

**Optoelectronic Quality and Stability of Hybrid Perovskites Determined by
Steady-State Luminescence Techniques**

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Abstract

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Hybrid perovskites are the most promising solution-processable semiconductor for low-cost, high efficiency photovoltaic applications to date. In particular, inorganic-organic lead halide perovskites are well suited for converting the sun's rays into electrical power. In addition to having the right light-absorbing and charge-carrier transport properties, hybrid perovskites may be synthesized via facile solution-based deposition techniques and demonstrate notably low amounts of heat-generating losses under illumination. Even polycrystalline films cast from hand-made inks can sustain very high concentrations of light-generated charge carriers, and in turn sustain large open-circuit voltages. Further, the three-component formula of ABX_3 (A = monovalent cation, B = divalent metal, C = halide) makes the composition space for hybrid

perovskites enormous. Each component can be alloyed to tune the bandgap for either single-junction or two-junction applications. In this dissertation, several methods centered around steady-state photoluminescence are detailed for characterizing this new class of materials. We explore the impact of composition, illumination time, charge-injection, and atmospheric conditions on the optoelectronic quality and stability of hybrid perovskites. We show that absolute intensity steady-state photoluminescence measurements of neat hybrid perovskite thin-films modeled with the Lasher-Stern-Würfel equation enables reliable prediction of device open-circuit voltages. Combinatorial spray coating and photoluminescence mapping of halide alloys reveals that the optoelectronic quality decreases with increasing bromide concentration. Finally, we present a scalable analysis tool-kit to analyze wide-field microscope videos of hybrid perovskite thin-film photoluminescence flickering.

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DEDICATION

This dissertation is dedicated to my wife, Kimberly. She deserves at least half of all the post-nominal letters I will ever acquire.

Chapter 1. INTRODUCTION

1.1 MOTIVATION

For the more than 50 years,¹ many generations of scientists and engineers have been developing photovoltaic (PV) technologies in order to harness the abundant solar resource that provides earth with on average about 9×10^4 Terawatts of power. Progress toward such a technological achievement has been hindered by economic variables such as panel cost per square meter, installation costs, soft costs, and energy market volatility. Since 2012, however, the levelized cost of PV produced electricity has plummeted mostly due to decreasing feed stock costs, learning curve improvements with scale-up, and this has resulted in a decrease in cost per peak Watt of utility-scale monocrystalline silicon-based (c-Si) solar power to \$0.64/W_p.² Indeed, the annual increase of U.S. domestic PV energy production increased from 2016 to 2017 by 40%.³

However, the U.S. consumed about 3×10^4 TW-hrs. total energy last year,⁴ and roughly 4000 TW-hrs. of that was in the form of electricity³. Overall this resulted in over 5 billion tons of CO₂ emissions, among other pollutants, to the Earth's atmosphere.⁴ In comparison, last year the U.S. produced 2.3×10^3 TW-hrs. total PV electricity.³ As grid parity is reached in wider regions around the world, the limiting factor for the penetration of PV into the electricity production sector is no longer the price, but rather the capacity to produce solar panels.

Solution-processed, thin film PV technologies are a promising alternative to c-Si technologies due to the potential accelerate solar panel production by reducing the capital intensity of building PV production plants.⁵ By realizing factories of reduced capital intensity, lower minimum sustainable cost per PV unit could be realized.⁶ Furthermore, if requiring cheaper feedstocks and processing equipment, thin film PV factories would be able to sell panels at a cheaper price and still make a profit in the long run even though it might cost a similar amount per unit to produce. For example, cadmium telluride (CdTe), albeit vacuum-based, is a

thin film PV technology that is cost competitive compared with silicon-based PV.⁷ Presently, the substrate and encapsulation make up a significant portion of the manufacturing cost of these mature thin-film technologies, enabling a U.S. dollar per square meter production cost of less than \$100 (compared to about \$130 for silicon-based PV);⁸ however, the scarcity of tellurium, indium and gallium casts doubt on the possibility of global scale production and long-term sustainability of such approaches.⁹ Therefore, there is a pressing need for a PV technology that meets four design constraints: (1) It must have a low economic barrier for entry into the production market (i.e. low CAPEX); (2) it must have low cost, earth-abundant feedstocks; (3) it must be stable to last significantly past its minimum time to ROI; and (4) it must be inherently environmentally benign.

Until very recently, the possibility of meeting this pressing need seemed decades away based on previous demonstrations of slow performance improvements.¹⁰ However, hybrid perovskite based PV (i.e. methylammonium lead iodide and variants thereof) has gone from birth as a technology¹¹ to achieving a 19.7% certified 1 cm² cell power conversion efficiency (PCE) in less than 10 years.¹² This rapid improvement can be owed to their high absorption coefficients,¹³ moderate charge carrier mobility,¹⁴ and significant defect tolerance. The ternary nature and geometric flexibility of the perovskite structure enables a wide range of alloys. Each cation and anion of the crystal structure can be mixed to control the material properties¹⁵⁻¹⁷, and surprisingly the compositions with increased complexity and manifold alloying are leading higher performance^{18, 19} – rather than material purity being the most important factor. Excitingly, the perovskite compositions with optimized performance for either single-junction or multi-junction photovoltaic applications have likely not been yet discovered.

Of the remaining hurdles for widespread adoption of hybrid perovskite thin-film photovoltaic technology, material stability²⁰ and toxicity²¹ remain the most significant. Since the multi-faceted metric of perovskite stability is composition dependent, the search for an optimal

perovskite composition which possesses both high optoelectronic quality and robust stability poses a significant challenge.

1.2 RESEARCH FOCUS

The goal of this work is to characterize the novel material class of hybrid perovskites based on the extent to which they can sustain large open circuit voltages (V_{oc}) under illumination for single junction and 2-terminal tandem PV applications. Further, considering the challenges that hybrid perovskites present with regard to photo-stability, an additional goal is to characterize the ability of variants within the hybrid perovskite material class to maintain these large V_{oc} 's over time under constant illumination. We will show how the combination of steady-state photoluminescence characterization and combinatorial materials screening can be a powerful tool to swiftly assess thousands of hybrid perovskite compositions for their optoelectronic quality; and we apply several steady-state luminescence techniques to evaluate the stability of these materials over time.

1.3 SIGNIFICANCE

This work makes at least three significant contributions to the larger body of hybrid perovskite thin film photovoltaics: (1) We demonstrate absolute intensity steady-state photoluminescence as an effective characterization technique for predicting optoelectronic quality of a material before carrying out device optimization; (2) we couple this characterization technique with combinatorial spray coating in order to map a wide range of hybrid perovskite alloys; and (3) we lay the groundwork to assess the environmental stability of various hybrid perovskite compositions by developing video analysis tools to characterize photoluminescence videos. Each of these items are outlined in Chapters 2-4, respectively. Perhaps the most significant observation made in this study was the decreasing optoelectronic quality with bromide composition, which is shown in Figure 3.4. The paradigm that improving the quasi-

Fermi level splitting determined by steady state photoluminescence measurements will lead to higher open circuit voltages was successfully implemented in this case, and our understanding of the inherent problem of low quasi-Fermi level splitting in most high bandgap hybrid perovskites gave us a substantial advantage while developing 2-terminal top cell perovskite materials.

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Chapter 2. PHOTOLUMINESCENCE TO ASSESS MAXIMUM OPEN-CIRCUIT VOLTAGE IN HYBRID PEROVSKITES AND OTHER PHOTOVOLTAIC MATERIALS

2.1 PREFACE

Quantifying and characterizing the photon flux emitted from a semiconductor thin-film under illumination is the fundamental theme of this entire work. Whether it is spectrally, spatially, temporally, or some combination thereof, our accurate quantification of the absolute intensity photon flux emitted from the material gives us insight into how well we would expect that material to perform in a photovoltaic device. This chapter sets the foundation by developing, critiquing, and demonstrating the photoluminescence characterization techniques used throughout this work. A specific thanks to John Katahara for bringing me up to speed on these topics in the beginning and to Thomas Kirchartz for the invitation to share the content of this chapter with the readers of the Journal of Physical Chemistry Letters.

This chapter was adapted from an invited perspective article for The Journal of Physical Chemistry Letters:

Braly, I.L.; Stoddard, Ryan J.; Rajagopal, Adharsh; Jen, Alex K-Y.; and Hillhouse, H.W. Photoluminescence and Photoconductivity to Assess Maximum Open-Circuit Voltage and Carrier Transport in Hybrid Perovskites and Other Photovoltaic Materials. *J. Phys. Chem. Lett.*, **2015**, *Submitted*.

Additionally, Section 2.5D was adapted from an accepted article which was an equal-contribution collaboration with Dane W. deQuilettes:

Braly, I.L.; deQuilettes, D.W.; Pazos-Outón, L.P.; Burke, S.; Ziffer, M.E.; Ginger, D.S.; and Hillhouse, H.W. Hybrid Perovskite Films Approaching the Radiative Limit with over 90% Internal Photoluminescence Quantum Efficiency. *Nat. Photonics*, **2018**, *In Press*.

2.2 ABSTRACT

Photovoltaic (PV) device development is much more expensive and time consuming than the development of the absorber layer alone. This chapter focuses on a method that can be used to

rapidly discover and develop promising PV absorber materials prior to, or in parallel with, PV device development. One of the main factors that determine the power conversion efficiency (PCE) of a PV device is the open-circuit voltage (V_{oc}). The quasi-Fermi level splitting under steady effective one-Sun illumination is an indicator of a material's ability to achieve high V_{oc} . The quasi-Fermi level splitting can be rapidly and simultaneously assessed by conducting steady-state absolute intensity photoluminescence measurements, is extremely useful for predicting the quality of PV materials prior to PV device development. Here, we summarize the method, discuss its strengths and weaknesses, and compare results on several PV materials (and their resulting devices) including methyl ammonium lead iodide HP, low bandgap HPs, high bandgap HPs, CISE CIGSe, CZTSe, and GaAs.

2.3 INTRODUCTION

Photovoltaic module costs have dramatically decreased over the past ten years¹, which can be attributed to concurrent improvements in module power conversion efficiency, stability, and manufacturing costs. While silicon based modules represent a majority of installed PV, CdTe and Cu(In,Ga)(S,Se)₂ thin-film PV modules have also experienced similar cost improvements.² Despite these encouraging trends, the capital expenditure required to build a 2 GW-per-yr. capacity PV c-Si module factory still requires on the order of US \$2 billion.³ This high entrance barrier creates substantial investment risk in an already uncertain market sector, and constrains the PV module manufacturing capacity growth. The commercialization of solution-processed photovoltaic technologies has the potential to decrease the capital expenditure by as much as 94%,³ which provides incentive for further research and development of new solution chemistry, materials, and processing strategies for Cu(In,Ga)(S,Se)₂,⁴ Cu₂ZnSn(S,Se)₄,^{5,6} hybrid perovskite⁷ (HP), inorganic perovskite,⁸ and quantum dot⁹ solar cells. During the development process, the quality of the absorber layer is often inferred from the performance of the completed PV device. However, while absorber material quality (after thin film deposition) sets upper limits for the

efficiency of the completed device, it is often unclear whether lower-than-optimal device performance is due to the optoelectronic quality of the absorber layer, due to the device architecture, or due to problems that are created during processing of the other layers. This ambiguity can result in missed opportunities (abandoning good materials because of poor device architecture) or misdirected efforts (searching for better architecture and subsequent layer processing when the starting quality of the absorber layer is poor). A more efficient strategy is to decouple absorber material quality evaluation from the engineering of a complimentary device architecture, particularly for new materials and devices.

Recently, hybrid perovskite materials have been developed into excellent optoelectronic quality absorber layers for high efficiency photovoltaic (PV) devices¹⁰ and have the potential to be cost-effective compared to existing commercial technology.^{11, 12} The relatively low purity required to achieve high optoelectronic quality polycrystalline perovskite films make these materials of considerable interest. Specifically, the superb open-circuit voltage (relative to the radiative-limit open-circuit voltage) achieved by perovskite devices^{13, 14} are unparalleled when compared to those utilizing other solution-processed absorber materials. The underlying electronic structure and defect tolerance¹⁵ are credited for enabling such high performance from such polycrystalline and defective absorber layers. Two lingering questions remain: What is the environmental impact related to producing lead-based hybrid perovskite PV modules? And will perovskite modules be able to last 20 years or more to achieve a reasonable levelized cost of energy? These questions motivate several active areas of research, including the development of lead-free hybrid perovskites,¹⁶ the understanding of fundamental perovskite degradation mechanisms,¹⁷ and long-term device stability testing.¹⁸ Several materials¹⁹ and materials discovery strategies^{20, 21} based on simulation have been proposed to find new PV-relevant materials with similar defect-tolerance as hybrid perovskites. Unfortunately, such simulation tools are not capable of yielding accurate and quantitative information about carrier recombination under illumination (e.g. steady-state quasi-Fermi level splitting, minority carrier

lifetime, diffusion length, etc.) that ultimately determine the open-circuit voltage and short-circuit current that a material will likely yield in an optimized PV device.

In this chapter, we review a method that can help improve existing PV materials and accelerate the search for new materials. Absolute intensity photoluminescence (AIPL) spectra are fit to a spectral emission model or uses the photoluminescence quantum yield (PLQY) to estimate the steady-state quasi-Fermi level splitting (QFLS or ΔE_F). We demonstrate the close correspondence between the $\Delta E_F/q$ (where q is the unit of fundamental charge) and the subsequently measured device V_{OC} , and show successful implementations of this model to screen thousands of solution processed semiconductor compositions to select for high open-circuit voltage. In addition, these measurements can be conducted with little more than a microscope with LED source, filter cubes, a monochromator, and detector with proper calibration. We review the strengths and weakness of the method, highlight situations where it is expected to provide excellent results, articulate situations where one should be cautious, and show how the results compare to measurements on completed PV devices.

2.4 MODELING STEADY-STATE BAND-TO-BAND PHOTOLUMINESCENCE

A. Quasi-Thermal Equilibrium Approximation

The charge carrier populations present in a semiconductor under illumination are not described by a single Fermi energy. The occupation of the energy levels in such non-equilibrium situations are often accurately described by making the quasi-thermal equilibrium approximation.²² This approximation assumes that all electrons in the conduction band are in thermal equilibrium with each other and with the lattice and that the occupation probability of the conduction band energy levels are well-described by a Fermi-Dirac distribution with a Fermi energy (unique to the conduction band) called the quasi-Fermi energy of the conduction band (E_F^{CB}). Likewise, all electrons in the valence band are assumed to be in thermal equilibrium with each other and the

lattice, and the occupation probability of the valence band energy levels are well-described by a Fermi-Dirac distribution with a Fermi energy (unique to the valence band) called the quasi-Fermi energy of the valence band (E_F^{VB}). The quasi-Fermi level splitting (QFLS or ΔE_F) is the difference between these two energies ($\Delta E_F = E_F^{CB} - E_F^{VB}$) at any given location. In common terms, a Fermi energy or a quasi-Fermi energy may be interpreted as a measure of the escaping tendency of an electron from a collection of electrons (for instance the conduction band electrons) at a given location. As a result, the quasi-Fermi level splitting at a given location is the driving force for all recombination processes (trimolecular Auger, bimolecular radiative, Shockley-Read-Hall, etc.). Thus, in principle, ΔE_F may be determined from the band-to-band radiative emission if it can be quantitatively measured. In general, ΔE_F is dependent on position, temperature, physical properties of the material, state of illumination or carrier injection, and if the material is at steady state (local electron and hole concentrations not changing with time).

ΔE_F also quantifies the maximum V_{OC} that a single material could generate in a PV device, $V_{OC}^{max} = \Delta E_F/q$.

B. Spectral Photoluminescence Flux from a Semiconductor Surface

The theory of how quasi-Fermi level splitting is connected to external radiative emission from a surface is well established (see publications by Lasher and Stern^{23, 24} and by Würfel,^{23, 24} and our previous paper on the method for more details²⁵). The spectral photoemission from a surface is given by the Lasher-Stern-Würfel (LSW) equation (also referred to as the Generalized Planck Law):

$$I_{PL}(\varepsilon) = \rho(\varepsilon) \cdot f_{BE}(\varepsilon, \Delta E_F, T) \cdot a(\varepsilon, E_F^{CB}, E_F^{VB}, T) \quad (2.1)$$

Where I_{PL} is the external spectral photon flux emitted (photons/(area·time·bandwidth)) from the surface of a semiconductor as a function of photon energy (ε); ρ is the photon density of states in

the external medium given by $2\pi \cdot \epsilon^2 / (h^3 \cdot c^2)$; f_{BE} is the Bose-Einstein distribution ($1/(e^{(\epsilon-\mu)/kT}-1)$) where the chemical potential of the bosons (the photons in this case, μ_γ) has been equated to the chemical potential difference between the electrons in the conduction band and valence band (which is just ΔE_F); a is the occupation and temperature dependent spectral absorptivity, and E_F^{CB} and E_F^{VB} are the quasi-Fermi energies of electrons in the conduction and valence bands, respectively. Equating the chemical potential²⁴ of photons with the quasi-Fermi level splitting may be understood by examining the “reaction,” $e^{CB} \rightarrow e^{VB} + \gamma$. This reaction may be considered to be at equilibrium when the sum of the chemical potentials equal zero ($\mu_e^{VB} + \mu_\gamma - \mu_e^{CB} = 0$, or $\mu_\gamma = \mu_e^{CB} - \mu_e^{VB} = \Delta E_F$). We note that the LSW equation only assumes microscopic reversibility, Lambertian emission from the semiconductor surface,²⁶ and quasi-thermal equilibrium.

It must be emphasized that the absorptivity given in eq 1 is not the typical absorptivity measured by a UV-vis experiment under low illumination conditions, but rather the occupation-dependent absorptivity which is valid at all injection levels.²⁷ The relationship between this absorptivity spectrum and the absorption coefficient will also depend on the sample specific characteristics (e.g. surface roughness, film thickness, back and front-surface reflectivity, etc.). The simplest case is for a smooth slab with no front or back surface reflectivity:

$$a(\epsilon, E_F^{CB}, E_F^{VB}, T) = 1 - \text{Exp} \left(-\alpha(\epsilon, T) \left(f_v(\epsilon, E_F^{VB}, T) - f_c(\epsilon, E_F^{CB}, T) \right) d \right) \quad (2.2)$$

where α is the joint-density-of-states based absorption coefficient (without consideration of occupation), f_v and f_c are the Fermi distributions for the valence and conduction bands, respectively, and d is the film thickness or the sum of the absorption length and diffusion length at the illumination wavelength (whichever is smaller). For the case of an intrinsic semiconductor with equal electron and hole effective masses, the two Fermi distributions can be simplified and expressed as a function of a single quasi-Fermi level splitting, ΔE_F :

$$f_v(\varepsilon, E_F^{VB}, T) - f_c(\varepsilon, E_F^{CB}, T) = 1 - \frac{2}{\text{Exp}\left(\frac{\varepsilon - \Delta E_F}{2kT}\right) + 1} \quad (2.3)$$

The result of substituting eq (2.3) into eq (6.1) can be further simplified (keeping the first term in a series expansion) to move the occupation correction factor out of the exponential and express it as a product with the other factors:

$$I_{PL}(\varepsilon) = \left(\frac{2\pi \varepsilon^2}{h^3 c^2}\right) \cdot \left(\frac{1}{\text{Exp}\left(\frac{\varepsilon - \Delta E_f}{kT}\right) - 1}\right) \cdot (1 - \text{Exp}(-\alpha(\varepsilon, T)d)) \cdot \left(1 - \frac{2}{\text{Exp}\left(\frac{\varepsilon - \Delta E_f}{2kT}\right) + 1}\right) \quad (2.4)$$

which is equivalent to eq 22 in Ref. 23.^{25, 28} To summarize, the first factor is the photon density of states (ρ), the second factor derives from the Bose-Einstein distribution (f_{BE}) and represents the main energy dependent driving force for emission, the third factor is the occupation independent absorptivity, and the fourth factor captures the occupation effects on absorptivity. If the quasi-Fermi level splitting is significantly lower than the energy of emitted photons being measured ($\varepsilon - \Delta E_F \geq 3kT$, as is common for experiments under effective one-Sun illumination intensities), then the occupation effects will be negligible (in which the last factor is approximately 1). In this case, one can also drop the negative one in the denominator of the f_{BE} to obtain a simple expression:

$$I_{PL}(\varepsilon) = \left(\frac{2\pi \varepsilon^2}{h^3 c^2}\right) \cdot (e^{-\varepsilon/kT} \cdot e^{\Delta E_f/kT}) \cdot (1 - e^{-\alpha(\varepsilon, T)d}) \quad (2.5)$$

Since ε is typically measured over a small range of energies near the bandgap, the density-of-photon-states (first factor in parentheses) is relatively constant and not the dominant ε -dependent factor. The first part of the second factor reveals that f_{BE} increases exponentially for

lower energy photons, and thus emission will occur through sub-bandgap states to the extent they are present. In fact, this factor reveals the requirement that the absorptivity below bandgap must decrease faster (as one examines decreasing photon energy below bandgap) than the increase in driving force in the first part of the second factor. The second part of the second factor reveals that the ε -independent component of f_{BE} increases exponentially with increases in the quasi-Fermi level splitting. Equations (2.4) or (2.5) are very useful. If one knows or has a model of the absorption coefficient (that includes sub-bandgap absorption), then one can fit the photoluminescence spectrum to obtain the quasi-Fermi level splitting. Alternatively, if one happens to know the quasi-Fermi level splitting, one can measure PL and determine the absorption coefficient spectrum.

C. Generalized Absorption Coefficient Model

Previously, a severe limitation of the LSW equation to predict or to fit photoluminescence spectra was the lack of generally applicable absorption coefficient models that included sub-bandgap states along with the above bandgap states. As a result, Katahara developed a general absorption coefficient model that includes sub-bandgap states^{25, 28} inspired by Kane's original treatment²⁹ (which is only valid in the semi-classical, Thomas-Fermi, limit). In our model we developed a two-parameter (γ and θ) sub-bandgap absorption function $\left(e^{|\varepsilon - E_g|/\gamma}\right)^\theta$ and combined it with a joint-density-of-states model for direct band-band transitions within the effective mass approximation ($\alpha_0\sqrt{\varepsilon - E_g}$) by using a convolution integral, which preserves the asymptotic behavior of the below and above bandgap models in their respective domain of relevance:

$$\alpha(\varepsilon) = \frac{\alpha_0 \sqrt{\gamma}}{2 \Gamma\left(1 + \frac{1}{\theta}\right)} \int_{-\infty}^{\Delta\varepsilon} \text{Exp}(-|\Delta\varepsilon'|^\theta) \sqrt{\Delta\varepsilon - \Delta\varepsilon'} d\Delta\varepsilon' \quad (2.6)$$

where α_o is a material dependent parameter related to the material oscillator strength; γ is the broadening energy of the sub-bandgap absorption distribution; θ defines the functional form of how the sub-bandgap states decay into the bandgap (where $\theta = 1, 1.25, 1.5$, and 2 correspond to Urbach, screened Thomas-Fermi with tunneling, Franz-Keldysh, and semi-classical Thomas-Fermi models, respectively); and $\Delta\varepsilon$ is a dimensionless energy parameter defined by $\Delta\varepsilon = (\varepsilon - E_g)/\gamma$. Note that Γ is the conventional gamma function, $\Gamma(x) = (x-1)!$, and is required for normalization of the integral of the sub-bandgap portion of the function. Absorption coefficients may be calculated at each energy given α_o , γ , θ , and E_g . The normalization prefactor of eq (2.6) is determined by insisting that the integral of the tail-state distribution over all energies is one. Problematically, the convolution integral is too slow computationally to be used effectively for non-linear least-squares fitting of measured photoluminescence (or absorption coefficient data) to determine α_o , γ , θ , and E_g . As a result, we have developed and reported data tables (used as numerical look-up tables) that enable rapid computation and fitting. Equation (2.6) is re-written as:

$$\alpha(\varepsilon) = \alpha_0 \sqrt{\gamma} G(\Delta\varepsilon, \theta) \quad (2.7)$$

where $G(\Delta\varepsilon, \theta)$ is a pre-calculated table of values.

D. Characteristics of the Combined Photoluminescence and Absorption Coefficient Model

The above absorption coefficient model is phenomenologically agnostic about the cause of sub-bandgap states and can model a very broad range of physical phenomena, from Urbach-based

short-range static and dynamic disorder ($\theta=1$), medium-range potential fluctuations and photon-enhanced tunneling ($1.25 \leq \theta \leq 2$), to long-range bandgap changes due to changing local stoichiometry ($\theta > 2$). To illustrate some spectral characteristics of the model, we examine the case for $\theta = 1$, where disorder is on the length-scale of the bond-length and gives rise to an Urbach tail.³⁰ We note that the absorption coefficient spectrum of GaAs near room temperature is well described by a direct bandgap density of states and an Urbach tail-state distribution.³¹ Figure 2.1 illustrates the relative importance of the different factors in the photoluminescence model described by eq (2.4).

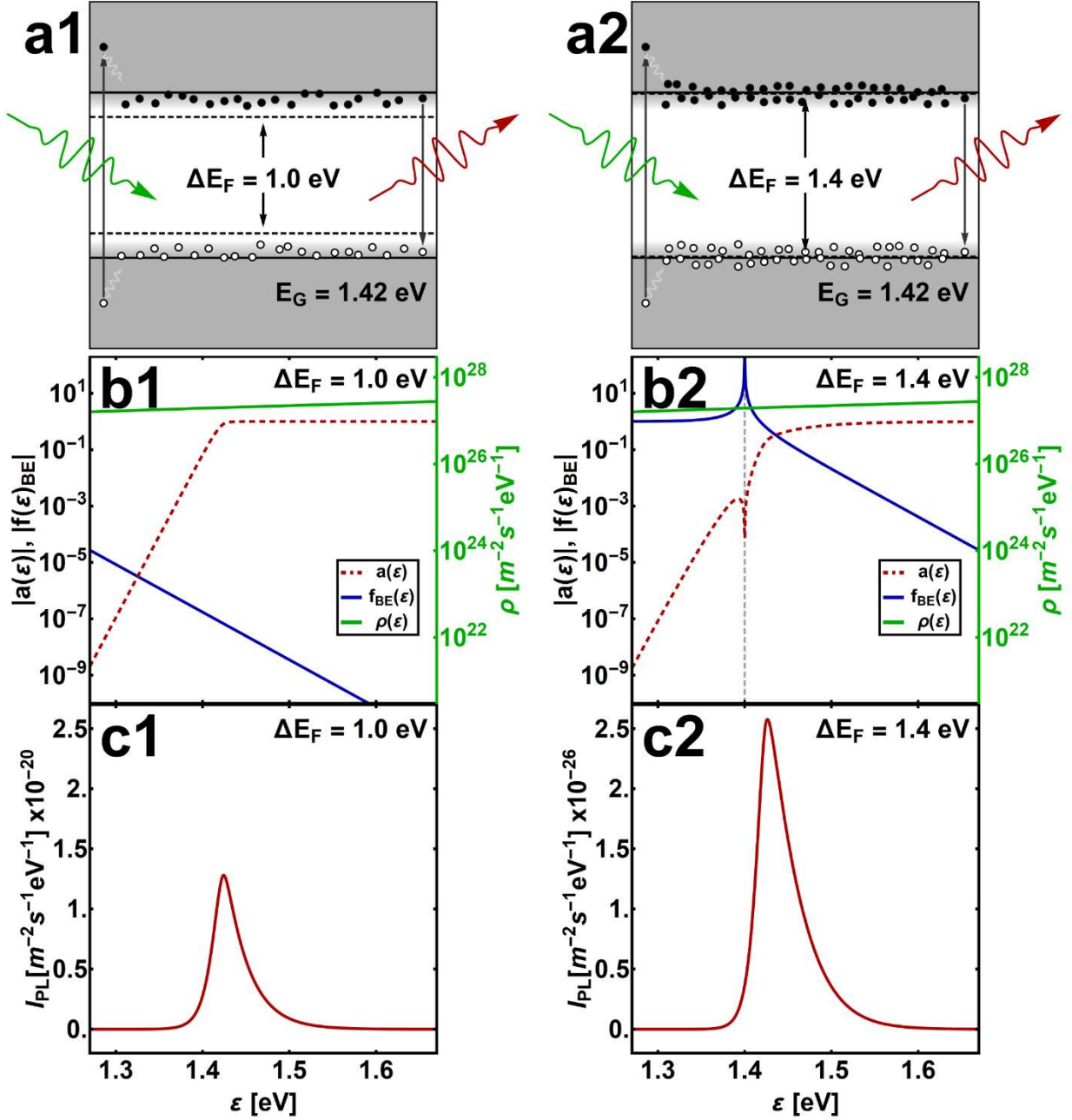


Figure 2.1 **Simulated photoluminescence spectra using eq 4** and parameters typical of GaAs: $E_g = 1.42$, $\theta = 1$, $\gamma = 7.5$ meV, and $\alpha_0 d = 40$. **Column 1** shows an example of $\Delta E_F = 1.0$ eV and **column 2** shows the example of $\Delta E_F = 1.4$ eV. **a**, energy diagram showing steady-state photoluminescence, including light absorption, hot-carrier relaxation, excess carrier population, and photon emission (not intended to portray location or direction of absorption/emission processes). The dark horizontal lines indicate the nominal band edge, while the grey shading into the bandgap indicates sub-bandgap states (the magnitude is exaggerated for illustrative purposes). The dashed lines indicate the quasi-Fermi levels. **b**, changes in the absorptivity spectrum (dashed red line), Bose-Einstein distribution (solid blue line), and photon density of states (solid green line). **c**, the modeled photoluminescence spectrum resulting from b. Note the six order of magnitude difference in emitted photon flux between c1 and c2, in addition to the absence of any pole in c2 despite the poles in b2.

Figure 2.1 b1 and b2 shows how changes in ΔE_F impact a and f_{BE} at room temperature, which results in photoluminescence peaks shown in Figure 2.1 c1 and c2. As can be seen by comparing the f_{BE} trends plotted in Figure 2.1 b1 and b2 with the resulting photoluminescence spectra plotted in Figure 2.1 c1 and c2, the energy-dependence of the high energy tail of the photoluminescence spectrum is dominated by the changes in the Bose-Einstein factor. Conversely, the energy-dependence of the low energy tail of the photoluminescence spectrum is dominated by the exponential decay of the sub-gap absorptivity factor. See 6.1 in the appendix for a discussion of the character of the photoluminescence model over a wide range of temperatures.

The factors in Figure 2.1b are plotted on a log-scale, therefore the absolute value of the a and f_{BE} are plotted since negative values are allowed for both of these cases (i.e. in the case of optical gain). This is important in the $\Delta E_F = 1.4$ eV case in Figure 2.1 b2 where the emission energy, ε , is equal to ΔE_F (i.e. where the vertical asymptote occurs in both a and f_{BE}). At energies below ΔE_F , a and f_{BE} are negative and their product is positive resulting in a positive emission flux. We have detailed the limitations of the model, achieving good fit of the entire photoluminescence peak, and other practical considerations in 6.3-5 of the appendix.

2.5 COMPARING CURRENT-VOLTAGE AND PHOTOLUMINESCENCE MEASUREMENTS

A. Does ΔE_F Determined from PL Match qV_{OC} Determined from Current-Voltage Measurements?

The steady-state quasi-Fermi level splitting in a neat absorber film under effective one-Sun illumination provides an estimate of the upper limit of the maximum-achievable open circuit voltage from a single-junction PV device that utilizes the film. We recently used this principle to guide the development of small and large bandgap perovskites for high efficiency two-terminal perovskite-perovskite tandem solar cells.³² Here, we collect AIPL from a wide variety of absorber

materials, fit the data using *eq* (2.5) to determine the quasi-Fermi level splitting, and measured the current-voltage characteristics of the completed devices to obtain the open-circuit voltage. Figure 2.2 shows these results for different PV absorbers including CuInSe₂⁴ (CISE), Cu(In,Ga)Se₂⁴ (CIGSe), Cu₂ZnSn(S,Se)₄⁵ (CZTSe), MA(Pb,Sn)I₃^{33, 34} (HP_{1.35}), MAPbI₃ (HP_{1.6}), and two recently developed HP compositions for overcoming the V_{oc} limitation in large bandgap perovskites (HP_{1.75} and HP_{1.82}). The abbreviations in parentheses will be used to refer to PV absorber type below. Also, note that for the HPs the number following “HP” indicates the bandgap in units of eV.

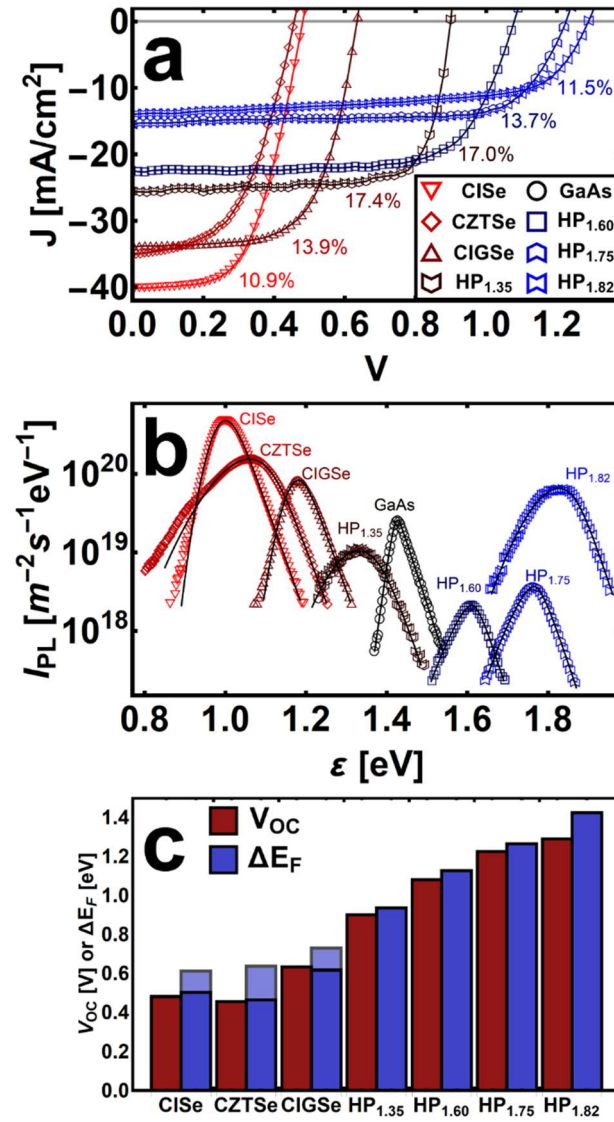


Figure 2.2 Device performance and photoluminescence: **a**, current density-voltage characteristics of CuInSe_2 (CIGSe, red triangles), Cu(In,Ga)Se_2 (CIGSe, red triangles), $\text{Cu}_2\text{ZnSn(S,Se)}_4$ (CZTSe, dark red diamonds), MA(Pb,Sn)I_3 (HP_{1.35}, black chevrons), MAPbI_3 (HP_{1.6}, blue squares), HP_{1.75} (upside-down blue chevrons) and HP_{1.82} (blue hexagons) PV devices. **b**, absolute intensity photoluminescence spectra collected at one-Sun equivalent light intensity from the same devices as **a**, with the addition of GaAs (black circles). **c**, comparison of device V_{OC} (red bars) and ΔE_F (blue bars). The light blue extension for the chalcogenides show the ΔE_F before intensity correction to 1 Sun while all dark blue bars are 1 Sun ΔE_F values.

The J-V characteristics of the PV devices are shown in Figure 2.2a and the device figures of merit are given in Table 1, and the photoluminescence spectra collected from the same PV devices are shown on a log-scale in Figure 2.2b and the model fitting parameters are given in Table 2. Reasonable fits were achieved for each photoluminescence spectrum in Figure 2.2b. The fitted temperatures ranged between near room temperature and 350 K (See 6.4E in the

appendix for discussion about fitted temperature and possible sources of error in slope of the high-energy tail). The extracted bandgaps agree with bandgaps determined by UV-Vis or EQE spectra. Values extracted for θ and γ are reasonable and provide additional information. The numerical values of θ between 1 and 2 is indicative of the length-scale of disorder. Note that the fit of the GaAs data yields parameters that are consistent with an Urbach tail with a broadening energy of 9 meV. The PL data from the chalcogenides were collected from absorber layers buried in the completed PV device, while the PL data from the perovskites were collected from neat films on glass. The CISE, CZTSe, and CIGSe spectra were collected at 68, 807, and 78 Suns, respectively. In the absence of a significant density of states within the bandgap, the quasi-Fermi level splitting is expected to increase logarithmically with light intensity. Therefore, we apply a correction to the ΔE_F values fit from the spectra collected at higher light intensities in order to predict the ΔE_F at one-Sun. The correction is calculated by subtracting $kT \cdot \ln(S)$ from the fit ΔE_F , where S is the number of equivalent Suns and is accurate when the steady-state excess carrier concentration is proportional to the incident photon flux³⁵ (see 6.5 of the appendix for details). The comparison between each extracted ΔE_F and device V_{OC} is shown in Figure 2.1c, and is shown to be in good agreement. While the intensity correction is valid when there is no density of states in the bandgap, if either of the quasi-Fermi levels are fully or partially pinned, the dependence of ΔE_F on intensity will be weaker. For the chalcogenide materials, this is a possibility.^{36, 37} Therefore we show the range of ΔE_F between the fit value at the elevated illumination intensity and the intensity-corrected value at one Sun in both Figure 2.2c and Table 2.1 and Table 2.2.

Table 2.1 PV Device Performance

Device	E_g [eV]	η [%]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]
CuIn(S,Se)₂	1.00	10.9	0.481	40.2	56.3
Cu₂ZnSn(S,Se)₂	1.11	8.2	0.456	35.0	51.4
Cu(In,Ga)(S,Se)₂	1.15	13.9	0.634	33.9	65.0
MA(Pb,Sn)I₃	1.35	17.4	0.900	25.6	75.5
MAPbI₃	1.60	17.0	1.081	22.4	70.3
HP_{1.75}	1.75	13.7	1.225	15.5	72.1
HP_{1.82}	1.82	11.5	1.290	13.8	64.0

Table 2.2 Data from Photoluminescence Fitting

Device	ΔE_F [eV]	T [K]	E_g [eV]	γ [meV]	θ
CuIn(S,Se)₂	0.50-0.61 [†]	330	1.02	47	2.0
CuInGa(S,Se)₂	0.62-0.73 [†]	330	1.19	39	1.8
Cu₂ZnSn(S,Se)₂	0.46-0.64 [†]	344	1.13	63	1.6
MA(Pb,Sn)I₃*	0.94	300	1.37	50	1.6
GaAs	0.95	310	1.43	9	1.0
MAPbI₃*	1.13	285	1.61	22	1.1
HP_{1.75}*	1.26	300	1.76	24	1.3
HP_{1.82}*	1.42	300	1.86	43	1.4

*Spectra collected from associated neat film prepared on a glass slide.

ΔE_F may be determined from PL from isolated films (separate from device layers), at any intermediate stage of device fabrication, and from buried absorber layers in completed devices. Each of these may be compared to qV_{oc} from the completed device, and each can reveal different but specific vital information. ΔE_F from an isolated absorber film, or from an absorber film grown during device fabrication but before overlayers are deposited, should provide the best estimate of the maximum possible qV_{oc} that the material could yield. If the measured device qV_{oc} is significantly less than this ΔE_F , it is a sign that either: (1) the absorber was damaged or

altered during overlayer deposition, (2) the interface between the absorber and overlayer has high interfacial recombination, or (3) there is a problem with band alignment with the overlayers. This is observed with the HP_{1.82} sample and suggests that even higher V_{OC} could be obtained with an alternate device structure. An extreme example of this is observed for BiI₃ (to be published data). The material has a bandgap of 1.8 eV, and AIPL measured from neat films yield a ΔE_F from of 1.0 eV, which is excellent and suggest high potential. However, the measured device V_{OC} is 0.4 V, which indicates significant issues with the device architecture or subsequent processing steps. This ability to determine the voltage generating potential of a material, prior to and separate from device fabrication, is a very strong advantage of this PL method. One can learn about the inherent quality of the thin film before other loss-mechanisms are introduced (if surface recombination at the air-absorber and absorber-glass interfaces do not dominate). Further, surface passivation^{38, 39} (see Section 2.5D) and other strategies⁴⁰ may be employed to inform appropriate materials selection for device engineering after the optoelectronic nature is better understood. When comparing the PL determined quasi-Fermi level splitting from a buried absorber layer in a completed device with the measured open-circuit voltage, it may also be observed that $\Delta E_F > qV_{OC}$, which further indicates band alignment issues. However, for buried absorber layers $\Delta E_F < qV_{OC}$ may be observed. In non-absolute intensity PL studies, some researchers have attributed the reduction in PL intensity in a buried absorber layer to be due to quenching (or the rapid transfer of photoexcited carriers into the adjacent material before radiative recombination can occur).⁴¹⁻⁴³

B. Connection between Photoluminescence Quantum Yield and Quasi-Fermi Level Splitting

Knowledge of the peak position and external photoluminescence quantum yield (PLQY or η) of a given material can allow a reasonable estimation of ΔE_F to be made, even if little else is known.

Ross developed a relationship between external photoluminescence quantum yield and ΔE_F by balancing the total recombination rate with the generation rate in a semiconducting material:⁴⁴

$$\Delta E_{F,\eta} = \Delta E_F^{max} + kT \ln(\eta) \quad (2.8)$$

where ΔE_F^{max} is the maximum quasi Fermi-level splitting, and η is the external photoluminescence quantum yield. This relationship accounts for losses due to non-radiative recombination which decreases η and the effects of temperature. Calculating $\Delta E_{F,\eta}$ is convenient because η can be measured using an integrating sphere⁴⁵ or calculated by integrating the spectral component of measured absolute-intensity photoluminescence spectra. In this “PLQY” method for estimating ΔE_F , the temperature to use must be chosen (not fit as above). Selecting an incorrect temperature when it is otherwise not possible to determine the surface temperature of the film under illumination can lead to significant error when $\eta \ll 0.01$. ΔE_F^{max} may be determined if the absorptivity spectrum is known by:

$$\Delta E_F^{max} = kT \ln \left(\left(\frac{h^3 c^2}{2\pi} \right) \frac{S \int_0^\infty a(\varepsilon) I_{in}(\varepsilon) d\varepsilon}{\int_0^\infty \varepsilon^2 a(\varepsilon) \exp\left(\frac{-\varepsilon}{kT}\right) d\varepsilon} \right) \quad (2.9)$$

Where I_{in} is the spectral photon flux incident to the material based on the AM1.5GT spectrum and S is the number of Suns. *Equation 9* makes the same simplifications and assumptions as eq 5, and the same correction. However, if the absorptivity spectrum is not known, ΔE_F^{max} may be approximated by assuming a step-function absorptivity (i.e. set $a = 1$ for $\varepsilon > E_g$ and 0 for $\varepsilon < E_g$). This is a similar treatment applied by Shockley and Queisser,⁴⁶ and comparisons of ΔE_F^{max} values using a step-function absorptivity (ΔE_F^{SQ}) to those using the actual absorptivity have been made for several materials elsewhere.⁴⁷ We compare device V_{OC} values from Table 1, ΔE_F values from Table 2, and $\Delta E_{F,\eta}$

Table 2.3 Comparing device V_{OC} , ΔE_F , and $\Delta E_{F,\eta}$

	V_{OC} [V]	ΔE_F [eV]	$\Delta E_{F,\eta}^*$ [eV]	$\Delta E_{F,\eta}^{**}$ [eV]
CuIn(S,Se)₂	0.481	0.50-0.61 [†]	0.55-0.65 [†]	0.57-0.67 [†]
Cu(In,Ga)(S,Se)₂	0.634	0.62-0.73 [†]	0.67-0.78 [†]	0.68-0.79 [†]
Cu₂ZnSn(S,Se)₂	0.456	0.46-0.64 [†]	0.53-0.70 [†]	0.59-0.76 [†]
MA(Pb,Sn)I₃***	0.900	0.94	0.88	0.92
MAPbI₃***	1.081	1.13	1.10	1.09
HP_{1.75}***	1.225	1.26	1.26	1.27
HP_{1.82}***	1.290	1.42	1.41	1.44

* Assumes $T = 300$ K, unit-step absorptivity, and E_g = Photoluminescence peak position

** Assumes $T = 300$ K, unit-step absorptivity, and E_g = Fit bandgap from Table 2.2

[†] Fit values with and without intensity correction.

*** Spectra collected from neat film prepared with the same ink batch as device

The quasi-Fermi level splitting obtained from spectral fitting and the quasi-Fermi level splitting obtained from the PLQY, ΔE_F and $\Delta E_{F,\eta}$, respectively, agree reasonably well. However, even with the intensity correction, the $\Delta E_{F,\eta}$ values for CISE, CIGSe, and CZTSe are significantly higher than the ΔE_F values from fitting the entire spectrum. This overestimation of ΔE_F based on the $\Delta E_{F,\eta}$ values calculated likely results from an underestimation of the effective electron temperature and an underestimation of the radiative losses. The purpose of presenting the $\Delta E_{F,\eta}$ model is to illustrate that it can give reasonable results when relatively little is known about a material, and to show the impact of making assumptions about the temperature and radiative losses.

C. Using ΔE_F Determined from PL for Materials Screening

Since the quasi-Fermi level splitting determined from photoluminescence is an excellent predictor for the maximum open-circuit voltage that a material may be able to generate, it is an excellent tool for discovering new promising photovoltaic materials or exploring trends over large composition spaces. However, when the bandgap changes with composition, it is more

appropriate to consider the ratio of the quasi-Fermi level splitting to the Shockley-Queisser quasi-Fermi level splitting as the parameter to maximize, $\chi = \Delta E_F / \Delta E_F^{SQ}$. For example, we previously screened the optoelectronic quality of over 6000 unique compositions of CZTSe by utilizing combinatorial spray-coating techniques,⁴⁸ see Figure 2.3. The experiments revealed the optimum composition regions (all off-stoichiometric, and copper deficient) for high open-circuit voltage. Measurements on devices confirmed this trend. Additional high throughput screening experiments were conducted to explore dopants and alloying in CZTSe and revealed beneficial effects of lithium and germanium. Subsequent scanning Kelvin probe microscopy and device development confirmed that lithium passivated CZTSe grain boundaries and led to device efficiency improvements⁵ while germanium alloying with tin led to record voltage efficiency in $\text{Cu}_2\text{Zn}(\text{Sn},\text{Ge})(\text{S},\text{Se})_4$.⁴⁹ In Chapter 3, we extend this composition screening technique (spray coating combined with the PL methods discussed above) to hybrid perovskites with ABX_3 stoichiometry in order to understand the optoelectronic quality trends with X-site alloying (iodide-bromide alloys) methylammonium lead halides.⁵⁰ The experiments show that increasing bandgap (via increasing bromide content) led to decreases in optoelectronic quality (separate from the phase segregation issue identified by Hoke et al.⁵¹). This trend was later observed as V_{oc} limitations for high bromide perovskites in numerous device focused publications.⁵² Based on the quasi-Fermi level splitting trends observed from PL, we postulated that the decreasing optoelectronic quality with increasing bromide content is consistent with a near band edge defect in the pure iodide material which transitions to become deeper in the bandgap for the mixed halide material. More recently, we have used the same composition screening tool to explore the wide space of A-site alloying in order to exceed the voltage limits encounter with the higher bandgap perovskites.⁵³ In particular, the method was able to identify specific A-site alloy mixed compositions of guanidinium (GA), formamidinium (FA), methylammonium (MA), and cesium (Cs) with exceptionally high ΔE_F and χ in the range of bandgaps ideal for tandem solar cells (both with silicon bottom cells and all perovskite tandems), see Figure 2.3c-d. Solar cells

from some of these compositions have yield record high open-circuit voltages for p-i-n devices in the bandgap range of 1.7 eV to 1.8 eV (1.24 V for a 1.75 eV bandgap),⁵³ which is the ideal range for many tandem solar cells with a perovskite top cell.^{32, 36, 54}

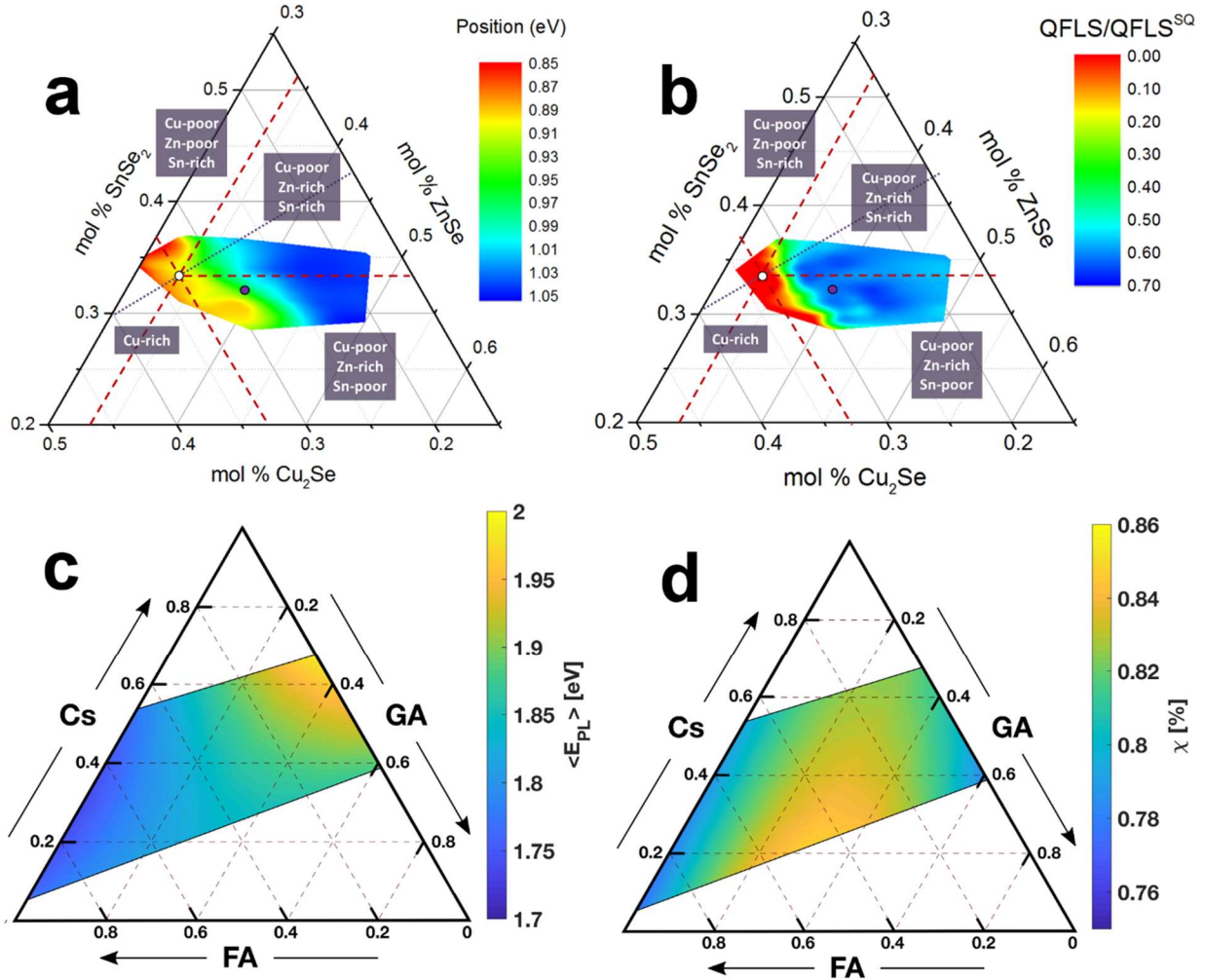


Figure 2.3 Ternary diagrams showing compiled photoluminescence performance for a wide range of CZTSe (a and b) and hybrid perovskite compositions (c and d). **(a)** Photoluminescence peak position map, and **(b)** measured to detailed-balance limit quasi-Fermi level splitting ratio (χ) map from CZTSe composition gradient library. **Reprinted with permission from IEEE Journal of Photovoltaics.** **(c)** Mean peak position map, and **(d)** χ map from hybrid perovskite A-cation composition gradient library for (GA,FA,Cs)Pb(I_{0.66},Br_{0.34})₃. **Adapted from Ref. 19.**

D. Using ΔE_F Determined from PL for Assessing Surface Passivation

We used confocal photoluminescence spectroscopy to study CH₃NH₃PbI₃ films before and after surface passivation. We prepared the perovskite precursor solution by mixing lead acetate and

methylammonium iodide in dimethylformamide and spin-coating this solution on a gold back reflector substrate with a SiO_x insulating layer³². We note that this type of geometry closely resembles a typical structure for a perovskite based photovoltaic device with Au serving as a back contact³³. Sister samples were subsequently surface treated with a dilute (0.025 M) solution of *n*-trioctylphosphine oxide (TOPO) in chlorobenzene. Others have previously shown that TOPO treatment reduces non-radiative recombination and is primarily confined to the surface, does not lead to any quantifiable changes in the film structure, and likely forms a new bond upon interaction with the perovskite surface⁵.

We measured the external photoluminescence quantum efficiency of a representative control sample and TOPO treated film at 1-Sun equivalent illumination intensity (continuous-wave, 60 mW/cm² at 532 nm). Figure 2.4a shows the control (red) and treated (blue) photoluminescence spectra on an absolute scale (calibrated to a black body source, details in Chapter 6, Section 6.6, Figures 6.4–6.6) with best fits to the data (black lines) using eq (2.4). See Chapter 6, Section 6.7 and Figure 6.7 for fitting parameters used for the control and TOPO treated film. The untreated film exhibited an average external photoluminescence quantum efficiency (η_{ext}) of $0.92 \pm 0.50\%$ (Figure 2.4b) and spatially averaged $\Delta\mu$ of 1.21 ± 0.02 eV ($N = 121$, 95% confidence) (Figure 2.4c), which is typical for films prepared from the lead acetate route and comparable to values reported for the highest performing devices⁸. Next, we fit the photoluminescence spectrum of a TOPO surface passivated film demonstrating an average η_{ext} of $20.3 \pm 5.6\%$ and extracted a $\Delta\mu = 1.28 \pm 0.01$ eV ($N = 121$, 95% confidence). Because the photoluminescence of polycrystalline perovskite thin films is known to be spatially heterogeneous³⁴, we report spatial averages, with the error intervals primarily reflecting the spatial heterogeneity in the film.

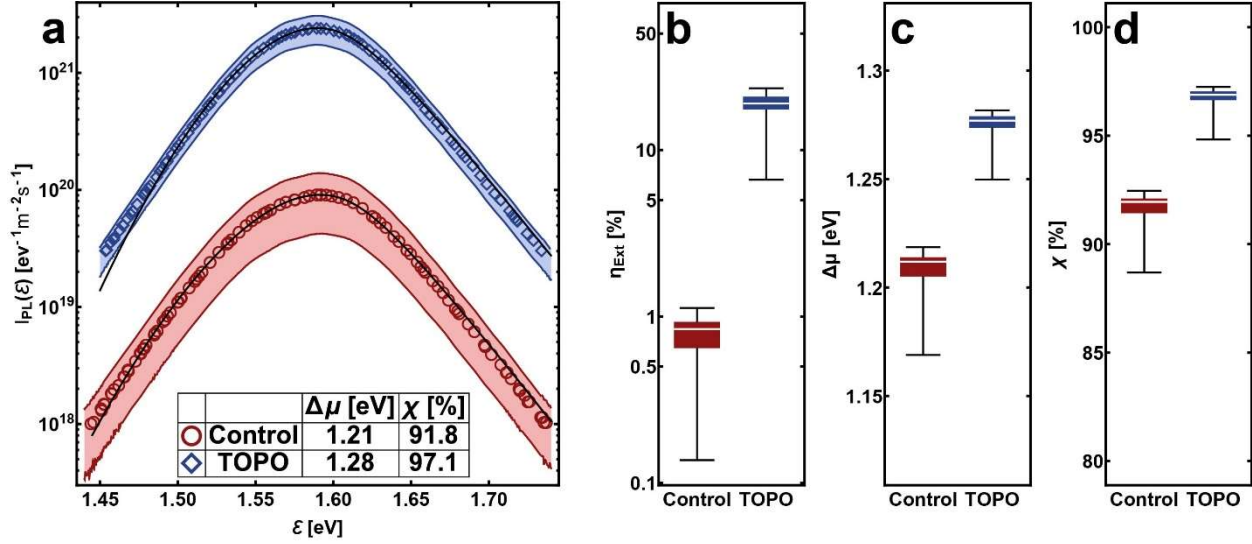


Figure 2.4 Absolute intensity photoluminescence spectra of control (red circles) and TOPO treated (blue diamonds) $\text{CH}_3\text{NH}_3\text{PbI}_3$ films deposited on an Au back reflector substrate measured in air. a, Log-scale photoluminescence spectra with fits to the data (black lines) using the generalized Planck model, shaded regions represent 95% confidence intervals for the spatial variation within the sample ($N = 121$). Quasi Fermi-level splitting ($\Delta\mu$) and percent of radiative limit quasi Fermi-level splitting (χ) are shown in the inset table. **b-d,** Parameter spatial statistics (min, first quartile, median, third quartile, and max. $N = 121$) of the control film and the TOPO treated film obtained from fits of spectra in **a**, showing external photoluminescence quantum efficiency (η_{ext}), $\Delta\mu$ and χ , respectively. Other fit parameters are reported in the SI (see Fig. S1).

The magnitude of this improvement in $\Delta\mu$ after TOPO treatment is impressive considering the logarithmic dependence of V_{OC} on η_{ext} (See eq (2.8)), where enhancements on a similar scale led to record efficiencies for GaAs³¹. Since the V_{OC} deficit for a given material depends on its bandgap, we use the modeled bandgap energy to calculate the radiative limit $\Delta\mu$ and compare to the observed $\Delta\mu$'s. The radiative limit is defined as the detailed balance limit for a material accounting for its real absorptivity spectrum (See Chapter 6, Section 6.8 and Figure 6.8). We note that this limit is dependent on several factors including film thickness and total sub gap absorptivity (See Figure 6.9). Using the extracted bandgap of 1.60 eV, Fig. 1d shows that the control film achieved $91.7 \pm 1.3\%$ of the radiative limit $\Delta\mu$, again consistent with high quality, untreated films that have been implemented in state-of-the-art devices⁸. The $\Delta\mu$ is enhanced to $97.1 \pm 0.7\%$ (Fig. 1d) of the radiative limit $\Delta\mu$ after TOPO surface passivation. We calculate this value to be only 40 meV less than the radiative limit $\Delta\mu$. To put this in context, if a passivated hybrid perovskite film such as the one studied here can be successfully implemented into a

device with appropriate selective contacts, then the resulting device ($V_{OC} = 1.28$ V) would be comparable to the 1.122 V achieved by the world record GaAs^{16,35}, which is 96.2% of the Shockley-Queisser limit V_{OC} for GaAs¹¹.

2.6 COMPARING STEADY-STATE PL WITH OTHER LUMINESCENCE EXPERIMENTS

A. Steady-State PL Quasi-Fermi Level Splitting versus Time-Resolved PL Lifetime

Time-resolved photoluminescence (TRPL) experiments using pulsed laser illumination are often used in the study of PV materials to learn about recombination dynamics⁵⁵⁻⁵⁷ and minority carrier lifetimes.^{42, 57, 58} The strength of the technique lies in its ability to reveal the mechanism and kinetics of recombination processes^{55, 59} (determining rate coefficients) as the carrier concentration decays and the material returns to its dark equilibrium state. However, the technique has two significant weaknesses in that the recombination processes are observed in the dark and not at steady state (making it quite different from the conditions in an operational solar cell). This may not be a significant issue in some ideal materials, but for materials (like hybrid perovskites) with light-sensitivity, phase segregation, or deep traps that can be photo-passivated, the technique becomes more complex and proper interpretation involves a much larger suite of experiments investigating the resting time between repeated experiments, fluence, and any pre-light soaking. A second weakness is that it is not clear which effective lifetime is appropriate to use for assessing its PV performance. Certainly, the long-time tail in TRPL experiments, which typically occurs for very low excess carrier concentrations is not typically the relevant lifetime.⁶⁰ At the same time, the initial effective lifetime may not be appropriate either since the steady-state carrier concentration in a solar cell at open circuit conditions is highly dependent on the overall recombination rate. In contrast, steady-state photoluminescence experiments observe the steady-state radiative emission that results from

the steady-state quasi-Fermi level splitting that results from all the recombination processes in the presence of a steady generation rate caused by light absorption.²⁴ It naturally avoids both weaknesses of TRPL. The down side is that one cannot extract kinetic rate coefficients for various recombination processes without performing detailed illumination intensity experiments, but the performing experiment under relevant PV operating conditions is straight forward and rapid.

B. Steady-State Photoluminescence versus Electroluminescence

The dependence of the flux and spectral distribution of electroluminescence on quasi-Fermi level splitting are the same as for photoluminescence, and therefore the emission model summarized in this perspective may be applied to electroluminescence as well. However, in electroluminescence, the electrons and holes are injected from opposite electrodes and must be transported across interfaces and through the absorber material to recombine radiatively; whereas in photoluminescence, the electrons and holes are generated in the same location do not rely on transport in order to interact. As a result, electroluminescence quantum efficiencies of thin-film heterojunction PV devices are typically lower than photoluminescence quantum efficiencies of the same devices.^{13, 61, 62} In addition, injecting current into a PV device with significant series resistance reduces the ΔE_F in the absorber material and therefore reduces the emission intensity. Walter et al. used combined electroluminescence and photoluminescence imaging data to observe local variations of series resistance in hybrid perovskite and PERL c-Si devices.⁶³ We consider the simplicity of execution to be a key advantage of photoluminescence experiments over electroluminescence experiments. Namely, devices need not be fabricated to assess the inherent optoelectronic quality of the prepared absorber material. As mentioned above, this has applications for screening new materials,⁶⁴ alloys,⁵⁰ dopants,^{5, 48} and surface treatments.^{38, 53, 65}

2.7 CONCLUSION

In this perspective, we present effective characterization tools for quantifying optoelectronic quality in a wide range of semiconducting materials. The intimate connection between excess carrier populations in an illuminated absorber material and the resulting emission is described, and an absorption coefficient model capturing sub-bandgap tail state distributions and carrier occupation effects is described for the implementation into the Lasher-Stern-Würfel equation emission. Advantages, analysis strategies, and pitfalls of this technique are discussed. We demonstrate the application of this model by accurately determining the maximum obtainable local V_{OC} by fitting ΔE_F for experimental photoluminescence data and comparing to J-V results from various PV technologies. Steady-state photoluminescence spectroscopy is compared with time-resolved experiments and electroluminescence experiments. The most significant advantage of this semiconductor characterization tool is that it is amenable to high-throughput experiments because and does not require device fabrication and optimization. High-throughput compositional screening with the photoluminescence characterization technique presented in this chapter very effective for rapidly discovering new high-performance PV materials.

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Chapter 3. OPTOELECTRONIC QUALITY AND STABILITY OF HYBRID PEROVSKITES FROM MAPbI₃ TO MAPbI₂Br USING COMPOSITION SPREAD LIBRARIES

3.1 PREFACE

In this chapter, the method outlined in Chapter 2 for rapidly exploring and characterizing hybrid perovskite compositions is demonstrated in detail. What is striking is that over two years later the trend given in Figure 3.10 is still relevant today in the search for perovskite compositions amenable to the 2-terminal tandem top cell application.

Most of this chapter has been accepted for publication in Journal of Physical Chemistry C:

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Sections 3.4G and H were adapted from the following equal-contribution publication in ACS Energy Letters:

Braly, I.L.; Stoddard, R.J.; Rajagopal, A.; Uhl, A.R.; Katahara, J.K.; Alex, K.-Y.; and Hillhouse, H.W. Current-Induced Phase Segregation in Mixed Halide Hybrid Perovskites and its Impact on Two-Terminal Tandem Solar Cell Design. *ACS Energy Lett.*, **2017**, *2*, 1841-1847.

3.2 ABSTRACT

The development of stable high-bandgap hybrid perovskites (HPs) with high optoelectronic quality may enable tandem solar cells with power conversion efficiencies approaching 30%. The halide composition of HPs has been observed to effect bandgap, carrier lifetime and material stability. Here we report optoelectronic quality and stability under illumination of thousands of compositions ranging from the pure iodide (CH₃NH₃PbI₃) to the diiodo monobromide (CH₃NH₃PbI₂Br). Hyperspectral maps of steady-state absolute intensity photoluminescence (AIPL) are used to determine the quasi-Fermi level splitting (QFLS) at each point after

synthesis. The QFLS upon first illumination increases with bandgap and reaches a maximum of 1.27 eV under 1 Sun illumination intensity for a bandgap of 1.75 eV. However, the optoelectronic quality (χ), defined as the ratio of the QFLS to the maximum theoretical QFLS for bandgap, decreases with bandgap from around 88% for 1.60 eV bandgap down to 82% for 1.84 eV bandgap. Further, we show that a reversible light induced defect forms that reduces the optoelectronic quality, particularly for high bandgap materials. Composition analysis shows that the halide to lead ratio, (I+Br)/Pb, decreases from 3 for the pure iodide to 2.5 for the diiodo monobromide, suggesting a role of halide vacancies or halide substitution defects in the light induced instability for this synthesis route. Even with phase segregation, stable QFLS of about 1.17 eV are possible. We further investigate the cause of phase segregation and provide direct experimental evidence that excess charge carrier populations provide the driving force for the growth of iodide-rich domains. Comparing our QFLS to V_{OC} values from HP devices reported in the literature indicates that higher open circuit voltages are possible but may require optimization of band alignment. Further, the spectral shape of the PL emission is found to be more commensurate with Franz-Keldysh broadening from local electric fields or from a screened Thomas-Fermi density of states (as opposed to a joint density of states due to Urbach disorder).

3.3 INTRODUCTION

Hybrid perovskites (HPs) can be engineered to have a wide range of light absorbing and electronic properties. Several variants within this class of materials, particularly methylammonium lead iodide (MAPbI_3), its mixed halide variants (MAPbX_3), and its formamidinium variants (FAPbX_3), are under intense investigation for their applications in photovoltaics (PV).^{1,2} A novel aspect of mixed halide HP's is their ability to achieve high open circuit voltages. Photovoltaic devices from HPs with a bandgap of 1.62 eV (extracted from white-light biased EQE data) have achieved open circuit-voltages of 1.17 V, which is 87% of their

theoretical limit.³ For comparison, record GaAs and single-crystalline Si achieve 97% and 84% of their detailed balance limit V_{oc} , respectively. Time-resolved photoluminescence (TRPL) measurements of solution processed MAPbX₃ films reveal that minority carrier lifetimes on the scale of hundreds of nanoseconds are possible.⁴ These already high lifetimes improve further upon interface passivation with treatment of small molecules with Lewis base sites.⁵

Perhaps the most exciting aspect of large bandgap HPs are their application as a top cell in a tandem device with more mature PV technologies like c-Si,⁶ CIGSe,^{7, 8} or CZTSSe.⁹ For these materials, a top-cell absorber with a bandgap of about 1.75 eV will be necessary for current matching in a two-terminal monolithic tandem architecture. Developing a catalogue of optoelectronic quality for HP materials with bandgaps in this range is important for the development of low cost, solution processed tandem technologies.

Lead iodide based hybrid perovskites can be alloyed in order to tune their bandgap energy. Bandgaps ranging between 1.57 and 2.2 eV are accessible by incorporating bromide into the metal halide inorganic structure of MAPbX₃.¹⁰ The shift occurs as the crystal lattice decreases in size, changing from tetrahedral to cubic between 13-20% relative bromide at room temperature.^{10, 11} Interestingly, the sub-bandgap absorption increases as the bromine content increases. Fitting the data with an Urbach model shows that the Urbach energy increases from 14 meV to 140 meV as the relative bromide content increases from 0 to 80%.¹² This indicates that some form of disorder is increasing with bromine alloying. We note that these results are from absorption experiments under weak excitation, and many reports have shown dramatic changes in hybrid perovskites under illumination intensities expected during photovoltaic device operation.

Solar cells with relative bromide contents ranging from 0-100% have been demonstrated,^{10, 13} and it has commonly been observed that the addition of chloride prior to film crystallization improves V_{oc} .^{14, 15} However, devices with greater than ~20% relative bromide tend to suffer from larger V_{oc} deficits,¹⁰ and undesirable photo-induced traps.¹⁶ Here, we demonstrate a high-

throughput composition screening technique¹⁷ for hybrid perovskites fabricated with the sequential-step deposition process. We show how the optoelectronic quality and stability under illumination change for HP compositions with high bandgap energies relevant to tandem applications with Si or CIGS bottom cells. We also show that the Urbach model is not accurate for the joint density of states that determine emission, at least under 1 sun illumination. We show that light-induced defects reduce the quasi-Fermi level splitting (QFLS) under constant illumination. However, iodobromides with bromine content less than ~20% stabilize and should be able to maintain QFLS of about 1.17 eV. Realizing stable mixed halide hybrid perovskites with high optoelectronic quality is essential if this material is to have impact on the PV industry.

10, 13, 14, 18, 19

3.4 RESULTS AND DISCUSSION

A. Synthesis

We use a sequential step deposition method combined with spray coating to make composition gradients varying from pure MAPbI_3 to MAPbI_2Br . The sequential step synthesis method has been outlined elsewhere,²⁰ and several reports establish this route as an effective method for device fabrication.^{14, 21} Detailed spray gradient fabrication and analysis details are given in Chapter 7, Sections 7.1A-C. Briefly, a mesoporous alumina scaffold is deposited by spin coating on a clean glass substrate. The porous layer is filled with lead iodide by precipitation upon spin coating (Figure 3.1a and c). Finally, methylammonium (MA) halide is introduced to the lead iodide films by spray coating an ethanol solution while heating the substrates on a hotplate (Figure 3.1b and d). Two syringe pumps, one containing a MAI solution and the other containing a MABr solution, are sequenced as the spray nozzle translates along a line of PbI_2 coated substrates, creating the composition gradient (Figure 3.2a). Samples are transferred to an air-tight KF-flange cell with a window for steady state absolute intensity photoluminescence

(AIPL) mapping. The samples are then exposed to lab air for the first time to measure UV-vis-NIR absorbance spectra. Finally, the samples are prepared for SEM and EDS for composition analysis.

SEM micrographs of samples before and after the reaction of PbI_2 with MAI are shown in Figure 3.1. Note that the conversion from PbI_2 to the HP material does not overfill the alumina scaffold. The average thickness of the filled mesoporous layer along the spray gradient was determined to be $2.1\ \mu\text{m}$ from profilometry data (See Chapter 7, Table 7.1).

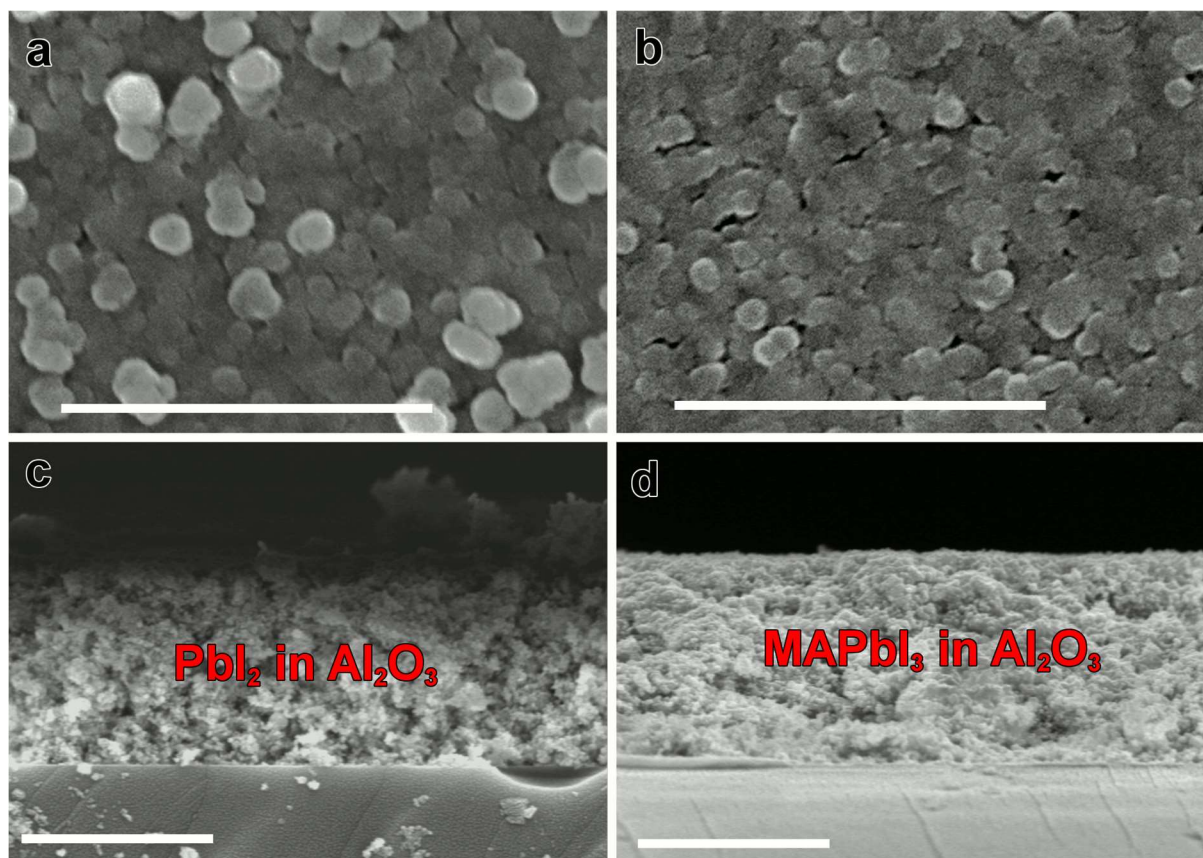


Figure 3.1. **SEM micrographs** - All white, horizontal scale bars are $1\ \mu\text{m}$. **a and c**, Spin-cast PbI_2 in MP Al_2O_3 . **b and d**, MAPbI_3 in Al_2O_3 after subsequent spray deposition of MAI.

The composition was measured by EDS along the length of the spray sample to verify the composition gradient. Figure 3.2b shows the relative bromide percent (i.e. $100x$ in $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$, referred subsequently as Br%) and total halide to lead ratio as a function of position on the spray line. The Br% data are used to construct an interpolating function for correlating position with bromide content in UV-vis and PL results. The systematic decrease of total halide to lead

ratio from 3.05 to 2.7 along the gradient may be due to the HP formation kinetics with these spray conditions.²²

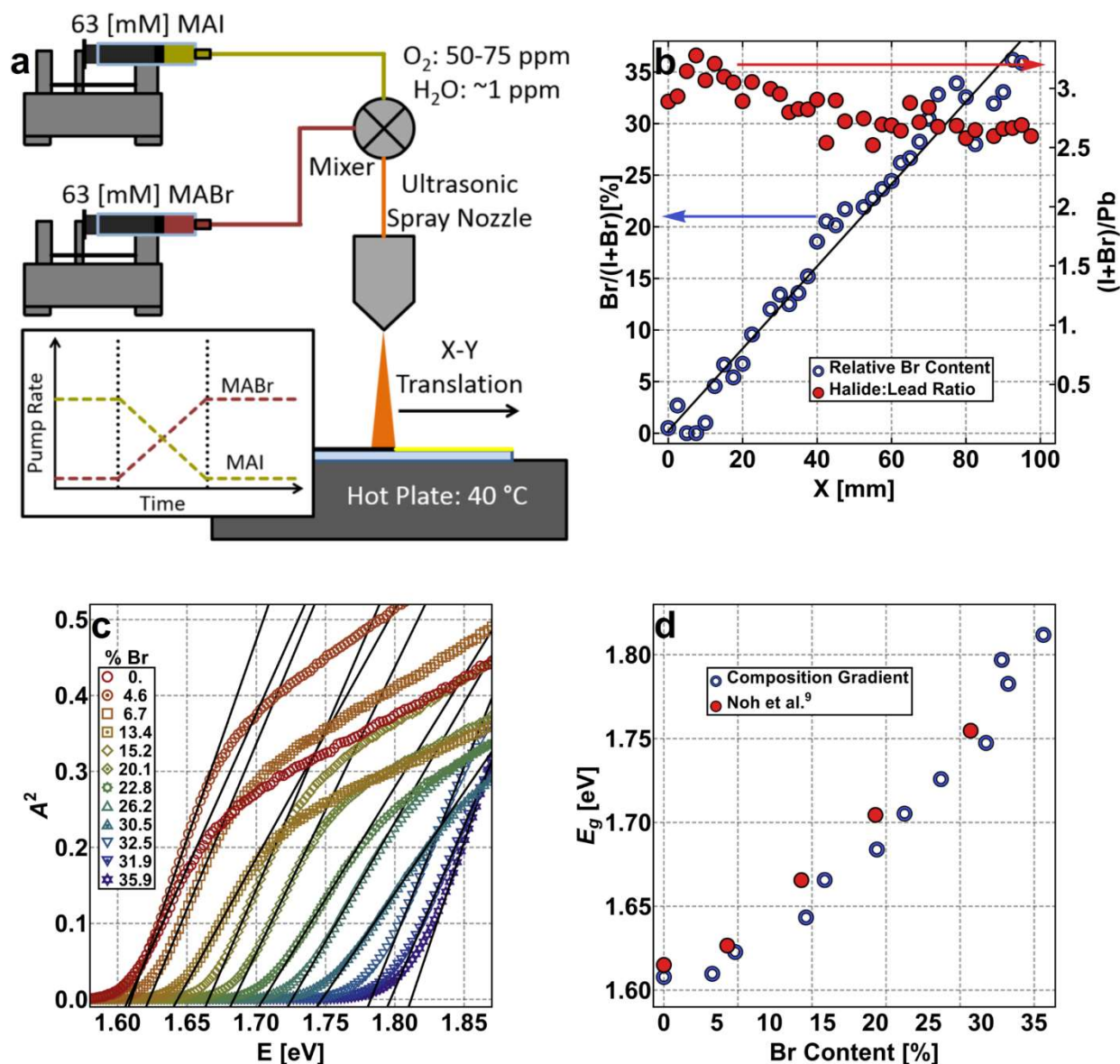


Figure 3.2 Figure 2. Composition gradient preparation and characterization. a, Illustration of spray coating setup used to achieve spray gradients. Pumps feed the ultrasonic spray nozzle while it translates across the sample. Inset: pump gantry used, including an initial delay time, pump ramp time and final hold time. **b, EDS results** – Relative bromide content (open blue circles) and halide to lead ratio (filled red circles) as a function of distance along the gradient profile as determined by EDS. The black line is to guide the reader's eye. **c, UV-vis-NIR results** – Absorbance squared spectra measured at several positions along the gradient with the relative bromide composition of each given in the legend. **d, Extracted bandgap data** from linear extrapolation shown as a function of relative bromide content from this work and from Noh et al. using red circles and black squares, respectively.

B. Determination of Bandgap

We measure UV-vis absorbance spectra in order to extract the bandgap for detailed-balance calculations. As a direct bandgap semiconductor and under the assumption of parabolic bands, HP's have a joint density of states that increases with the square-root of energy above the bandgap. Therefore, we plot the absorbance-squared versus photon energy (Figure 3.2c). The bandgap is determined by extrapolating the linear region above the band edge to zero absorbance. The incorporation of bromide into the sprayed film, as anticipated, shifts the absorption edge to higher energies. The bandgap increases from 1.6 to 1.83 eV, which includes the desirable bandgap energy range for tandem solar cells with silicon or CIGS. The composition–bandgap relationship observed here (Figure 3.2d) agrees well with the bandgap determined from data collected by Noh et al.¹⁰ Note that the reported bandgaps by Noh et al. are lower since they are determined by extrapolating absorbance versus energy. The Noh et al. bandgap data shown in Figure 3.2d is obtained by plotting the Noh et al. data as absorbance squared versus energy and extrapolating, consistent with this data set.

C. Determination of Quasi-Fermi Level Splitting (QFLS or $\Delta\mu$) and Optoelectronic Quality (χ).

Assuming quasi-thermal equilibrium (See 1.1A), the quasi Fermi-level splitting is the non-equilibrium Fermi-level of the conduction band (CB) minus the non-equilibrium Fermi-level of the valence band (VB). Thus, the QFLS is the driving force for electron transfer from the CB to the VB. Radiative recombination in response to this driving force is unavoidable, and the rate of radiative recombination is directly connected to the QFLS. Thus, measurements of the absolute rate of radiative recombination (absolute intensity photoluminescence or AIPL²³) contain information about the QFLS. Below, we briefly summarize three methods to extract the QFLS from AIPL. Note that the QFLS is a thermodynamic property that quantifies the maximum possible work that can be done by an electron-hole pair. Under illumination (and open-circuit

conditions), the QFLS (divided by the unit of fundamental charge) gives the maximum possible open-circuit photovoltage that a material could be used to generate. For a semiconductor in the dark in thermal equilibrium with its surroundings, the QFLS is zero. Also, since the theoretical maximum QFLS ($\Delta\mu_{max}$) increases as the bandgap increases, we define a parameter, χ , which is the ratio of ($\Delta\mu/\Delta\mu_{max}$) to capture the true optoelectronic quality of any given composition independent of bandgap. Unless otherwise noted, we calculate χ using $\Delta\mu_{max}$ of a semiconductor at 300 K and at 1 sun AM1.5GT illumination, which can simply be calculated using the formula $0.932 E_g - 0.167$ (See Chapter 7, Section 7.3 and Figure 7.1 for more details).

QFLS from AIPL Peak Fit: The Lasher-Stern-Würfel equation^{24,25} for external photoluminescence in terms of spectral photon flux is:

$$I_{PL}(E) = \frac{2\pi}{h^3 c^2} \frac{E^2 a(E)}{\exp\left[\frac{E - \Delta\mu}{kT}\right] - 1} \quad (3.10)$$

where h is Planck's constant, c is the speed of light, E is photon energy, $a(E)$ is the spectral absorptivity, k is the Boltzmann constant. We account for occupation of states by assuming symmetric splitting of the quasi Fermi-levels from mid-gap (valid for intrinsic materials), which yields an expression for AIPL flux at the surface of a semiconductor at non-zero absolute temperature (see ref. 23 for details of derivation):

$$\alpha(E) = \frac{\alpha_0}{\gamma 2\Gamma\left(1 + \frac{1}{\theta}\right)} \int_{-\infty}^{\infty} \left(\exp\left(\left|\frac{u}{\gamma}\right|^{\theta}\right) \sqrt{(E - E_g) - (E' - E_g)} \right) du \quad (3.11)$$

where α_0 is related to the oscillator strength, γ is a characteristic sub-bandgap energy broadening parameter, Γ is the gamma function, θ is an exponent that characterizes the functional form of the sub-bandgap tail, and E_g is the characteristic energy of emission (i.e. the bandgap for band-band transitions). Note that an Urbach tail model corresponds to $\theta=1$. $\Delta\mu$, T ,

E_g , θ , γ , and the product $\alpha_o d$ are determined using a Levenberg-Marquardt non-linear least-squares fit of the spectral AIPL data.

QFLS from AIPL High-Energy Tail: The quasi-Fermi level splitting can also be determined by fitting the AIPL peak high energy tail (HT) to a generalized Planck law model. At energies far enough above bandgap, the absorptivity can be assumed to be close to one and Eq. 1 can be rearranged to

$$\ln \left[\frac{I_{PL}(E) h^3 c^2}{2\pi E^2} \right] = -\frac{1}{kT} E + \frac{\Delta\mu}{kT} \quad (3.12)$$

using the Wien approximation. Thus, the QFLS and carrier temperature may be extracted from the slope and intercept of the linear region of the AIPL above bandgap (plotted on a log-scale).

QFLS from Photoluminescence Quantum Yield (PLQY): Ross²⁶ showed that the QFLS can be related to the external photoluminescence yield (PLQY_{Ext}) with the following expression:

$$\Delta\mu = \Delta\mu_{max} - kT \ln \left[\frac{1}{PLQY_{Ext}} \right] \quad (3.13)$$

where $\Delta\mu_{max}$ is the QFLS in the radiative limit. Note that $\Delta\mu$ and $\Delta\mu_{max}$ depend on the bandgap, temperature, and the illumination intensity. $\Delta\mu_{max}$ is calculated by a detailed balance calculation (similar to Shockley and Queisser²⁷) assuming a temperature and an incident photon flux based on the measured intensity of the laser excitation (see supplementary information for more details). We also note that this model assumes that all photoemission is above the bandgap. In the presence of sub-bandgap emission, this may overestimate the QFLS.

We distinguish quasi Fermi-level splittings calculated using a full-peak fit, high-energy-tail fit, or photoluminescence quantum yields with $\Delta\mu_{FP}$, $\Delta\mu_{HT}$, and $\Delta\mu_{QY}$, respectively.

Comparison of the Three Methods: Each of the three methods above were used to extract $\Delta\mu$ and T for four different HP compositions and a GaAs wafer (used as a control), as shown in *Fig. 3*. With the full peak fit method, additional parameters E_g , θ , and γ are determined. The AIPL spectra and the fits are shown in Figure 3.3*a and b*. All fitted parameters are summarized in Table 3.1 – Table 3.4, organized to compare the results from each AIPL analysis methods.

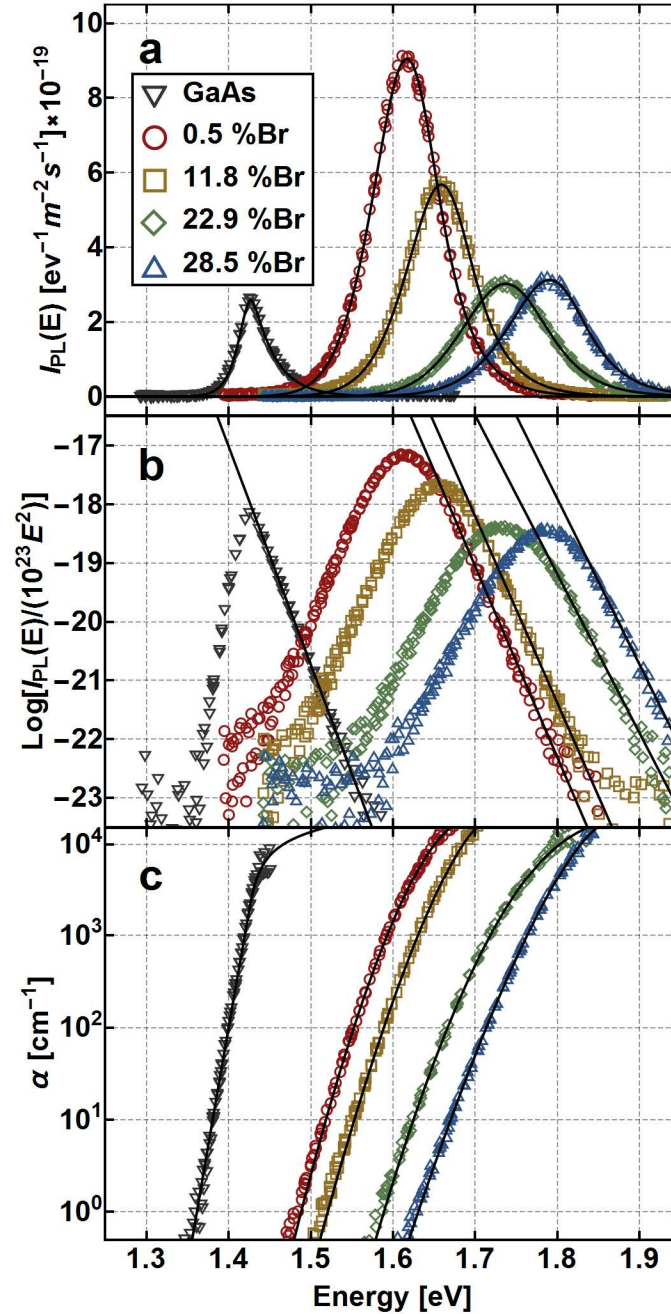


Figure 3.3 **Absolute intensity photoluminescence (AIPL).** **a,** A series of AIPL spectra shown along with model fits to equation 4 are shown for four bromide compositions ranging from roughly 0 to 30 % Br. The AIPL and model fit from a GaAs standard is shown as a reference for peak shape and intensity. **b,** The same spectra plotted on a log scale. Straight lines show the high energy tail fits assuming that absorptivity is unity. **c,** Absorption coefficient as a function of energy calculated from the AIPL using the quasi-Fermi level splitting and temperature determined the full model fits in part a.

Table 3.1 Absorptivity Parameters Fit from AIPL

Sample Name	GaAs	HP 0.5% Br	11.8% Br	22.9% Br	28.5% Br
θ	1.02	1.55	1.45	1.7	1.4
γ [meV]	9	42	39	60	44
α_o [cm ⁻¹ ev ^{-1/2}]	5.04x10 ⁴	9.85x10 ⁴	1.03x10 ⁵	7.95x10 ⁴	1.16x10 ⁵

Table 3.2 Transition Energy Parameters

Sample Name	GaAs	HP 0.5% Br	11.8% Br	22.9% Br	28.5% Br
$E_{g,UV-vis}$ [eV]	1.42	1.61	1.65	1.71	1.74
$E_{g,FP}$ [eV]	1.43	1.64	1.68	1.78	1.82
$E_{Max PL}$ [eV]	1.43	1.61	1.65	1.74	1.75

Table 3.3 Fit QFLS Values

Sample Name	GaAs	HP 0.5% Br	11.8% Br	22.9% Br	28.5% Br
$\Delta\mu_{FP}$ [eV]	0.95	1.10	1.10	1.10	1.14
$\Delta\mu_{HT}$ [eV]	0.95	1.14	1.15	1.12	1.19
$\Delta\mu_{QY}$ [eV]	0.96	1.13	1.15	1.20	1.23

Table 3.4 Fit Temperature Values

Sample Name	GaAs	HP 0.5% Br	11.8% Br	22.9% Br	28.5% Br
T_{FP} [K]	310	364	380	417	428
T_{HT} [K]	310	344	353	410	399
T_{QY} [K]	310	350	350	350	350

The fitted parameters for GaAs in Table 3.1 and Table 3.2 agree with previous reports (i.e. a bandgap of 1.42 eV, θ of 1 and γ of 9 meV). The θ values for the four HP compositions hover around 1.5, which may be indicative that internal electric fields are playing a dominant role in the sub-bandgap absorption behavior (*via* a local Franz-Keldysh effect),²³ as opposed to simple short-range disorder that results in Urbach-like sub-bandgap absorption. After fitting, the $\Delta\mu$ and T may be held fixed, and the model can then be used to extract a model independent absorption coefficient directly from the AIPL. These absorption coefficient spectra are shown in Figure 3.3c along with the model dependent absorption coefficient (plots of *eq* (3.12) using

values of E_g , θ , and γ determined by the fit). We assume α_0 for GaAs to be $5.04 \times 10^4 \text{ cm}^{-1} \text{ eV}^{-1/2}$, and d for the HP films to be their film thicknesses. The absorption coefficient for GaAs has a steep sub-bandgap absorption edge (due to the low Urbach energy) and follows the expected square root dependence above bandgap, while the HP films demonstrate a more gradual band edge that slowly turns over above bandgap. This is a direct result of the higher broadening energies for the HP material and larger θ exponent. Note that the absorption coefficients determined for the HP are effective absorption coefficients that include the alumina scaffold. We note that, unlike analyzing PL for other materials such as CZTSSe or CIGSe,²³ fitting the AIPL high energy tail for peaks such as those given in Figure 3.3b is unambiguous; there is a distinct linear region that extends nearly the entire high energy side of the peak.

The quasi-Fermi level splittings are shown in Table 3.3. The QFLS calculated using the high energy tail model agree well with the more rigorous full peak fit model based on the subbandgap absorptivity model described above for the GaAs, a hybrid perovskite with 0.5%Br and 11.8%Br. However, not all peaks fit the full spectrum model well. For example, the temperatures calculated for the 22.9%Br and 28.5%Br peaks are unphysically high. This is largely in part due to the development of a shoulder on the high energy tail of the peak, particularly in high Br% regions of the gradient. Further, some regions of the gradient did not provide sufficient signal to confidently fit the AIPL peak tails. Therefore, we calculated quasi-Fermi level splittings using the PLQY method assuming a temperature of 350 K, the temperature extracted using the high energy tail method on single AIPL peaks with strong signal in the tail regions. In contrast to the full spectrum fit and high energy tail fit methods, the PLQY method is less susceptible to signal-to-noise errors in calculation since the integrated AIPL flux is used in the calculation. It is also reassuring that all three models yield similar QFLS (within 5%).

The fitted temperatures are shown in Table 3.4. The fitted temperature in GaAs was 312 K, which is reasonable for the approximately 2 suns equivalent illumination. In comparison, the

lowest fit temperature for the HP samples in Table 1d is 344 K. The higher temperatures extracted for these AIPL peaks may be real and a signature of important physics. The elevated temperatures do not appear to be artifacts since the same measurement method for GaAs leads to reasonable temperatures. However, a non-linear detector response cannot be ruled out at this stage. The elevated temperatures are also not due to convolution of multiple PL peaks (since the high energy tail is unambiguously linear) or due to a non-unity absorptivity at the high energy tail (we calculate this to have at most a reduction in the fit temperature by about 5°C). We hypothesize two possible explanations for these elevated temperatures. First, the MAPbI₃ crystal lattice is expected to be quite labile, with the ability of the inorganic framework to rock and MA cations to rotate. As a result, extremely low thermal conductivities have been observed for HP's under dark conditions.²⁸ This thermal conductivity (approximately 100 times smaller than that of GaAs) would result in significant local heating from non-radiative recombination and thus an increase in the lattice temperature.

Alternatively, the high temperatures may be a sign of hot carriers. The fitted temperature is actually the carrier temperature (not necessarily equal to lattice temperature). Under quasi-thermal equilibrium, the carrier temperature is assumed to be equal to the lattice temperature. However, if this assumption is not valid, it would manifest as an elevated fitted temperature. Excited charge carriers that are generated deep in the bands by far above bandgap photons have been predicted to relax slowly to the band edge.²⁹ A significant population of these hot carriers could exist under steady illumination, which would be observed in the AIPL peak as a high energy tail that decays more slowly with increasing energy and explain the higher fitted temperature. These two phenomena – a low thermal conductivity and the existence of long-lived hot carriers – both have significant implications to possible device applications for HPs. Highly doped HPs with extremely low thermal conductivity could be used as low-cost thermoelectric materials; while a HP with long lived hot carriers could be used in PV devices that sustain even higher voltages without current losses.

D. Effects of Composition

The effects of halide composition on the AIPL peak position, QFLS, and optoelectronic quality are shown in *Fig. 4*. The 2-D color maps above each plot in *Fig. 4a* and *4b* show the spatial distribution of AIPL peak position and PLQY, respectively. Using the composition profile in *Fig. 2b*, we transform x-values in our AIPL maps from position values to composition values. The plots in *Fig. 4* show the y-position averaged AIPL parameters as a function of bromide composition for each gradient processing stage. *Fig. 4a* shows the peak position as a function of halide content. The peak position begins at 1.62 eV at 0%Br, and increases to 1.82 eV at 37%Br.

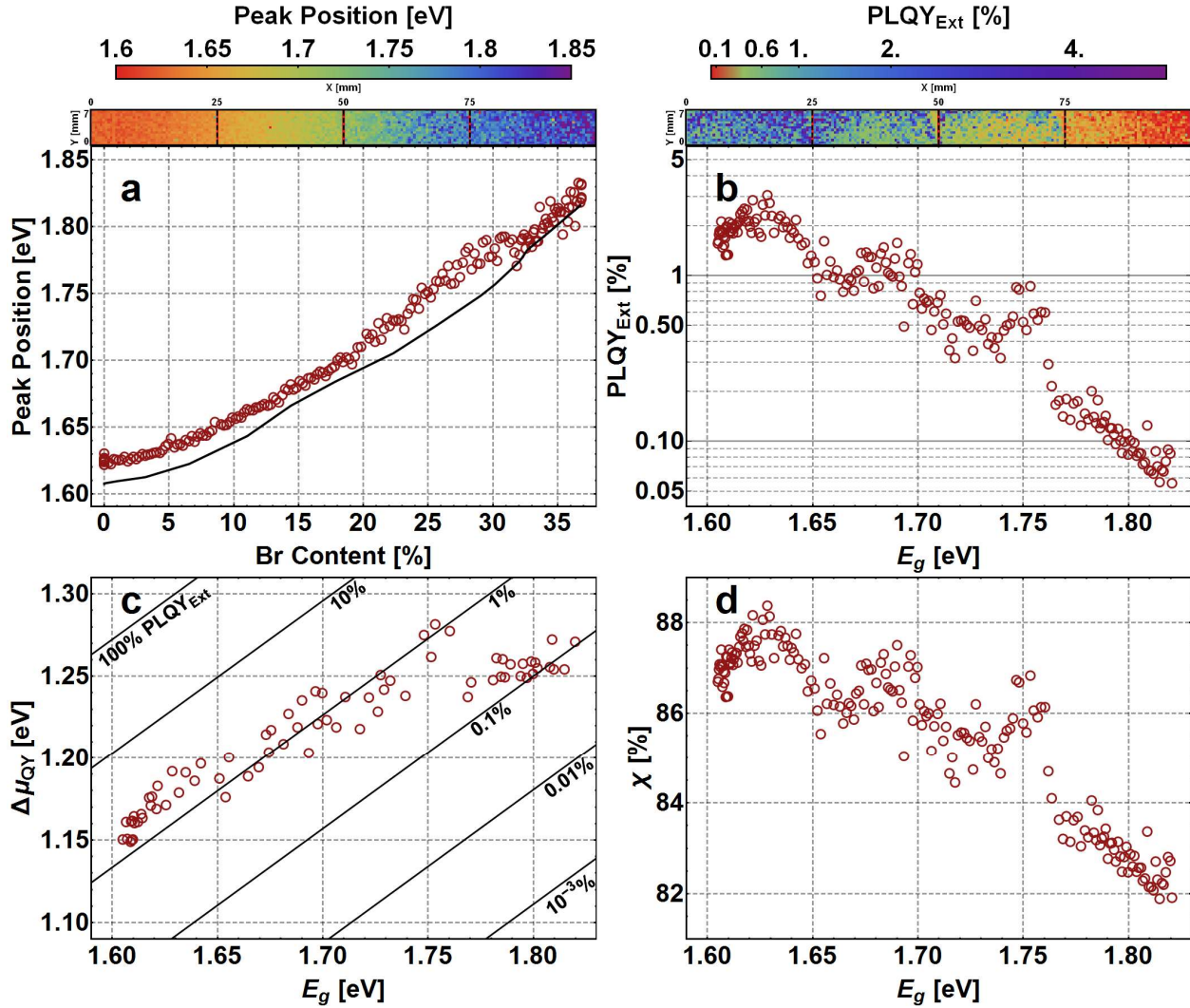


Figure 3.4 **AIPL collected at 1 sun of composition spread library.** **a**, Spatial map of local peak position with color scale given above. Y-position averaged peak position as a function of Br content, with the black line representing the UV-vis determined bandgap trend. **b**, Spatial map of local external photoluminescence quantum yield ($PLQY_{Ext}$) with log-scale color bar given above. Y-position averaged $PLQY_{Ext}$ given as a function of bandgap. **c**, Quasi Fermi-level splitting determined from PLQY, $\Delta\mu_{QY}$, given as a function of bandgap with black lines representing lines of constant PLQY assuming a lattice temperature of 350 K. **d**, Optoelectronic quality parameter, χ calculated as a percent from $\Delta\mu_{QY} / \Delta\mu_{max}$ given as a function of bandgap.

The $PLQY_{Ext}$ is plotted on a log scale as a function of bandgap in Figure 3.4b. The PLQY of the halide composition gradient observed here decreases exponentially rather than remaining constant as would be the case for a material with constant optoelectronic quality. This is a result of increasing non-radiative recombination with bromide incorporation. Figure 3.4c shows QFLS calculated using the $PLQY_{Ext}$ method and assuming a material temperature of 350 K.

The χ parameter trend follows the same behavior as the PLQY trend plot plotted on the log scale due to the logarithmic relationship between PLQY and quasi Fermi level splitting in Figure 3.4d. MAPb(I,Br)₃ compositions with χ larger than 85% are demonstrated for bandgaps less than 1.75 eV. Therefore, even though the optoelectronic quality decreases with Br incorporation, these results show that high-optoelectronic quality materials can be achieved within the desirable bandgap range for tandem applications. The decrease in optoelectronic quality with Br incorporation may be explained by: (1) an increasing population of defects arising due to the increasing presence of Br; (2) an increasing population of defects arising due to increasing halide vacancies or MA vacancies (see Fig 1b where (I+Br)/Pb decreases from 3 to 2.5 over the gradient); (3) a constant defect population that becomes an increasingly detrimental SRH recombination center as the bandgap increases; or (4) an increasing population of surface recombination centers caused by changing crystallization dynamics as a function of relative bromide composition. The above explanations can be divided into two categories: Changes in defect concentrations (1, 2 and 4), and changes in defect energy relative to the band edges (3). We evaluated the plausibility for each of these categories by simulating steady-state charge-carrier populations while considering radiative and non-radiative recombination pathways. At steady-state and open circuit voltage conditions, the recombination rate equals the injection rate. Here, we assume that Auger recombination is negligible and the quasi Fermi-level splitting can be determined implicitly with the equation $G = U_{\text{Rad}}(\Delta\mu) + U_{\text{SRH}}(\Delta\mu)$, where G is the volumetric generation rate, U_{Rad} is the volumetric radiative recombination rate and U_{SRH} is the volumetric Shockley-Read-Hall (SRH) recombination rate. The simulation results (See Chapter 7, Section 7.4 and Figure 7.2 - Figure 7.7 in the appendix) show that a constant defect concentration with a changing constant defect energy level (but moving relative to the band edges caused by the increasing bandgap) is sufficient to explain the linear decrease in χ . This would occur if the defect was relatively shallow (close to the valence band edge) in the pure iodide but became deeper in the iodobromide due to a downshift of the valence band edge.

There may also be an increase in the defect concentration; however, that is not necessary to explain the exponential decrease in the PLQY or the linear decrease in optoelectronic quality with increasing bandgap. Regardless, further improvements in optoelectronic quality of the high bandgap hybrid perovskites may be realized via defect passivation, surface passivation, recrystallization, or alternative syntheses.

E. Effects of Illumination Intensity

The instantaneous optoelectronic quality of HPs increases with increasing illumination intensity. Figure 3.5 shows the effect of excitation intensity on AIPL flux from. Figure 3.5a is plotted on a linear scale, with GaAs AIPL peaks shown for reference. The peak position and shape remains constant for both GaAs and the HP sample as the excitation intensity increases. The black lines in the log-scale plots in Figure 3.5c represent the high energy tail model fits for each of the AIPL peaks shown. For both GaAs and the HP data, the slope of these lines remains the same for each excitation intensity and are shifted vertically for both GaAs and HP data, indicating that the quasi Fermi-level splitting is increasing as excitation intensity increases.

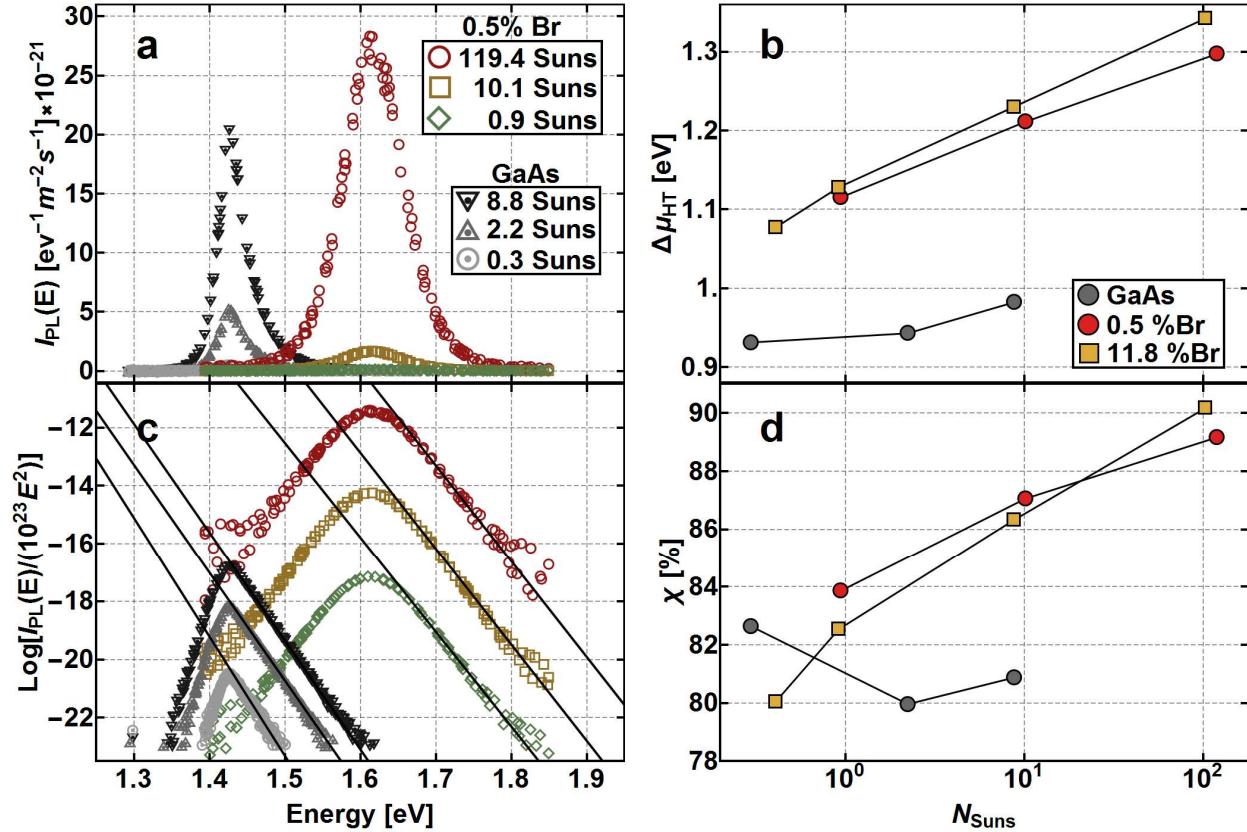


Figure 3.5 **Effect of excitation intensity ranging from 1 to 100 suns** for 0.5%Br GaAs. **a**, AIPL flux on a linear scale shown against photon energy. GaAs AIPL peaks are shown for reference. **c**, AIPL flux on a logarithmic scale. Lines are the high energy tail model fits used for extracting $\Delta\mu_{HT}$ and T for each peak. Red arrows are to guide the reader's eye along the peak maxima. GaAs is shown with no scaling factor. **b** and **d**, $\Delta\mu_{HT}$ and χ , respectively, for 0.5 %Br, 11.8%Br and GaAs plotted against excitation power.

Figure 3.5b summarizes how quasi Fermi-level splitting increases with excitation intensity for two different HP halide compositions and GaAs. In order to compare these increases in quasi Fermi-level splitting between each sample in a fair manner, the χ percentage is calculated by considering the bandgap and equivalent number of suns for each sample and displayed in Figure 3.5d. The increase in quasi Fermi-level splitting in the GaAs sample is due solely to the increase in excitation, as seen by the lack of any significant trend in optoelectronic quality. Both HP samples of different halide compositions, on the other hand, increase in optoelectronic quality as the excitation intensity increases from 1 to 100 suns.

Previously, improving photoluminescence quantum yields using higher excitation intensities have been observed in iodochloride HP films.³⁰ Larger excitation intensities were

presumed to fill more trap states present in the film and possibly increase the exciton population making generated charge carriers less susceptible to charged recombination centers. Further, the excitation intensity-dependent behavior was shown to become less significant when the chloride-containing films were treated with a Lewis base, indicating that the same recombination centers being passivated with the light in the untreated films were being passivated by the solvent treatment at the surface of the film.⁵ We show that the same photo-passivation phenomena exists for bromide containing films, making surface passivation routes a promising candidate to further improve HP materials in this composition space.

F. Effects of Steady-State Illumination

In addition to collecting high resolution spatial AIPL maps of the composition gradient, we also observe the slow transient behavior of select halide compositions by collecting AIPL as a function of time. Figure 3.6*a* and *c* show the time-dependent behavior of the peak position and quasi Fermi-level splitting, respectively, under constant laser illumination for relative halide compositions ranging from 0 to 29%Br. The AIPL peak position begins to noticeably red-shift with time once the bromide content reaches 11.8%Br. This behavior has previously been observed and hypothesized to be the result of reversible photo-induced traps.¹⁶ Since the local bandgap under illumination is likely changing with time as well, we approximate the local bandgap for each composition at each time by assuming a constant offset from the peak position (16 meV) based on average bandgap-peak position offset observed in Figure 3.4*a*. Despite the increasingly dramatic red shift of AIPL peak position at higher halide compositions, we show the stabilized QFLS still increases with bromide incorporation up to 22.9%Br, and the maximum stabilized quasi Fermi-level splitting is 1.17 eV. Additionally, the 0.5%Br QFLS time profile shows a slight but steady increase during the 20 minutes of constant illumination.

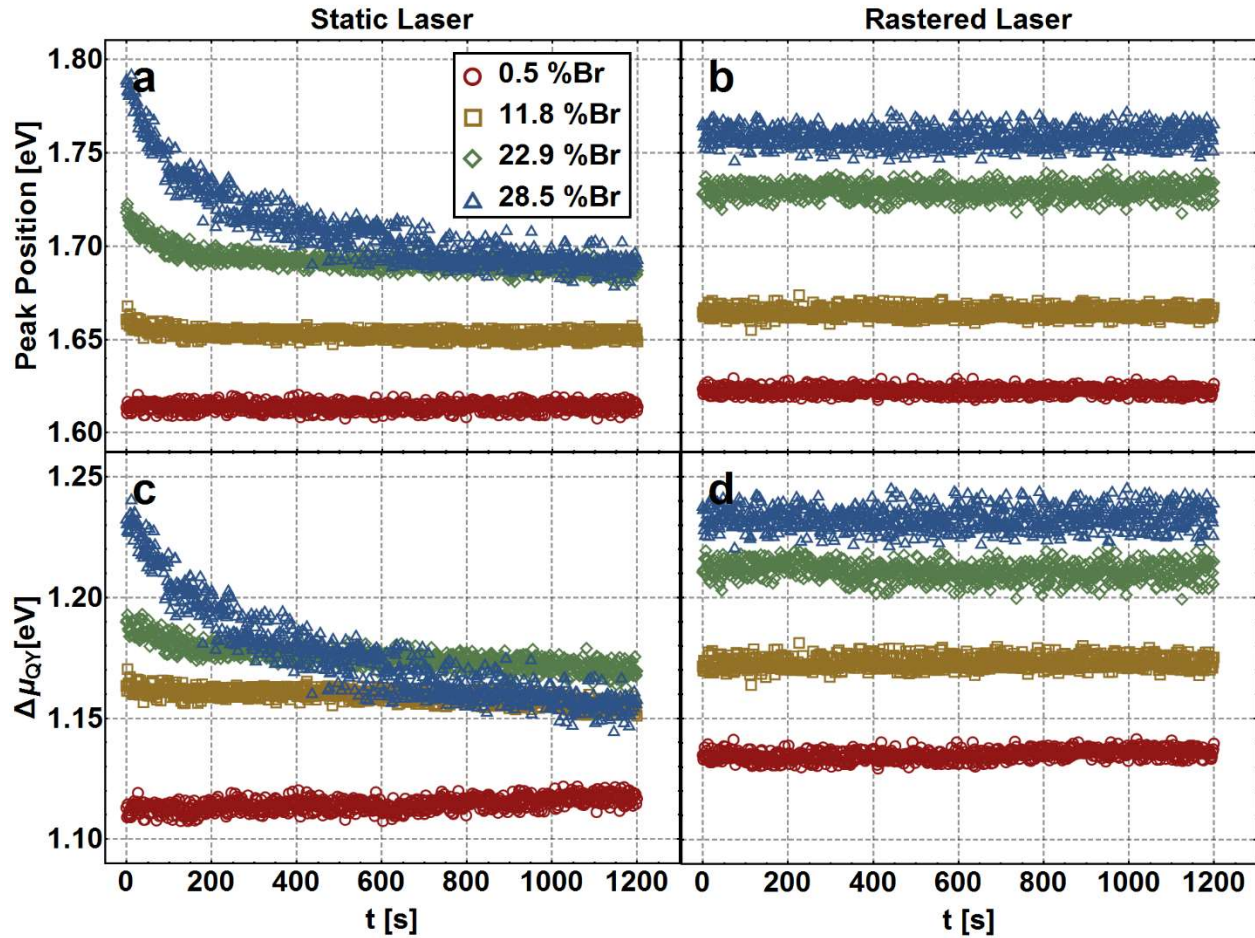


Figure 3.6 **Slow transient AIPL behavior** collected at 1 sun illumination for four HP halide compositions ranging from roughly 0-30%Br. **a and b**, peak position over the first 1200 s of CW and rastered laser illumination, respectively. **c and d**, $\Delta\mu_{QY}$ during the first 1200 s of CW and rastered laser illumination, respectively.

In order to separate the effects of illumination and time, measurements were repeated at the same locations on the gradient using a rastered laser. Two computer controlled mirrors are used to repeatedly raster the laser beam over the field of view of the objective lens with a frequency of 2-100 Hz. The peak position and quasi Fermi-level splitting with time for four halide compositions are shown in Figure 3.6b and 6d. Note that the transient behavior is eliminated for all compositions. This shows that the photo-induced defect formation process that is occurring under constant illumination conditions is reversible on the time scale of less than 0.5 seconds under one sun equivalent illumination.

G. Effects of Charge-Injection

To investigate the origin of phase segregation in mixed-halide perovskites we measured spectrally resolved electroluminescence (EL) of devices and photoluminescence (PL) of neat hybrid perovskite films. The device used for this EL study, having a $\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ absorber, exhibited a power conversion efficiency (PCE) above 10%, with device parameters comparable to other studies in this bandgap range³¹⁻³³ (see Chapter 7, Section 7.1E for device fabrication methods; and see Section 7.5 and Figure 7.8 for device performance metrics). Relevant 1 Sun carrier densities were achieved by setting the current injection density to the Shockley-Queisser limit short-circuit current density ($J_{\text{SC,SQ}}$) for a 1.81 eV material (19.2 mA/cm²), and by setting the continuous wave (CW) photoexcitation intensity to the above-bandgap photon flux for a 1.75 eV material (1.3×10^{21} photons/m²/s) for EL and PL experiments, respectively. We chose to inject with $J_{\text{SC,SQ}}$ for EL measurements instead of device J_{SC} to prevent from providing a carrier density lower than present under AM1.5 illumination for devices with transport-limited J_{SC} .

Results for the EL and PL experiments are presented in Figure 3.7. Figure 3.7a shows absolute intensity electroluminescence evolution with time for a $\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ device. In five minutes, the electroluminescence spectrum peak position red-shifts from 1.8 eV to 1.63 eV while the emitted flux increases by 50-fold. This agrees with the formation of the smaller bandgap iodide phase and shows, for the first time, phase segregation in the absence of photoexcitation. Figure 3.7b depicts the mean emission spectrum energy ($\langle E \rangle$) over time during continuous current injection or photo-excitation. The parameter $\langle E \rangle$ is simply the first moment of the emission spectrum and has been employed previously to quantify peak shifts due to phase segregation³³. $\langle E \rangle$ decreases from 1.8 eV to ~1.65 eV in five minutes for both EL (current injection) and PL (photoexcitation). This data strongly confirms the hypothesis that excess charge carrier density is the origin of phase segregation. Moreover, this finding aligns with mechanisms suggested previously, i.e. excited charge carriers inducing lattice strain via

electron-phonon coupling which results in the nucleation of I-rich clusters near the borders of morphological domains.³⁴ Our findings refine this mechanism by suggesting that the I-rich clusters are not light-stabilized, but rather sustained by a high carrier density. The high carrier density that results in phase segregation can be achieved by either photo-excitation or current injection.

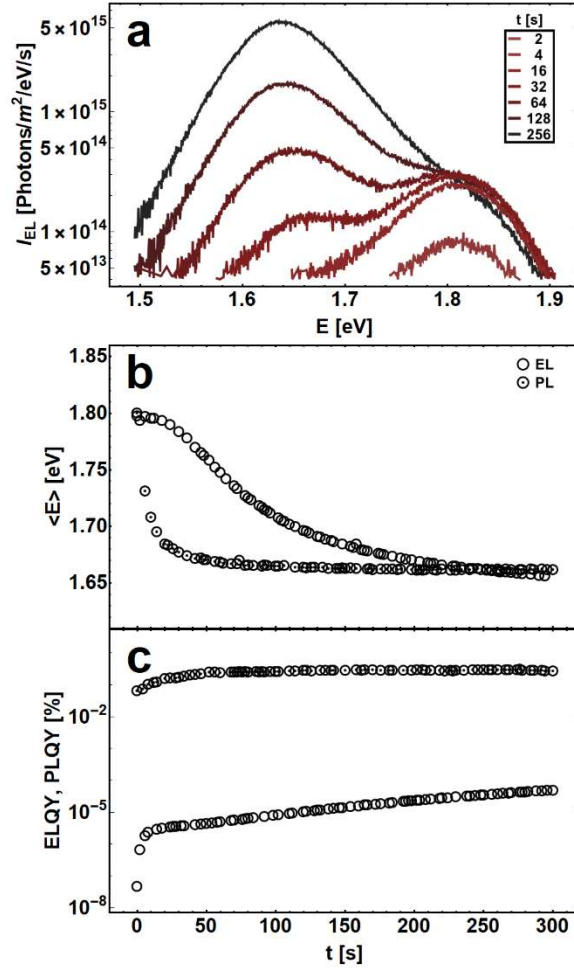


Figure 3.7 **Electroluminescence and photoluminescence measurements over time.** **a**, electroluminescence spectra at selected times of a MAPb(I_{0.6}Br_{0.4})₃ device being injected with a constant current density of 19.2 mA/cm² for five minutes. **b**, mean electroluminescence and photoluminescence emission energy of a device utilizing a MAPb(I_{0.6}Br_{0.4})₃ absorber. **c**, external electroluminescence and photoluminescence quantum yield from the same experiment.

Figure 3.7c shows EL and PL quantum yield (ELQY and PLQY) for the MAPb(I_{0.6}Br_{0.4})₃ device and neat film. The increase in PLQY and ELQY in the phase segregating MA material has been proposed to be due to carrier funneling into the locally smaller bandgap, I-rich domains as

demonstrated elsewhere³⁵⁻³⁷. This mechanism could be present, but we note that the driving force for photoemission becomes exponentially stronger for states at lower energy, thus even without any carrier funneling mechanism, one should expect significantly higher QY simply due to the appearance of lower energy states (see Chapter 7, Section 7.6 and Figure 7.9). The several orders-of-magnitude difference between ELQY and PLQY is likely due to additional recombination pathways that are present in devices (e.g. interfacial recombination) and carrier separation at the ETM/HP and HTM/HP interfaces.

H. Effects of Applied Electric Field

To verify that the presence of excess charge carrier populations alone is responsible for phase segregation in mixed-halide perovskites we measured spectrally resolved photoluminescence of a neat MAPb(I_{0.6}Br_{0.4})₃ film deposited on an insulated interdigitated back contact substrate. Figure 3.8 shows the top-down image of the back-contact substrate. See the appendix for details about the fabrication of the back-contact substrate. Briefly, patterned gold was coated with atomic-layer deposition aluminum oxide so that a lateral electric field could be applied across the 10 μm channel while avoiding charge injection into the hybrid perovskite thin film above.



Figure 3.8 Microscope images of the insulated interdigitated back contact substrates used to determine the impact of electric field only on phase segregation of a MAPb(I_{0.6}Br_{0.4})₃ film. (Left) A 10x magnification image of one of the gold contact pads shown in the top left portion of the image and a 10 μm channel spanning from the top to bottom of the image. (Right) a 50x magnification image of the 10 μm channel.

In order to probe phase segregation in the $\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ film, photoluminescence spectra were collected from within the $10\ \mu\text{m}$ channel every 30 s. The 532 nm CW-laser ($12\ \mu\text{m}$ beam diameter) was turned on for less than a second for each collection, keeping the film in the dark for the remainder of the experiment. After 230 s, 60 V were applied across the $10\ \mu\text{m}$ channel, and at 730 s the applied voltage was switched off. Figure 3.9a shows $\langle E \rangle$ over time before, during and after the application of the device-relevant electric field strength.

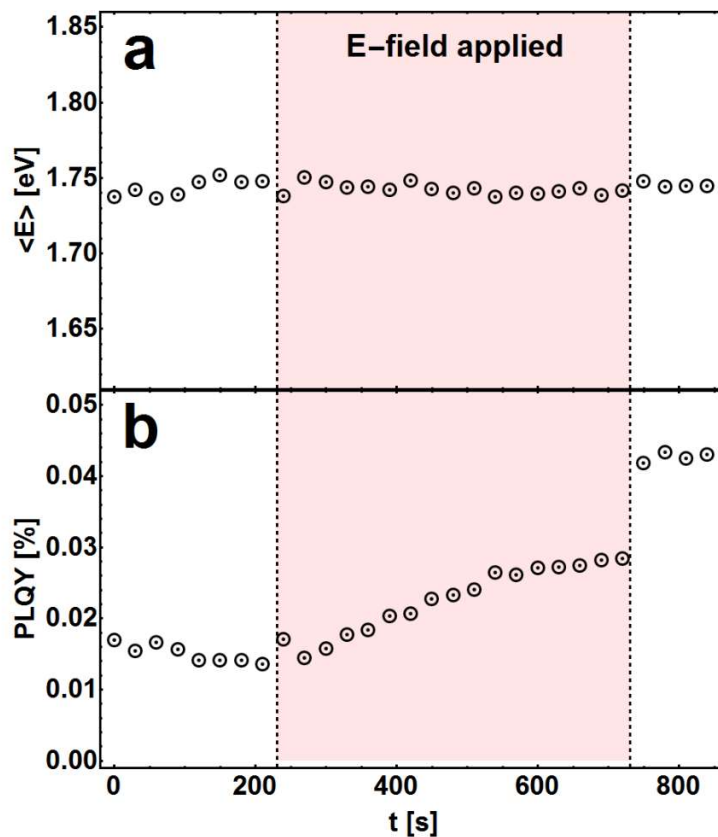


Figure 3.9 **PL of an MA film deposited on insulated interdigitated back-contacts.** **a**, Mean photoluminescence emission energy over time. **(b)** Photoluminescence quantum yield over time. The light red region depicts the period which 60 V were applied across the $10\ \mu\text{m}$ channel.

The red-shift in the PL peak position is not observed, indicating that an applied electric field (in the absence of charge injection) does not cause phase segregation. However, gradual PLQY increase during electric field application followed by a jump in PLQY is observed upon field cessation (Figure 3.9b). This is likely related to the build-up and relaxation of energy

storage from ionic charge separation induced by the electric field application, however the authors can only speculate without a further detailed study.

I. Comparison of QFLS to Measured Device Open-Circuit Voltages

Finally, to compare our QFLS results to reported devices in the literature we plot the initial quasi Fermi-level splitting of the compositional gradient in Figure 3.10 as a function of bandgap. V_{oc} values of devices are also shown in Figure 3.10. In particular, V_{oc} 's are reported for devices using pure MAPbI₃,³ binary halide MAPb(I,Br)₃,^{10, 18} ternary halide HP's,^{14, 15} and mixed organic-mixed halide combinations are utilized.³⁸ So far, the reported device with the highest V_{oc} for its bandgap achieves a $\chi_{\Delta\mu}$ value of 87% through the optimization of the electron transport layer band alignment with the pure iodide.³ Besides this device, the quasi Fermi-level splitting values demonstrated by the composition gradient reported here are well above the demonstrated V_{oc} values for most reported devices, showing that the use of transport materials with passive interfaces and well-aligned bands are essential to fabricating high V_{oc} devices.

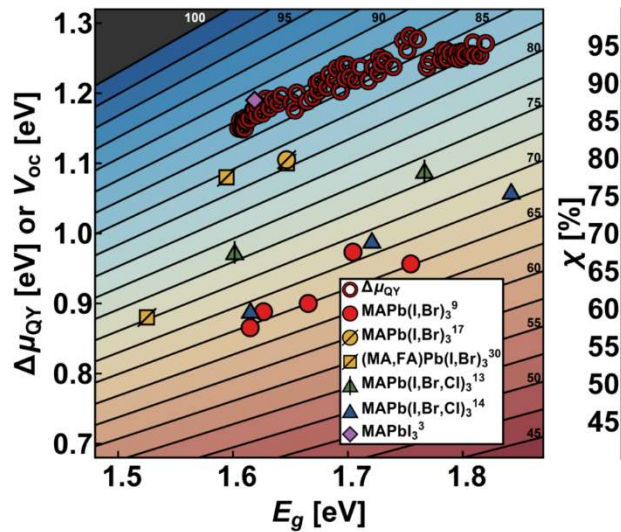


Figure 3.10 **Comparison of $\Delta\mu_{QY}$ to reported device V_{oc} values** plotted against EQE- or UV-vis-extracted bandgap. Contours represent lines of constant χ , and the color scale for χ is shown to the right.

3.5 CONCLUSIONS

We prepared HP halide composition gradients *via* combinatorial spray coating methods and determine the optoelectronic quality of the film using AIPL measurements. The instantaneous QFLS steadily increases from 1.15 eV to 1.25 eV with bromide incorporation up to 30%Br. For HP compositions with bandgaps below 1.75 eV, 85% of the theoretical maximum QFLS is achieved, providing a promising halide composition range for tandem applications. Modeling the absorption coefficient from our AIPL measurements suggests that local electric fields may be responsible for the functional form of the absorption coefficient below the HP bandgap, rather than phenomena related to Urbach tailing. Some degradation in optoelectronic quality is observed when tested under constant laser illumination, however stable performance is sustained if an intermittent excitation source is used. The highest stabilized quasi Fermi-level splitting value observed under constant laser illumination is 1.18 eV at 22.9%Br. We observe abnormally elevated local temperatures in HP films under laser light illumination, which we attribute to either the low thermal conductivity of HP's or to the presence of hot carriers. Additionally, we show phase segregation in a high bandgap HP in the presence of steady current injection, consistent with excited-state lattice strain sustained by a high carrier density; in contrast to the lack of evidence we show for phase segregation in the presence of device-relevant electric fields. When comparing our results to demonstrated device performances reported in the literature, it shows that improving band alignment of the selective transport layers in completed devices is an essential step towards improving HP solar cell Voc.

3.6 REFERENCES

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Chapter 4. ANALYSIS OF PHOTOLUMINESCENCE VIDEOS OF HYBRID PEROVSKITE THIN FILMS

4.1 PREFACE

The follow-up study in this chapter adds depth to the exploration and understanding of high bandgap hybrid perovskites which has been developed in the previous chapters. This project in some ways began back in 2015 while the data from the photoluminescence-time data in Chapter 3 were being collected. Even though spectra were only collected with an exposure time of 1 second, we found that the photoluminescence intermittency of certain localities in the mixed halide gradient was measurably higher than that observed in samples such as GaAs. At the same time, the first reports of photoluminescence blinking and intermittency were coming out for hybrid perovskite islands and nanocrystals. Ultimately, the time resolution of the confocal photoluminescence instrument prevented us from making any new discoveries about the intermittent photoluminescence in the mixed-halide hybrid perovskite films at that time. However, when a faster camera was obtained for collecting wide-field images which could resolve the photoluminescence brightness of thousands of individual grains simultaneously, we immediately began looking for clues about the dynamic processes occurring within the perovskite samples under illumination.

At the time of submission, this chapter has yet to be submitted for peer review and consists entirely of unpublished data. Many thanks to Ryan Stoddard and Ray Palmer for their discussions and assistance during the development of the analysis tools described in this chapter.

4.2 ABSTRACT

Hybrid perovskite compositions which can withstand 1 Sun illumination for multiple decades are necessary for the successful commercialization of hybrid perovskite photovoltaics. Scalable accelerated testing methods which probe the relevant degradation pathways in hybrid perovskite compositions are important for the discovery of such hybrid perovskite compositions. We simultaneously measured wide-field micro-photoluminescence videos and lateral DC photoconductivity of various hybrid perovskite thin-films under concentrated illumination in lab air and nitrogen environments in order to track carrier diffusion while observing grain-level changes in photoluminescence. The formamidinium containing perovskite was stable under 100 Suns equivalent photon flux and flowing nitrogen for longer than 7 hours, while the methylammonium containing perovskites completely degraded under the same illumination conditions within 7 hours in all atmospheres tested. In each case, high or increasing levels of spatial heterogeneity of photo-brightening or photo-dimming was associated with losses in carrier diffusion. These insights guide future developments of contactless methods for determining carrier transport in perovskites.

4.3 INTRODUCTION

Hybrid perovskite (ABX_3) solar cells are being developed as a commercial technology.¹ However, long-term material and device stability is a serious technical challenge. Discovering hybrid perovskite alloys, device architectures, and encapsulation procedures that yield module lifetimes of at least 20 to 25 years will be necessary to compete with existing commercial PV technologies.² There are several possible perovskite material degradation pathways³ including moisture uptake, thermal decomposition, and deprotonation. For methyl ammonium lead triiodide perovskite, the later decomposition route involves the deprotonation of the organic cation and the formation of HI, methyl amine, and lead iodide.⁴ This reaction is accelerated by the

presence of oxygen or water and photoexcited or injected electrons via the formation of O_2^- , a highly oxidative superoxide radical anion.⁵⁻⁷ The interplay of material compositions, micron-scale grain structures,^{8, 9} film interfaces,¹⁰ and contacts¹¹⁻¹³ influences the stability of perovskites to withstand combinations of oxygen,⁶ moisture,¹⁴ heat,¹⁵ and light.^{5, 7, 16, 17} In general, smaller grain size is associated with faster perovskite degradation rate in the presence of moisture.¹⁸ Recently, promising progress in perovskite module performance stability has been achieved through the use of hydrophobic electrodes and a low-dimensional perovskite interface,¹⁹ however there is still much room for improvement upon this strategy – namely in short-circuit current collection.

Recently, we reported simultaneous photoconductivity-photoluminescence measurements on perovskite thin-films undergoing degradation that yield the root mean square of the electron and hole diffusion length and the quasi-Fermi level splitting, which are proxies for the short-circuit current and maximum open-circuit voltage.^{20, 21} During degradation, after an initial period of increasing performance, the diffusion length begins to drop. However, simultaneous with this loss of transport, the photoluminescence quantum yield (PLQY) increases (i.e. photo-brightening).²⁰ While increases in PLQY are typically taken to be good (a sign of reduced non-radiative recombination), these observations reveal that photo-brightening in perovskites is not unambiguously positive and could be a sign of connected grains becoming insulated from each other while their surfaces degrade to a passive PbI_2 . It has been postulated that PLQY enhancements from $MAPbI_3$ under illumination are the result of the annihilation of Frenkel-defects that reduce non-radiative recombination rates.²² Photo-brightening has also been associated with halide redistribution,²³ which may be enabled by photo-enhanced ion conductivity.²⁴ The atmosphere,²⁵ light intensity, and film preparation method²⁶ have also been shown to impact the extent to which photo-brightening occurs. On the microscale, photo-brightening occurs locally in domains which initially exhibit low PLQY over the course of several minutes to an hour.^{23, 25}

On much shorter time-scales, intermittent photoluminescence, which is likely distinct from photoluminescence quantum dot blinking,²⁷⁻²⁹ has been observed in a host of all-inorganic³⁰ and hybrid perovskite³¹ nanocrystals, nanorods, and polycrystalline microscale islands.^{32, 33} However, the nanoscale origin or mechanism of intermittent photoluminescence is not well understood. Fluorescence video analysis techniques originally developed for microbiological applications were applied to intermittent photoluminescence in hybrid perovskite materials.³⁴ Super-resolution microscopy³⁵ and localization fluorescence microscopy in tandem with electron microscopy were used to infer the nature and location of non-radiative recombination centers in micro-scale hybrid perovskite island domains. To add to this picture, the magnitude of intermittent photoluminescence in methylammonium lead bromide microcrystals was observed to increase at higher relative humidity atmospheres.³⁶

In this chapter, we report simultaneous photoluminescence video-photoconductivity measurements and relate spatial and temporal changes in photoluminescence to changes in carrier transport. In this way, we could observe both fast and slow dynamics of spatial photoluminescence in perovskite films, and relate them to changes in carrier transport during degradation. By observing MAPbI₃, MAPb(I_{0.6}Br_{0.4})₃,³⁷ and (FA_{0.84}Cs_{0.16})Pb(I_{0.85}Br_{0.15})₃³⁸⁻⁴⁰ under 100 Sun equivalent photon flux in both humid air and nitrogen conditions, we find that increases in or high levels of variance in a local least-squares fit slope parameter precedes the decay of charge-carrier transport. Since the variance in this parameter captures photo-brightening and photo-dimming processes occurring in hybrid perovskite grains, these results give additional insight about the implication of observed photocuring effects on device stability. Our work enables qualitative determination of carrier transport properties without having to make electrical contact to the material, creating opportunities for high-throughput, contactless material stability studies.

4.4 RESULTS

We simultaneously collected photoluminescence video and photoconductivity data of perovskite compositions to study the relationship between local recombination dynamics and material stability. Perovskite thin films having compositions of MAPbI_3 ,³⁷ $\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$,³⁷ and $(\text{FA}_{0.84}\text{Cs}_{0.16})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ ³⁸⁻⁴⁰ (MA = methylammonium and FA = formamidinium) were prepared using a solvent wash technique as described in the methods section. An evaporation mask was used to deposit gold contacts with a $100\ \mu\text{m}$ channel. Scribe-lines were made on either side of the $100\ \mu\text{m}$ channel to minimize the dark current (see *Figure 8.1* and *Figure 8.2* in Appendix C). *Figure 4.1* shows the experimental scheme and a bright-field microscope image of the perovskite sample with the narrow channel. Micro-photoluminescence images and videos were collected with a microscope and a filter-cube fitted with a long-pass filter. During continuous 100 Sun illumination ($6000\ \text{mW}/\text{cm}^2$ and $4500\ \text{mW}/\text{cm}^2$ 545 nm LED illumination for 1.6 eV and 1.85 eV bandgap material, respectively), photoluminescence videos of the center of the channel were collected every two minutes. Each video consisted of 500 frames, each frame having a 10 ms exposure time. In this fashion, we gained insight into short time-scale changes in local photoluminescence, long time-scale changes in the average photoluminescence intensity, as well as the degradation of the sample through the lateral photoconductivity trend. We used a high magnification objective (100x) to resolve individual perovskite grains. The resulting small field-of-view ($120\ \mu\text{m}$) required similar channel dimensions to illuminate the entire channel for photoconductivity measurements.

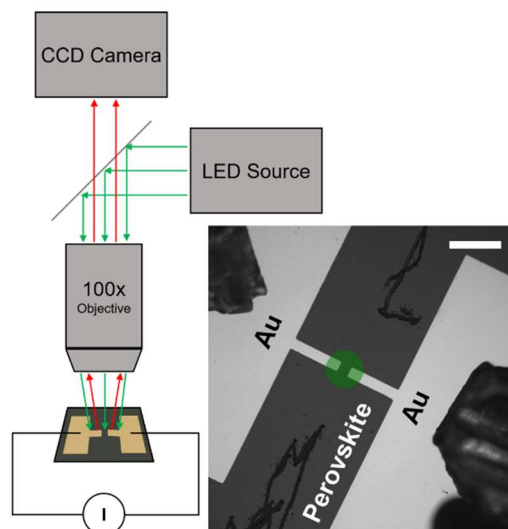


Figure 4.1 Experimental schematic of the high-magnification photoluminescence-photoconductivity experiment. A green LED with mean emission wavelength of 545 nm illuminates a $100\ \mu\text{m}$ perovskite channel between two lateral gold contacts. A voltage of 1 V is applied across the channel and the photocurrent is measured simultaneously while photoluminescence videos are collected with CCD Camera through the NIR long-pass filter. (Inset) A bright-field low magnification optical microscope image of a MAPbI_3 sample illustrating the channel geometry and scribe-lines, with a $500\ \mu\text{m}$ scalebar, and a green circle showing the illumination area and perovskite channel location.

Wide-field photoluminescence videos were collected every two minutes over the course of 3.5 hours for samples measured in humid air, 7 hours for samples measured in nitrogen, and over 12 hours for the $(\text{FA}_{0.84}\text{Cs}_{0.16})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ sample. This resulted in a massive amount of photoluminescence video data on the order of 1000 videos. In order to aid in the interpretation of these perovskite photoluminescence videos, we fabricated simulated videos that exhibit various properties we observe typically in perovskite samples. Figure 4.2a-c shows example frames from one such simulated video that contains 100 randomly dispersed emitters, which have a Gaussian spatial intensity distribution. The two-dimensional Gaussian distributions were used in order to represent point-source emitters. The intensity of these emitters vary with time by flickering (i.e. random intensity fluctuations), and also by photo-brightening or photo-dimming at random rates (i.e. gradual increase or decrease in intensity). The rate of photo-brightening or photo-dimming of each pixel is visualized in Figure 4.2d as a color-density plot, which shows the linear regression rate of intensity change of each pixel. We refer to this type of

plot subsequently as the linear regression slope image. The slope is calculated by performing a least-squares regression with time for each pixel. The yellow and red regions show emitters that exhibit moderate to fast photo-brightening, while the light blue regions show emitters that exhibit slight photo-dimming. This example illustrates that the linear regression slope has a maximum at the center of a Gaussian emitter, instead of the linear regression slope parameter being spatially uniform. In the supplementary information, we show results from other simulated videos, which exhibit different phenomena such as binary blinking, flickering of well-defined domains, and white noise (see *Figure 8.3* and *Figure 8.4* in Appendix C).

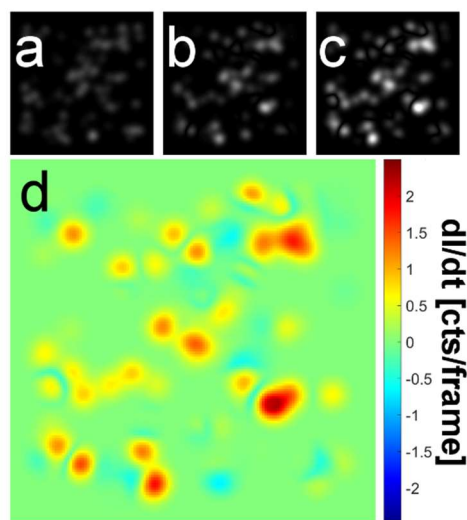


Figure 4.2 Simulated photoluminescence video results. (a-c) Time-sequence series showing the first, 50th, and 100th frame of the simulated photoluminescence video of randomly distributed gaussian emitters, some of which exhibit photobrightening and others exhibit photodimming. (d) Image showing the linear regression slope of each pixel.

Linear regression slope images are shown in Figure 4.3a and Figure 4.3d for MAPbI₃ after 2 minutes and 122 minutes, respectively. Short time-scale photoluminescence trends extracted from the 500 frame, 5 ms exposure time videos are shown for example pixels which exhibited photo-dimming or photo-brightening in Figure 4.3b-c and Figure 4.3e-f (locations for these pixels are shown in Figure 4.3a and Figure 4.3d, respectively). The slopes of the red lines Figure 4.3b-c and Figure 4.3e-f are examples of what is being imaged in Figure 4.3a and Figure 4.3d. While these example linear regression models do not reproduce all of the features in the data,

the red lines do represent the general trend in photoluminescence intensity with time. The regression images are consistent with the modeled Gaussian emitter video, with round domains and local extrema in the regression parameter. As others have noted,^{32, 33} these films exhibit photoluminescence flickering, as can be seen by the *ms* time scale fluctuations in the time-trends in Figure 4.3b-c and Figure 4.3e-f. Upon comparison of Figure 4.3a and Figure 4.3d, we observe the spatial heterogeneity of the slope parameter to have increased significantly. We discuss this in more detail below.

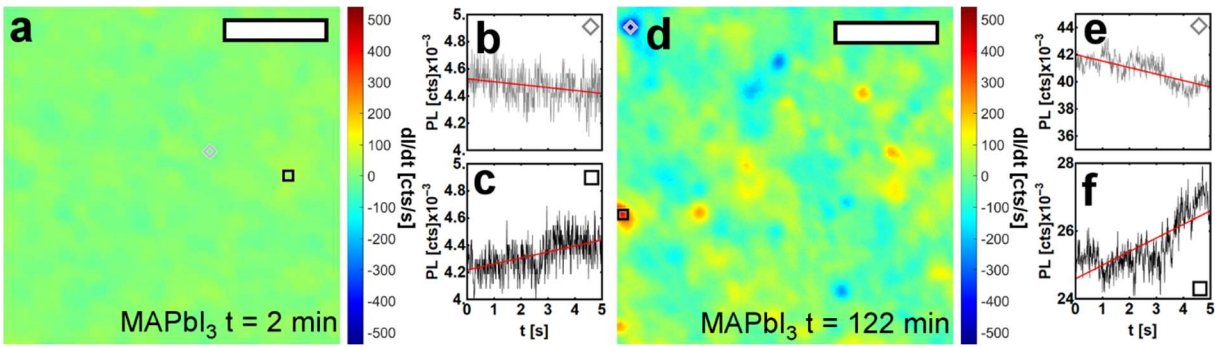


Figure 4.3 Linear regression slope image analysis of 100 Sun, 40%RH, MAPbI₃ photoluminescence videos. (a) Linear regression slope image after 2 minutes of illumination. (b and c) Photo-brightening and photo-dimming pixels located at the gray diamond and black square, respectively, in (a). Red lines represent linear regression of the time series data. (d) Linear regression slope image after 122 minutes. (e and f) Same as (b and c) but with respect to the gray diamond and black square in (d). Scalebars are 4 μm.

The summary statistics of photoconductivity and photoluminescence results for each composition and environmental condition are shown in Figure 4.4. The red trends represent samples exposed to concentrated illumination under lab air conditions controlled to 40%RH for 220 minutes. The blue trends represent samples exposed to the same illumination conditions, but under flowing nitrogen. The root mean square electron and hole diffusion length, L_D , is calculated from the photoconductivity measurements as described in Stoddard et al using.²⁰

$$L_D = \sqrt{\frac{\sigma_{ph} kT}{2q^2 G}} \quad (4.1)$$

Here, σ_{ph} is the photoconductivity, k is the Boltzmann constant, T is the temperature, and G is the volumetric generation rate. We refer to L_D as the carrier diffusion length in the following. The diffusion length trends are plotted with time in Figure 4.4a, d, and h; and the average photoluminescence intensity trends relative to the initial value are plotted with time for each composition and condition in Figure 4.4b, e, and i. We note that the diffusion length values calculated here are lower than we previously calculated by a factor of 2-3.²⁰ This is most likely a result of using a two-point contacting scheme, which is vulnerable signal decrease due to contact resistance; and also a result of contact quenching edge effects, where the photoluminescence is quenched near the gold contacts. The length-scale over which we observe a decrease in photoluminescence due to the perovskite-gold interface is unusually high (about 12 μm , see *Figure 8.5* in Appendix C), and as a result has a significant impact on the photoconductivity signal. The origin of this phenomenon may be due to a mechanism other than the interface recombination rates and charge-carrier diffusion; however, this is beyond the scope of this work. We assume this edge effect impacts each perovskite sample in a similar way, and so we are confident the trends with time and between perovskite samples are accurate reflections of those trends in lateral carrier transport.

Under these illumination conditions, the MAPbI₃ and MAPb(I_{0.6}Br_{0.4})₃ samples exhibit monotonic decline in the carrier diffusion length with time. The MAPbI₃ films in lab air and nitrogen undergo rapid degradation at 100 and 300 minutes, respectively, according to both the diffusion length and photoluminescence intensity trend; whereas the MAPb(I_{0.6}Br_{0.4})₃ films in the same conditions undergo a slower degradation at earlier times (50 and 80 minutes, respectively). Similar to our previous results,²⁰ the photoluminescence dramatically increases during the first half of the illumination stress-test, and then dramatically declines as the carrier

transport becomes compromised. Contrarily, the $(\text{FA}_{0.84}\text{Cs}_{0.16})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ sample demonstrates rather stable diffusion length with time in nitrogen and 100 Sun illumination conditions after an initial decay, and the photoluminescence trend of the same sample shows slow, monotonic decay. In every case observed here, the thin film eventually undergoes electronic and morphological degradation, as can be seen by the photoluminescence images and bright-field images taken before and after prolonged exposure to illumination (See *Figure 8.6* and *Figure 8.7* in Appendix C). In general, samples exposed to high intensity illumination under nitrogen conditions are observed to be more stable than those exposed to the same illumination under 40%RH humidity air. Photoluminescence videos of a p-GaAs wafer piece were also collected over the course of four hours as a control. Figure 4.4b, e, and i show GaAs to be by far the most stable, with the average photoluminescence intensity decaying less than 2% over the course of the two-hour experiment. This small decay is likely due to surface oxidation leading to higher surface-recombination velocities.

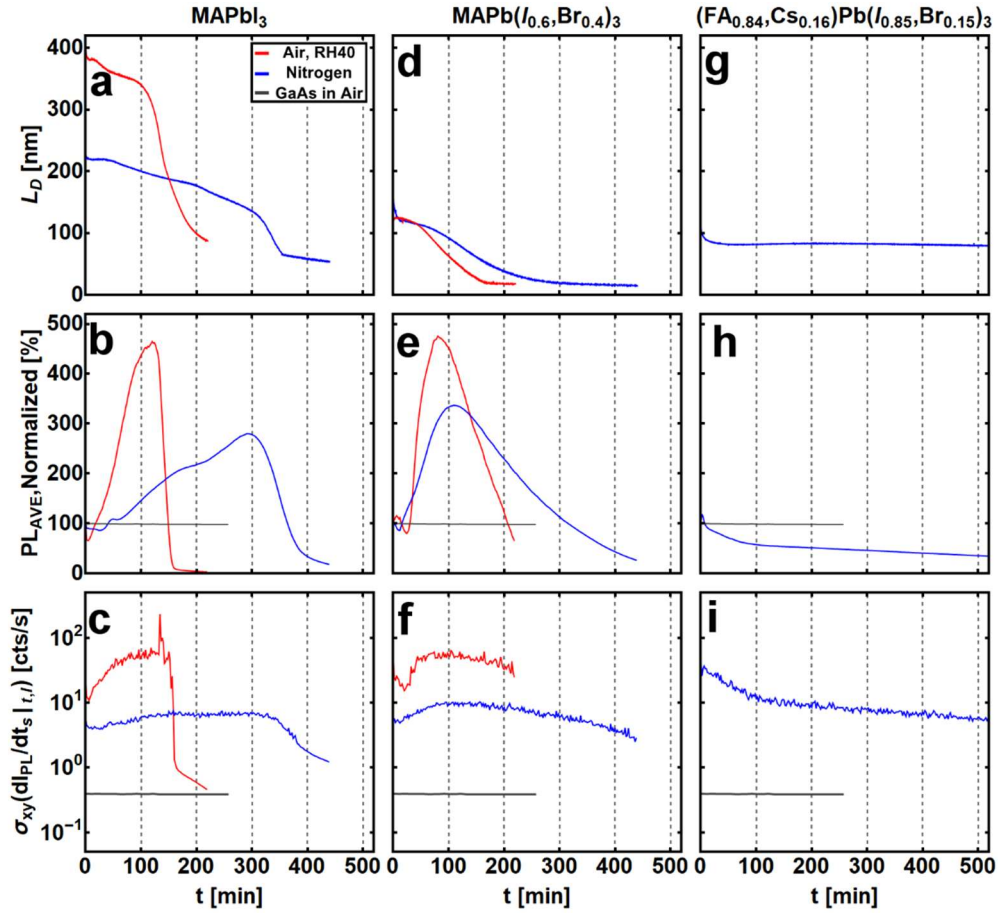


Figure 4.4 Photoluminescence-photoconductivity results for MAPbI_3 , $\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$, and $(\text{FA}_{0.84}\text{Cs}_{0.16})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ samples illuminated with 100 Suns equivalent photon flux in 40%RH (red traces) and nitrogen (blue traces) atmospheres. Mean carrier diffusion length, average PL intensity, and standard-deviation of the linear regression slope parameter vs. time for MAPbI_3 (a-c), $\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ (d-f), and $(\text{FA}_{0.84}\text{Cs}_{0.16})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ (g-i), respectively. Gray traces are GaAs reference data.

The spatial standard deviation of the linear regression slope parameter was calculated for each photoluminescence video and plotted with time in Figure 4.4c, 4f, and 4j. We observe that increasing or high values of spatial variance in the linear regression slope are associated with degradation of carrier transport. Initially, the MA containing films show an increase in PL intensity over time under illumination; however, the mean carrier diffusion length is monotonically decreasing. The spatial variance in the photoluminescence linear regression slope parameter fills in this picture by revealing how the heterogeneity in photo-brightening

and photo-dimming develops over time. Namely, the local changes in photoluminescence intensity for MA containing films within the first 10 minutes are relatively homogeneous; however, as the film begins to degrade, the spatial variance in the linear regression slope parameter increases and plateaus. Notably, the MAPbI₃ sample exposed to 40%RH lab air exhibited an enormous spike in the spatial standard deviation of the linear regression slope parameter at about 130 minutes which is just before the final and rapid decay of the mean carrier diffusion length. While the photoluminescence trend does not track with the photoconductivity trend in the early developments of the MA-containing perovskite films, both the photoluminescence and the photoconductivity in these films undergo a rapid decline at similar times in each case (e.g. 120 minutes for MAPbI₃ in 40%RH). We hypothesize that the increase in spatial heterogeneity of the photobrightening and photodimming of the perovskite film is associated with the loss of intergrain carrier transport. Explaining further, once the film begins to be composed of hybrid perovskite islands insulated from each other by lead iodide interfaces, we would expect spatial heterogeneity to increase since local trends in charge carrier recombination rates due to ionic transport, etc. would also become isolated from effects of neighboring domains.

Further support of this connection between mean carrier diffusion length and spatial heterogeneity in photoluminescence trends can be found in the observed trends of the (FA_{0.84}CS_{0.16})Pb(I_{0.85}Br_{0.15})₃ film under nitrogen. The (FA_{0.84}CS_{0.16})Pb(I_{0.85}Br_{0.15})₃ film shows the highest values of spatial variance in the linear regression slope parameter at early times while

the mean carrier diffusion length is changing the most. After the carrier diffusion length stabilizes for the FA containing film, the spatial variance in the linear regression slope parameter decreases and becomes nearly stable within the 500 minute time-frame. In the supplementary information, we show that the photoconductivity decreases to 50% of its initial value and that the photoluminescence signal decreases to less than 10% of its initial value over the course of 2500 minutes of constant illumination in nitrogen. The enhanced stability of the $(\text{FA}_{0.84}\text{CS}_{0.16})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ composition relative to the methylammonium-based hybrid perovskites has been hypothesized to result from the lower vapor pressure of the formamidinium salt and possibly the lower Lewis-acidity of the hydrogen atoms on the formamidinium cation.⁴¹ We observe the limit to which this formamidinium containing perovskite composition is stable within the a few days of experimentation despite the fact that this composition has been shown to withstand over 1000 hours of constant illumination under 1 Sun conditions³⁹. This shows the utility of using concentrated light to accelerate the determination of perovskite composition stability while also setting the bar for future promising perovskite compositions. In contrast to the perovskite samples, the GaAs sample standard deviation of the linear slope parameter trend is constant and orders of magnitude lower. This is unsurprising considering the chemical stability of GaAs and the fact that the sample is a single crystal.

4.5 CONCLUSION

In summary, we simultaneously measured photoluminescence videos and photoconductivity data of methylammonium and formamidinium films in lab air and flowing nitrogen environments. We compared the experimental results to simulated photoluminescence videos in order to gain intuition about the nature of perovskite emitters. The hybrid perovskite photoconductivity trends all exhibited significant film degradation within the 7 hours, with the exception of photoconductivity trend for the $(\text{FA}_{0.84}\text{Cs}_{0.16})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ film. In every case, increasing or high values of the standard deviation of the linear regression slope parameter is associated with losses in carrier transport. We show that collecting photoluminescence videos with short exposure time enables insight into the phenomena occurring on short time-scales, and collecting videos periodically over the course of hours enables insight into the slower processes such as degradation. This technique is well suited as a tool to study accelerated degradation, focusing on excess charge carrier concentration via high illumination intensities as the primary source of degradation in these materials. By studying spatial heterogeneity in the local photoluminescence trends, we can learn more about what is happening with regard to carrier transport in the films without having to make electrical contact to the films. Future studies expanding upon the different environments, encapsulation techniques, etc. will be useful for the continued development of stable and high-performance hybrid perovskite materials. The video analysis techniques described in this work will prove useful for scaling up the search for stable materials via high-throughput, combinatorial spray coating techniques.

4.6 METHODS

A. Ink Preparation

Pure iodide and mixed-halide methylammonium-based perovskite inks were prepared at 1 [M] concentration using a 7:3 v:v mixture of γ -butyrolactone (GBL) and dimethylsulfoxide (DMSO).

The MAPbI₃ ink was composed of 0.7 mL GBL, 0.3 mL DMSO, 1 mMol MAI, and 1 mMol PbI₂.

The MAPb(I_{0.6},Br_{0.4})₃ ink was composed of the same solvent amounts, 0.6 mMol MAI, 0.4 mMol MABr, 0.6 mMol PbI₂, and 0.4 mMol PbBr₂.

The mixed halide formamidinium-cesium-based perovskite ink was prepared at 1 [M] concentration using a 9:8 v:v mixture of n-methyl-2-pyrrolidone (NMP) and n,n-dimethylformamide (DMF). The (FA_{0.84}Cs_{0.16})Pb(I_{0.85}Br_{0.15})₃ ink was composed of 1.05 mL NMP, 0.94 mL DMF, 0.2856 g FAI, 0.0883 g CsI, 0.1630 g PbBr₂, and 0.6989 g PbI₂.

B. Film Preparation

Microscope glass scribed and cut to be 15 mm x 15 mm was cleaned for 10 minutes sequentially in deionized water, acetone, isopropanol, and argon plasma. The methylammonium perovskite films were spin-cast using a toluene solvent wash technique. The perovskite ink was dispensed onto the substrate with a volume of 70 μ L. The spin rate profile was 5 s at 500 RPM, 60 s at 1000 RPM, and then 45 s at 5000 RPM using maximum acceleration for each step. The spinning substrate was flooded with 0.7 mL toluene when 18 s remained on the last spin step. The resulting perovskite films were annealed for 10 min on a hotplate set to 100 °C.

The formamidinium-cesium-based perovskite films were spin-cased using a chlorobenzene solvent wash technique. The perovskite ink was dispensed onto the substrate with a volume of 70 μ L. The spin rate profile was 4000 RPM for 45 seconds using maximum acceleration. The spinning substrate was flooded with 0.7 mL chlorobenzene when 20 s remained. These films were also annealed for 10 min on a hotplate set to 100 °C.

C. Video Acquisition

An Olympus BX53M microscope equipped with a motorized z-axis controller, a CMOS camera (Hamamatsu C11440 Orca Flash 4.0), a 545 nm LED (Lumencor), 665 nm dichroic beamsplitter and a 664 nm long-pass filter were used for collecting fluorescence videos. The total

illumination intensity of the incident light within the field of view was measured by closing the iris diaphragm of the illumination path such that the total area of illumination was visible in the field of view and measuring to total power within that area using an optical power meter (Oriel). The exposure time used for the fluorescence videos was 10 ms, and the duration of each video was 500 frames. A region of interest (ROI) spanning 200 pixels by 200 pixels in the center of the 100 μm channel was used to minimize processing time and achieve the 10 ms exposure time. Videos were collected every 2 minutes, and the 100 Sun illumination was continuously incident on the perovskite sample during the stability test.

Humidity control for the lab-air experiments was achieved by collecting photoluminescence videos in an atmosphere controlled room set to 70 °F and 40%RH. The videos were collected with a 100 $\times$ objective with a 0.21 mm working distance (Olympus MPLN 100 $\times$). The nitrogen atmosphere experiments were performed using a window-containing flow-cell with inlet and outlet ports for high-purity nitrogen flow. Due to the window of the flow-cell, a 100 $\times$ objective (M Plan APO NIR 100 $\times$) with a longer working distance (12 mm) was used for the nitrogen environment videos.

D. Photoconductivity Measurements

A Keithley model 2400 was used to measure the photocurrent across the 100 μm channel while a bias across the channel of 1 V was applied. Measurements were made every 5 s during continuous bias application. The contact and scribing geometry of the samples are shown in *Figure 8.1* in Appendix C.

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Chapter 5. CONCLUSION

5.1 SUMMARY AND DISCUSSION

This dissertation details our efforts to characterize a wide range of hybrid perovskite compositions for their application to single junction and multijunction photovoltaic technologies. Absolute intensity photoluminescence measurements served as the primary means for comparing absorber materials with their respective limit based on detailed balance calculations. While the compositions explored in this work is by no means exhaustive, it outlines several considerations that must be made when contributing to the broader hybrid perovskite composition optoelectronic quality library.

In Chapter 2, we set out to apply a previously developed model to several notable hybrid perovskite thin films. The model, which describes spectral photoluminescence flux emitted from a smooth semiconductor surface, is applied using non-linear regression and enables the quantification of the quasi-Fermi level splitting. By comparing the quasi-Fermi level splitting of films to the V_{OC} 's of associated devices, we experimentally demonstrate the paradigm which is relied upon for the rest of this work: $\Delta E_F = V_{OC,Max}$. In words, the quasi-Fermi level splitting we measure with the absolute intensity photoluminescence technique gives us a glimpse of the potential a given material has to sustain high V_{OC} 's. We leverage this relationship between photoluminescence and device performance to predict further improvements of hybrid perovskite device power conversion efficiencies to beyond 25% *via* effective integration of surface passivation into device architectures. Such advancements in surface passivation are forecast to improve device V_{OC} 's to approach 1.3 V for the 1.6 eV bandgap perovskite.

In Chapter 3, we apply the PL method given in Chapter 2 to combinatorial composition screening. The goal of this chapter was to assess Iodide-Bromide alloys for their top-cell potential in a 2-terminal tandem device architecture. We developed a spray coating technique

for preparing a halide gradient spanning MAPbI_3 to MAPbI_2Br with high resolution. The incorporation of bromine, while successfully tuning the bandgap within the tandem relevant energies, has two negative impacts on the material quality: (1) The initial optoelectronic quality upon illumination decreases, and (2) the phase stability of the iodide-bromide alloys becomes significantly compromised at about 20% bromide replacement. Though many other wide bandgap hybrid perovskite compositions have been applied to photovoltaic devices, they are predominately plagued by the former limitation – even when all evidence of the latter limitation is absent. We hypothesized that the decrease in optoelectronic quality with bromide incorporation is due to a defect population which energetically is deeper into the bandgap for the large bandgap materials, which in turn enables efficient non-radiative recombination. Without eliminating this defect population, or possibly engineering the absolute-energies of the band edges to keep the defect population energy out from near the middle of the bandgap, the large bandgap hybrid perovskite variants will not serve effectively as a top-cell absorber in tandem devices.

In Chapter 4, we simultaneously measured photoconductivity and photoluminescence videos over time in order to link photoluminescence dynamics with charge carrier transport and film stability. We observed that the $(\text{FA}_{0.84}\text{Cs}_{0.16})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ films were the most stable and could withstand 100 Sun illumination for more than 8 hours. We proposed a link between charge carrier transport and spatial heterogeneity of photobrightening and photodimming. This work sets the stage for future stability studies to make further connections between stability and photoluminescence dynamics in hybrid perovskites.

5.2 FUTURE WORK

There are several opportunities for subsequent studies and developments based on the learnings reported in this dissertation. These can be categorized into model development, composition exploration, and scaled-up accelerated testing.

Based on the limitations of the photoluminescence model presented in 6.2 of the appendix, a broader set of materials and samples could be appropriately characterized if alternative joint-density of states models were implemented into the general absorptivity model. For example, G-function tables could be calculated for indirect-gap, excitonic, and low dimensional above bandgap density of state models. Further, alternative thin-film geometries could be considered when calculating the absorptivity spectrum from the modeled absorption coefficient spectrum. Presently, the model only accounts for optical outcoupling in the case of a planar film and ignores interference effects. Extending the absorptivity model to include the impact of rough or very thin films may enable further improvements in the accurate determination of material properties such as the subbandgap absorptivity exponent or disorder energy parameter. We acknowledge, in light of the already six fitting parameters required to generate a photoluminescence peak, any extensions of the photoluminescence model presented in Chapter 2 must be carefully considered in terms of the number of additional fitting parameters the model extension contributes.

The composition space explored in Chapter 3 was by no means exhaustive. The sequential-step deposition method limited the components which could be included in the composition gradient application were limited to the organic cation and one third of the halide composition. Therefore, it will be very important to continue development of single-step ink formulations amenable to the spray coating of perovskite thin films with controllable thickness, coverage, and morphology. For example, approaches such as the one presented by Stoddard et. al may be translatable to perovskite alloys. Besides exploring for high- and low-bandgap perovskite compositions which are amenable for tandem photovoltaics, it would be incredibly valuable to also measure carrier concentration with either indirectly using illumination intensity dependent photoluminescence experiments or directly using van der Pauw method Hall effect experiments. A method for doping perovskite thin films to moderate concentrations (i.e. $>10^{16} \text{ cm}^{-3}$) would

enable an entirely new realm of device optimization strategies, likely leading to device fill-factor and V_{OC} improvements.

Regarding the photoluminescence video analysis studies, a future direction with high potential impact is to expand this work to previously unexplored compositions in order to find compositions which are stable at high illumination conditions. Additionally, these techniques could be implemented to study the stability of hybrid perovskite materials interfaced with metal electrodes or transport materials.

5.3 THE FINAL WORD

Fundamentally, there is a direct relationship between steady-state photoluminescence from a given material and its potential device performance. The aim of this body of research was to demonstrate that this principle is relevant to both hybrid perovskites specifically and to all potential PV materials broadly. We leveraged steady-state photoluminescence mapping to begin a catalogue of hybrid perovskite compositions and their optoelectronic materials. During this process, we came across special considerations regarding material stability that needed to be addressed, such as phase segregation and temporal photoluminescence fluctuations. We have shown that coupling steady-state photoluminescence modeling with high-throughput exploration is an efficient means to discover new photovoltaic materials with high optoelectronic quality and stability.

Chapter 6. APPENDIX A: ADDITIONAL INFORMATION FOR CHAPTER 2

6.1 CHARACTER OF THE PHOTOLUMINESCENCE MODEL -- TEMPERATURE

Figure 6.1a shows how changes in temperature impact the absorptivity and Bose-Einstein distribution, which results in the photoluminescence peaks shown in Figure 6.1b. In this case, the known temperature-dependence of the direct bandgap and Urbach energy for GaAs¹ are included.

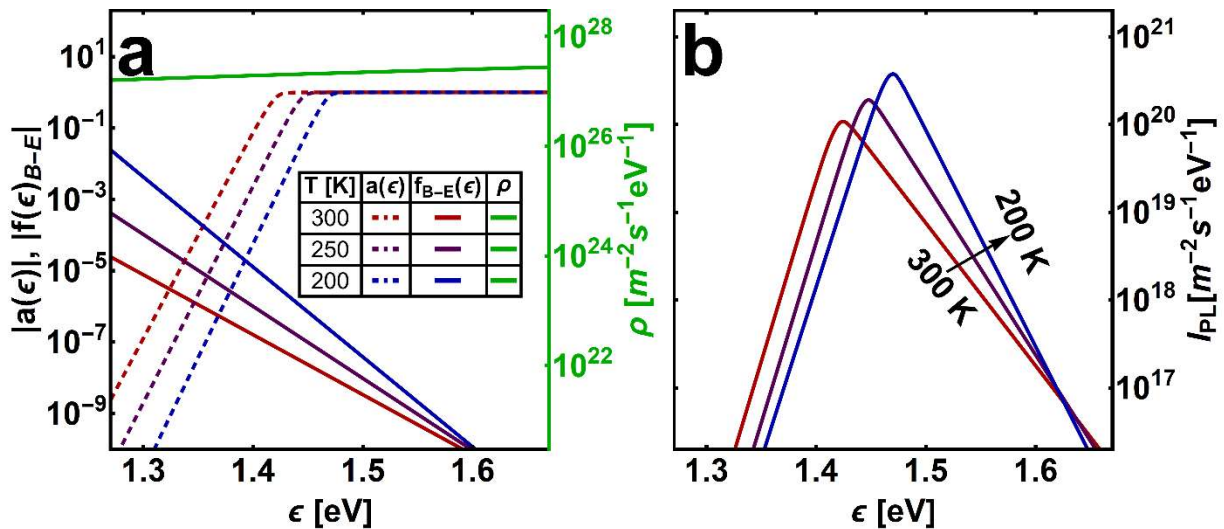


Figure 6.1 Illustrating of the contributing factors of photoluminescence spectra as a function of temperature. The excess carrier concentration is held constant and the temperature is decreased. **a**, changes in the absorptivity spectrum (dashed lines), Bose-Einstein distribution (solid lines), and photon density of states (solid green line). **b**, the modeled photoluminescence spectra resulting from **a**. Note the increasing slope and intensity with decreasing temperature of the high energy tail.

Importantly, ΔE_f is shown to increase with decreasing temperature, even as the excess charge carrier population density is kept constant – a consequence of the Fermi occupation function becoming sharper at lower temperatures. While this model correctly predicts non-zero emission near 0 K (see Figure 6.2), several commonly observed physical phenomena are left out of this model as presented and therefore do not accurately describe the low temperature limit of GaAs photoluminescence behavior. The most significant omission in this model is exciton

recombination, which dominates when kT becomes on the order of the exciton binding energy of the material. Extending the absorptivity model to include exciton absorption would be sufficient to accurately predict the commonly observed low-temperature photoluminescence spectra observed elsewhere.²

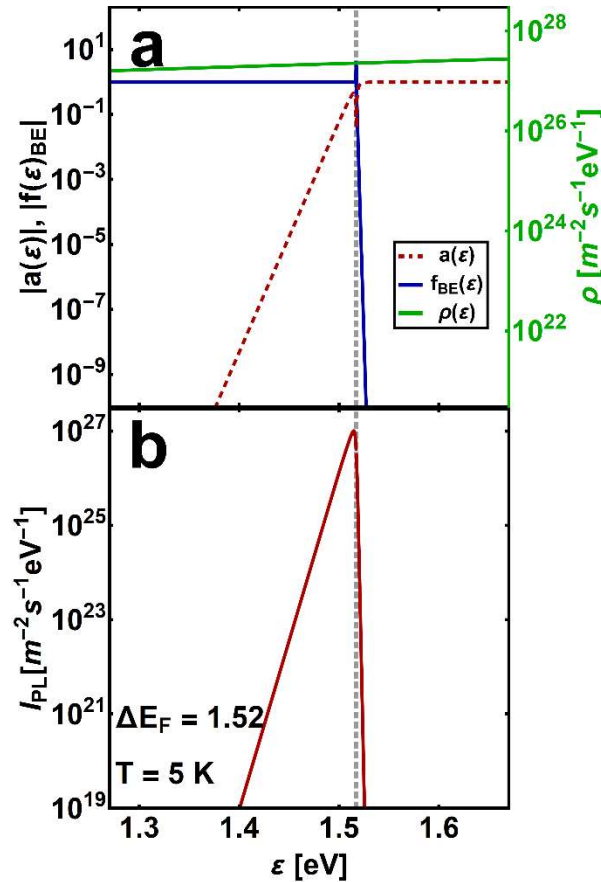


Figure 6.2 **Modeled band-band radiative recombination at very low temperature. a**

The absorptivity spectrum (red dashed line), Bose-Einstein distribution (blue), and photon density of states (green). **b** the modeled photoluminescence spectra resulting from a. Note that almost all emission is from below the quasi Fermi-level splitting energy.

6.2 LIMITATIONS OF THE COMBINED PHOTOLUMINESCENCE AND ABSORPTION MODEL

It is important to consider some limitations related to applying the above photoluminescence model. The following list briefly presents several cases where additional care should be taken.

- *Violation of quasi-thermal equilibrium.* Transient measurements on short time-scales and very low temperatures, particularly in the presence of defect populations, will cause the quasi-thermal equilibrium assumption to become invalid. Additionally, hot carrier distributions are not accurately described using the quasi-thermal equilibrium assumption. Gibelli et al expand the Lasher-Stern-Würfel equation to account for hot carrier populations to model emission from III-V multiquantum wells and extract accurate values of ΔE_F .³
- *Inappropriate density-of-states model.* Indirect-gap and excitonic materials are examples where the model as stated above using a direct-gap joint density of states will break down. Calculating a new G-function and look-up tables for each density-of-states model would be necessary. For example, 2D density-of-states direct bandgap model convoluted with a tail-state distribution was necessary to accurately model electroluminescence spectra collected from a highly crystalline rubrene/C₆₀ heterojunction interfaces.⁴
- *Inappropriate absorptivity model.* Very thin films, very rough films, or films of very high index of refraction would likely cause some error related to its deviation from the planar absorptivity model we have used above.
- *Shoulders and multiple peaks in measured PL.* This can be caused by compositional heterogeneity or optical transitions other than band-band recombination. If the high-energy side of the peak is well fit by an absorptivity of 1, a so-called 'high-energy tail fit' may be used to determine ΔE_F and T, without determining θ and γ .⁵
- *Depth variation of ΔE_F .* Variation of ΔE_F with depth is expected. For instance, ΔE_F is expected to decrease with depth for low quality films with short carrier diffusion lengths. On the contrary, for high quality films with long carrier diffusion lengths, but non-passivated surfaces, ΔE_F may increase with depth. Regardless, the ΔE_F

determined by the technique will be dominated by the high ΔE_F regions, and thus gives an upper limit for achievable Voc.

- *Lateral variation of ΔE_F .* If local variations in optoelectronic quality exist that are larger than the illumination area, then spectra can and should be collected over different locations to quantify. If the spatial variation is smaller than the illumination area, then the spectral characteristics will be dominated by the high ΔE_F regions.
- *Extremely thin films.* For the case of very thin films where the absorptivity is low for all wavelengths measured, $\alpha_o d$ and ΔE_F become correlated and may be difficult to simultaneously fit. The $\alpha_o d$ product may be made smaller and smaller by a least-squares fitting algorithm while compensating with a larger ΔE_F . If $\alpha_o d$ is known independently it can be held fixed.

6.3 ACHIEVING A GOOD FIT OF THE ENTIRE PHOTOLUMINESCENCE PEAK

We have previously detailed the calibration and validation methods that were performed in order to characterize the instrument response in terms of an absolute photon flux.^{6,7} The photoluminescence and absorption coefficient model as given in this perspective only accounts for one band-band transition and one tail-state distribution; therefore, it is unreasonable to expect this form of the model to accurately reproduce multiple transitions (i.e. multiple or convoluted peaks) or more complicated tail-state distributions (more than one length-scale of electrostatic fluctuations, for example). Additionally, most of the model parameters are sensitive to the far high (i.e. T and ΔE_F) and low (i.e. γ and θ) energy tails. We recommend plotting the absolute-intensity photoluminescence peaks on a logarithmic scale to check the quality of the fit and shoulders in either of the tails (see CZTSe peak in Figure 2.2b as an example). Further, performing a logarithmic transform of the absolute intensity data and non-linear fit model

before minimizing the residual error can improve the quality of the fit in the far-tail regions, particularly the high energy tail.

A common behavior we have observed in multiple materials (CISe, and CIGSe in Figure 2.2b of the main text are good examples) is deviations of the model from experimental data in the far low-energy tail. Contrary to the accelerating exponential decays that result from higher values of θ , the experimental results appear linear on a logarithmic scale, which suggests the presence of an Urbach tail. On the contrary, the entire photoluminescence peak is not well described by a simple exponential tail because the behavior at the peak-maximum is not nearly as sharp as one would expect from a pure Urbach tail (GaAs in Figure 2.2b, for example). Multiple length-scales of disorder may account for these changes in the exponential slope of the low energy tail, but this is outside the scope of this model. Indeed, observations of the very far low energy tail (absorption coefficient data of order $\sim 10^{-3} \text{ cm}^{-1}$) demonstrate deviations from this Urbach behavior.⁸

6.4 SOME PRACTICAL CONSIDERATIONS FOR FITTING PHOTOLUMINESCENCE SPECTRA

We optimize the fitting parameters of the photoluminescence model using a non-linear least squares fitting technique (e.g. Levenberg-Marquardt method) to describe the observed photoluminescence spectra. The most immediate concern of doing this is the large number of fitting parameters required. If none of the properties are known, then E_g , θ , γ , $\alpha_0 d$, T , and ΔE_F , must be used as fitting parameters to describe the observed photoluminescence peak. Typically, we only fit E_g , θ , γ , T , and ΔE_F . Our initial guess for the fit temperature is the resulting temperature from a high energy tail fit,⁹ and we calculate $\alpha_0 d$ based on available material properties. We discuss below each of the fitting parameters of the model, strategies for constraining certain parameters, and other necessary considerations when fitting photoluminescence data.

A. Fitting E_g

The bandgap is a useful parameter to fit, particularly when a relationship between bandgap and material composition is known. Fixing this parameter to be the bulk bandgap determined from UV-vis experiments may be reasonable, however local variations in the bandgap will be ignored in this case and the absorptivity model will be forced to fit variations in photoluminescence peak position with γ and θ .

B. Fitting θ

The exponent θ depends on the energy-scale and length-scale of electrostatic potential fluctuations.¹⁰ If the dominant physical mechanism responsible for the electrostatic potential fluctuations is known or hypothesized (e.g. Urbach Tails,¹¹ screened Thomas-Fermi potential fluctuations,¹² Franz-Keldysh effect from charged impurities,¹³⁻¹⁵ bandgap fluctuations,¹⁶ etc.), then the exponent may be fixed. For example, $\theta = 1$ was used for GaAs nanowires in order to model cathodoluminescence spectra,¹⁷ $\theta = 2$ and $\theta = 1.25$ were hypothesized to analyze CZTS photoluminescence-excitation¹⁸ and photoluminescence spectra,¹⁹ respectively. We typically keep the tail distribution exponent θ as a fitting parameter because sub-bandgap absorptivity is often dependent on composition and defect chemistry.²⁰

C. Fitting γ

The broadening energy is strongly coupled with θ , since they both impact the slope of the low energy tail of the absorption coefficient spectrum. One useful alternative to allowing both θ and γ to float as fitting parameters is to constrain θ to a limiting case, and to assign physical meaning to the fit γ . For example, typical Urbach energies extracted for hybrid perovskites range from 12-16 meV.^{21, 22} By fixing $\theta = 1$ and simultaneously fitting high and low energy photoluminescence tails, this Urbach energy may be obtained. γ is simply an energy in each case, but it has different meaning. For the Urbach model, γ is simply called the Urbach energy. For the Thomas-Fermi

model with tunneling, γ is related to the barrier height. For the Franz-Keldysh model, γ is related to the average local electric field strength. For the semiclassical Thomas-Fermi model, $\gamma/\sqrt{2}$ is the root-mean square of the depth of the potential well created by charged impurities.

D. Fitting $\alpha_0 d$

These two parameters always appear together as a product (which is dimensionless) when modeling absorptivity or photoluminescence. Fitting $\alpha_0 d$ for very thin films is inappropriate because this parameter is weakly coupled to ΔE_f in this case. Therefore, the observation depth, d , for thin films may be obtained simply by measuring the film thickness; and d for thick samples such as wafers may be obtained by adding the diffusion length and the absorption length. The α_0 parameter may be extracted from literature absorption coefficient data, or estimated using the $k \cdot p$ approximation:

$$\alpha_0(\varepsilon) = \left(\frac{q^2 \hbar}{6\pi \epsilon_{\text{vac}} m_e c} \right) \left(\frac{2m_r^*}{\hbar^2} \right)^{3/2} \left(\frac{E_{\text{Kane}}}{\varepsilon} \right) \quad (6.1)$$

Where m_e is the electron mass, m_r^* is the reduced effective mass, and E_{Kane} is the Kane energy (estimated by $E_{\text{Kane}} = E_g(m_e/m_r^* - 1)$).²³ For GaAs, $E_{\text{Kane}} = 22.7$ eV and does not vary much for any of the III-V semiconductors. The energy dependence of this parameter is typically ignored since it varies slowly with emission energy relative to the other energy-dependent factors being considered (i.e. joint density of states and the exponential tail of the sub-bandgap absorptivity distribution). Typical $\alpha_0 d$ products for III-V, chalcogenide, and hybrid perovskite semiconductor thin films are 30-50, 10-20, and 2-5, respectively. Importantly though, small errors in $\alpha_0 d$ do not significantly affect the fitting results for E_g , θ , γ , and ΔE_F .

E. Fitting T

The temperature used for modeling the photoluminescence spectra is the only parameter which determines the slope of the high energy tail plotted on a logarithmic scale, as seen in Figure 1e. One exception is when the $\alpha_0 d \ll 1$ in which case changes in the $\alpha_0 d$ product will have an impact on the slope of the modeled high energy tail. Presuming the spectra were collected at ambient temperatures and one-Sun equivalent photon fluxes, the extracted temperature should be between 300 - 350 K. Low radiative efficiencies, low thermal conductivities,²⁴ slow hot-carrier relaxation,²⁵ and higher photon fluxes may cause further elevated temperatures, however detector non-linearity (in terms of signal or spectral responsivity) may also be considered as explanations of erroneously high fit temperatures. This effect is shown in Figure 6.3 shows reasonable temperature fits from the Lasher-Stern-Würfel equation using the generalized sub-bandgap absorptivity model; however, the error in the fit temperature increases with decreasing signal strength

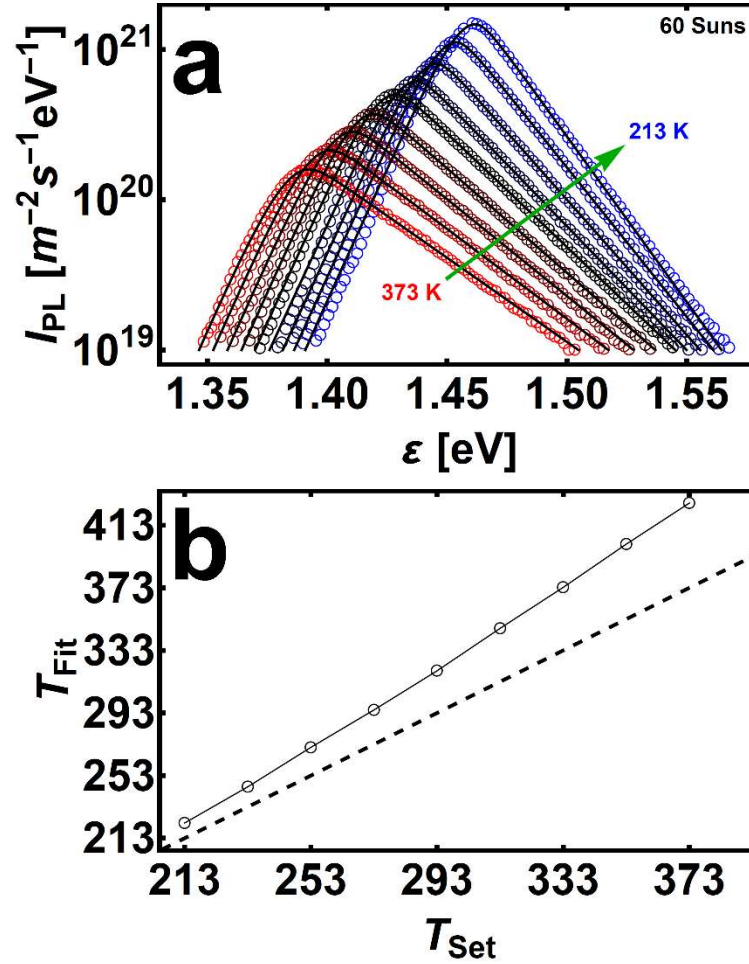


Figure 6.3 Evaluating the accuracy of fitting the local temperature of a GaAs wafer using absolute-intensity photoluminescence analysis. A GaAs sample was placed in a cold-stage, and spectra were collected as a function of temperature while noting the stage temperature at each collection. **a** absolute-intensity spectra plotted on a log scale. **b**, the fit temperature as a function set-point temperature.

6.5 ΔE_F VERSUS LIGHT INTENSITY

Learning about the material-limited V_{OC} from extracted ΔE_F values of steady-state photoluminescence measurements is most useful when the illumination conditions are as close to AM1.5GT as possible. As most photoluminescence experiments are performed using monochromatic light sources, there are some limitations in fully reproducing standard operating conditions. The way that we address this problem is to match the photon flux of the monochromatic light source with the above-bandgap photon flux of the AM1.5GT solar

spectrum (even better would be to match the absorbed photon flux to that of the AM1.5GT spectrum). Depending on the excitation source wavelength used, film thickness, and carrier diffusion length, the steady-state carrier density profile through the depth of the film may also differ in the monochromatic case compared to the AM1.5GT illumination spectrum.

For certain materials it is not possible to observe photoluminescence under one-Sun equivalent absorbed photon flux due to material quality limitations, or more often the lower detector efficiencies (higher dark currents) for NIR detectors. Such is the case with the CISE, CIGSe, and CZTSe spectra shown in Figure 2.2. To compensate for this, we increased the measured photoluminescence signal by exposing the CISE, CIGSe, and CZTSe samples to 68, 78, and 807 Suns, respectively, and made a correction for the best-case relationship between ΔE_F and light intensity which is shown in eq S21,

$$\Delta E_F(T, 1 \text{ Sun}) = \Delta E_F(T, S) - kT \log(S) \quad (6.2)$$

where S is the number of equivalent Suns. This correction assumes that the carrier concentration is proportional to the square-root of the incident photon flux (i.e. $n \cdot p \propto S$), which is equivalent to assuming an ideality factor of one. This assumption is correct in for either (1) a doped semiconductor at low injection with monomolecular non-radiative recombination dominating, (2) a doped semiconductor at low injection with radiative recombination dominating, or (3) a semiconductor with bimolecular radiative recombination dominating. For undoped semiconductors with dominant monomolecular non-radiative recombination, ΔE_F has a higher dependence on the illumination intensity – as high as $2kT \log(S)$. The excess carrier concentration in this case is assumed to be directly proportional to the illumination intensity (i.e. $n \cdot p \propto S^2$).

If a significant density of states exists within the bandgap, then the quasi-Fermi levels can become pinned, and the above relationship no longer holds because the dependence of ΔE_F on light intensity weakens. In such cases, the light-intensity dependence of ΔE_F may be measured

to determine the ideality factor of the material in the low-series resistance limit. Gunawan and Gokmen performed light intensity and temperature dependent V_{OC} and J_{SC} experiments²⁶ to better understand the V_{OC} deficit in CZTSe, CIGSe, and c-Si devices using the relationship $n_s = [kT d\ln(S)/dV_{OC}]^{-1}$, where n_s is the ideality factor.²⁷ They found that the CZTSe device V_{OC} saturated at about 0.55 V, causing the effective ideality factor to be zero at high illumination intensities. In the same study, the CIGSe devices demonstrated an ideality factor between 1 and 1.5 over light intensities ranging from 1 to 100 Suns. Therefore, the possibility for various recombination kinetics within the absorber and the possibility for defect density distributions to exist in the gap complicates the ΔE_F light intensity correction. Collecting photoluminescence data at multiple illumination intensities can assist in determining the one-Sun ΔE_F .

6.6 ABSOLUTE-INTENSITY PHOTOLUMINESCENCE SPECTRA CALIBRATION

We use a blackbody cavity at a temperature of 1050 °C to perform both the spectral shape correction and the absolute intensity spectral photon flux calibration for the confocal photoluminescence instrument used in this study. Figure 6.4 shows the geometry of the blackbody source emission cone and the confocal objective collection cone.

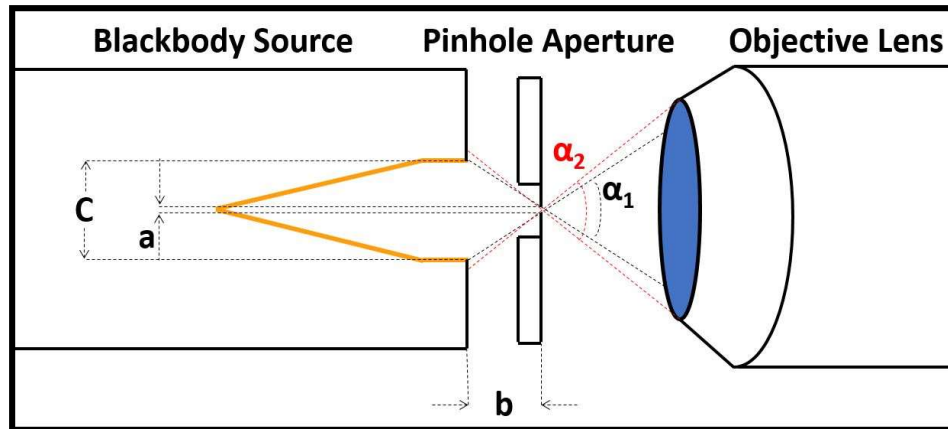


Figure 6.4 **The blackbody calibration geometry.** The blackbody source (**left**), having maximum cavity diameter C , is masked and collimated by a pinhole aperture (**middle**) having a diameter a and is offset from the blackbody cavity entrance by b . After the pinhole, the blackbody source is slightly collimated by the pinhole such that the intensity distribution is Lambertian from normal incidence to an angle of $\alpha_1/2$. This cone angle is compared to the collection cone angle $\alpha_2/2$, the microscope objective one-half angle aperture.

The calibration is performed by collecting a spectrum of the NIST calibrated blackbody source through a pinhole aperture of known diameter and setting the spectral photon flux collected to that determined by eq (6.3).

$$I_{BB}(\epsilon) = \left\{ \frac{2\pi\epsilon}{h^3c^2} \right\} \left\{ \frac{1}{\exp\left(\frac{\epsilon}{kT}\right)} \right\} \quad (6.3)$$

where I_{BB} is the spectral blackbody photon flux and ϵ is the photon energy. Eq (6.3) assumes a Lambertian angular distribution, which is valid so long as the microscope objective is completely filled by the blackbody emission cone. Otherwise, any underfilling of the microscope objective collection cone can be accounted by using a geometric correction factor. To calculate this correction factor, one must first calculate the blackbody emission cone angle using eq (6.4).

$$\alpha_1 = 2 \tan^{-1} \left(\frac{a - c}{2b} \right) \quad (6.4)$$

where α_1 is the emission cone angle, a is the pinhole aperture diameter, c is the maximum blackbody cavity diameter, and b is the distance between the blackbody entrance and the pinhole. This emission cone angle must be compared to the collection cone angle of the microscope objective, calculated using eq (6.5).

$$\alpha_2 = n \sin^{-1}(NA) \quad (6.5)$$

Here, α_2 is the collection cone angle, n is the index of refraction of the imaging medium, and NA is the numerical aperture of the objective. These parameters are summarized in Table 6.1.

Table 6.1 Blackbody Calibration Geometry Parameters

Variable	Description	Value
C	Maximum blackbody cavity diameter	6.35 mm
b	Distance between aperture plane to blackbody cavity entrance	13 mm
a	Aperture diameter	0.01 mm
α_1	Blackbody cavity emission cone angle	27.4°
α_1	Objective lens collection cone angle	29.0°
Ω_1/Ω_2	Solid angle correction factor	0.895
$f(\Omega_1)/f(\Omega_2)$	Cosine-corrected factor	0.898

An Olympus MPLN 10x objective is used for the confocal photoluminescence experiments, which has an NA = 0.25. The solid angle of the emission and collection cones can be found by using eq (6.6) and the cone angles α_1 and α_2 , respectively.

$$\alpha_2 = n \sin^{-1}(NA) \quad (6.6)$$

where Ω is the solid angle of either the emission cone or the collection cone. Table 6.1 shows the blackbody emission cone fills 89.5% of the collection cone. Alternatively, the Lambertian distribution can be considered, which requires multiplying the surface integration in spherical coordinates by a factor of $\cos(\alpha)$. The result of this integration is shown in eq (6.7).

$$f(\Omega) = \pi(1 - \cos^2[\alpha/2]) \quad (6.7)$$

where $f(\Omega)$ is the cosine-weighted surface integral over the solid angle of either emission or collection. The extent to which the collection cone is underfilled by the blackbody emission is calculated using this approach to be 89.8%, very similar to the simple fraction of the solid angles. This similarity is due to the small collection and emission angles. There would be a bigger difference between the solid angle and the Lambertian-corrected value for larger

numerical apertures, since the Lambertian distribution tends to 0 as the collection angle approaches 90° . Therefore, we use a geometric correction value of 0.895 to correct the absolute intensity photoluminescence spectra.

The accuracy of the integrating sphere setup for measuring external photoluminescence quantum efficiency was verified using a known fluorescence standard. A solution of the Rhodamine 6G at a concentration of 9.91×10^{-6} M in ethanol was prepared by serial dilution. The solution was dispensed into a 10 mm path-length cuvette for placing in the centre-mount position of the integrating sphere. The excitation wavelength used was 487 nm, which was obtained by filtering a xenon-mercury lamp with a monochromator. Figure 6.5 shows the excitation and fluorescence spectra, and the measured photoluminescence quantum efficiency was determined to be $93.3 \pm 2.0\%$ ($N = 5$), which agrees with the known photoluminescence quantum efficiency of Rhodamine 6G (94%)²⁸.

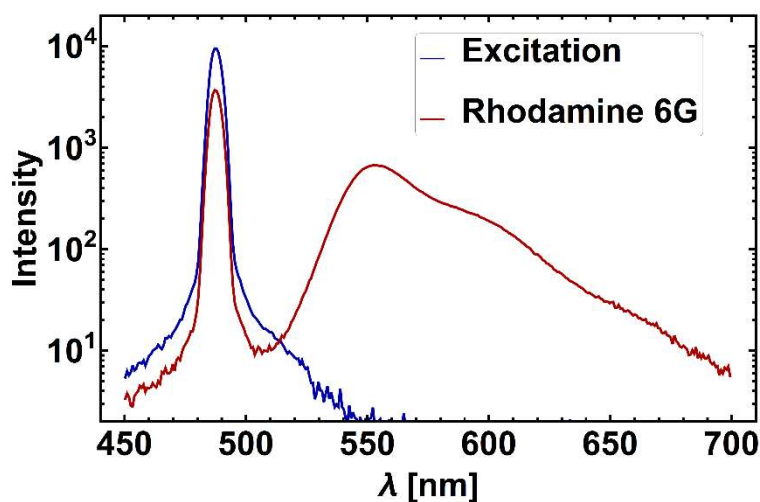


Figure 6.5 Spectra collected in the integrating sphere instrument of (blue) pure ethanol, and (red) Rhodamine 6G in ethanol at a concentration of 9.91×10^{-6} M.

The confidence interval spectra for the spatially varied data collected by the confocal instrument and compared it to the integrating sphere spectra of the same treated and untreated sample. These are shown in Figure 6.6.

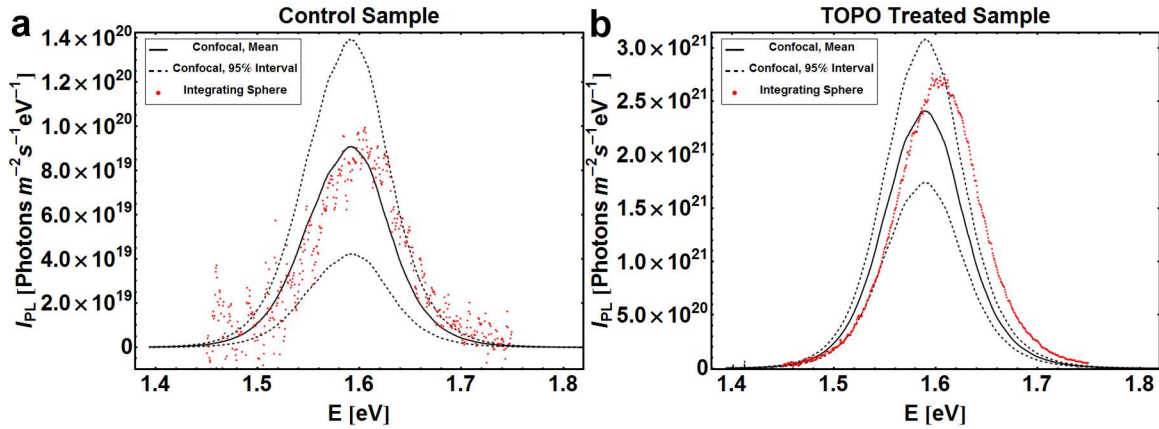


Figure 6.6 **Comparison between the independently calibrated confocal and integrating sphere spectral photoluminescence flux data** of **a** the untreated sample and **b** the TOPO treated sample. The dashed lines and solid black lines represent the 95% confidence interval and mean spectra, respectively, capturing the spatial variation within the sample. The red data represent the integrating sphere data calibrated by measuring the incident laser light with a power meter.

The integrating sphere data falls within the confidence interval of the spatial statistics collected by the confocal instrument over a majority of the peak for both the control and TOPO treated sample, including the region of maximum intensity. It is important to note that the high energy tail of the integrating sphere spectra fall outside of the 95% confidence interval of the confocal instrument spectra. This is likely due to the apparent peak shift between the spectra collected by the two instruments. For all confocal measurements, the spectrometer position is calibrated daily using a two-point calibration (the o-order reflection of the grating and the silicon Raman peak).

The results can be further compared by looking at the integrated photoluminescence flux of the spectra collected with both the confocal instrument and the integrating sphere in

Table 6.2.

Table 6.2 Total Photoluminescence Flux [photons/(s•eV•m²)]

	Integrating Sphere	Confocal Measurement
Control	9.89x10 ¹⁸	9.45x10 ¹⁸ ± 5.08x10 ¹⁸
TOPO	2.78x10 ¹⁸	3.35x10 ²⁰ ± 9.3x10 ¹⁹

Additionally, we can use the absorbed photon flux from the integrating sphere data (the absorbed photon flux was not measured using the confocal instrument and is not needed for the $\Delta\mu$ analysis) to calculate the external photoluminescence quantum efficiency as shown in Table 6.3.

Table 6.3 External Photoluminescence Quantum Efficiency [%]

	Integrating Sphere	Confocal Measurement
Control	0.96	0.92 ± 0.50
TOPO	23.5	20.3 ± 5.6

For both the total photoluminescence flux and the external photoluminescence quantum efficiency, the integrating sphere values fall within the confidence interval of the confocal instrument measured value. We note that the above integrating sphere photoluminescence quantum efficiency measurement of 23.5% is not the highest value that was measured during this study, however it does describe a representative sample measured by the two instruments.

6.7 PHOTOLUMINESCENCE MODEL PARAMETERS FOR CONTROL AND TOPO SAMPLES

Fig. S1 shows box-and-whisker plots of the photoluminescence fitting parameter results from collecting several spectra across the area of both a control and treated film deposited on gold.

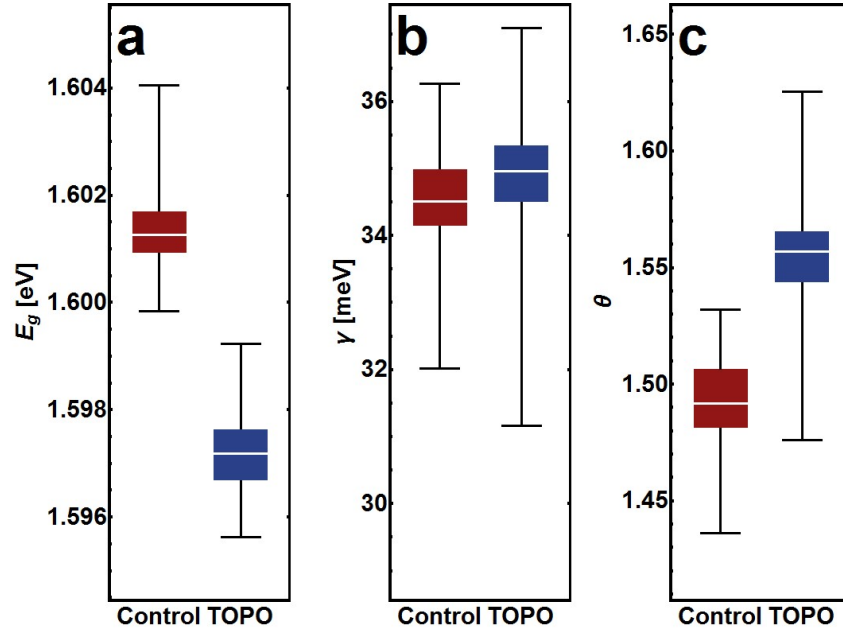


Figure 6.7 **Sub-gap absorptivity model parameters extracted absolute intensity photoluminescence spectra of the control and TOPO samples. a**, bandgap (E_g), **b** broadening energy (γ), and **c** tail exponent (θ). The sample size is 121 and the box-and-whisker statistics shown are the minimum, first quartile, median, third quartile, and maximum, respectively.

The temperature parameter was fixed to be 285 and 291 K for the Control and TOPO treated sample, respectively. The median fit bandgap for the control and TOPO treated film were 1.601 eV and 1.597 eV, respectively. This slight red-shift of the band-edge can be recognized by observing the peak shift and broadening of the intense TOPO treated absolute intensity photoluminescence peak. The small red-shift in the bandgap energy for the TOPO treated sample could be attributed to a reduction in surface-dominated behavior and a larger contribution from the bulk (i.e. single crystal generally exhibited red-shifted optical properties)²⁹. The median broadening energy for both the control and TOPO treated film was 34.4 meV. This value is closely coupled with the exponent, which were fit to be 1.49 and 1.56, for the control and TOPO treated films, respectively. Such a high fit exponent indicates potential disorder on the length scale exceeding the lattice constant. This is not surprising considering the plethora of disorder-inducing mechanisms that have been observed in these materials³⁰⁻³².

6.8 RADIATIVE LIMIT CALCULATIONS FOR THE SURFACE PASSIVATION EXPERIMENT

Calculations similar to Shockley and Queisser's derivations were carried out as described previously³³. Here, we assume radiative losses only occur at the front surface (perfect back-reflector) and assume an illumination spectrum equivalent to the AM1.5GT solar spectrum. The radiative limit $\Delta\mu$ for the perovskite films deposited on a gold back reflector was calculated by following the general procedure summarized below:

- (1)** Extract the absorptivity spectrum using the absolute intensity photoluminescence spectrum.
- (2)** Use the absorptivity spectrum to calculate the generation rate under AM1.5GT conditions.
- (3)** Equate the generation rate to the total recombination rate described by photoluminescence equation and solve for $\Delta\mu$.

Detailed Description of Procedure:

(1) Absorptivity spectra were calculated from the absolute intensity photoluminescence spectra reported in Fig. 1a in the main text using the generalized Planck Law solved for absorptivity as shown in eq (6.8).

$$a(\varepsilon) = I_{PL}(\varepsilon) \frac{\text{Exp}\left(\frac{\varepsilon - \Delta\mu}{kT}\right) - 1}{\varepsilon^2 \frac{2\pi}{h^3 c^2} \left(1 - \frac{2}{\text{Exp}\left(\frac{\varepsilon - \Delta\mu}{2kT}\right) + 1}\right)} \quad (6.8)$$

We used the $\Delta\mu$ and T extracted from fitting the photoluminescence spectrum with eq (6.8), and the measured photoluminescence flux for each energy to calculate the absorptivity spectrum, as shown in Figure 6.8.

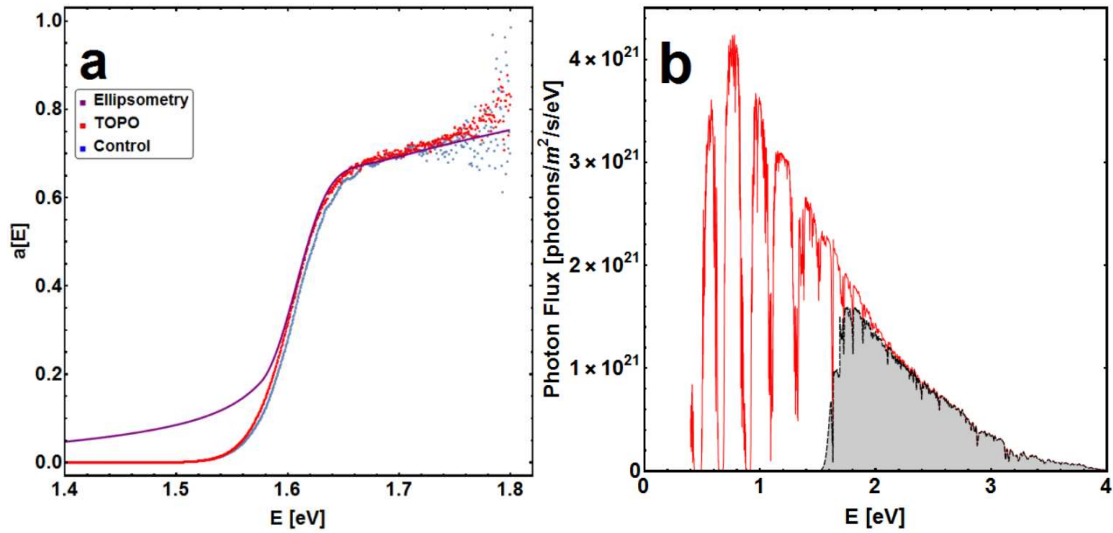


Figure 6.8 **a**, Absorptivity spectra calculated from TOPO and control absolute intensity photoluminescence spectra using the fit quasi-Fermi level splitting and temperature values. Absorptivity calculated from absorption coefficient spectrum determined by ellipsometry is shown in purple as a reference. **b**, Generation rate visualized as the integrated AM1.5 GT spectrum times the extracted hybrid perovskite absorptivity spectrum (shown as the grey area). The full AM1.5 GT spectrum is shown in red for reference.

We note that the absorptivity spectrum is film thickness dependent, and therefore so is the radiative limit quasi Fermi-level splitting. We show this in Fig. S4a and S4b with a representative absorption coefficient spectrum of an ideal direct gap semiconductor, and that of methylammonium lead iodide.

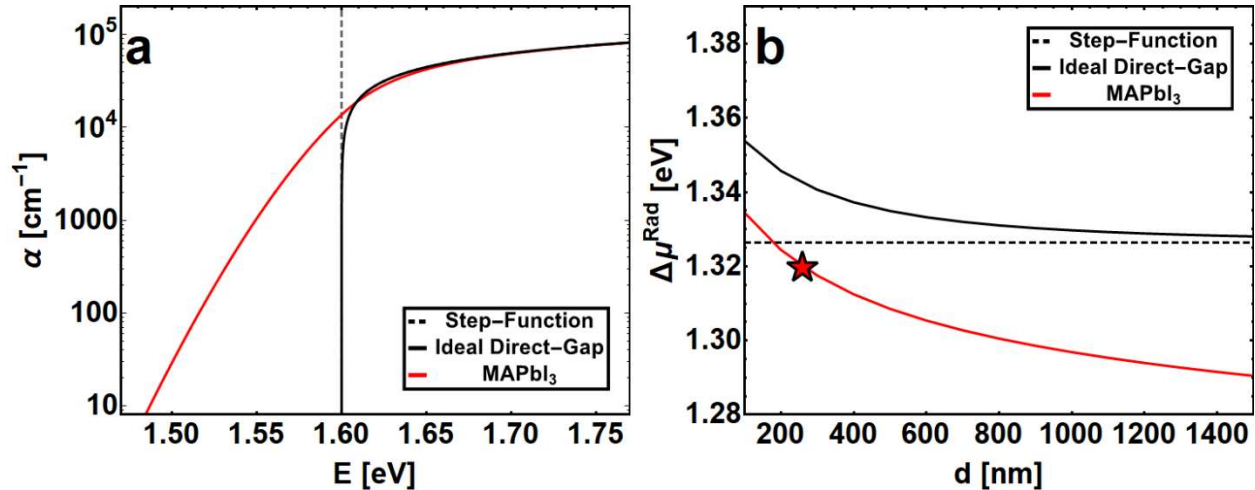


Figure 6.9 a, Absorption coefficient spectra and b, corresponding radiative limit quasi-Fermi level splitting for (i) a step-function absorptivity (dotted lines), (ii) an ideal direct-gap (solid black line) with characteristic square-root dependence, and (iii) the experimental data for the perovskite studied in this report (experimental data) all with a bandgap of 1.6 eV. Note that the radiative limit quasi-Fermi level splitting for the ideal direct gap case and perovskite case depend on thickness.

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Chapter 7. APPENDIX B: ADDITIONAL INFORMATION FOR CHAPTER 3

7.1 METHODS

A. Mesoporous Alumina Layer Deposition

Borosilicate glass substrates measuring 25 mm x 25 mm were sonicated for 10 minutes each in the following solvents: 2% alconox, UPW, acetone and 2-propanol. The substrates were then exposed to an O₂ plasma for 10 minutes. The mesoporous alumina dispersion was prepared by diluting 2-propanol solution of Al₂O₃ nanoparticles (Sigma Aldrich 702129) with 2-propanol by volume (2:1 Al₂O₃ solution:2-propanol), stirring vigorously for 10 minutes and sonicating in a sonicating horn for 30 minutes prior to coating. Clean substrates were coated with the alumina dispersion by spin casting at 5500 RPM and 3500 RPM/s for 45 seconds in lab atmosphere. A 1.2 µm Teflon syringe filter was used while applying the Al₂O₃ nanoparticle dispersion to the substrates in order to exclude large nanoparticle aggregations. Sufficient volume was used to completely cover the substrate with the alumina ink. Two applications were deposited in this manner. The substrates were dried on a hot plate set to 130°C for 30 minutes. Profilometry measurements confirmed a film thickness averaging 2.1 µm.

B. Lead Iodide Deposition

A 1 M solution of lead iodide in dimethylformamide was prepared and then preheated and stirred on a hot-plate (set to 90°C) prior to spin coating. The alumina coated substrates were also allowed to sit on the same hot plate prior to placing on the spin-coating chuck. The hot lead iodide ink was pipetted onto the substrates at a volume of 200 µL and spin cast at 5500 RPM, 5000 RPM/s for 5 s in lab atmosphere. The wet lead iodide coated substrate was quickly transferred back to the hotplate and allowed to dry with a hotplate setting of 90 °C for 50

minutes. The spin time was minimized to avoid needle-like PbI_2 crystals that form on the surface of the film if the dispensed liquid cooled too much during spin casting.

C. Spray Coating of Composition Gradient Perovskite Sample

Methylammonium iodide and methylammonium bromide (MAX) were each dissolved in ethanol to prepare separate 62.91 μM solutions for spray coating (typical amounts of 0.3 g methylammonium iodide and 0.2117 g methylammonium bromide each dissolved in 30 mL ethanol). The hybrid perovskite composition gradient was formed on the lead iodide coated substrates using a custom-built deposition system based on a Sono-Tek ultrasonic spray coater fitted into a nitrogen-filled glovebox (<150 ppm O_2 and <1 ppm H_2O). A MAX ink concentration gradient was fed to the spray nozzle with two independently operating syringe pumps – one programmed to ramp up and the other programmed to ramp down while keeping the total feed rate constant. The total flow rate being sent to the spray nozzle was fixed at 200 $\mu\text{L}/\text{min}$, and each syringe pump ramped between 200 and 0 $\mu\text{L}/\text{hr}$. over 1 minute 30 seconds. After a delay time of 1 minute 40 seconds (as determined by a 300 μL and 65 μL purge and delay volume, respectively), the spray nozzle translated at a speed of 1 mm/s along the 100 mm sample array while the spray nozzle also oscillated laterally at a speed of 40 mm/s while the MAX ink concentration gradient was being dispensed onto the glass substrate. The substrates were on a hot plate set at 40°C. Spray gradient samples were transferred into a KF-flanged cell to prevent oxygen or humidity exposure while transferring to the AIPL instrument.

D. Neat $\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ Film Preparation

Sequential steps of ultrasonication for 10 min in detergent, deionized water, acetone, and isopropanol alcohol were used to clean glass substrates. $\text{MAPb}(\text{I}_{0.66}\text{Br}_{0.34})_3$ and $(\text{MA}_{0.9}\text{Cs}_{0.1})\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ precursor solutions were prepared from MAI, CsI, PbI_2 , and PbBr_2 in mixed solvent (volume ratio 3:7) of DMSO and γ -butyrolactone (GBL); solutions were

stirred at 60 °C for 1 h. Cleaned substrates were transferred into N₂-filled glovebox for film deposition. The perovskite precursor solution was spin coated onto the substrate using 2-step spin program (1000 rpm for 15 s and 4000 rpm for 45 s); during the last 20-10 s of the second spin-coating step, 0.7 ml toluene was dropped onto the spinning substrate and the substrates were annealed at 100°C for 10 min. The thickness of the MA and MACs films were measured by profilometry to be 202 nm and 194 nm, respectively.

E. MAPb(I_{0.6}Br_{0.4})₃ Device Fabrication

ITO glass was cleaned with sonication and UV ozone treatment as described above. A NiOx precursor solution was prepared by dissolving 124.4 mg of Nickel (II) acetate tetrahydrate in 5 mL ethanol and 30 µL ethanolamine was added to it; the mixture was stirred at 60 °C for 2 h. The NiOx precursor was spin coated onto the clean ITO glass at 3000 rpm for 60 s and annealed at 400°C for 1 h in ambient. Next, films were transferred into a N₂-filled glovebox for perovskite layer deposition as described above for MA containing films. For the ETL precursor solution, 15 mg/mL PC61BM was dissolved in chloroform and stirred at 80 °C for 30 min. The PC61BM solution was spin coated using 4000 rpm for 45 s followed by annealing at 100 °C for 5 min. For the fullerene surfactant solution, 2 mg/mL Bis-C60 in isopropyl alcohol was dissolved using sonication (typically 1 h). The bis-C60 surfactant solution was spin coated on top at 3000 rpm for 60 s. Finally, 150 nm thick silver (Ag) electrode was evaporated under high vacuum ($<1 \times 10^{-6}$ Torr) with shadow masks (3.14 mm²). All solutions were filtered with 0.22 µm PVDF filters before spin coating.

F. Non-Injecting Interdigitated Back Contact Substrates for Electric Field Experiment

Lateral devices with back contact architecture were used to separate the effect of electric field and charge injection on phase segregation. Each device consisted of two Au electrodes separated

by a 10 μm channel (Figure S6). A dielectric layer was deposited on top of the electrodes to prevent direct charge injection into the perovskite material deposited within the channel. Devices were fabricated at the Washington Nanotechnology Facility (WNF) using photolithography and liftoff. 100 mm Si wafers with a 1 μm layer of thermal oxide were coated with a thin layer of NR9 negative photoresist (3000py) through spin coating followed by a post-bake at 150 $^{\circ}\text{C}$ for one minute. The photoresist was exposed for 40s under UV excitation in an ABM contact aligner, followed by a 40 s post bake at 110 $^{\circ}\text{C}$. After the resist was developed, the wafers were coated with 10 nm Ti (adhesion layer) and 150 nm Au through e-beam evaporation. After liftoff in an acetone bath, the wafers were coated with 50 nm of Al_2O_3 through thermal atomic layer deposition at 300 $^{\circ}\text{C}$.

G. Absolute Intensity Photoluminescence Measurements

The experimental set up used for AIPL measurements were adapted from previous work.²² Spectra were acquired using a modified Horiba LabRAM HR-800, a 532 nm laser diode excitation source, and a 10x objective (NA=0.25). The adjustable confocal hole before the monochromator was set at 800 μm . A 150 gr/mm Czerny-Turner monochromator blazed at 1200 nm was used, and the emitted light was collected with a silicon CCD array detector. For maps, the PL collection time was set to 1 s, and the amount of time that the laser stayed at any given location was less than 1.5 s. This reduces the effects of any transient behavior and gives the initial condition of each HP composition. Spectral artifacts caused by the detector and the optical path between the sample and detector were accounted for by creating a relative correction file with a black body source (IR-301, Infrared Systems Development Corporation) set to 1050 $^{\circ}\text{C}$. A 10 μm pin-hole was used to fix the spectral photon flux to the detector and allow an absolute photons per count calibration factor to be measured. An Oriel optical power meter and beam profilometer were used to measure the illumination intensity and excitation diameter, respectively, for various laser power and filter combinations. The N_{Suns} illumination

intensity was calculated by dividing the photon flux inside the FWHM of the Gaussian beam by the above-bandgap photon flux of the AM1.5 GT solar spectrum. The laser diameter was measured to be 10 μm and the FWHM of the Gaussian distributed laser intensity was measured to be 6 μm . All AIPL measurements were conducted with the HP samples in a nitrogen-filled KF-flanged cell with a Kodial borosilicate glass window.

In order to separate the effects of illumination and time, an AIPL data was collected while the laser was continuously rastered in two directions across a square measuring 110 μm x 110 μm . The time required to complete a full rastering cycle was exactly 1 second, which was the minimum collection time for all measurements taken in this manner. This means that each position in the 110 μm box on the sample was illuminated for a total of 0.5 seconds each second with an on-off illumination frequency between 2 and 100 Hz during the rastered laser slow transient study.

Additionally, the neat $\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ film was measured in a closed, N_2 -filled stage (Linkam Scientific LTSE420-P) with continuous N_2 purge at 70% of maximum flow, with the stage temperature regulated to 20 $^\circ\text{C}$.

H. Electroluminescence Measurements

Electroluminescence data was collected with the same set up as confocal PL (Horiba Labram with 150 gr/mm grating blazed at 500nm), but using current injection with Keithley 2400 rather than 532nm photoexcitation. EL experiments were also conducted in N_2 -filled Linkam stage with constant N_2 purge and temperature regulated to 20 $^\circ\text{C}$.

I. Composition Measurement and Imaging

Aluminum, lead, iodine and bromine content along the spray gradient were measured using an FEI XL830 Dualbeam SEM-FIB workstation equipped with an Altura EDS probe. A working distance of 5 mm, accelerating voltage of 20 keV, spot size of 5 and magnification of 150x was

used. The X-ray spectra were collected with a process time of 4 and a count limit of 1×10^6 . Due to the overlap of the Al K α (1.486 keV) and Br L α (1.48 keV) peaks, the less intense Br K α (11.922 keV) peak was used to quantify the Bromide atomic composition. Average composition values for the entire field of view were determined every 3 mm along the center of the spray line. Top-down and cross-section images of gold-sputtered spray-coated HP samples were collected using an FEI-Serion-XL30 SEM.

J. Current-Voltage Measurements

J-V measurements were conducted in air using a Keithley 2400 SourceMeter Newport Oriel Sol3a Class AAA Solar Simulator calibrated to 1 Sun AM1.5 GT using Newport 91150V Si reference diode. J-V curves were collected with a reverse voltage sweep at a slow sweep rate of 75 mV/s. Device area was 3.14 mm² defined by Ag contact area (valid due to high resistance in all HP/ETL/HTL layers).

K. Absorbance Measurements

Absorbance spectra were collected using a Perkin Elmer Lambda 1050 UV/vis/NIR spectrometer equipped with a 150 mm InGaAs integrating sphere in lab atmosphere. The light beam was masked to collect local absorbance spectra every 7.5 to 10 mm (3 measurements per substrate) along the gradient, and a background subtraction spectrum was collected using a glass slide coated with a mesoporous alumina layer.

7.2 PROFILOMETRY RESULTS ALONG THE GRADIENT SAMPLE

Table 7.1 Film Thicknesses as Measured by Profilometry

X [mm]	t [μm]
5	1.96
10	2.01
15	2.07
20	1.92
30	1.89
35	1.68
40	2.06
45	1.99
55	2.14
60	2.25
65	2.27
70	2.20
80	2.35
85	2.44
90	2.51
95	2.30

7.3 DETAILED BALANCE CALCULATIONS

We determine the open-circuit voltage for any given bandgap by using a detailed balance (i.e. a Shockley-Queisser¹ style analysis). The assumptions are:

1. Incident photon flux is based on ASTM G-173 standard experimental AM1.5GT data.
2. Single bandgap semiconductor, E_g .
3. No reflectivity at the front surface.
4. All photons with $E > E_g$ are absorbed.
5. Photons with $E < E_g$ are not absorbed.
6. Each absorbed photon generates one electron-hole pair.

7. Only radiative recombination is present.
8. Perfect reflection at the back surface.
9. No parasitic effects from series or shunt resistances.

Detailed Balance at Open-Circuit Conditions

$$Generation = Recombination \quad (7.1)$$

Generation rate per unit area due to incident photon flux:

$$G = \int_{E_g}^{\infty} b_s(E) dE \quad (7.2)$$

where G is the total generation per unit area, and b_s is the photon flux per spectral bandwidth defined by the ASTM G173 standard AM 1.5 GT solar spectrum.

Recombination rate due to emitted photon flux:

$$R = \int_{E_g}^{\infty} [b_e(E, \Delta\mu, T) - b_a(E, T)] dE \quad (7.3)$$

where R is the total recombination rate per unit area, E_g is the absorber bandgap (unit step absorptivity), b_e is the non-equilibrium Planck Law that governs the emitted photon flux, and b_a is the photon flux emitted at equilibrium.

b_e is determined by eq (7.4),

$$b_e(E, \Delta\mu, T) = \frac{2\pi}{h^3 c^2} \left(\frac{E^2}{\exp\left\{\frac{E - \Delta\mu}{k T}\right\} - 1} \right) \quad (7.4)$$

where h is Planck's constant, c is the speed of light, E is photon energy, $\Delta\mu$ is the quasi Fermi-level splitting, k is the Boltzmann constant and T is the absorber temperature.

b_a is determined by equation S4.

$$b_a(E, T) = \frac{2\pi}{h^3 c^2} \left(\frac{E^2}{\text{Exp}\left\{\frac{E}{kT}\right\} - 1} \right) \quad (7.5)$$

Practically, eq (7.5) can be ignored since T is typically around room temperature making the thermal emission from the sample negligible. The quasi Fermi-level splitting is determined by equating G and R and solving implicitly for $\Delta\mu$. Figure S1 shows the detailed balance calculations for absorbers with bandgaps varying from 0.9 to 2.2 eV.

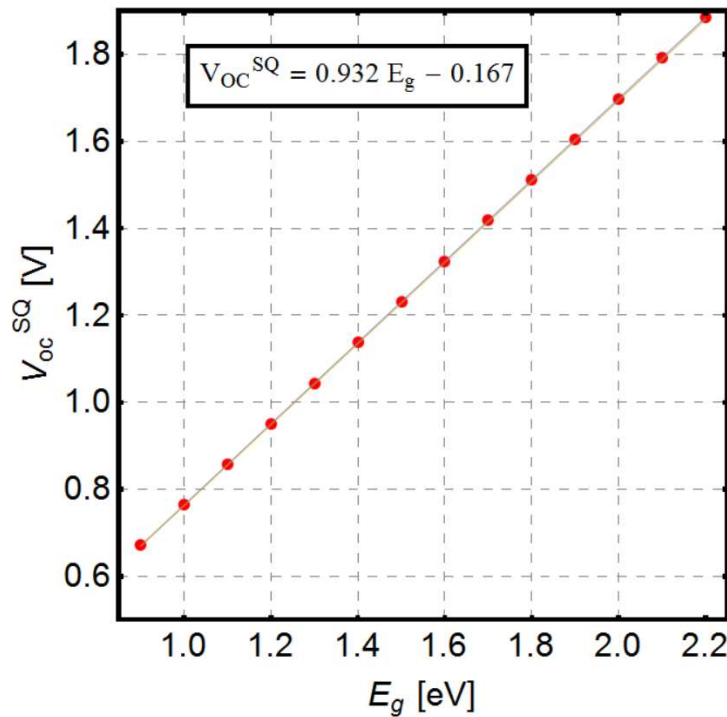


Figure 7.1 Relationship between Bandgap and Open-Circuit Voltage in the Radiative Recombination Limit. The line is the linear regression line fit to the detailed balance results (red dots). The fit parameters are shown in the inset.

In general, the linear fit equation in the inset of Figure S1 is valid for direct and indirect semiconductors within bandgap range of 0.9 and 2.2 eV. These limiting V_{oc} values can only be exceeded if one of the above assumptions become invalid (e.g. multi-exciton generation, hot-carrier collection, etc.).

7.4 CHANGES IN OPTOELECTRONIC QUALITY (χ) AS A FUNCTION OF BANDGAP

To estimate the effects of changing bandgap and potentially changing various recombination parameters on the quasi-Fermi level splitting, optoelectronic quality χ , and the PLQY, we employ a simplified model where the carrier concentrations are assumed to be spatially uniform. At open circuit conditions, the rate of generation is equal to the rate of recombination (assumed to be only radiative recombination and Shockley-Read-Hall recombination). The generation rate is known (since we are using a calibrated laser). Thus, given models of the radiative recombination and SRH recombination, one can solve for the quasi-Fermi level splitting and thus calculate the PLQY and χ . We simulated the effects of bandgap changes (changes in the defect energy relative to the band edges), defect concentration, and doping on χ for MAPb(I,Br)₃. We present the equations used below and the assumed parameters (such as effective masses and capture cross sections). Figures S2-S7 show the results of these simulations.

A. Semiconductor Equations

$$N_V = 2 \left(\frac{m_h kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \quad (7.6)$$

The effective density of states in the conduction and valance bands assuming parabolic bands are given in eq (7.7) and (7.6),

$$N_C = 2 \left(\frac{m_e kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \quad (7.7)$$

where N_C (N_V) is the effective density of states of the conduction (valance) band, m_e (m_h) is the relative mass of electrons (holes) and $\hbar$ is the reduced Planck constant. Knowledge of the

bandgap and carrier relative masses allow the intrinsic carrier concentration (eq (7.8)) and the intrinsic equilibrium Fermi-level to be calculated (equation (7.9)),

$$n_i = \sqrt{N_c N_v} e^{\frac{-E_g}{kT}} \quad (7.8)$$

$$E_i = \frac{1}{2} E_g + \frac{3}{4} kT \ln \left(\frac{m_h}{m_e} \right) \quad (7.9)$$

where n_i is the intrinsic carrier concentration and E_i is the intrinsic equilibrium position of the Fermi-level.

B. Shockley-Read-Hall Recombination

Non-radiative recombination is modeled assuming the Shockley-Read-Hall (SRH) mechanism with a single energetic position of defects in the bandgap. We calculate the volumetric recombination rate using the full SRH recombination expression,

$$U_{SRH} = \frac{np - n_i^2}{\frac{1}{\tau_n} (p + p^*) + \frac{1}{\tau_p} (n + n^*)} \quad (7.10)$$

where U_{SRH} is the volumetric recombination rate, n (p) is the non-equilibrium population of electrons (holes), τ_n (τ_p) is the electron (hole) lifetime and n^* (p^*) is the electron (hole) concentration when the trap energy is equal to the intrinsic equilibrium Fermi-level. The carrier lifetimes are modeled using eq (7.11) and (7.12),

$$\tau_n = \frac{1}{N_d \sigma_{cap} v_{th}} \quad (7.11)$$

$$\tau_p = \frac{1}{N_d \sigma_{cap} v_{th}} \quad (7.12)$$

where N_d is the recombination center concentration, σ_{cap} is the capture cross-section area of the recombination center, and v_{th} is the thermal velocity. n^* and p^* are given by equations (7.13) and (7.14),

$$n^* = n_i e^{\frac{(E_d - E_i)}{kT}} \quad (7.13)$$

$$p^* = n_i e^{\frac{(E_i - E_d)}{kT}} \quad (7.14)$$

where E_d is the recombination center energy relative to the valance band maximum.

C. Radiative Recombination

Radiative recombination can be modeled as a second-order reaction rate with a bimolecular recombination constant (eq (7.15)),

$$U_{Rad} = b_o(np - n_i^2) \quad (7.15)$$

where U_{Rad} is the volumetric radiative recombination rate and b_o is the bimolecular recombination constant. This recombination constant is calculated assuming an absorption coefficient model and setting the macroscopic recombination rate as determined by the emitted flux of a semiconductor in non-equilibrium (eq (7.4)) with the microscopic recombination rate (eq (7.15)) and solving for b_o (eq (7.16)),

$$b_o = \frac{\int_0^\infty \alpha(E)(b_e(E, \Delta\mu, T) - b_e(E, 0, T))dE}{np - n_i^2} \quad (7.16)$$

where $\alpha(E)$ is the spectral absorption coefficient, which we model as a direct semiconductor in eq (7.17)

$$\alpha(E) = \begin{cases} \alpha_o \frac{(E - E_g)^{\frac{3}{2}}}{E} & \text{for } E > E_g \\ 0 & \text{for } E < E_g \end{cases} \quad (7.17)$$

where α_o is related to the oscillator strength.

Under open circuit conditions assuming radiative and SRH recombination, the steady-state balance equation is given in equation S18 assuming open circuit conditions, radiative and SRH recombination.

$$G = U_{Rad}(\Delta\mu) + U_{SRH}(\Delta\mu) \quad (7.18)$$

D. Non-Equilibrium Carrier Concentrations

Assuming the material is not degenerate, the carrier statistics at non-equilibrium are:

$$np = n_i^2 e^{\left(\frac{\Delta\mu}{kT}\right)} \quad (7.19)$$

Thus, for an intrinsic material, where $\Delta n = \Delta p$ and $\Delta n \gg n_o$ and $\Delta p \gg p_o$:

$$n \approx n_i e^{\left(\frac{\Delta\mu}{2kT}\right)} \quad (7.20)$$

$$p \approx n_i e^{\left(\frac{\Delta\mu}{2kT}\right)} \quad (7.21)$$

For a doped semiconductor, we can also derive a simple connection between n or p and the quasi-Fermi level splitting. Using eq. (7.19), the assumption that $N_D \gg p_0$ for an n-doped material, and the quadratic formula, n and p are given by:

$$n \approx N_D + \frac{1}{2} \left(-N_D + \sqrt{N_D^2 - 4n_i^2 e^{\frac{\Delta\mu}{kT}}} \right) \quad (7.22)$$

$$p \approx \frac{n_i^2}{N_D} + \frac{1}{2} \left(-N_D + \sqrt{N_D^2 - 4n_i^2 e^{\frac{\Delta\mu}{kT}}} \right) \quad (7.23)$$

Likewise, the equations for non-equilibrium carrier concentrations in a p-doped semiconductor is given by:

$$p \approx N_A + \frac{1}{2} \left(-N_A + \sqrt{N_A^2 - 4n_i^2 e^{\frac{\Delta\mu}{kT}}} \right) \quad (7.24)$$

$$n \approx \frac{n_i^2}{N_A} + \frac{1}{2} \left(-N_A + \sqrt{N_A^2 - 4n_i^2 e^{\frac{\Delta\mu}{kT}}} \right) \quad (7.25)$$

Thus, given the parameters: E_d (relative to the valence band edge position), N_d , σ_{cap} , v_{th} , G , α_o , m_e , m_h , and (if doped) N_A or N_D , the quasi-Fermi level splitting is the only unknown.

E. Values used for Simulations

The relative band edge positions of MAPbBr₃ to MAPbI₃^{2,3} and charge carrier relative masses⁴ have been either simulated or experimentally observed previously. Table 7.2 and S3 summarizes

these as well as other relevant parameters used in the simulation. A common capture cross section of 10^{-14} cm^2 is used. The actual capture cross section in perovskites is not known. This value is typical of many defects in semiconductors. However, it is important to note that the actual magnitude is not important since we are only looking at the functional form of the effect of parameters on QFLS.

Table 7.2 Simulation Parameters

m_e	$0.23 m_o$	kg
m_h	$0.29 m_o$	kg
t_{he}	1×10^7	cm/s
α_o	10^5	cm^{-1}
σ	10^{-14}	cm^2
G	1.3×10^{20}	$\text{cm}^{-3}\text{s}^{-1}$

Table 7.3 Assumed Hybrid Perovskite Relative Band Structure

	MAPbI₃	MAPbBr₃
E_{CBM} [eV]	1.6	1.609
E_{VBM} [eV]	0	-0.26

The band structure is assumed to vary linearly with bandgap between the two cases as a simple approximation.

F. Results of the Model

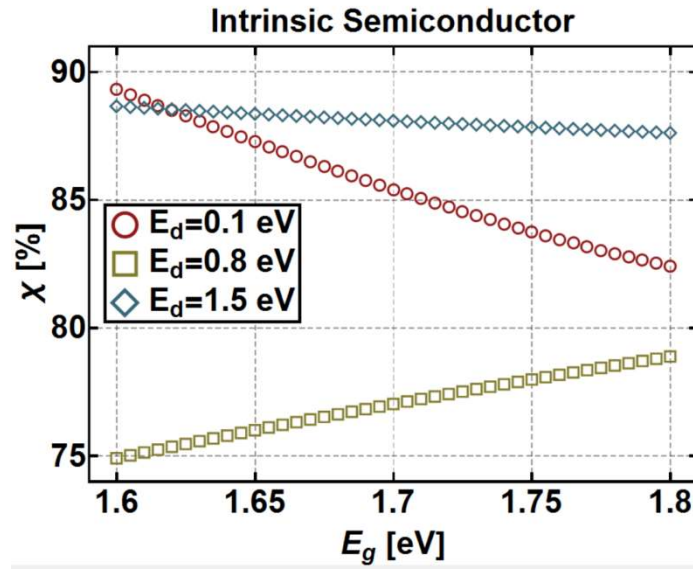


Figure 7.2 χ as a function of bandgap assuming an intrinsic semiconductor for three different defect levels relative to the valence band maximum.

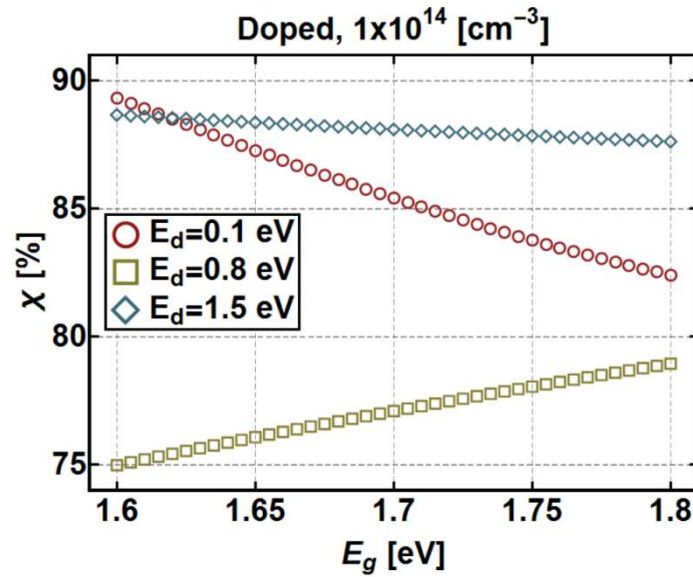


Figure 7.3 χ as a function of bandgap assuming a weakly doped semiconductor for three different defect levels relative to the valence band maximum.

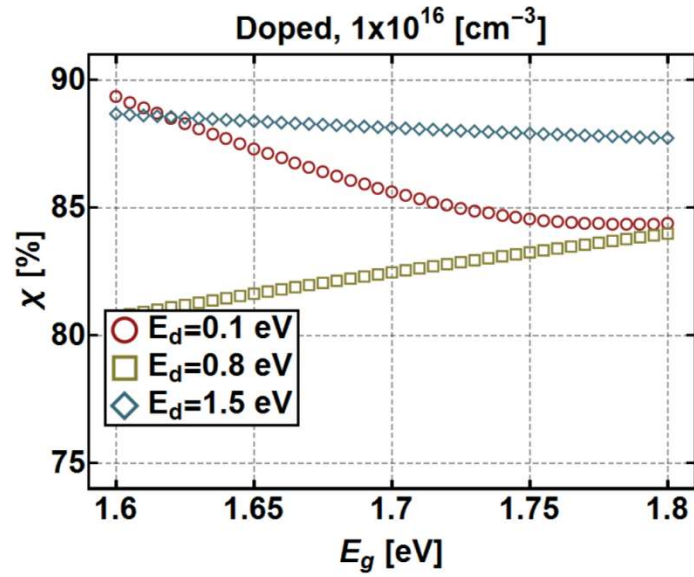


Figure 7.4 χ as a function of bandgap assuming a moderately semiconductor for three different defect levels relative to the valence band maximum

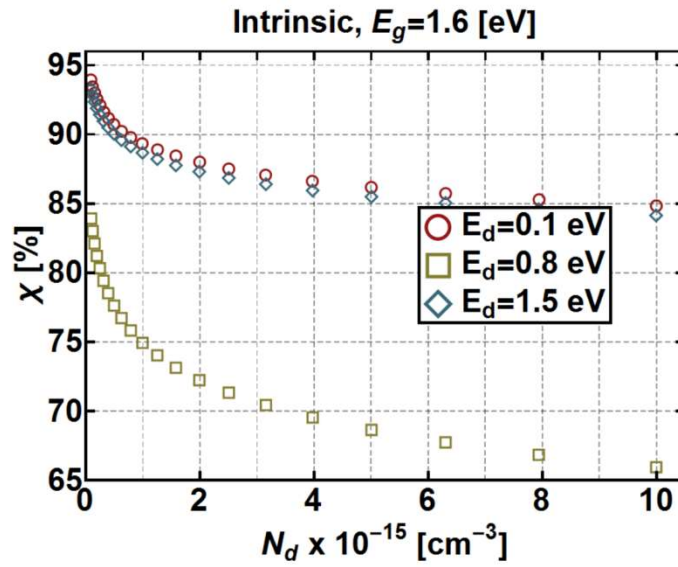


Figure 7.5 χ for an intrinsic semiconductor as a function of defect concentration.

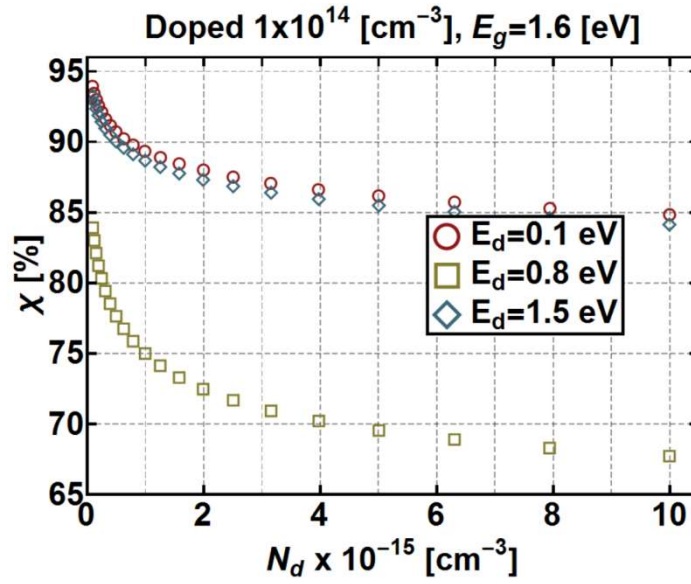


Figure 7.6 χ for a weakly doped semiconductor as a function of defect concentration.

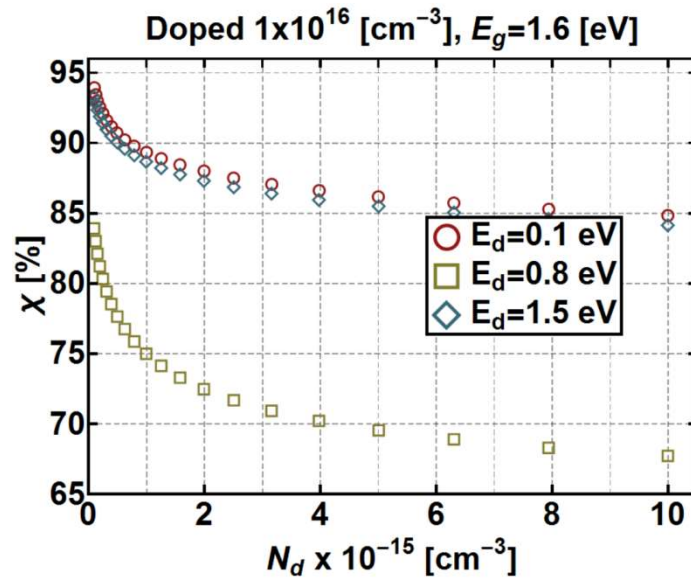


Figure 7.7 χ for a moderately doped semiconductor as a function of defect concentration.

7.5 PERFORMANCE METRICS OF DEVICE USED FOR ELECTROLUMINESCENCE EXPERIMENT

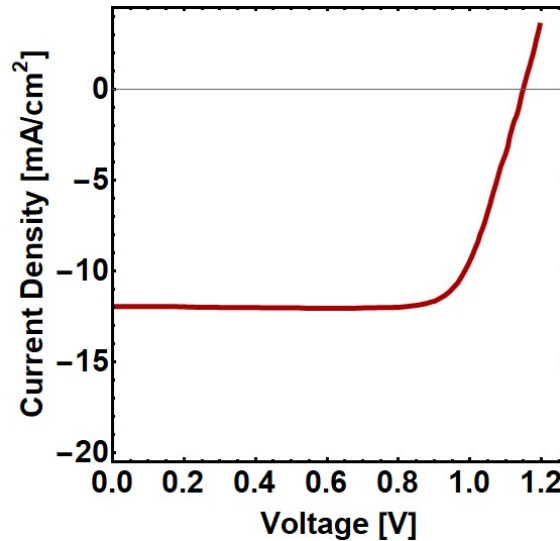


Figure 7.8 **Current-voltage (JV) sweeps of a device** utilizing a 202 nm MAPb(I_{0.6},Br_{0.4})₃ absorber.

The power conversion efficiency, open circuit voltage, short circuit current, and fill-factor were measured to be 10.6%, 1.15 V, 11.8 mA/cm², and 78.1%, respectively.

7.6 ENERGY-DEPENDENCE OF THE DRIVING-FORCE FOR EMISSION

In the Chapter 3, we claimed that, in addition to carrier funneling, the forcing function that governs photon emission will make the intensity of the low energy peak stronger relative to the high energy peak during luminescence of a phase segregating hybrid perovskite film. Consider two cases, where in the initial case a large-bandgap material with a steep subbandgap tail is emitting photons commensurate with a quasi-Fermi level splitting of $\Delta\mu_1$; and in the final case the material has developed a broader subbandgap tail extends to lower energies similar to what is observed in a phase segregating large-bandgap hybrid perovskite, but is still emitting photons commensurate with a quasi-Fermi level splitting of $\Delta\mu_2 = \Delta\mu_1$. We are interested in the relative emission intensity at two energies, E_1 and E_2 , which have the same absorption coefficients, $\alpha_1(E_i)$

and $\alpha_2(E_2)$. Since the subbandgap tail is broader and red shifted, E_1 is larger than E_2 .

Summarizing the two cases,

$$\alpha_1(E_1) = \alpha_2(E_2) \quad (7.26)$$

$$\Delta\mu_1 = \Delta\mu_2 \quad (7.27)$$

$$E_1 > E_2 \quad (7.28)$$

The emission in each case will be determined by the Generalized Planck Law, shown in Equation S1,

$$I_{PL}(E) = \left\{ \frac{2\pi E^2}{h^3 c^2} \right\} \left\{ \frac{1}{\exp\left(\frac{E - \Delta\mu}{kT}\right) - 1} \right\} a(E) \quad (7.29)$$

where the expression in the first curly brackets is the photon density of states, the expression in the second curly brackets is the Bose-Einstein distribution, and the final term is the absorptivity. Taking the ratio of the final emission intensity at E_f to the initial emission intensity at E_i , taking the Wein approximation, and cancelling equal terms,

$$I_{PL,2}/I_{PL,1} = \frac{E_2}{E_1} \exp\left[\frac{E_2 - E_1}{kT}\right] \quad (7.30)$$

Figure S6 shows Equation S5 plotted assuming E_1 is 1.75 eV and T is 298 K.

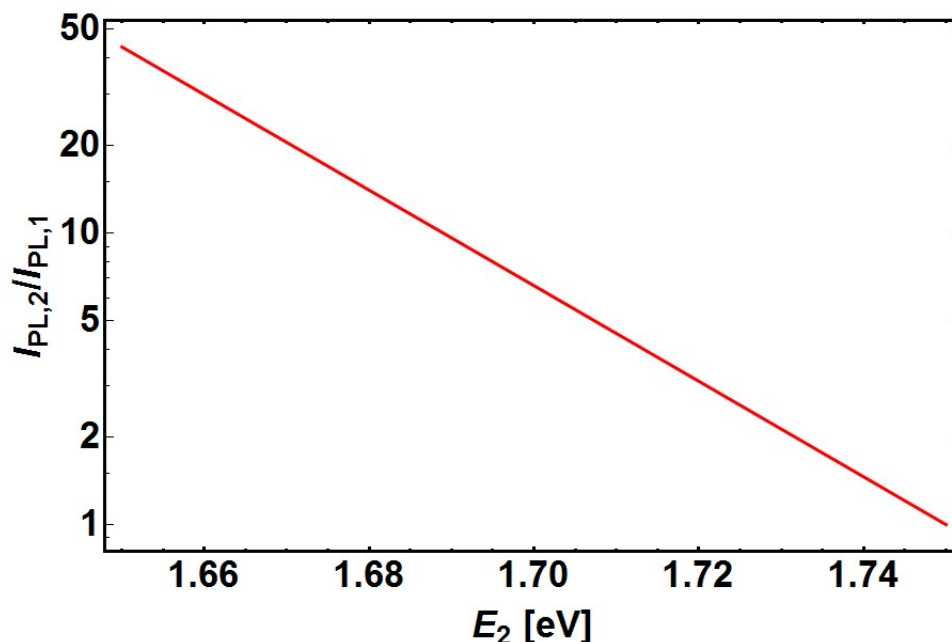


Figure 7.9 **Final luminescence intensity at E_2 relative to that at E_1** as a function of final luminescence energy E_2 for a red-shifting band edge, assuming no change in quasi-Fermi level splitting and assuming no change in the density of states (only a shift of the density of states to a lower energy).

The luminescence intensity at lower energy grows exponentially as the band edge red shifts from 1.75 to 1.65 eV, increasing by a factor of 50 assuming no changes in the quasi Fermi level splitting and that the density of states does not change in magnitude but only shifts to lower energy. The increase should not be this high since not all the film phase segregates and the density of states at the lower energy is likely lower. But without measurement of the density of states of the phase segregated domains and the extent of phase segregation, the increase in PLQY cannot be precisely allocated to either the carrier funneling mechanism or the expected increased driving for emission.

7.7 REFERENCES

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3. Hao, F.; Stoumpos, C. C.; Chang, R. P. H.; Kanatzidis, M. G., Anomalous Band Gap Behavior in Mixed Sn and Pb Perovskites Enables Broadening of Absorption Spectrum in Solar Cells. *Journal of the American Chemical Society* **2014**, 136 (22), 8094-8099.
4. Giorgi, G.; Fujisawa, J. I.; Segawa, H.; Yamashita, K., Small Photocarrier Effective Masses Featuring Ambipolar Transport in Methylammonium Lead Iodide Perovskite: A Density Functional Analysis. *Journal of Physical Chemistry Letters* **2013**, 4 (24), 4213-4216.

Chapter 8. APPENDIX C: ADDITIONAL INFORMATION FOR CHAPTER 4

8.1 PHOTOCONDUCTIVITY EXPERIMENT DEVICE GEOMETRY

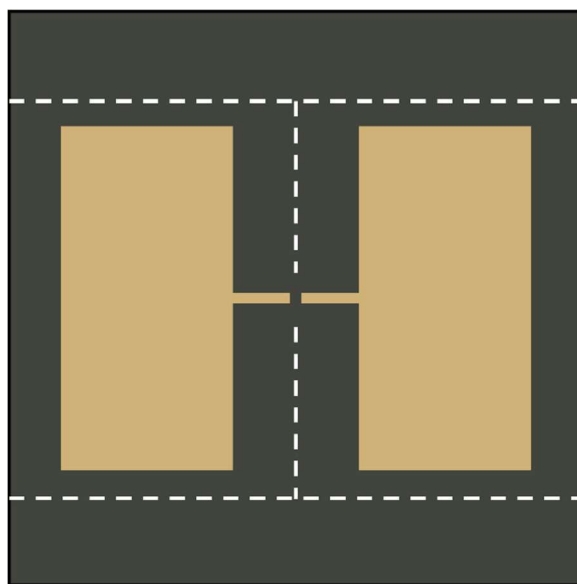


Figure 8.1 Top-down illustration of the high magnification photoconductivity contacting scheme. Dark regions are regions of exposed perovskite film, gold regions are the gold contacts, and white dashed lines are the scribe-lines.

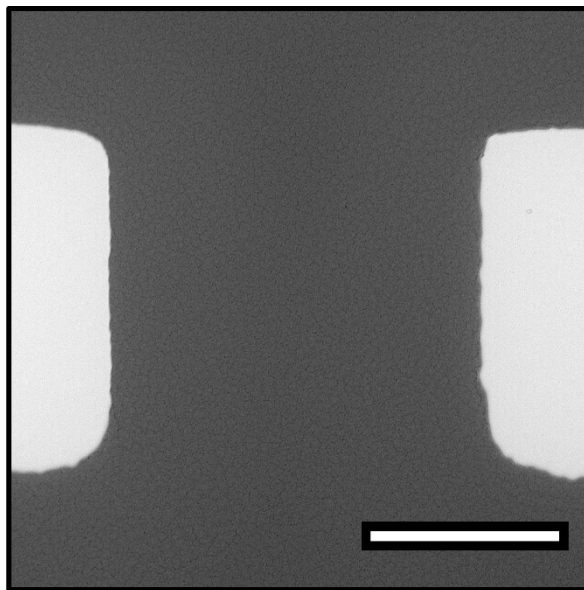


Figure 8.2 Top-down SEM micrograph of the photoconductivity channel. The lighter regions are each end of the gold contacts, and the darker regions are the MAPbI₃ thin film. The scalebar is $50\ \mu m$, and the channel dimension is measured to be $98.5\ \mu m$.

8.2 EXAMPLE VIDEOS AND SIMULATIONS FOR ANALYSIS

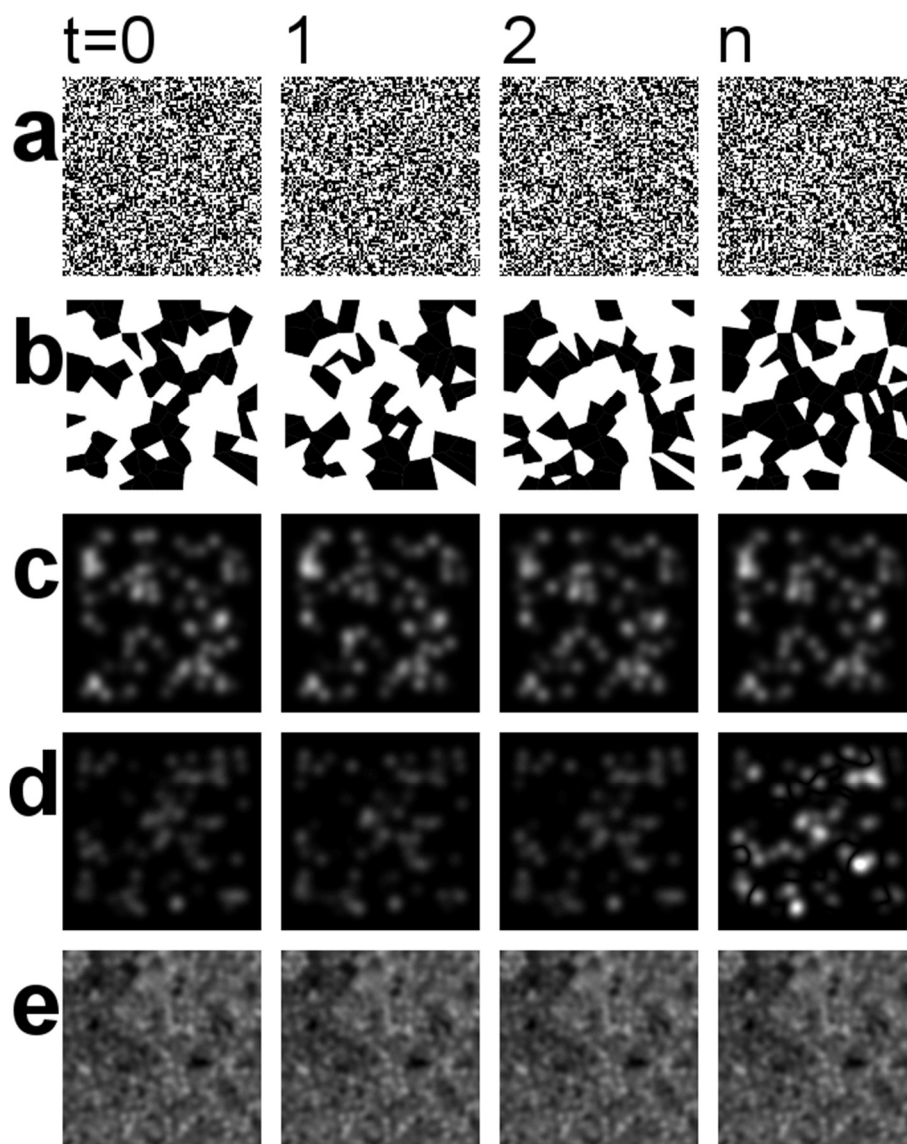


Figure 8.3 Selected frame sequence from synthesized random white noise videos for methods development, where domains are either white or black. **a White Noise:** Each pixel blinks independently with time. **b Voronoi Domains:** Randomly shaped domains defined by a Voronoi mesh blink white or black. **c Gaussian:** Point emitters modeled as 2-D Gaussian distributions are randomly positioned, and the intensity of these emitters randomly switches between two intermediate values. **d Gaussian 2:** The same as **c**, but each domain either brightens or dims at random rates. **e MAPbI₃:** High magnification photoluminescence video collected from a MAPbI₃ film exposed to lab air controlled to 40% relative humidity.

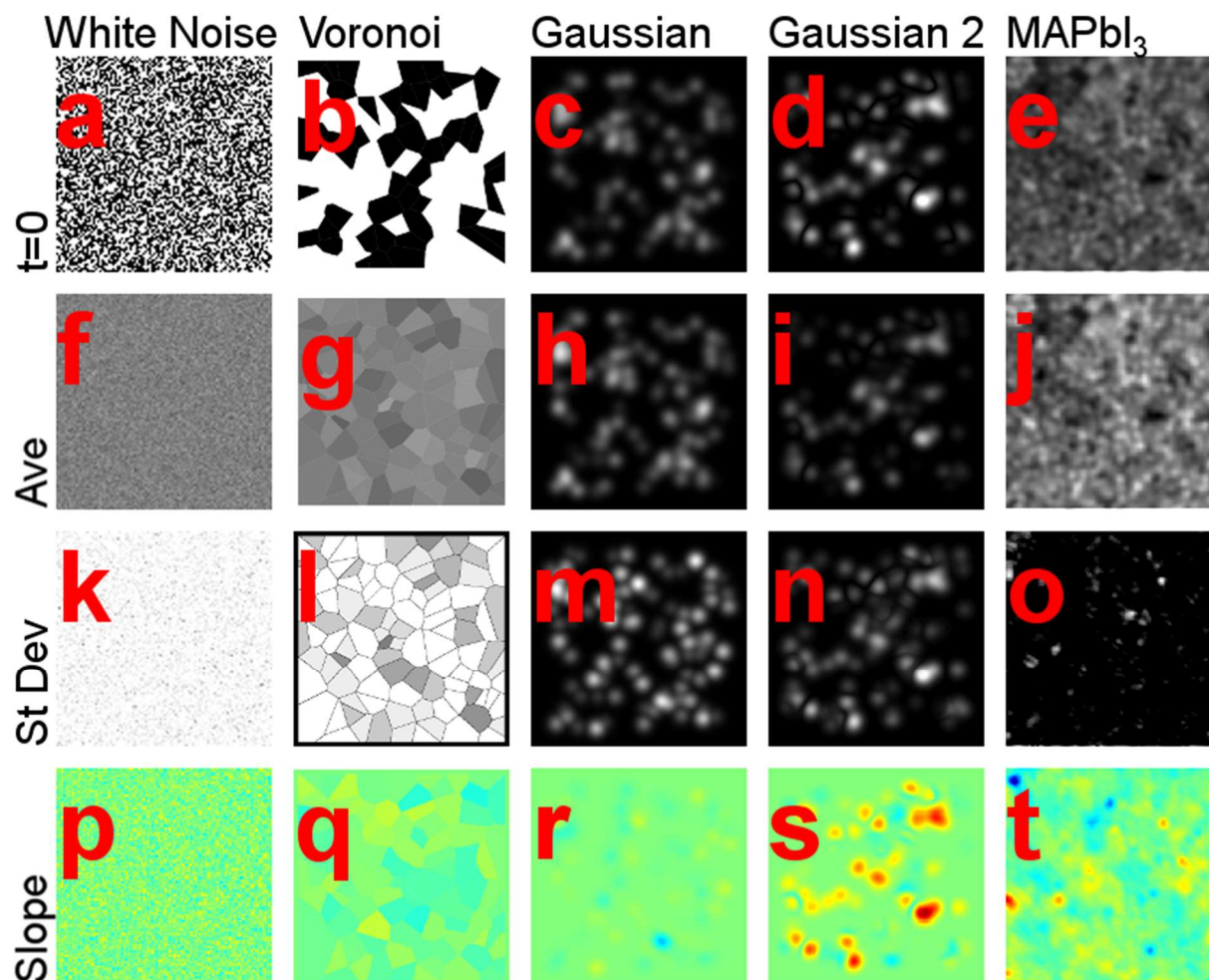


Figure 8.4 Plot montage showing (in row order) an example image, time-average image, time-standard deviation image, regression slope image for the videos given in Figure 8.3.

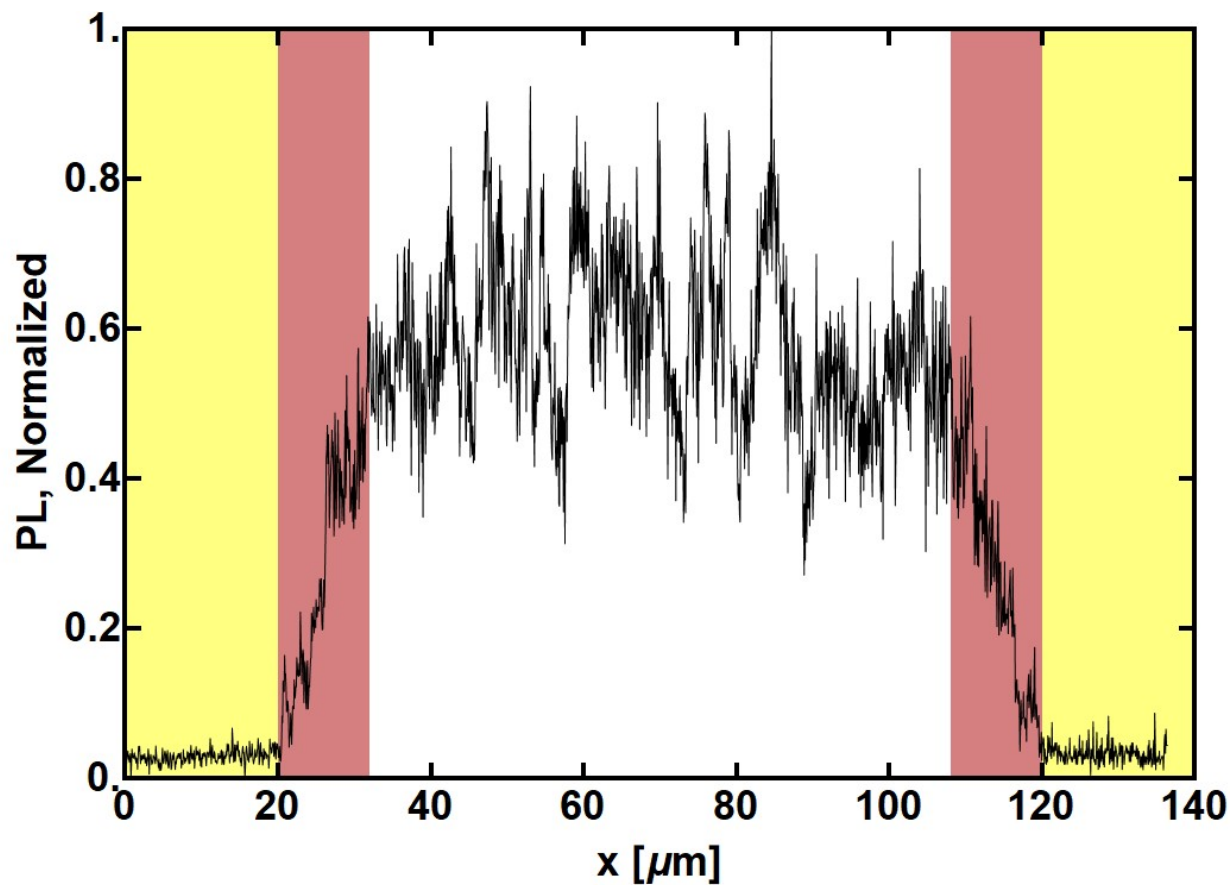


Figure 8.5 Photoluminescence signal profile across the channel before degradation. The yellow regions are of the gold contacts, and the red regions are those effected by the metal-perovskite interface. These edge effect regions extend $12\ \mu\text{m}$ into the channel on each side in this case, making up about a quarter of the channel dimension.

8.3 ADDITIONAL PEROVSKITE SAMPLE DEGRADATION RESULTS

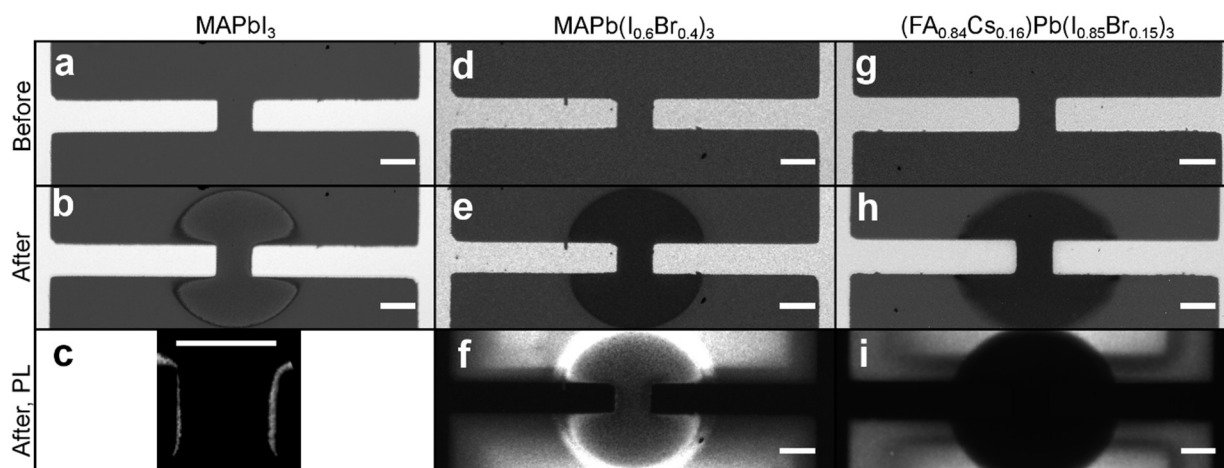


Figure 8.6 . Microscope images before and after illumination stress test conducted *in nitrogen*. (a) Bright-field images before and (b) after degradation, and (c) photoluminescence image after degradation for the MAPbI₃ sample, respectively. (d) Brightfield images before and (e) after degradation, and (f) photoluminescence image after degradation for the MAPb(I_{0.6}Br_{0.4})₃ sample, respectively. (g) Bright-field images before and (h) after degradation, and (i) photoluminescence image after degradation for the (FA_{0.84}Cs_{0.16})Pb(I_{0.85}Br_{0.15})₃ sample, respectively. Scalebars are the SEM-verified channel width of 98.5 μm .

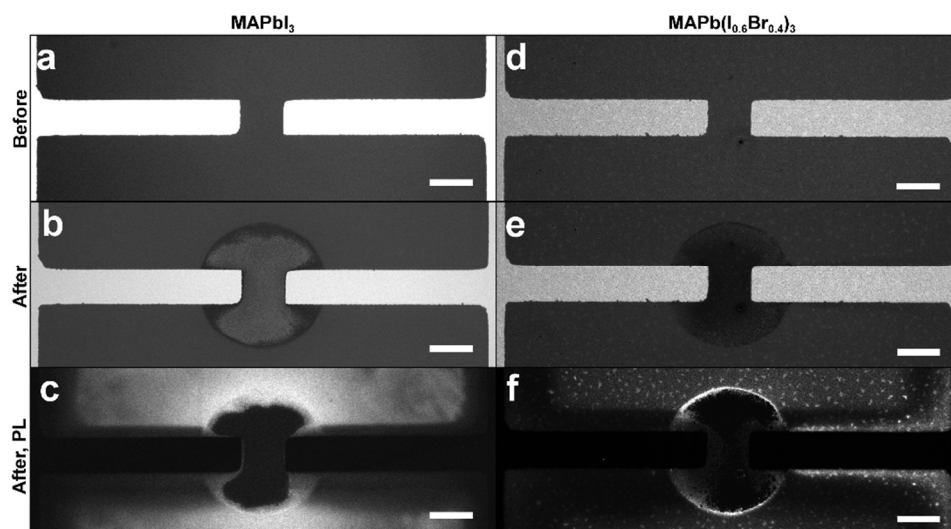


Figure 8.7 Microscope images before and after illumination stress test conducted *in 40% relative humidity air*. (a) Bright-field images before and (b) after degradation, and (c) photoluminescence image after degradation for the MAPbI₃ sample, respectively. (d) Bright-field images before and (e) after degradation, and (f) photoluminescence image after degradation for the MAPb(I_{0.6}Br_{0.4})₃ sample, respectively. Scalebars are the SEM-verified channel width of 98.5 μm .

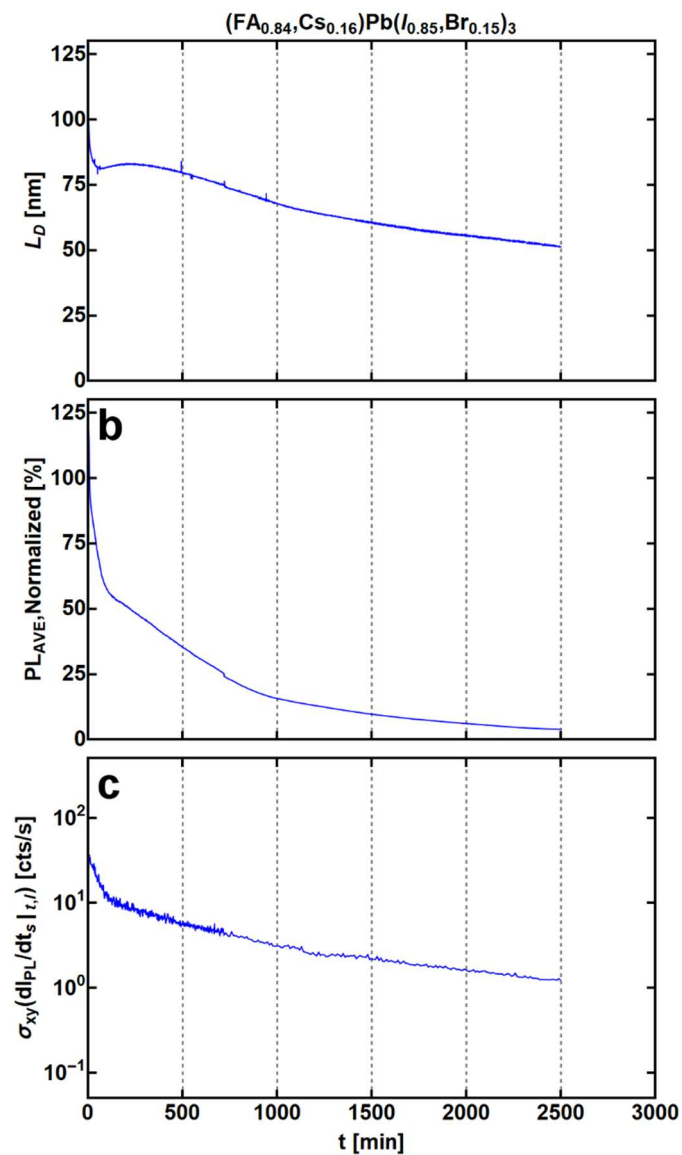


Figure 8.8 Photoluminescence-photoconductivity results for the $(\text{FA}_{0.84}\text{Cs}_{0.16})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ sample illuminated with 100 Suns equivalent photon flux under flowing nitrogen. (a) Mean carrier diffusion length, (b) average PL intensity, and (c) standard-deviation of the linear regression.

VITA

Ian L. Braly was born and raised in the Willamette Valley of Oregon. Ian did not travel far from home to study Chemical Engineering at Oregon State University before entering graduate school at the University of Washington in 2012. While working in the Hillhouse research lab, Ian had several opportunities to give hybrid perovskite demonstrations to prominent figures such as former Secretary of Energy Dr. Ernest Moniz and Washington Governor Jay Inslee. Ian's fondest memories of his time in the UW Chemical Engineering Department are of lunch discussions and group game-nights and outings.