

## Bandgap Tuneability for High-Voltage Lead-Halide Perovskite Materials

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Organic-metal halide perovskite materials have after just a few years of intensive research reached energy conversion efficiencies of 22%. [1] These solution-processable materials have ideal properties to develop efficient hybrid tandem devices concepts and other high-bandgap/high-voltage applications, which is the most promising technological application for evolving photovoltaic materials. [2,3] Lead halide perovskite semiconductors can very feasibly be tuned by chemical substitution and alloys, allowing the exploration of a wide parameter space of metal halide perovskite compounds with the generalized formula:  $ABX_3$  with  $A = Cs, Rb, MA, FA$  or a mixture of these monovalent cations,  $B = Sn, Pb$ , or a mixture of those, and  $X = Cl, Br, I$  or a mixture of halides.

Comparing a reported experimental values suggests that metal halide perovskites are a class of semiconductors with complete bandgap tunability ranging from 1.2 eV for  $MA(Sn_zPb_{1-z})I_3$  to about 2.3 eV for  $MAPbBr_3$  and even higher energies for Cl-containing compounds. There are, however, apparent deviations of the expected trends in the experimental data sets suggesting the existence of a miscibility gap or fundamental thermodynamic instability of compounds comprising halide mixtures. Hoke et al. first described photo-induced phase-segregation effects [4] indicated by the formation of lower-energy emitting sites during steady state photoluminescence measurements. There is an ongoing debate in the literature whether these low-energy sites are present in materials as-prepared or dynamically formed due to photo-induced ion migration phenomena. Theoretical calculations predict a thermodynamic limitation of the miscibility in  $AB(Br_xI_{1-x})_3$  alloys. [5] The consequence for solar cell devices is that the compositional range exhibiting photo-induced ion migration effects coincides with a drop in the photoluminescence quantum yield [6] limiting the open circuit voltage due to these lower energy sites determining the quasi-Fermi levels for electrons and holes in these materials. Figure 1 shows an overview of reported power conversion efficiencies as a function of the perovskite absorption onset. This graph on the one hand shows, how close reported device efficiency metrics are to theoretically limiting efficiencies indicated in grey (assuming 100% IQE, no absorption losses and minimal voltage losses of 0.3 eV).

To understand the limited band gap miscibility, we performed in-situ UV-Vis experiments monitoring the absorption spectrum of as deposited films during annealing. For bromide ratios of  $> 0.5$  and  $< 1$  in  $MAPb(Br_xI_{1-x})_3$ , the spectral signature of wet-films indicate the presence of a mixed precursor phase from which a bromide and an iodide rich phase crystallize out in the initial stages of the annealing process. Annealing causes ions to some extent to equilibrate but the presence of a small amount of residual low-energy phases impurities or a phase gradient is prone to remain in the samples as prepared.

The presence of lower energy sites by themselves however is not sufficient to explain the evident increase in phase segregation observed under illumination. As this effect [4] is a function of the illumination intensity and pulse repetition rate, it has been suggested that the underlying driving force for ion migration is the presence of photo-induced polar states that are long lived.[7] While having been referred to as “polarons” it is currently unclear what exact physical state these states are and whether they would also be present in all types of halide perovskite semiconductors creating local fields in the absorber layers that have also been postulated to transient effects in the solar cell device response. Slow transient phenomena have giving rise to hysteresis effects and ion migration under device operation is an important failure mechanism to be considered in the reliability of ABX<sub>3</sub> based solar cell devices.

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