Novel inorganic-organic perovskites for solution processable photovoltaics

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This report is presented in two parts summarizing our progress on 1) advancing perovskite-based devices and 2) on synthesizing and studying new perovskite absorbers

Abstract
We have fabricated semi-transparent perovskite solar cells with an efficiency of over 12%. This has enabled us to make 4-terminal hybrid tandem solar cells which comprise of a semi-transparent large bandgap (MA)PbI$_3$ (MA = CH$_3$NH$_3^+$) perovskite solar cell stacked on top of a smaller bandgap CIGS or silicon solar cell, achieving efficiencies over 18% in the case of the CIGS-perovskite tandem. As the reliability of the perovskite material remains the greatest technical risk in commercialization of perovskite photovoltaics, we have made several important discoveries regarding instabilities of the perovskite to electrical bias and illumination. In particular, we have found that perovskite solar cells in planar architectures typically exhibit hysteresis with voltage, and a decline in performance under steady-state conditions that can be reversed by forward biasing the device. These observations are consistent with electromigration of ions within the device during operation. We have also found that larger bandgap perovskites incorporating mixed halides, such as CH$_3$NH$_3$Pb(I$_{1-x}$Br$_x$)$_3$, generally undergo a halide segregation process under illumination. This produces domains with a smaller bandgap than the starting material and limits the open circuit that can be achieved by these materials.
We have synthesized new materials and developed methods to address the intrinsic instability and toxicity of the rapidly developing 3D perovskite solar-cell absorbers (MA)PbX$_3$ (X = Br or I). Our major accomplishments within this time period include:
1) The first demonstration that 2D perovskites can serve as solar-cell absorbers with enhanced moisture stability compared to the 3D perovskite (MA)PbI$_3$.
2) Identification of the source of light-induced traps that form in mixed-halide perovskites, which limit the obtainable voltages from these absorbers. We further showed that application of mechanical pressure can mitigate this effect and may allow for higher voltages to be realized from mixed-halide perovskite solar cells.
3) The first demonstration that double perovskites can be used to substitute nontoxic bismuth for lead. Our preliminary photophysical investigations show that the bismuth double perovskite has long carrier recombination lifetime and much higher stability to heat and moisture compared to (MA)PbI$_3$, which is promising for photovoltaic applications.
Part 1: Devices

Introduction

The objectives of this work are to design, synthesize and characterize new families of inorganic-organic perovskites for the application of low cost, hybrid tandem photovoltaics with efficiencies above 25%. For this application, the perovskite device needs to obtain high power conversion efficiencies over 15% and large open circuit voltages of over 1.2 V, be stable for many years and be safe for consumers and the environment. To meet these criteria, we are varying the stoichiometry of the inorganic constituents in the 3D perovskites as well as develop new layered (2D) perovskites to study the effect of the structure on the bandgap and electrical properties of the material and increase the open circuit voltage of devices. We are engineering perovskites with functionalized organic cations to promote stability of the material. We are also characterizing the optoelectronic properties of numerous lead-free perovskite materials to avoid the toxicity concerns of the lead-based perovskites.

Background

The efficiency of solution-processable perovskite solar cells has continued to advance at a rapid pace over the past year. After only a few years of research as photovoltaic material, devices based on the perovskite CH$_3$NH$_3$PbI$_3$ have in the past few months achieved certified power conversion efficiencies of over 20% in the laboratory[1] (Figure 1). Recent advances have involved further optimization of the perovskite ink solution and processing conditions to obtain a more uniform film morphology, and slight modifications to the perovskite stoichiometry to tune the perovskite bandgap and absorption onset.[2,3]

![Figure 1: Efficiency of record lab-scale perovskite devices.](image)

Hybrid perovskite materials have a relatively large optical bandgap (above 1.5eV for lead containing perovskites) and can obtain large open circuit voltages in excess of 1.1V.[2] This opens the possibility of making perovskite-silicon and perovskite CIGS tandem solar cell where the perovskite subcell absorbs the high energy photons and transmits lower energy photons to the CIGS or silicon device. A material with a bandgap of approximately 1.8 eV is needed to achieve current matching when paired with a conventional silicon solar cell. We and others[4] have
previously demonstrated that the bandgap of CH$_3$NH$_3$Pb(I$_{1-x}$Br$_x$)$_3$, can be continuously tuned from 1.6 to 2.3 eV by replacing iodide with bromide.

Hybrid perovskite photovoltaics currently face significant stability challenges which pose the greatest technical risk towards the commercialization of these devices. The most commonly studied perovskites are hydroscopic and degrade in the presence of moisture. We show that this degradation mechanism can be significantly suppressed by adding hydrophobic layers to the perovskite,[5] and potentially can be solved with appropriately engineered module encapsulants. However, there is a growing body of evidence from our research and from other laboratories that ion migration occurs in the material in the presence of electric fields, and for mixed-halide composition perovskites, in the presence of light. Ion migration can cause changes in the electric field distribution in the device. This has been hypothesized to cause the output power of perovskite solar cells to fluctuate and decline with time. Perovskite devices frequently exhibit hysteresis with voltage bias, which may also be a consequence of ion drift in the devices.

Results

In this report we first highlight our first demonstration of a mechanically stacked, 4-terminal tandem solar cell utilizing a semi-transparent perovskite device as the large bandgap junction. We also present our investigations into understanding the hysteresis and stability of perovskite devices under electrical bias, and the photo-stability of mixed-halide perovskites. We demonstrate improved stability to moisture using new layered perovskite materials. Most of the topics presented in this report have been published in peer reviewed journals over the past year that are listed in the Publications and Patents section of this report.

4-terminal, perovskite hybrid tandem photovoltaic solar cells

Perovskite solar cells have made rapid progress in the last few years at a pace unmatched by any other photovoltaic technology. These thin film perovskite solar cells have primarily been developed for single-junction modules, but we feel the greatest advantage of this new material is the ability to make low-cost tandems using conventional low-bandgap materials in the bottom cell. All Si and CIGS modules have a glass cover sheet to provide transparency, mechanical rigidity, and environmental sealing. The opportunity now exists to expand the functionality of the cover glass by depositing a string of perovskite cells onto the glass (Figure 2). This upgrade to the cover glass and module is expected to improve the module efficiency by 15-30\% (relative). On the timescale of 5 years, perovskite on high-quality Si tandems are expected to reach 30\% efficiency. Since the layers of the perovskite cells can be printed at low cost with high-throughput tools, and the modules will not be substantially modified, we estimate the cost per area will only increase by ~5\% and new factories will not be needed. By controlling the size of the perovskite cells, the separate top and bottom cell strings can be current-matched at the module level (Figure 2). This allows the module to be operated with only two wires leaving the module and requiring only a single system-level inverter.
Figure 2: (Left) Schematic of a mechanically-stacked tandem fabricated in this work with a perovskite solar cell as the top cell and Si or CIGS as the bottom cell. (Right) Current-matching at the module level. An example perovskite/silicon module with a simplified geometry and current density to demonstrate how current-matching at the module level can occur with a mechanically-stacked tandem. In this example module, the filtered silicon produces half the photocurrent density of the perovskite, so the silicon cells are twice as large to match the current of the perovskite cells. In this example, all cells are strung together in series; the total voltage of the module is the sum of the individual cell voltages.

Mechanically-stacked tandems require a semi-transparent top cell. The perovskite solar cell architecture used in this study uses a mesoporous titanium dioxide (TiO\(_2\)) layer infiltrated with the perovskite and contacted on either side by electron-selective (compact TiO\(_2\)) and hole-selective (2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene, spiro-OMeTAD) contacts. For compatibility with these existing electron- and hole-selective contacts, we use the MAPbI\(_3\) perovskite rather than the optically ideal MAPbBrI\(_3\). MAPbBrI\(_3\) was also not chosen due to a photo-instability observed in this material.[6] The transparent front electrode is fluorine-doped tin oxide (FTO) coated glass. Typically, a perovskite solar cell is opaque with an approximately 100 nm thick metal back electrode of either Au or Ag. This metal back electrode provides a low-resistance electrical contact and a reflective surface, giving the perovskite a second chance to absorb any light that was not absorbed on the first pass. To enable the transparency required to make a mechanically-stacked tandem, we needed a transparent top electrode.

The technical constraints that the top transparent electrode must meet are stringent. The electrode must be highly transparent in the critical 600–1000 nm window where the perovskite is not absorbing all of the light and the bottom cell has significant external quantum efficiency (EQE). The sheet resistance of the transparent electrode should be at most 10 Ω/□ because the transparent electrode must have high lateral conductivity to minimize resistive loss when carrying the large
current density generated in the perovskite cell. Perhaps most importantly, this electrode must be applied after deposition of the spiro-OMeTAD layer onto a temperature- and solvent-sensitive perovskite solar cell without damaging it. For these reasons, high-performance transparent conductive oxides widely used in industry cannot be directly sputtered onto a perovskite solar cell without a buffer layer. An electrode meeting these criteria has not been demonstrated before now. We use a silver nanowire (AgNW) mesh electrode which has been shown in other cases to have a low sheet resistance and high optical transmission and develop a new method of depositing this electrode onto our perovskite cell in a room-temperature solvent-free process. This AgNW electrode serves as the linchpin for our mechanically-stacked tandem architecture.

We first form our AgNW transparent electrode on a flexible polyethylene terephthalate (PET) film by spray deposition. The resulting AgNW film has a sheet resistance of 12.4 $\Omega/\square$ and exhibits 90% transmission between 530 and 730 nm falling off to 87% at 1000 nm. The AgNW film is then completely and uniformly donated from the PET to the top spiro-OMeTAD layer of the perovskite solar cell by mechanical transfer ideally without damaging the sensitive AgNW or perovskite films. Because this is a research-stage procedure, the applied force of the mechanical transfer was manually rather than automatically controlled. Variability in the applied force can cause shorting (high pressure) as well as incomplete transfer (low pressure), resulting in a spread of device efficiencies. Automated precise control of the applied force is expected to remove these inconsistencies. As a result of the transfer, the conductivity of the AgNW film typically improves by 2 $\Omega/\square$. The primary reason for this increase in conductivity is the planarization of the AgNW film due to the downward force of the transfer lamination process, which reduces the resistance of junctions between wires.[7] A secondary effect is that the AgNWs have been embedded into the moderately conductive spiro-OMeTAD layer ($10^{-3} \text{ S cm}^{-1}$) on top of the perovskite device. This transfer step decouples the fabrication of the perovskite solar cell from that of the electrode, allowing each to be optimized independently. Independent fabrication eliminates any thermal or solvent damage that the spiro-OMeTAD or perovskite may otherwise incur during the AgNW deposition process. We complete the semi-transparent solar cell by depositing two lithium fluoride (LiF) anti-reflective (AR) coatings, 133 nm onto the glass surface and 176 nm on top of the AgNW electrode to improve transmission through the device.

The current–voltage curves and metrics of the semi-transparent perovskite cells and opaque control devices are shown in Figure 3. The loss in absorption in the perovskite due to the removal of the opaque metal back electrode was offset by reduced reflection from the glass surface by the AR coating, yielding comparable $J_{sc}$ between the semi-transparent and opaque cells. We note that if the opaque cell had an AR coating, it would have approximately 0.5 mA cm$^{-2}$ higher photocurrent. We control our measurements for hysteresis in accordance with a paper by Unger et al.[8] We found a 5 s delay time between stepping the voltage and measuring current necessary to achieve steady state and remove any semblance of hysteresis. This procedure for removing hysteresis was corroborated and confirmed by NREL when a device was sent for certification. Shadow masks were used to define the illuminated area of a device. Opaque devices were illuminated through a 0.12 cm$^2$ mask and semi-transparent devices were illuminated through a 0.39 cm$^2$ mask.
Figure 3: Perovskite device results. (a) Current–voltage curves comparing best opaque vs. semi-transparent perovskite devices. (b) EQE of semi-transparent device and opaque device. Note that the opaque device does not have AR coatings. (c) Transmission through semi-transparent perovskite with AR coatings. Peak transmission is 77% around 800 nm.

Figure 3c shows that the transmission through the semi-transparent device peaks at 77% around 800 nm, the center of the 600–1000 nm transmission window that is critical for tandems. Much of the transmission loss is due to parasitic absorption in the FTO electrode, AgNW electrode, and spiro-OMeTAD layer. Uniquely, our semi-transparent device has both a high below-bandgap transmission and a high efficiency. There remains significant room for improvement in the transmission. Low-temperature processes would allow for fabrication of the perovskite cell on ITO, which is more transparent than FTO. A more transparent hole-transporter than spiro-OMeTAD, which in its oxidized form absorbs light throughout the visible and infrared, would also improve transmission.

We have made tandems with both Si and CIGS as bottom cells. Both have a bandgap around 1.1 eV, which is sub-optimal for a single-junction solar cell but optimal for a double-junction tandem, and are commercially successful solar technologies. We use a 17.0% laboratory-scale CIGS device made using previously reported procedures.[9] Although CIGS cells with 21% efficiency can be made, we chose a cell with a more modest efficiency for this demonstration to illustrate how cells that can be made at scale could be enhanced with a perovskite top cell. The current–voltage curves and external quantum efficiency of the semi-transparent perovskite solar
cell, the CIGS solar cell and the CIGS solar cell underneath the perovskite solar cell are shown in Figure 4. To arrive at the efficiency of the 4-terminal tandem, the efficiency of the semi-transparent perovskite cell is added to the efficiency of the CIGS solar cell when underneath the perovskite cell. With our 12.7% semi-transparent perovskite cell, we improve the 17.0% CIGS cell to 18.6% in a tandem (Table I) as measured in-house. This cell was not sent for certification due to scratching of the electrode from excessive handling. A different cell was sent to NREL and was certified as 17.3% with an 11.7% semi-transparent perovskite cell which was slightly higher than our in-house measurement of 17.1%. The good agreement between the in-house and certified measurements lends credence to the other values reported herein.

### Table I: Performance metrics of semi-transparent perovskite cell, CIGS cell, TI-Si cell, and the resulting tandem efficiencies

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (mV)</th>
<th>FF (−)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semi-transparent perovskite</td>
<td>17.5</td>
<td>1025</td>
<td>0.71</td>
<td>12.7</td>
</tr>
<tr>
<td>TI-Si – unfiltered</td>
<td>29.3</td>
<td>582</td>
<td>0.667</td>
<td>11.4</td>
</tr>
<tr>
<td>TI-Si w/IR-ARC – filtered</td>
<td>11.1</td>
<td>547</td>
<td>0.704</td>
<td>4.3</td>
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<tr>
<td>Tandem w/perovskite + TI-Si</td>
<td></td>
<td></td>
<td></td>
<td><strong>17.0</strong></td>
</tr>
<tr>
<td>CIGS – unfiltered</td>
<td>31.2</td>
<td>711</td>
<td>0.768</td>
<td>17.0</td>
</tr>
<tr>
<td>CIGS – filtered</td>
<td>10.9</td>
<td>682</td>
<td>0.788</td>
<td>5.9</td>
</tr>
<tr>
<td>Tandem w/perovskite + CIGS</td>
<td></td>
<td></td>
<td></td>
<td><strong>18.6</strong></td>
</tr>
</tbody>
</table>

Perovskite solar cells are already efficient enough to upgrade the performance of silicon solar cells made with low-quality silicon using the polycrystalline tandem approach. Here, we explore lower-quality sources of Si including cast multicrystalline silicon (mc-Si) wafers made from feedstock with high impurity content recycled from the top 10% of other cast multicrystalline ingots (TI-Si) (Figure 4 / Table I) and cast mc-Si wafers grown using 4.5 N (99.995% pure) upgraded metallurgical-grade Si (UMG-Si) instead of the more expensive Siemens-grade polysilicon (9 N, or 99.9999999% pure). Low-quality Si sources generally are not commercially viable today in single-junction devices because the material cost advantage of low-quality Si is offset by the reduction in performance due to impurities and crystal defects. We improve an 11.4% low-quality Si cell to 17.0% as a tandem, a remarkable relative efficiency increase of nearly 50%. Such a drastic improvement in efficiency has the potential to redefine the commercial viability of low-quality Si. Another tandem cell was sent to NREL for certification using a 17% silicon bottom cell. The tandem was certified as 17.9% efficient.
Figure 4: Perovskite and CIGS/Si tandem results. (a) Current–voltage and (b) EQE of semi-transparent perovskite cell, unfiltered CIGS cell, and CIGS cell filtered by the perovskite cell. (c) IV curves and (d) EQE of semi-transparent perovskite cell, unfiltered TI-Si cell, and TI-Si cell with an infrared-optimized anti-reflection coating filtered by the perovskite cell.

When making tandems as opposed to single-junction devices, some design parameters change for the bottom cell. The tandem relaxes the design constraints for both the Si and CIGS top layers. For example, the 20–50 nm CdS window layer used in commercial CIGS devices results in a photocurrent loss of 0.5 mA cm$^{-2}$ due to reduced EQE from 400–550 nm caused by parasitic light absorption in the CdS layer. However, this does not affect the EQE of a tandem because the 400–550 nm light is already absorbed in the top cell, decoupling the optimization of the electronic and optical properties of the CdS layer. In single-junction Si cells, there is a strict tradeoff of the series resistance vs. EQE from 400–550 nm due to minority carrier recombination in the emitter layer. As the bottom cell in a tandem, the emitter thickness or doping can be increased without an EQE penalty. In this work, the Si has a 35 Ω/□ phosphorus-diffused emitter as opposed to 100 Ω/□ in industry. Lower sheet resistance in the emitter layer means bus bar spacing can be increased, reducing shading losses. The design parameters also change for the optimal anti-reflection coatings used in a tandem. All commercial solar cells use AR coatings to improve the transmission into the solar cell. For a single-junction cell, the AR coating on top of the cell is optimized for a broad spectral range from 400–1100 nm and necessarily suffers in performance at the edges of this range. However, for the bottom cell in a tandem, the AR coating is optimized for a much narrower spectral range between 800 and 1100 nm, and can maintain a much higher performance through this
narrower spectral range. Full consideration of the different design parameters between single-junctions and tandems such as these examples could yield further improvements in the future. Perovskite solar cells, in both their opaque and semi-transparent versions, are still in their infancy. As perovskite cells continue to improve, tandems employing them will directly benefit from these improvements. We note that the benefit of the tandem instead of a single junction cell is maximized when the top and bottom cells have approximately equivalent single-junction device performance. While we have not yet demonstrated a tandem that can compete directly in efficiency with record single-junction CIGS, Si, or perovskite cells, we estimate that converting the current record perovskite efficiency of 22.1% from an opaque to a semi-transparent cell and coupling it with a 21–22% single-crystal Si solar cell would result in a 28% efficient tandem.

**Hysteresis and slow transient behavior in perovskite photovoltaics:**

Early in our research, we observed slow transient effects in perovskite-absorber devices that severely affect current–voltage measurements from which device performance metrics are commonly derived. Slow transients give rise to hysteresis between IV-measurements performed at different scan rates and directions, which can cause both over- and underestimated efficiency values. Hysteretic effects during IV-measurements have been observed in both mesoscopic[10] and thin-film perovskite photovoltaics.[11] In impedance measurements, illuminated perovskite-absorber devices exhibit an additional capacitance at low frequency caused by slow dynamic processes in the device that give rise to hysteresis in IV-measurements.[10,12] These effects can lead to erroneous device performance metrics if the slow device response is not considered during IV-measurements. Hysteresis in perovskite-absorber devices has been speculated to originate from trapping/de-trapping of charge carriers, changes in absorber or contact conductivity, ferroelectricity and ion migration.[10–12] Field-dependent orientation effects of the MA$^+$-dipoles and lattice distortion have been proposed to give rise to polarization effects that affect the charge carrier dynamics.[13] In addition, metal halides and metal halide perovskites can exhibit significant halide ion mobilities[14] that are often accelerated by photoexcitation.

We compared meso-porous titania based perovskite devices to solution-processed thin film devices. Hysteretic effects are observed in both type of architectures. We found that the device performance metrics derived from current–voltage measurements crucially depend on the scan direction and delay time after each voltage step before the measurement is taken. **In Figure 5, IV-curves were measured with either a 10 ms or 5 s delay after each 50 mV voltage step.**

![Figure 5: Current–voltage measurements of mesoporous-TiO$_2$ based perovskite-absorber device (a) and thin film device (c). Different scan directions (pos: 0 V to forward bias, neg: forward bias to 0 V) and delay times (0.01 s for fast scan and 5](image)
s for slow scan) are compared. (b & d) Corresponding short-circuit current transients when switching the devices from $V_{oc}$ to $J_{sc}$ during illumination.

At a short delay time of 10 ms, significant hysteresis is observed for both the mp-TiO$_2$ based devices (Figure 5a) and the thin film devices (Figure 5c). For the mp-TiO$_2$ based device shown in Figure 5c, the efficiency at a 5 s delay time is 12.3% but would be overestimated to be 13.6% when measured with 10 ms delay time in the negative scan direction or underestimated to be 11.9% when measured rapidly in the positive scan direction. For the thin film device, measurement at 10 ms delay time in the negative direction results in an 11.2% device efficiency, while the scan in the opposite direction yields a power conversion efficiency of 6.07%. At a delay time of 5 s, the positive and negative scans converge with an efficiency of 8.5 ± 0.1%.

The meso-porous titania based devices exhibited less hysteresis and a weaker dependence of the device efficiency on the measurement delay time compared to the thin-film devices. On average, the meso-scopic devices exhibited a negative scan efficiency of 12.5% and 11.3%, using a delay time of 10 ms and 5 s, respectively. For the thin film devices investigated, the average device efficiency between a fast scan and slow scan in the negative scan direction was 10.1% vs. 6.7%.

We find that the conditions prior to the IV-measurement have a huge effect on the performance of thin film devices. After storage in the dark and prior to any light-soaking, thin-film devices often exhibited IV-curves with a slight s-shape and rather low performance as shown in (Figure 6a). Light-soaking at far-forward bias conditions ($J > 0$) dramatically improved the fill factor and photocurrent of this device leading to a power conversion efficiency increase from about 2% to about 4%. For some devices, we were able to further improve the device efficiency to about 7% by cycling the device between forward bias and 0 V under illumination several times prior to performing the IV-measurement. Illumination under reverse bias conditions, where the current flows in the opposite direction, had the opposite effect causing the IV-curves to become more s-shaped over time and the photocurrent to decrease. This can explain the observed slow decrease in short-circuit photocurrent with time. We found that we repeatedly improve or diminish the device efficiency by cycling the voltage bias conditions during light soaking, indicating that there are reversible processes occurring in perovskite-absorber solar cells. In contrast, meso-porous titania based devices performed fairly independently of illumination and bias conditions prior to the measurements.

**Figure 6:** (a) Light-soaking at forward bias positively affects the current–voltage and hence the performance of thin film perovskite-absorber solar cells. (b) The
reverse effect is observed after light soaking under reverse bias conditions with the IV-curves developing an s-shape.

The transient processes responsible for hysteresis appear to originate from the processes in the bulk of the perovskite-absorber. We have observed hysteresis in all of the perovskite device architectures that we have examined, irrespective of contact materials. When omitting the spiro-OMeTAD from our devices and contacting the perovskite-absorber directly with gold, hysteresis persisted. This suggests that hysteretic effects are neither solely caused by the perovskite/spiro-OMeTAD interface nor diffusion of Li+, introduced to the device with the hole-transporting medium. We have found that contacts can influence the size and direction of the transients and hysteresis. Inverted thin film devices using PEDOT:PSS and PC60BM as hole and electron-selective contacts exhibit hysteresis at fast scan rates but the photocurrent appears to be lower rather than higher at fast scan rates. These observations are consistent with a mechanism where transient polarization of the perovskite absorber results in changes in charge carrier extraction efficiency at the carrier-selective contacts. In inverted devices, we found the photocurrent not to be as dependent on IV-scan delay time. This suggests that the charge extraction efficiency is not as severely affected by changes in perovskite polarization in these type of devices.

It is not yet clear whether the current transients in response to changes in the applied voltage have a similar origin to the slower processes occurring during pre-conditioning of the devices. The strong influence of bias pre-conditioning on IV-measurements suggests that polarization-induced changes in the device may play an important role in the observed current transients and device hysteresis. This polarization could be caused by diffusion of ionic species or alignment of methylammonium dipoles within the metal-halide lattice[10–13] under an applied voltage bias, resulting in changes in ability for photocurrent to be extracted from the device. Recent impedance studies on perovskite-absorber solar cells analyzing low-frequency phenomena observed slow transients with similar time-constants.[12] They arrive at a similar conclusion, that the observed transiently higher photocurrent cannot be explained by charge-carrier accumulation but is likely due to ferroelectric MA+ re-orientation and lattice distortion effects giving rise to polarized domains.

We propose that ion migration may also play a role in slower processes occurring during pre-conditioning of the devices. We suggest that photo-excitation of MAPbI3 may enhance the ionic conductivity of the material, resulting in the observed transient currents and hysteresis when a bias is applied to the device. This process is well known to occur in metal halides, including PbI2 where photo-excitation creates halide vacancies that enable the migration of halide ions.[15] Once these vacancies are created, an applied external bias can result in a redistribution of ions within the device, producing electric fields that aid or counteract charge carrier extraction. This can explain why under continuous illumination, the external quantum efficiency and photocurrent slowly decreases in perovskite solar cells and why applying a large forward bias to reverse the current direction causes the photocurrent to recover. Applying a reverse bias or short circuit conditions during illumination is expected to cause negatively charged ions such as I in the perovskite to migrate towards the titania cathode and positive ions such as MA+ and Li+ towards the hole-selective contact. This may create an extraction barrier for both electrons and holes at their respective contact, resulting in the observed s-shaped IV behavior (Figure 6). Forward-biasing the device during illumination can drive these ions in the opposite direction, potentially allowing the device photocurrent to recover if the pre-conditioning forward bias is applied for an adequate time.
This redistribution of ions under illumination can explain why the current–voltage behavior of perovskite devices is sensitive to the pre-conditioning bias history before the measurement.

Since ion migration is particularly sensitive to the concentration of mobile vacancies (or interstitials depending on the mechanism), this proposed mechanism would suggest that the transient behavior of perovskite devices should be influenced by the precise stoichiometry of the perovskite material, as well as the degree of crystallinity and the size of crystalline domains. The significant differences in the transient behavior that we observed between the meso-scopic and thin-film devices may be a consequence of differences in stoichiometry or morphology due to the differences in processing. The thin film devices may contain trace amounts chloride due to the employed deposition procedure. As any ion migration will likely be detrimental for the long-term reliability of perovskite-absorber devices, reducing any ion-migratory effects in hysteresis may be an important step for improving long-term reliability.

**Photostability of mixed-halide perovskites:**

We investigated the opto-electronic properties of various compositions of the perovskite family CH$_3$NH$_3$Pb(Br$_x$I$_{1-x}$)$_3$ to assess which stoichiometries are best suited for a tandem solar cell. One attractive attribute of hybrid perovskites as photovoltaic absorbers is the ability to continuously tune the absorption onset by alloying different halides into the structure. For example, the bandgap of (MA)Pb(Br$_x$I$_{1-x}$)$_3$ (MA = CH$_3$NH$_3$) can be continuously tuned over the range 1.6–2.3 eV,[4] making these materials suitable both for single-junction solar cells and for the larger bandgap absorber of tandem solar cells. Photovoltaic devices containing (MA)Pb(Br$_x$I$_{1-x}$)$_3$ have demonstrated PCEs of 4–16% for a wide range of halide ratios,[2,4,16–18] and an open circuit voltage (V$_{OC}$) of 1.5 V has been achieved using the largest bandgap perovskite of this family: (MA)PbBr$_3$.[19] Although solar cells containing (MA)PbI$_3$ have obtained V$_{OC}$’s of up to 1.15 V,[20] solar cells with mixed-halide perovskites have so far not produced the larger V$_{OC}$’s that may be expected from their larger bandgaps. Several groups have reported a decrease in V$_{OC}$, despite the increase in optical band gap, in (R)Pb(Br$_x$I$_{1-x}$)$_3$ (R = CH$_3$NH$_3$ or HC(NH$_2$)$_2$) absorbers for $x > 0.25$.[4,16,17,21]

We examined the optical properties of (MA)Pb(Br$_x$I$_{1-x}$)$_3$ thin films to understand the poor voltage performance of solar cells with the bromide-rich alloys. Surprisingly, for perovskites with $0.2 < x < 1$ we find that a second PL peak forms at ~1.68 eV and grows in intensity under continuous illumination (Figure 7a). The position of this new peak is independent of halide composition and bandgap (Figure 7b). After less than a minute of continuous visible-light soaking (argon ion laser, 457 nm, 15 mW/cm$^2$) the PL intensity from the new low-energy peak becomes more than an order of magnitude more intense than the original peak (Figure 7c). We find that this PL spectral change is not dependent upon the spectrum or coherence of the light source and that it occurs as long as the light is absorbed by the perovskite. Notably, these changes are reversible; the original PL spectra return after the materials are left in the dark for 5 minutes. Moreover, the spectra can be repeatedly cycled between these two states by turning on and off the excitation light (Figure 7c).
Figure 7: (a) Photoluminescence (PL) spectra of an $x = 0.4$ thin film over 45 s in 5-s increments under 457 nm, 15 mW/cm$^2$ light at 300 K. Inset: temperature dependence of initial PL growth rate. (b) Normalized PL spectra of (MA)Pb(Br$_x$I$_{1-x}$)$_3$ thin films after illuminating for 5-10 minutes with 10-100 mW/cm$^2$, 457 nm light. (c) PL spectra of an $x = 0.6$ thin film after sequential cycles of illumination for 2 minutes (457 nm, 15 mW/cm$^2$) followed by 5 minutes in the dark.

To understand the origin of the new PL feature, we performed photocurrent spectroscopy measurements on photovoltaic devices containing (MA)Pb(Br$_x$I$_{1-x}$)$_3$ before and after light soaking to characterize absorption from band-edge states (Figure 8). A new absorption shoulder forms around 1.7 eV after light soaking, which completely disappears after the devices are left in the dark for 1 h. We speculate that these new PL and absorption features in the light-soaked mixed-halide perovskites are due to the formation of small, iodide-enriched domains with a lower bandgap compared to the alloy. The absorption shoulder in the light-soaked $x = 0.6$ alloy has an absorption coefficient similar to the expected value if ~1% of the material converted into the $x = 0.2$ perovskite (Figure 8). The observations of this absorption shoulder and additional PL peak at 1.68 eV were recently reported for (MA)Pb(Br$_{0.4}$I$_{0.6}$)$_3$ and were attributed to the existence of multiple phases.[22] However, the role of light soaking in producing these features was not examined.

Figure 8: Absorption spectra of an $x = 0.6$ film before (black) and after (red) white-light soaking for 5 minutes at 100 mW/cm$^2$, and after 1 h in the dark (blue). A scaled absorption spectrum of an $x = 0.2$ film (dashed green) is shown for comparison.
In order to reversibly create iodide-rich domains, the bromide concentration should be slightly enhanced elsewhere in the films. To test this hypothesis, we performed XRD measurements on \( x = 0.6 \) thin films before and after light soaking. We observe splitting of all XRD diffraction peaks with light soaking, and regeneration of the original sharp diffraction patterns after the films are left in the dark (Figure 9a). Since perovskites with higher bromide content have a smaller lattice constant than those with higher iodide content, this splitting is consistent with the presence of a minority phase with significantly enhanced \((x \sim 0.2)\) iodide content and a majority phase with slightly enhanced bromide content \((x \sim 0.7)\) compared to the original material (Figure 9b). These phase compositions would suggest that the minority phase is about 20% of the material in these particular samples. If we compare the magnitude of XRD intensity from the two phases, we estimate that the minority phase makes up 23% of the material, after accounting for differences in structure factor for the two hypothesized phases. These values are substantially higher than the 1% minority phase estimated from the absorption measurements by photocurrent spectroscopy on mesoporous devices (Figure 8). We suggest that differences in morphology between the mesoporous devices and planar thin films may be responsible for the different minority phase yields under similar illumination conditions.

![Figure 9: XRD patterns](image)

We monitored the PL spectral evolution under constant illumination at different temperatures to study the kinetics of this conversion. The low-energy PL peaks also form below room temperature \((200 - 280 \text{ K})\), indicating that the spectral change is due to photoexcitation and not heating from the light. The initial growth rate in the low-energy PL peak follows Arrhenius behavior with an activation energy of 0.27 ± 0.06 eV (Figure 7a, inset). This value is similar to the activation energies attributed to halide migration in the perovskites \( \text{CsPbCl}_3, \text{CsPbBr}_3, \text{KMnCl}_3, \text{CuCdCl}_3, \text{KPbI}_3, \text{CuSnI}_3, \text{and CuPbI}_3 \), which span the range 0.25–0.39 eV.[14,23–25] Light-induced halide migration has also been reported to occur in metal halides such as PbBr\(_2\) and PbI\(_2\).[15,26] and is the basis for latent image formation in photography using Ag\(_2\).[27] While halide mobilities in hybrid lead-halide perovskites have not yet been reported, ion conductivities of \(7 \times 10^{-1}\)
and $3 \times 10^{-9}$ S/cm have been reported for K Pb I and Cu Pb I, respectively.[23] Since the (MA)Pb(Br<sub>x</sub>1-x)I<sub>3</sub> valence band is dominated by contribution from the halide p orbitals,[28] we speculate that formation of iodide-enriched domains stabilizes holes, which could provide a driving enthalpy for halide segregation under illumination (Figure 10). When these trapped holes are filled, entropy and lattice strain may cause the phase segregated material to relax back to the well-mixed alloy. Light-induced, reversible structural changes in PbBr<sub>2</sub> have been attributed to self-trapping of such photogenerated holes.[29] Alternatively, since iodide-rich domains have a smaller bandgap, they lower the energy of excitons, which could drive halide segregation. It is not yet clear whether these structural and spectroscopic changes can be induced by electrical excitation. Spectrally stable red-emitting (MA)PbBr<sub>2</sub>I LEDs have been recently demonstrated.[30] This suggests that the application of an electrical bias might not produce the large changes in emission that are observed under photoexcitation and that photogenerated excited states may play an important role in the transformation mechanism. It is also not yet clear why photo-induced defects resemble the $x = 0.2$ perovskite for a range of bulk perovskite stoichiometries.

![Energy level diagram](image)

**Figure 10:** Schematic of the proposed mechanism for photo-induced trap formation through halide segregation. Photogenerated holes or excitons may stabilize the formation of iodide-enriched domains which then dominate the photoluminescence. The valence band (VB) and conduction band (CB) energies with respect to vacuum were estimated by interpolation of published values obtained from ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) for the endpoint stoichiometries.[31]

This ion-transport mechanism suggests that crystallite size and quality should influence its kinetics. Accordingly, we have seen variations between samples in the rate of their light-induced changes. We see the growth of the low-energy PL even in single crystals of (MA)Pb(Br<sub>x</sub>1-x)I<sub>3</sub>, indicating that significant grain boundaries or surface defects are not required for this transformation. We have also observed this new phase upon light exposure (for both white LED and 457 nm excitation at 10–100 mW/cm<sup>2</sup>) in (MA)Pb(Br<sub>x</sub>1-x)I<sub>3</sub> thin films formed from a PbCl<sub>2</sub> precursor,[16] sequentially-deposited dip-converted[17] and vapor-converted[32] thin films, and in (HC(NH<sub>2</sub>)<sub>2</sub>)Pb(Br<sub>x</sub>1-x)I<sub>3</sub> thin films,[21] all processed following the procedures described in the references. Approx. 10 s of continuous visible-light soaking at 10 mW/cm<sup>2</sup> (0.1 J/cm<sup>2</sup>) was typically required for these PL spectral changes. We postulate that previously reported PL studies on mixed-halide perovskites,[21,22,33] in many cases done with ultrafast pulsed excitation, may have used much smaller light-soaking dosages that were insufficient to produce these changes.
In summary, we have observed the formation of a new low energy PL feature upon light soaking of (MA)Pb(Br\textsubscript{x}I\textsubscript{1-x})\textsubscript{3} and other mixed-halide perovskites. This spectral change, accompanied by the growth of sub-bandgap absorption states and a splitting of XRD peaks, is consistent with photo-induced halide segregation. In the case of (MA)Pb(Br\textsubscript{x}I\textsubscript{1-x})\textsubscript{3} solar cells, the red-shift in PL upon light illumination indicates a reduction in the electronic bandgap and quasi-Fermi level splitting, reducing their achievable $V_{OC}$’s. This photo-induced instability suggests that significant halide migration can occur in the perovskite, which we expect has serious implications for the stability of perovskite photovoltaics. We are planning to continue to study the mechanism of light-induced trap formation to better understand its potential impact on device reliability, and access strategies to mitigate it. The results from this study indicate that the perovskite compositions (MA)Pb(Br\textsubscript{x}I\textsubscript{1-x})\textsubscript{3} with $0 \leq x \leq 0.2$, or $x=1$ that do not undergo halide segregation are best suited for making perovskite tandems.

Part 2: Materials

_A Layered Hybrid Perovskite Solar Cell Absorber with Enhanced Stability Towards Atmospheric Moisture_

As solar cells with perovskite absorbers reach commercially viable efficiencies, their stability to manufacturing and operating conditions must also be considered. The lead-iodide perovskites decompose upon exposure to relative-humidity levels as low as 11% over several days. Motivated by our observations that the structurally related two-dimensional perovskites readily formed high-quality films that appeared more resistant to humidity than the three-dimensional analogs, we sought to assess if the layered materials could act as solar-cell absorbers. We synthesized the 2D perovskite (PEA)\textsubscript{2}(MA)\textsubscript{2}[Pb\textsubscript{3}I\textsubscript{10}] (1, PEA = C\textsubscript{6}H\textsubscript{5}(CH\textsubscript{2})\textsubscript{2}NH\textsubscript{3}\textsuperscript{+}, MA = CH\textsubscript{3}NH\textsubscript{3}\textsuperscript{+}) and showed that it can serve as an absorber in a solar cell with an open-circuit voltage of 1.18 V and a PCE of 4.73%. Subsequent to our work, several other groups have reported on 2D perovskite solar cells. Although our first generation devices had lower efficiencies compared to 3D perovskite cells, we showed that the layered structure brings distinct advantages:

1) High-quality films of 1 can be easily deposited through one-step spincoating under ambient humidity and annealing steps are not required for device processing. Similar processing of 3D perovskites do not afford continuous or phase-pure films.

2) These films are far more resistant to moisture compared to (MA)PbI\textsubscript{3}, and do not require anhydrous conditions for device processing or operation.

3) Higher voltages are accessible from solar cells with 2D perovskite absorbers.
The layered perovskite structure can be derived from the three-dimensional analog by slicing along specific crystallographic planes.[34,35] The thickness of the inorganic layers can be controlled by choice of organic cation. Each inorganic layer in 1 consists of three sheets of corner sharing Pb-X octahedra (denoted \( n = 3 \)). The structure contains two types of organic cations: the smaller \( \text{CH}_3\text{NH}_3^+ \) molecules fit in the cavities defined by eight corner sharing Pb-I octahedra while the larger phenethylammonium (PEA = \( \text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3^+ \)) cations form an ordered bilayer that templates the inorganic layers (Error! Reference source not found.) Reducing the dimensionality of the inorganic components from the three-dimensional structure causes an expected increase in bandgap. The \( n = 1, 2, \) and 3 structures have bandgaps of 2.4, 2.2, and 1.8 eV, respectively. We chose the \( n = 3 \) material for this study as it has the closest bandgap to the three-dimensional perovskite while affording new properties emerging from the hybrid layered structure. While this bandgap is larger than the ideal value of 1.4 eV calculated to be the Shockley-Queisser limit[36] it can absorb a significant fraction of the solar spectrum. It is also the ideal value for the higher bandgap absorber in a tandem solar cell, which can exceed the Shockley-Queisser limit.

Layered perovskites form oriented films on substrates through simple one-step dropcasting or spincoating techniques. Unlike \((\text{CH}_3\text{NH}_3)[\text{PbI}_3]\) that crystallizes as dodecahedra at room temperature, 1 forms plates indicating faster crystal growth in the \( ab \) plane along the inorganic sheets. Powder x-ray diffraction (PXRD) patterns of 1 on glass or titania substrates show only 00l reflections revealing long-range order along the crystallographic \( c \) axis perpendicular to the inorganic sheets. Similar processing of three-dimensional perovskites do not afford continuous films. Films of comparable quality of \((\text{CH}_3\text{NH}_3)[\text{PbX}_3]\) can be obtained by thermal evaporation, or two-step vapor- or dip-conversion from \( \text{PbI}_2 \) or \( \text{PbCl}_2 \). In contrast to the three-dimensional analogs, the layered perovskites do not require high-temperature annealing for good device performance, allowing for simpler device fabrication.

Perovskite 1 is the first \( n = 3 \) lead-iodide perovskite to be crystallographically characterized and is similar in structure to the \( n = 3 \) tin-iodide perovskite \((\text{BA})_2(\text{CH}_3\text{NH}_3)_2[\text{Sn}_3\text{I}_{10}]\) (BA = butylammonium) [34]. Devices utilizing 1 as the absorber were constructed using a typical

![Figure 11: A) Crystal structures of the 3D perovskite (MA)PbI\(_3\) and B) the n = 3, 2D perovskite (PEA\(_2\)(MA)\(_2\)[Pb\(_3\)I\(_{10}\)] (1, PEA = 2-phenylethylammonium). Turquoise, purple, blue, and gray spheres represent Pb, I, N, and C atoms, respectively. Disordered atoms and hydrogens omitted for clarity. (Figure from reference 5)
perovskite-based device architecture employing TiO\textsubscript{2} and 2,2′,7,7′-tetrakis-(N,N-di-p-methoxyphenylamine)9,9′-spirobifluorene (spiro-OMeTAD) as the electron- and hole-selective contacts, respectively. Films of 1 were deposited from a N,N-dimethylformamide solution containing stoichiometric quantities of PbI\textsubscript{2}, (CH\textsubscript{3}NH\textsubscript{3})I and (PEA)I using a single spin-coating step. Importantly, films of 1 can be processed under ambient humidity levels, which do not degrade the films. This allows for easier device processing compared to (CH\textsubscript{3}NH\textsubscript{3})[PbI\textsubscript{3}] films, which require anhydrous deposition conditions, and multistep deposition methods,[37] or high-temperature annealing steps. A scanning-electron microscopy (SEM) image of the full device is shown in Figure 11. Typical thicknesses of the layers of TiO\textsubscript{2}, 1, Spiro-OMeTAD, and gold are 50, 450, 125, and 60 nm, respectively.

**Figure 11:** SEM cross section of planar devices utilizing 1 as the absorber layer. Figure from reference 5.

We obtained \(JV\) curves of these devices using simulated AM1.5 solar illumination (Figure 12). The open-circuit voltages (\(V_{oc}\)) for these devices routinely exceed 1.0 V; the best devices show a value of 1.15 V. Owing to the larger bandgap of the two-dimensional material, these \(V_{oc}\) values are higher than for optimized cells containing (CH\textsubscript{3}NH\textsubscript{3})[PbI\textsubscript{3}][37] These devices display fill factors of ca. 0.65 and afford a maximum power of 4.73 mW/cm\textsuperscript{2} for 100 mW/cm\textsuperscript{2} solar intensity, resulting in a 4.73\% PCE. The current density under short-circuit conditions (\(J_{sc}\)) is 6.72 mA/cm\textsuperscript{2}. Slow scan rates were used for these measurements to avoid current from capacitive cell charging and similar \(JV\) profiles were obtained for both forward and reverse scans (Figure 12). An external-quantum efficiency (EQE) of 50\% was obtained for devices illuminated by monochromatic light and the integrated photocurrent density from these measurements matched the \(J_{sc}\) obtained from voltammetry corroborating the efficiencies calculated using the \(JV\) curves. Faster scan rates for the \(JV\) curves afforded currents as high as 11.5 mA/cm\textsuperscript{2}, but these voltammograms showed large hysteresis between forward and reverse scans and the higher PCEs of 6.1\% calculated through these measurements were not matched by the EQE measurements. The layered structure of the material likely affects charge extraction from these devices as carrier transport in the inorganic sheets is highly anisotropic, with no direct path between inorganic layers. Low-dimensional inorganic materials have previously been effectively used in photovoltaic devices,[38,39] and device optimization should afford improvements in \(J_{sc}\) and overall efficiency.
Figure 12: Current-voltage (JV) curves of the devices. Figure from reference 5.

Upon exposure to humid atmospheres at room temperature, black \(\text{(CH}_3\text{NH}_3)_4\text{[PbI}_3\text{]}\) converts to a bright-yellow solid that has been formulated as the hydrated structure \(\text{(CH}_3\text{NH}_3)_4\text{[PbI}_6\text{]}\cdot\text{2H}_2\text{O}\). The tetragonal phase of \(\text{(CH}_3\text{NH}_3)_4\text{[PbI}_3\text{]}\), which is the stable structure at room temperature, is prone to this reactivity with water, whereas the high-temperature cubic phase is more resilient. To assess the stability of 1 and \((\text{MA})\text{PbI}_3\) to humidity we used spincoated films of both materials on glass substrates. These films were exposed to relative-humidity levels of 52% and their PXRD patterns were periodically recorded (Figure 14). The 3D perovskite film shows a new PbI₂ phase after only 4 days, which dominates the pattern after 46 days of humidity exposure. In contrast, the PXRD pattern of 1 does not show additional reflections throughout the 46-day experiment, demonstrating its resilience to humidity.

Importantly, 2D perovskites are far more amenable to synthetic tuning compared to 3D perovskites. We proposed that thicker inorganic layers can be used to mimic the properties of the 3D perovskites while the organic layers bring new functionality

Figure 13: PXRD patterns of films of \((\text{PEA})_2(\text{MA})_2[\text{Pb}_3\text{I}_{10}]\) (1), \((\text{MA})[\text{PbI}_3]\) formed from PbI₂ (2a), and \((\text{MA})[\text{PbI}_3]\) formed from PbCl₂ (2b), which were exposed to 52% relative humidity. Films of 2a and 2b were annealed at 100 °C for 15 and 80 minutes, respectively, prior to humidity exposure. Asterisks denote the major reflections from PbI₂. Figure from reference 5.

Post-synthetic Halide Exchange in \((\text{MA})[\text{PbX}_3]\) Perovskites

Although many deposition methods have now been developed for forming continuous films of \((\text{MA})\text{PbI}_3\), high-quality films of \((\text{MA})\text{PbX}_3\) (\(X = \text{Cl}\) or \(\text{Br}\)) are more difficult to form. We found a
simple way to transform high-quality films of (MA)PbI to equally good (MA)PbX (X = Cl or Br) films without purification or annealing steps[41] The perovskite (MA)PbBr₃ has been targeted as the higher bandgap absorber in a tandem solar cell, while both (MA)PbBr₃ and (MA)PbCl₃ have been used as LEDs and lasers. All these applications require high-quality films.

Exposure of (MA)PbI₃ films to Cl₂ or Br₂ gas cleanly transforms the film to (MA)PbX₃ (X = Cl or Br). This reaction occurs through electron transfer from Cl₂ or Br₂ gas to I⁻ in the perovskite. Importantly, the morphology of the lead-iodide film is retained in the lead-bromide and lead-chloride films (Figure 15) and all reaction byproducts are volatile.

**Figure 15:** SEM images of 3D perovskite films. A) A film of (MA)PbI₃. Films prepared directly from PbX₂ and (MA)X solutions are shown on the left (B and C) and films formed using halogen gas are shown on the right (D and E). Figure from reference 41.

Lead-free double perovskites as solar-cell absorbers.

The toxicity of lead is a primary concern for the wide-scale use of this technology, particularly in light of the material’s water solubility. The analogous tin perovskite (MA)SnI₃ (MA = CH₃NH₃⁺) has been explored as a non-toxic alternative and efficiencies of devices employing these absorbers have reached ca. 6%.[42, 43] However, the tin perovskites are unstable to oxidation in air, limiting their viability. Bismuth has been used for decades as a nontoxic replacement for Pb.[44] We therefore focused our efforts on incorporating Bi³⁺ as a B-site cation in the ABX₃ (X = halide) perovskite framework. To accommodate the trivalent Bi³⁺ ion in the 3D perovskite lattice we
decided to use the double-perovskite structure: $A^1_2B^I_{III}X_6$. Accordingly, we synthesized the double perovskite: $\text{Cs}_2\text{AgBiBr}_6$ (2).[45] Large single crystals of 2 can be crystallized from a concentrated HBr solution containing stoichiometric CsBr, AgBr, and BiBr$_3$. The perovskite shows the characteristics of an indirect bandgap semiconductor with a shallow absorption region beginning at 1.8 eV followed by a sharp increase in absorption near 2.1 eV. A Tauc plot of the data, assuming an indirect allowed transition, shows the expected phonon-assisted processes with transitions at 1.83 eV and 2.07 eV occurring with absorption and emission of a phonon, respectively. This allows us to estimate the indirect bandgap as 1.95 eV with an assisting phonon energy of 0.12 eV. We anticipate that 2 could be used as the higher-bandgap absorber in a tandem solar cell. Four- and two-terminal tandem cells with Si absorbers require higher-bandgap absorbers with ideal bandgaps of 1.8 – 2.0 eV and 1.8 – 1.9 eV, respectively.[46]

To determine if photogenerated carriers were long-lived enough to produce photocurrent in a solar cell we then obtained room-temperature, time-resolved PL data of 2 (Figure 4). The PL intensity shows a fast initial drop followed by a slower decay. While analysis of the short-lived process’s lifetime is limited by our instrumental resolution the magnitude of this process (PL intensity × time) is larger in the powder (5%) than in the single crystal (0.02%). Because powders typically have much more defects and surface states than a single crystal, this suggests that the shorter processes may originate from trap and/or surface-state emission. The long PL decay time of ca. 660 ns does not vary significantly between single-crystal and powder samples and likely gives the material’s fundamental recombination lifetime. Long carrier recombination lifetimes are indicators of good photovoltaic performance. These values are significantly higher than those for high-quality (MA)PbBr$_3$ films of 170 ns[47] and approach those for optimized (MA)PbI$_3$ films of 736 ns[48] - ca. 1 μs.[49] Although indirect bandgap semiconductors should have longer PL lifetimes compared to direct bandgap materials, the long lifetime in 2 is unusual, especially for powders. Integrating the PL traces, we estimate that 85% of excited carriers emit via a long-lived recombination process ($\tau \geq 660$ ns) in the crystal compared to 80% for the powder (See SI for details). The ratio of these values indicates that faster PL decay components increase by only 6% in powders compared to crystals, attesting to the material’s robustness to defects.

Figure 16: Left: X-ray structure of the ordered double perovskite $\text{Cs}_2\text{AgBiBr}_6$ (2). Orange, gray, turquoise, and brown spheres represent Bi, Ag, Cs, and Br atoms, respectively. Right: Time-resolved room-temperature photoluminescence (PL) and fits for the PL decay time ($\tau$) in powder and single-crystal samples of 2. Figure from reference 45.
We investigated the stability of 2 to both light and moisture. Freshly prepared powders of 2 were stored either in the dark at 55% relative humidity or irradiated at 50 °C with a broad spectrum halogen lamp (0.75 Sun) under dry N₂ for 30 days. PXRD patterns of 2 after moisture or light exposure showed no evidence of material decomposition (Figure 5). After 15 days some of the irradiated samples showed small localized surface discolorations. These spots recovered their original color upon storing the sample in ambient light for two days. Thermal stability is also important for solar-cell absorbers, which can reach temperatures of ca. 50 – 70 °C during typical device operating conditions[50] and still higher temperatures during device fabrication. Thermogravimetric analysis (TGA) shows that 2 is stable to mass loss up to 430 °C and differential thermal analysis indicates no phase transitions within this temperature range (Figure S6). PXRD patterns obtained after heating 2 at 100 °C in air for 72 h confirms structural integrity (Figure 3B). The absence of volatile organic components likely increases 2’s thermal stability with respect to (MA)PbX₃ (X = I[51, 52] and Br), as shown for CsPbBr₃.[53] Although TGA data collected at fast heating rates suggest material stability, (MA)PbX₃ slowly loses CH₃NH₂ and HX even at modest temperatures.[52] PXRD data of (MA)PbX₃ heated at 60 °C for 72 h in air show decomposition to PbX₂ (Figure 5). Although encapsulation may impede this decomposition pathway, inherent thermal stability is an advantage for material processing and its long-term usage.

Importantly, the double perovskite lattice is far more accommodating for substitutions. Here, many combinations of metals in different oxidation states can be incorporated into the B/B’ sublattices, both organic and inorganic cations can be incorporated into the A sites, and the halide can be varied. Our studies show that inorganic and hybrid halide double perovskites should be further investigated for photovoltaic and other optoelectronic applications.

Effects of pressure on 3D perovskites.

We recently reported the high-pressure single-crystal structures of the 3D perovskites (MA)PbX₃ (X = I or Br).[54] Material compression within diamond-anvil cells (DACs) causes both bond compression and tilts between metal-halide octahedra. We also investigated the high-pressure properties of mixed halide perovskites. As mentioned earlier in the report, we found that light soaking causes a reversible redshift in the PL of mixed-halide perovskites, which we

Figure 17: (A) PXRD patterns of 2 after exposure to humidity (55% RH) or light (0.75 Sun). Asterisks denote signals from the sample holder. (B) PXRD patterns of 2 before (orange) and after (red) 72 h at 100 °C, (MA)PbBr₃ before (turquoise) and after (blue) 72 h at 60 °C, and (MA)PbI₃ before (light green) and after (dark green) 72 h at 60 °C. Vertical bars denote reflections from PbBr₂ or PbI₂. (C) CBM and VBM of 2 and other materials relevant to photovoltaic devices with perovskite absorbers. Figure from reference 45.
attributed to halide segregation. Because our proposal for halide segregation under illumination requires halide migration, we reasoned that lattice compression should affect the thermodynamics or kinetics of this effect.

We measured PL spectra over the course of ca. 150 s for (MA)Pb(Br$_{x}$I$_{1-x}$)$_{3}$ powder compressed within helium-loaded DACs. This experiment was repeated from ambient conditions to pressures at which the PL disappeared. Compiled spectra at four selected pressures are shown for the $x = 0.6$ material in Figure 6. At 0.2 GPa the PL band redshifts and increases in intensity with increased duration of light exposure, similar to its ambient-pressure behavior. At 0.6 GPa, however, a second, higher-energy peak (hereafter designated as peak 2) is visible, which is invariant with light soaking. The lower-energy peak (peak 1) still redshifts with light exposure. Upon increasing pressure to 0.7 GPa, peak 1 is barely visible and peak 2 has increased in relative intensity. At 0.9 GPa only peak 2 is visible and above ca. 1.6 GPa no PL is visible from the sample. Importantly, the energy to which peak 1 redshifts with light exposure increases with increasing pressure. We see similar behavior in the $x = 0.4$ and 0.2 materials.

Our results suggest that peak 2, which is only visible at high pressures, may arise from the native material where halide segregation is suppressed by lattice compression. Furthermore, even when considering peak 1, higher-energy steady-state PL is obtained at higher pressure. The formation of low-energy trap states upon light exposure can impede the use of these mixed-halide perovskites in high-voltage solar cells. Although application of very high pressures may be impractical, our results show that some amount of material compression can mitigate this PL redshift. This compression may be attained through mechanical or chemical means. For example, substitution of larger ions into the perovskite lattice induces steric compression that can mimic the effects of mechanical compression.

5) Identifying structural heterogeneity on the surfaces of (MA)PbI$_{3}$ crystals.
Through collaboration with researchers at Istituto Italiano di Tecnologia we also showed that the photoluminescence emitted from edge sites of (MA)PbI$_3$ single crystals differ from that of the bulk.[55] The higher-energy PL observed from the crystal edges more closely matches the PL originating from perovskite films. This suggests that lattice reconstructions at crystal edges (and at grain boundaries) in these perovskites lead to a widening of the optical bandgap. We find that this inhomogeneity is further enhanced when the crystal is exposed to humidity, as water intercalates into the material as the first step to hydration-induced decomposition. This PL signature from moisture-exposed surface sites can serve as the first indication of material decomposition.

Figure 19: Microscopic PL spectra recorded at edge sites of a single crystal show a blue shift in energy, which intensifies when the crystal is exposed to moisture. Figure from reference 55.

Conclusions

We have fabricated 4-terminal hybrid tandem solar cells which comprise of a semi-transparent perovskite solar cell stacked on top of a CIGS or silicon solar cell. The semi-transparent perovskite solar cells have power conversion efficiencies of over 12%. When combined with commercial-grade CIGS solar cells we have achieved power conversion efficiencies of over 18%. This work has enabled the development of the first monolithic silicon-perovskite tandem solar cells that have so far achieved over 13% power conversion efficiency.[56] There are now many research groups developing these kinds of tandems and pushing them towards commercialization.

Our discovery of hysteresis and light-induced phase segregation in perovskites with mixed halides identified two significant problems that needed to be addressed by the perovskite community and have been a very valuable contribution to this community. Our suggestions for how to accurately measure the efficiency of perovskite solar cells are now widely used and researchers are careful to avoid compounds that undergo light-induced phase segregation.

We have made substantial advances in understanding degradation pathways in perovskite solar cells due to the presence of electrical bias, light and moisture. The results we obtained in the first year of our GCEP-funded research enabled us to obtain additional funding from the Department of Energy. With those funds, we have gone on to improve the stability of perovskite solar cells by many orders of magnitude by replacing methylammonium with cesium, replacing the silver nanowire electrodes with indium tin oxide and using industry standard packaging.
With GCEP support over the past 3 years we have identified and proposed solutions for the intrinsic instability and toxicity of the 3D perovskites (MA)PbX₃ (X = Br or I). We provided the first demonstration that 2D perovskites can serve as solar-cell absorbers with enhanced moisture stability compared to the 3D perovskite (MA)PbI₃. We also first identified that double perovskites can be used to substitute nontoxic bismuth for lead. Our preliminary photophysical investigations show that the bismuth double perovskite has long carrier recombination lifetime and much higher stability to heat and moisture compared to (MA)PbI₃, which is very promising for photovoltaic applications. Despite the massive interest in perovskite photovoltaics, the AⅡBⅡⅢX₃ (X = halide) lattice has proved restrictive for incorporating stable and nontoxic metals. Double perovskites of the form A₂BB’X₆ provide a more accommodating platform for substitutions. Our studies show that inorganic and hybrid halide double perovskites should be further investigated for photovoltaic and other optoelectronic applications.

We have performed preliminary optical and cost calculations on using perovskite solar cells in hybrid tandems to “upgrade” a conventional silicon solar cell. Monolithically adding a few material layers of the perovskite solar cell on top of a conventional 20% efficient silicon device can increase the device efficiency to over 25% and potentially at an additional cost of only $10-14/m². Assuming that the stability of perovskite solar cells can be improved, perovskite hybrid tandem solar cells have the potential to decrease the cost-per-watt of the current largest market-share solar cells, accelerating the world-wide adoption of solar energy and reducing green-house gases.

Professor McGehee and Colin Bailie founded Iris PV to commercialize tandems with perovskite on top of silicon. Colin has won the Forbes 30 under 30 Award and was selected for the second cohort in the Cyclotron Road startup incubator program at the Lawrence Berkeley Laboratory.

**Publications and Patents**


Presentations

McGehee

Karunadasa
3. 41st International Conference on Coordination Chemistry (ICCC41), Singapore, July 2014.
4. National University of Singapore, Department of Chemistry, August 2014.
7. 80th Israel Chemical Society Meeting, Tel Aviv, Israel, February 2015.
8. Weizmann Institute, Department of Materials and Interfaces, Israel, February 2015.
12. Nanyang Technological University, Energy Research Institute, Singapore, August 2015.
17. Pennsylvania State University, Department of Chemistry, March 2016.
19. Texas A&M University, Department of Chemistry, April 2016.
References


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