

# Novel inorganic-organic perovskites for solution processable photovoltaics

## Investigators

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## Abstract

We have fabricated 4-terminal hybrid tandem solar cells which comprise of a semi-transparent large bandgap  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite solar cell stacked on top of a smaller bandgap 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 and some silicon solar cells, the tandem produces more power than the CIGS or silicon solar cell by itself. In order to raise the open circuit voltage produced by the perovskite solar cell in a hybrid tandem, we have raised the bandgap of the perovskite by gradually replacing iodide with bromide. We have investigated the optical and structural properties of these perovskite alloys and have used them to make working devices. As the toxicity of lead in these perovskites is a potential challenge for manufacturing and consumer adoption of perovskite solar cells, we have investigated the properties of a family of non-toxic tin-based perovskites,  $\text{CH}_3\text{NH}_3\text{Sn}(\text{Br}_x\text{I}_{1-x})_3$ . We have identified that these materials are highly unstable to oxygen and have short carrier lifetimes of less than a nanosecond, making them less suitable for photovoltaic applications. As solar cells with perovskite absorbers reach commercially viable efficiencies, their stability to manufacturing and operating conditions must also be considered. We have investigated the stability of thin films of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  to moisture and find that they decompose upon exposure to relative-humidity levels as low as 11% over several days. We are functionalizing the organic groups in these materials and have identified modifications that result in improved moisture resistance.

## Introduction

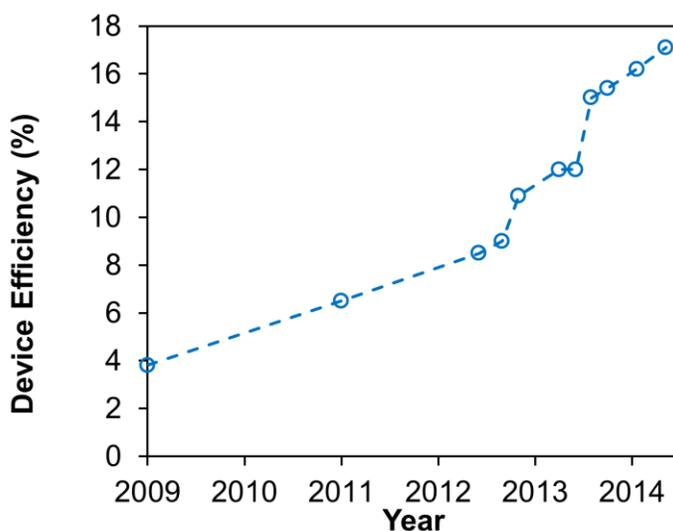
The objectives of this work are to design, synthesize and characterize new families of inorganic-organic perovskites for the application of low cost, hybrid tandem photovoltaics with efficiencies above 25%. For this application, the perovskite device needs to obtain high power conversion efficiencies 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  $\text{CH}_3\text{NH}_3\text{PbI}_3$  have in the past few months achieved certified power conversion efficiencies of over 17% in the laboratory (Figure 1).[1] Much of the progress in the past year can be attributed to optimization of the processing of perovskite material to improve the film morphology. Notably, the Grätzel group at EPFL found that the perovskite material could be more uniformly and consistently deposited in a two-step process where a precursor  $\text{PbI}_2$  is first spin-cast and then converted to the perovskite by exposing the film to solutions of  $\text{CH}_3\text{NH}_3\text{I}$ . [2]

The understanding of perovskites as a photovoltaic material has also advanced considerably in the past year. Perovskite devices based on  $\text{CH}_3\text{NH}_3\text{PbI}_3$  can be considered to be p-i-n heterojunction solar cells where the perovskite acts as the intrinsic light absorber. The perovskite material predominately generates free carriers which can have long carrier lifetimes of 300 ns and diffusion lengths exceeding  $1 \mu\text{m}$  in polycrystalline thin films.[3] In our lab we have measured an upper bound of 70 cm/s for the surface recombination velocity in the perovskite. Band structure calculations have indicated that the origin of these impressive carrier lifetimes and diffusion lengths are likely due to the lack of deep trap defects with low formation energies which would act as recombination sites.[4] The defect tolerance of the perovskite  $\text{CH}_3\text{NH}_3\text{PbI}$  enables the material to achieve a high open circuit voltage of 1.07 V with its moderate bandgap of 1.6 eV. The large open circuit and high efficiencies of these perovskite devices make them excellent candidates for the large bandgap junction in a hybrid tandem solar cell.



**Figure 1:** Efficiency of record lab-scale perovskite devices.

## Results

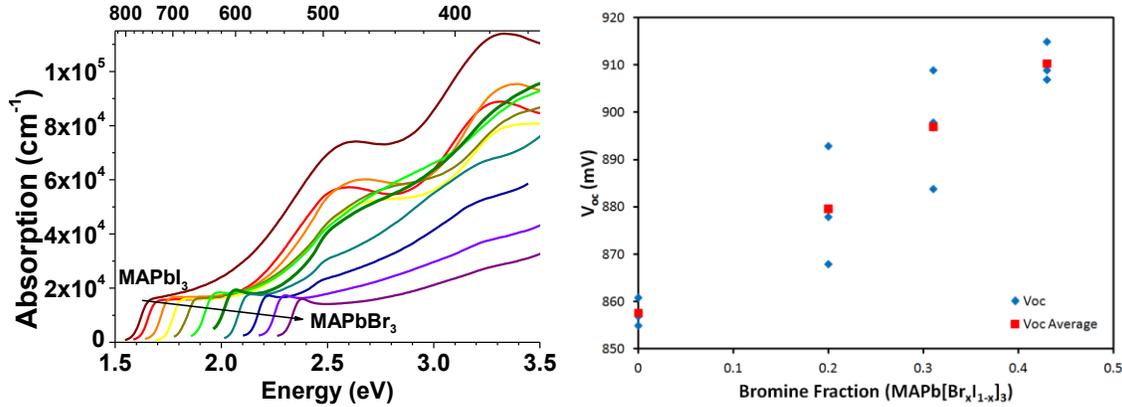
In this report we will highlight our work to increase the bandgap and open circuit voltage of perovskite solar cells by halide substitution, the investigation of the properties of a family of tin perovskites as a non-toxic replacement for lead, and the stability and device performance of perovskites with modified organic cations. A manuscript describing the details of the work engineering 4-terminal hybrid tandems with semitransparent perovskite solar cells is currently under peer-review and is available to GCEP sponsors upon request.

### *Bandgap tuning of $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ perovskites:*

The bandgap of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  can be gradually increased by replacing iodide with increasing amounts of bromide. Since the bandgap of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (1.6 eV) is smaller than optimal for the large bandgap junction of a tandem solar cell with silicon or CIGS ( $\sim 1.8\text{eV}$ ), mixed perovskites of the formula  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ , can potentially result in a larger open circuit voltage as well facilitate current matching in a tandem solar cell.

We have performed diffuse reflectance and transmission measurements on thin films of  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$  of varying halide content as well as highly sensitive photothermal deflection spectroscopy (PDS) measurements to determine the absorption coefficient above and below the bandgap (Figure 2, left). We find for all compositions studied that there is a sharp absorption onset, which suggests that the material is homogenous and does not contain substantial minority phases with lower bandgaps that would act as detrimental traps in a solar cell. X-ray diffraction studies on thin films and single crystals of  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$  over varying compositions also indicate that the alloys contain a single phase.

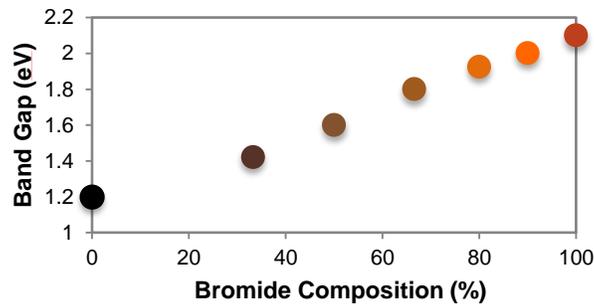
$\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$  mesoscopic devices were fabricated using a two-step dip-conversion process of the perovskite material analogous to the procedure developed by Burschka et al.[2] These devices have the architecture: fluorine-doped tin oxide (FTO)/compact titania/mesoporous titania/perovskite/spiro-OMeTAD/gold. The perovskite material was deposited by first spincoating  $\text{PbI}_2$  and then soaking the films in solutions containing mixtures of  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{CH}_3\text{NH}_3\text{Br}$  in isopropanol to convert the  $\text{PbI}_2$  into the mixed-halide perovskites. The stoichiometry of the mixed perovskite formed in this manner was determined by comparing the absorption and XRD spectra to thin films of  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$  deposited from known stoichiometric solutions in a single step process. The final stoichiometry of the dip-converted mixed perovskite films was found to depend upon the solution mixture of  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{CH}_3\text{NH}_3\text{Br}$  as well as the soaking time. We were able to fabricate devices with moderate photovoltaic power conversion efficiencies of 8-10.5% over the stoichiometric range  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ ,  $x=0-0.4$ . The open circuit voltage was found to increase with increasing bromine content, though by a smaller amount than expected from the change in optical bandgap (Figure 2, right). We are currently investigating whether contacts or defects in the perovskites may be limiting the voltage in these mixed  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$  devices.



**Figure 2:** (Left) Absorption coefficient of mixed perovskites  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$  and (right) open circuit voltage obtained by mixed perovskites fabricated in a two-step conversion process.

*Properties of non-toxic tin perovskites:*

The acute toxicity of lead is a concern for the scale up and commercialization of the perovskite solar cell technology. This, coupled with the novelty of perovskite photovoltaics in general, motivates the investigation of other non-lead perovskite materials for solar cells. With this aim, we began our investigation for lead replacements by investigating the  $\text{CH}_3\text{NH}_3\text{Sn}(\text{Br}_x\text{I}_{1-x})_3$  perovskite.



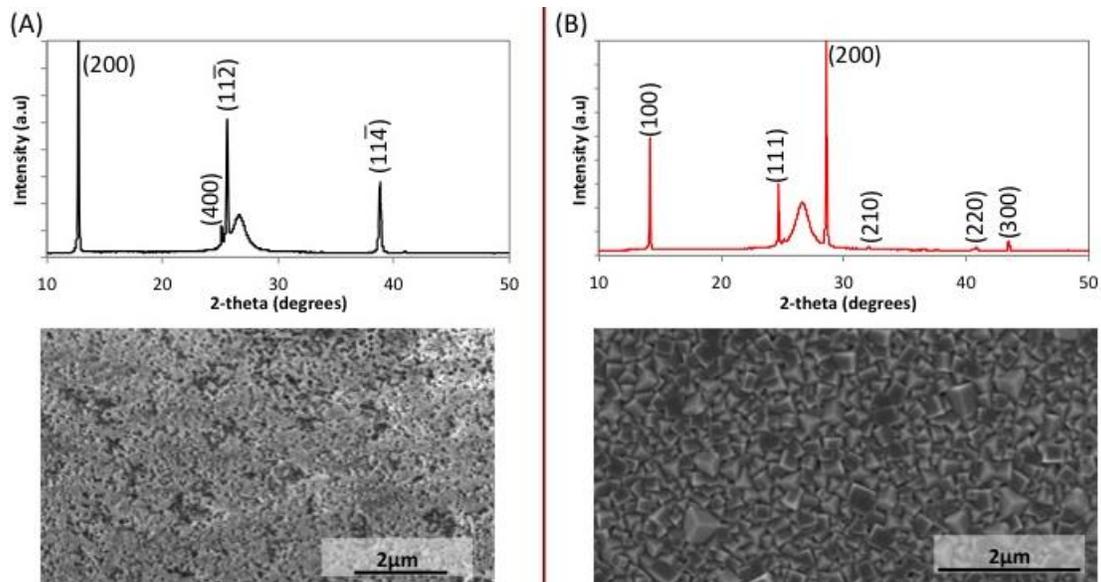
**Figure 3:** Control of band gap by bromide composition in  $\text{CH}_3\text{NH}_3\text{Sn}(\text{Br}_x\text{I}_{1-x})_3$  perovskites.

Before developing the processing of the perovskite material for thin film and device application, we first demonstrated we could synthesize the  $\text{CH}_3\text{NH}_3\text{Sn}(\text{Br}_x\text{I}_{1-x})_3$  family perovskites (Figure 3). Similar to the lead compounds, the band gap of the absorber can be tuned by varying the bromine content in the perovskite, from 1.2-2.1 eV.

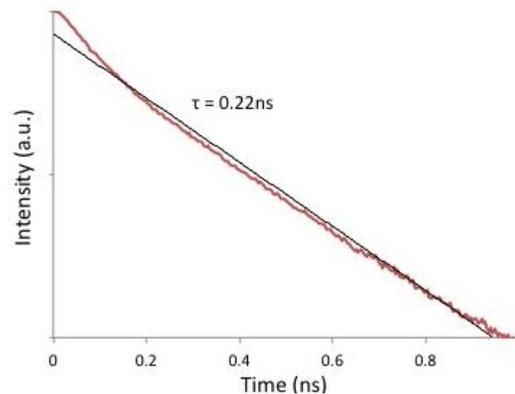
For a single junction solar cell, the maximum theoretical efficiency can be achieved with a ~1.4 eV band gap absorber, which would correspond to a perovskite with the composition  $\text{CH}_3\text{NH}_3\text{SnI}_2\text{Br}$ . These films appear to absorb strongly and are therefore a good candidate as a lead replacement when considering these optical properties. Moving forward we would want to incorporate these mixed-halide perovskites into devices,

however for the ease of processing we have been on our efforts focusing on the  $\text{CH}_3\text{NH}_3\text{SnI}_3$  perovskite.

A variety of thin film processing techniques have been demonstrated for the synthesis of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films. One that has been notably successful is the dip-conversion of  $\text{PbI}_2$  to the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite by immersion in a solution of  $\text{CH}_3\text{NH}_3\text{I}$ . We have successfully applied a similar processing technique to the tin perovskites to synthesize thin films of the  $\text{CH}_3\text{NH}_3\text{SnI}_3$  perovskite. Evidence of complete conversion of the precursors can be evaluated by X-Ray Diffraction (Figure 4). From SEM it is clear that we can get uniform coverage of the film by first evaporating  $\text{SnI}_2$  and then dipping the films into  $\text{CH}_3\text{NH}_3\text{I}$ , forming perovskite crystals hundreds of nanometers in size (Figure 4). This uniform coverage will be an asset when we make devices, preventing the formation of pinholes through the device where there are gaps in the absorber.



**Figure 4:** X-ray diffraction spectra and scanning electron micrographs before evaporated  $\text{SnI}_2$  films before (A) and after (B) dip-conversion to the full perovskite  $\text{CH}_3\text{NH}_3\text{SnI}_3$ .



**Figure 5:** Decay in photoluminescence of  $\text{CH}_3\text{NH}_3\text{SnI}_3$  (red) and fit (black) for a charge carrier lifetime of 0.22 ns.

Beyond the correct band gap and good absorption properties, the materials must have good electrical properties as well. Chief among those properties is charge carrier lifetime, which is essential for both extracting photogenerated charges and reducing the detrimental effects of dark current on the Voc. To evaluate the charge carrier lifetime we performed time-resolved photoluminescence measurements on dip-converted  $\text{CH}_3\text{NH}_3\text{SnI}_3$  films. The results show charge carrier lifetimes of 0.22 ns (Figure 5), three orders of magnitude shorter than the charge carrier lifetimes of the lead-containing compounds.

At this time it remains unclear why the lifetimes of the tin perovskite are so much shorter than those of lead, but until resolved it is unlikely that tin can be utilized as a less-toxic alternative in perovskite solar cells. One potential reason for this discrepancy is a variation in the number of defects or defect energies for the tin samples as compared to their lead counterparts. Since defects serve as traps for recombination, if we can reduce the number of defects in our films we should be able to improve the carrier lifetimes.

To this end we will be pursuing alternative synthesis techniques, such as solvent annealing, to improve the film quality of the  $\text{CH}_3\text{NH}_3\text{SnI}_3$  materials. Additionally, we will continue to pursue other non-lead absorbers in addition to the tin perovskites. One promising alternative is to incorporate Bismuth into the structure as it is of a similar size to lead, which is important as steric effects have large impacts on the optoelectronic properties of the material.

Along with developing absorbers containing less toxic materials, we are also working on optimizing the lead-based perovskite absorbers. 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. We are functionalizing the organic groups in these materials to improve their moisture resistance.

### **Progress**

We have already 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 and some silicon solar cells, the tandem produces more power than the CIGS or silicon solar cell by itself. 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/m<sup>2</sup>. Hybrid tandem solar cells utilizing perovskite 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 greenhouse gases.

## Future Plans

The toxicity of lead and the stability of perovskite materials containing CH<sub>3</sub>NH<sub>2</sub> to moisture are significant challenges that may need to be overcome in order to commercialize perovskite hybrid tandem solar cells. We are functionalizing the organic groups in these materials to improve their moisture resistance. We are beginning to investigate perovskite materials based on germanium as well as bismuth to replace lead. We are also developing one-step deposition methods for forming continuous films of perovskites which may result in improved film quality and device performance. These processes also avoid the multi-step conversion process of forming the perovskite and high-temperature vapor annealing steps, which may be less suitable for large scale manufacturing.

## Publications and Patents

1. Hoke, E.T. *Charge Recombination and Transport in Hybrid Perovskite Solar Cells*, Oral presentation at the Materials Research Society Fall Meeting, Boston, December 2013.
2. McGehee, M.D. *Optimizing Perovskite Semiconductors for Tandem Solar Cells*. Invited talk at the Materials Research Society Spring Meeting, San Francisco, April 2014.

## References

1. Park, N.G. *Smart Photovoltaic Material: Organolead Halide Perovskite*. Materials Research Society Spring Meeting, San Francisco, April 2014.
2. Burschka, J.; Pellet, N.; Moon, S.-J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Gratzel, M. *Nature* **2013**, *499*, 316.
3. Stranks, S.D. et al. *Science* **2013**, 341-344.
4. Yin, W.-J. et al. *Appl. Phys. Lett.* **2014**, *104*, 063903

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