

## What's Holding Back Perovskite Photovoltaics?

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### Background

Fossil fuels, in addition to being a limited resource, are a major contributor to anthropogenic climate change.<sup>1</sup> As a primary use of fossil fuels is for electricity generation, one method to combat climate change is to replace electricity from fossil fuels with electricity from low-carbon sources such as photovoltaic (PV) cells. In the semiconductors which comprise the working part of a PV cell, there are two electronic bands of interest. The valence band is mostly or entirely filled, while the conduction band is mostly or entirely empty, and these bands are separated in energy by an amount known as the band gap. When a photon of sufficient energy strikes the surface of the material, an electron from the valence band is promoted into the conduction band, leaving behind a positively-charged hole, and this newly-mobile electron and hole are harvested for energy generation.<sup>2</sup>

This photovoltaic effect consists of two basic steps, first, charge separation by light absorption, and second, transport and harvesting of the charge.<sup>2</sup> The primary PV cell in use today is based on doped silicon, and although it is efficient at charge transport, silicon has a low absorption coefficient for the photons of interest.<sup>3</sup> This has led to the development of dye-sensitizers, compounds with a higher absorption coefficient which can be coupled with the silicon cell. Although the original dye-sensitizers were organic compounds,<sup>4,5</sup> interest has shifted towards lead perovskites, namely methylammonium lead(II) triiodide  $\{(\text{CH}_3\text{NH}_3^+)\text{PbI}_3\}$ , since the discovery of their photovoltaic properties in 2009.<sup>6</sup> This increase in absorption is largely due to the perovskites having a direct bandgap, whereas silicon has a phonon-mediated indirect bandgap.<sup>7,8</sup> These perovskite sensitizers have many advantages over traditional solar cells, namely that they can be manufactured using currently-available techniques, and allow for the use of less silicon within a cell, while having higher effective absorption cross-sections than identically-sized silicon cells.<sup>8</sup>

### Water Sensitivity

A major impediment to the implementation of dye-sensitized solar cells is the water sensitivity of  $(\text{CH}_3\text{NH}_3^+)\text{PbI}_3$ , which is due largely to the hygroscopicity of the methylammonium ion. However, this ion rests in the cuboctahedral cavity formed from  $\text{PbI}_6$  octahedra which share corners (Figure 1) and is already approaching the size limit of the cavity, making substitution nontrivial. By only connecting the  $\text{PbI}_6$  octahedra in two dimensions, a more hydrophobic ion, such as (2-phenylethyl)ammonium (PEA), can be substituted. However, this creates a layered structure which imposes penalties on charge transport.<sup>8</sup>

As a compromise between these considerations, the octahedra can be connected in all three dimensions, but for a very limited number of layers ( $n=2, 3$ ) in one direction, giving rise to the mixed PEA/methylammonium structure shown in figure 2.<sup>8</sup> This substituted perovskite remains unaffected after 46 days of exposure to 52% humidity, while the original perovskite has completely decomposed under these conditions. However, at 66% humidity, the PEA/methylammonium perovskite shows significant decomposition after 9 days. To combat this, the authors substituted the PEA ion for its monofluorinated analog, (2-(4-fluoro)phenylethyl)ammonium (FPEA), which shows even greater water resistance.

Unfortunately, these modified perovskites have an efficiency of only ~5%, compared to the 22% of the original, and it remains to be seen whether this limitation can be overcome.<sup>8</sup>

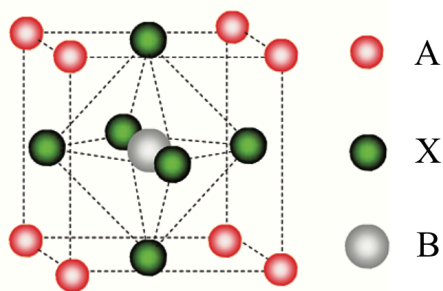


Figure 1: The perovskite structure

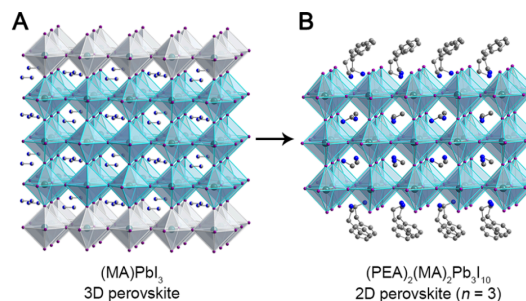


Figure 2: Relationship between 3D and 2D perovskite

### Issues of Composition

Even if issues of water sensitivity are overcome, the presence of lead makes development unattractive. It would be desirable to develop compounds with similar absorptive properties, but less toxicity and environmental persistence. To this end, Cortecchia *et al.* developed a series of compounds of the form  $(\text{CH}_3\text{NH}_3^+)_2\text{CuCl}_x\text{Br}_{4-x}$ , where  $x$  is between 0.5 and 4.0.<sup>9</sup> Due to the size difference between copper and lead, these copper perovskites are two-dimensional irrespective of the cation used. This series exhibits peak absorbance ranging from 500 nm – 689 nm with increasing bromide concentration. This absorption is primarily a Ligand-Metal Charge Transfer, and longer absorption maxima are desirable to harvest more thermal photons.

However, a series of issues plague these lead-free perovskites. The crystal growth pattern places the layers of the structure parallel to the surface, while it would be desirable for the layers to grow perpendicular to the surface to facilitate charge transport. Additionally, the presence of the bromide ion causes reduction of some copper(II) centers to copper(I) during annealing, decreasing efficiency. Together, these effects lead to a sub 1% efficiency.<sup>9</sup>

Elements more similar to lead have also been investigated. Tin perovskites show PV properties, but tin(II) oxidizes easily to tin(IV), which does not have the desired properties. Bismuth(III) perovskites, in large part due to the higher charge, tend to crystallize in chains, impeding charge transport. Additionally, bismuth has a lower-energy conduction band than lead, leading to difficulties with hole transport above what is due to topology.<sup>19</sup>

### Summary

Lead perovskites offer a promising option for next-generation photovoltaic cells. Their water sensitivity impedes implementation, but cation substitution offers a partial solution, if efficiency lost by substitution can be regained. Other metals, such as copper, bismuth, and tin, have been investigated to replace the toxic lead, but copper and bismuth have low efficiencies, while tin is susceptible to oxidation.

### References

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