Performance-limiting processes in $Cs_2AgBiBr_6$ solar cells

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Highly-efficient perovskite solar cells contain the heavy metal lead. One way to avoid lead consists of employing double perovskite materials. One of the most common representatives in photovoltaics research is $Cs_2AgBiBr_6$, so far commonly yielding power-conversion efficiencies below 5%. Although the potential of this material as an absorber in solar cells is limited due to an absorption onset above 2 eV, it is a highly interesting optoelectronic material. Understanding its properties might contribute to pave the way for the development of further lead-free perovskite(-similar) materials.

In this contribution, the performance-limiting factors in $Cs_2AgBiBr_6$ solar cells are discussed based on a temperature-dependent study of the optoelectronic properties. The findings are very distinct from the lead-halide perovskites, which can be described as a semiconductor, where e.g. the common reciprocity relations are applicable.

The large Stokes shift between absorption (peak at 2.8 eV) and emission (peak at 2.0 eV) of $Cs_2AgBiBr_6$ and the broad emission were early observations that gave rise to still ongoing debates. We find that it is indeed not straight-forward to employ reciprocity relations to deduce radiative open-circuit voltage (Voc) limits from sensitive measurements of the photocurrent onset. Fitting a Gaussian allows to calculate a radiative Voc limit of 1.95 V and roughly reproducing the photoluminescence (PL) spectra. However, using an exponential fit, a strongly temperature dependent Urbach energy with a value of ca. 50 meV at room temperature can be found. Furthermore, the PL, which increases by two to three orders of magnitude when decreasing the temperature to 100 K, can be separated into two peaks: One (630 nm), whose shape is hardly affected by temperature similarly to the absorption peak and a second one further in the red (670 nm) that shows a stronger temperature dependence. The first confirms earlier suggestions of a rather localized excitonic transition in contrast to a transition between a valence and conduction band of the crystal. Since the absorption peak remains mainly unaffected by temperature as well, this indicates the same origin of absorption and PL despite the large shift. Temperature-dependent photocurrent and -voltage that strongly drop for temperatures below 200 K indicate that charge separation requires temperature activation. From impedance spectroscopy, we deduce a dielectric constant of 21, which indicates efficient charge screening. Analyzing light- and temperature dependent open circuit voltage data in the range above 250 K allows for a linear extrapolation to values at 0 K, which are strongly dependent on the illumination intensity. The open-circuit voltage is limited by non-radiative recombination as electroluminescence yields of 1e-8 show, where interestingly the EL spectrum is further redshifted compared to the PL. One part of the rather low Voc of 1.1 V can be explained by poor contact selectivity as voltage-dependent external quantum efficiency measurements indicate. Also scan-rate dependent current-voltage curves unravel slow processes that counteract efficient charge collection. Adding a 2D perovskite layer on top of the 3D one could slightly attenuate these losses.

The overall goal of this contribution is to put above mentioned observations into perspective also in comparison to the lead-halide perovskites and stimulate discussions regarding their origins and consequences.