase the NMR signal and sensitivity by several orders of magnitude.³⁸ Figure 4c shows applied DNP enhanced ¹H-²⁰⁷Pb cross-polarization MAS (CPMAS) spectra of microcrystalline and nanocrystalline CH₃NH₃PbBr₃ impregnated with tetrachloroethane solution of the biradical polarizing agent TEKPol. In these experiments, the



Figure 4. (a) ²⁰⁷Pb ssNMR spectra acquired with 50 kHz MAS and a 1.3 mm probehead vs a static sample and a 4.0 mm probehead (" $CH_3NH_3PbI_{1.5}Br_{1.5}$ " samples made by different methods). Experiment times were 1.2 vs 34.4 h, respectively. (b) Directly detected vs a ¹H detected ²⁰⁷Pb ssNMR spectrum of $CH_3NH_3PbBr_{1.5}Cl_{1.5}$ obtained with 50 kHz MAS (sensitivity of the ¹H detected spectrum is approximately 7 times higher). Experiment times were 6.9 min vs 29 min, respectively. (c, d) 400 MHz/263 GHz DNP vs ¹H-²⁰⁷Pb CPMAS ssNMR spectra of microcrystalline and nanocrystalline $CH_3NH_3PbBr_3$ (²⁰⁷Pb indirect DNP signal enhancements, $\varepsilon_{Pb CP}$, are indicated). Experiment times were less than 5 min.

protons in CH₃NH₃⁺ cations within the particles are remotely polarized by spin diffusion of DNP enhanced magnetization from their surface. The relatively large particle size of microcrystalline CH₃NH₃PbBr₃ leads to a modest DNP signal enhancement of ca. 3. However, it is still possible to obtain high-quality ²⁰⁷Pb ssNMR spectra in minutes with DNP signal enhancements and the additional improvements in sensitivity from reduced temperatures. In the case of nanocrystalline $CH_3NH_3PbBr_3$, a substantial DNP signal enhancement of 13 was obtained, allowing us to obtain a high-quality ${}^{1}\text{H}{-}^{207}\text{Pb}$ CPMAS ssNMR spectrum from ca. 35 mg of material. The larger remote DNP signal enhancements are a consequence of the small particle size, suggesting that DNP enhanced ssNMR spectroscopy will be most useful for characterization of low-dimensional lead halide perovskites.

Advances and Challenges in Optical Spectroscopy. The optical properties of lead halide perovskites are of critical importance as nearly all applications revolve around these properties. While a majority of reports focus on the construction of photovoltaic devices.^{39,40} a better understanding of the fundamental photophysics of perovskites not only will aid device construction but also may generate new uses for these unique materials. Our first report in this area, in 2015, focused on spectral characterization of the ensemble and the correlation between nanocrystal morphology and single-particle luminescence.⁹ Interestingly, several types of CH₃NH₃PbX₃ nanocrystals display synchronous luminescence across entire particles, even long-aspect-ratio nanorods, that is, there are no areas of anisotropic luminescence hot spots, such as the ends of the nanorods. In addition, there are very few OFF (dark) events as a result of blinking behavior.9 In 2016, others reported similar characteristics for CH₃NH₃PbI₃ nanorods through single-crystal photoluminescence blinking measurements combined with super-resolution localization microscopy.⁴¹ More specifically, nanorods showed synchronous blinking and power law dependence of ON and OFF times, suggesting surface trapping and detrapping processes are behind this phenomenon. In addition, a strong environmental dependence on blinking behavior was observed.

In a further study published in 2017, we carried out a more detailed analysis of the time-correlated luminescence and showed that mixed-halide CH₃NH₃PbBr_{3-a}I_a nanocrystals are more likely to exhibit luminescence intermittency than their CH₃NH₃PbI₃ and CH₃NH₃PbBr₃ counterparts.⁴² Still, at most only 26% of the nanocrystals of any mixed-halide composition exhibited some degree of intermittency. For these luminescence measurements, nanocrystals suspended in toluene were drop cast onto clean glass coverslips and allowed to dry prior to imaging. Further analysis of these time-correlated luminescence data show a power law dependence of OFF times for the mixed-halide CH₃NH₃PbBr_{3-a}I_a nanocrystals, and Figure 5 shows representative data from CH₃NH₃Pb(Br_{0.75}I_{0.25})₃ nanocrystals. As stated previously, a power law dependence is strong evidence for surface trap involvement in the ON and OFF states. Others showed that CH₃NH₃PbI₃ crystals photobrighten upon mechanical grinding from greater than 2 μ m down to 100 nm in size.⁴³ The size dependence on the rate of photobrightening led to the conclusion that the entire crystal volume contains charge traps, not just the surface. In addition, super resolution localization demonstrated nanometer-scale emitting sites on micrometer-sized crystals, hypothesized to be either small defect-free crystal grains that confine the charge carriers or small, localized defects that attract charge carriers to recombine at certain locations. Because organolead halide perovskites can become unstable under illumination,^{44,45} efforts to synthesize a robust, all-inorganic perovskite were undertaken by others. Thus far, single- and mixed-halide cesium perovskites with compositions spanning from CsPbCl₃ through CsPbI₃ showed size- and composition-dependent luminescence maxima from 400-700 nm, as well as quantum yields between 50-90%.¹⁰



Figure 5. (a) Single-particle luminescence intensity of a $CH_3NH_3Pb(Br_{0.75}I_{0.25})_3$ nanocrystal over 250 s with inset images for the indicated frames. The scale bars are 2 μ m. (b) Power law plot of the probability of an OFF event vs its duration measured for multiple $CH_3NH_3Pb(Br_{0.75}I_{0.25})_3$ nanocrystals. OFF times were graphed because even intermittent particles are ON the vast majority of time. The coefficient for the power law fit is -1.54, based on statistics from 330 OFF events. (Panel a reproduced with permission from ref 42. Copyright 2017 The Royal Society of Chemistry.)

Another technique that is well-suited to the study of inorganic nanocrystal systems is Raman spectroscopy. Insights into the optical phonons of crystalline materials give structural information that is unique and supplementary to the more common XRD and the advanced NMR-based characterization discussed above. Two key lead halide perovskite properties to be considered prior to subjecting these to Raman spectroscopy studies have been outlined: First, the heavy Pb atoms in the lattice result in low-energy vibrational modes ($\leq 200 \text{ cm}^{-1}$) that are within the range attenuated by conventional laser notch filters. Thus, efficient collection of Raman data requires specialized Rayleigh filtering to access many of the vibrational modes of lead-based perovskites. Second, the photostability of lead perovskite materials is inherently low (see above).⁴ Thus, Raman studies of these materials should use (and report) low irradiances-power per unit area illuminated-as well as illumination wavelength, with meaningful data requiring excellent instrument throughput or long acquisition times.

The Raman spectrum of CH₃NH₃PbI₃, along with DFT calculations for various possible crystal structures, has been reported in 2014, although experimental irradiances for this

study were not.⁴⁶ Based on reported laser powers used in this study, reasonable calculations suggest the irradiance to be at least 3600 W/cm² and higher. Later reports of Raman spectra reveal some disagreement with the original data reported in 2014, most notably two strong bands at 92 and 106 cm^{-1.47}. These correlate well to the Raman spectrum of PbI₂ (Figure 6),



Figure 6. (a) False color plot of the evolution of the Raman spectrum of " $CH_3NH_3PbI_3$ " over 120 min of illumination, collected at 60 s intervals using a laser intensity of 150 W/cm² and (b) comparison between the Raman spectra of a $CH_3NH_3PbI_3$ sample irradiated with 150 and 75 W/cm² for various intervals and neat PbI₂. The spectra shown in panel b have been normalized and scaled for easier comparison. The spectra collected at 1 min overlap at this scale.

which is a known degradation product of lead iodide perovskites.⁴⁸ It is important to note the inconsistencies between the reported Raman spectra are related to the phonon modes of the inorganic cage that appear below $\sim 200 \text{ cm}^{-1}$, not the vibrational modes of the organic component. Even moderate laser intensities ($\sim 1250 \text{ W/cm}^2$) in the visible range cause sample degradation during Raman data acquisition,⁴ ⁹ which corroborates similar results found for perovskite photostability studies.⁴⁴ Figure 6 shows Raman spectra of a powder sample of CH₃NH₃PbI₃ collected on a triple-grating spectrograph with 532 nm excitation at 150 W/cm² and 75 W/cm². The false color plot shows the evolution of the spectrum over 120 min for 150 W/cm^2 , and the graph shows the spectra at the start of illumination and after 120 min of illumination for both intensities with a neat sample of PbI₂ for comparison. Interestingly, there is no recorded signal above the noise for the first ~ 15 min using 150 W/cm^2 , but over time, bands evolve that are consistent with PbI_2 . This indicates the sample has degraded under 150 W/cm² laser illumination. The onset of degradation using 75 W/cm² occurs after 45 min of illumination. These data make it clear that obtaining a degradation-free Raman spectrum for lead halide perovskites will be challenging and require some form of complementary validation, as the material tends to degrade and, at

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least for $CH_3NH_3PbI_3$, the relative Raman cross section of the perovskite is much lower than that of PbI_2 , i.e., no signal is observed until the material degrades under these conditions.

Moving forward, the challenges and opportunities for optical spectroscopy in the field of lead halide perovskites are exciting. Much research has been performed on the luminescence of organolead perovskites, and this will aid the development of new types of perovskite materials, such as Ge- or Sn-based perovskites, which have gained recent attention due to the absence of Pb in their composition. Future directions for luminescence studies should include advanced imaging techniques to study single nanocrystals in more dense systems (i.e., films for real devices), such as stimulated emission depletion (STED) or other super-resolution microscopies. Subdiffraction imaging studies on

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functional devices will allow for a better understanding of the role of small defects on conversion efficiencies. On another front, all-inorganic CsPbX₃ perovskites have been demonstrated to have tunable PL in the visible range and high quantum yields, but detailed studies using several characterization techniques are lagging. In addition, Raman spectroscopy data for methylammonium lead halide materials are not well agreed upon in the literature. Computational methods with an appropriately high level of theory (at least using the generalized gradient approximation or hybrid functionals) should accompany future Raman studies to provide further evidence that observed bands correspond to the nondegraded perovskite structure. As new classes of perovskites emerge, understanding their fundamental chemistry will increase their application potential and enable advances in their device performance.

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Summary and Future Outlook. Lead halide perovskite semiconductors have quickly become a highly versatile platform to build photovoltaic solar cell and light emitting devices. Organolead halides, the first heavily studied members of this family of compounds, have a limited thermal stability range, but this can be extended with inorganic perovskites. More widespread among different halide perovskites are moistureand photoinstability issues whose origin has been harder to pin down. Hybrid mixed-halide perovskites enable the construction of more stable and better performing devices and have thus gained considerable attention. Initial ²⁰⁷Pb ssNMR experiments have allowed us to gain deeper insights into the structure and composition of these materials. We have discovered that spontaneous spinodal decomposition and amorphous impurities permeate mixed-halide perovskites. We have successfully removed the amorphous impurities by introducing a new solvent-free synthesis that benefits from facile halide diffusion in the solid state. The application of more advanced ssNMR techniques such as fast MAS and DNP will greatly shorten the acquisition time required for ²⁰⁷Pb and other NMR experiments on other hybrid perovskites. This will allow for more in-depth studies of impurities and stability factors that are unique to these materials and their devices. Advanced optical spectroscopy is similarly critical to the study of lead halide perovskites. Evaluating the ensemble and singleparticle photoluminescence stability and intermittency of these materials is a key to their continued viability in future applications. Finally, Raman spectroscopy could provide complementary vibrational data about the structure and stability of perovskites, so long as it is carefully performed to eliminate the possibility of laser-induced sample degradation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.6b00674.

Video file describing the work being done on hybrid perovskites at Iowa State University (AVI)

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