

Organo-metal-halides: dynamic materials for solar energy conversion

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Organo-metal-halides are still a soaring and exciting field of research. Certified power conversion efficiencies of 20% have been achieved after a very brief period of intensive research. This family of semiconductor materials holds great potential for single junction and tandem photovoltaic technology. Still, many of the underlying material properties that have led to their break-through in photovoltaics are just beginning to be understood. This presentation will summarize various different findings of dynamic changes in organo-metal-halides when exposing these materials to light, heat and bias. These phenomena are of significant magnitude and play a role in the current-voltage hysteresis observed in solar cells based on organo-metal-halides,^{1,2} photo-induced ion migration phenomena,³ changes and degradation of the material when exposed to light, heat and ambient atmosphere⁴ as well as intermittent photo-induced curing of defect states.^{5,6} Dynamic changes in the intrinsic material properties such as polarization, defect state density distribution and material composition present a challenge to study these materials and are the cause for large discrepancies between results obtained in different research laboratories.

Hysteretic phenomena in current-voltage measurements of organo-metal-halide perovskite solar cells have been linked to bias-induced changes in the device polarization affecting the charge carrier generation efficiency. Stricter requirements for reporting solar cell device data have been imposed by scientific journals but the origin of hysteresis and the effect of selective contacts and intrinsic material quality are still not fully understood. We recently proposed time-resolved staircase voltammetry measurements as a mean to both assess sufficiently long delay times to perform current-voltage measurements under steady-state conditions but also found that solar cells based on organo-metal-halides exhibit transient phenomena on various different time-scales and might never be in true equilibrium.²

For their use in hybrid tandem solar cells, organo-metal-halides with higher bandgaps are being investigated. Mixed bromide-iodide compounds of methylammonium-lead-halides can be feasibly obtained. Thermal annealing was found to be not only important as a drying step but directly affect the ionic heterogeneity of the mixed halide compounds leading to the formation of close to fully mixed single bandgap phases (subject of master thesis conducted under my

supervision). Illumination of the mixed halide compounds however, led to the segregation of phases³ indicative of ion migration caused by either the activation energy provided or an electric field generated in the material upon light absorption.

Organo-metal-halide compounds are intrinsically very sensitive to heat, light and ambient atmosphere and are found to rapidly degrade. Even moderate temperatures of 100°C cause methylammonium iodide to evaporate over time leaving causing a degradation to lead iodide. Subjecting samples to heat and light simultaneously resulted in an accelerated degradation with lead oxide being the possible degradation product. Polymeric encapsulation layers of PMMA were found to slow down degradation by preventing exposure of samples to ambient atmosphere and creating a physical barrier to the evaporation of methylammonium iodide. Furthermore, we found that even the deposition of the polymer layer and storage of samples in the dark may affect the samples microstructure and charge carrier dynamics dramatically.⁷

In spectroscopic studies of organo-metal-halide samples, we found the preparative methods and conditions employed to deposit the samples to critically affect the charge carrier dynamics. Mechanical scratching leads to the disintegration of methylammonium lead iodide into small crystallites that exhibit strong enhancement of the photoluminescence when illuminated continuously under oxygen atmosphere. This indicates photo-induced curing of defect states in these materials decreasing non-radiative recombination.

All in all, there are still many aspects of organo-metal-halide semiconductors that are not understood and need to be investigated further to make reliable predictions about their long-term stability and suitability for the technological applications.

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