Chlorine and the kinetics of formation of $CH_3NH_3PbI_{3-x}Cl_x$ for perovskite solar cells

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The inclusion of chlorine has been shown to improve carrier diffusion lengths in methylammonium lead triiodide perovskite films ($CH_3NH_3PbI_{3-x}Cl_x$) [1], though the cause of this improvement is not understood.

We have investigated the amount of Cl and its chemical state in $PbCl_2$-derived perovskite films throughout the annealing process. This was done through the use of in-situ X-ray absorption near edge spectroscopy (XANES) and X-ray fluorescence (XRF) at the Cl K-edge. Films were prepared in a nitrogen glovebox; in-situ XANES and XRF measurements were then performed while the films were annealed in a helium environment.

We have previously reported that Cl leaves the film during annealing through sublimation of MACl [2] and that the final amount of Cl in the film corresponds to x=0.05 Cl atoms per Pb atom [3]. In this new study, we have used in-situ XRF to elucidate the kinetics of Cl evolution. Along with in-situ XRD measurements, we can compare these kinetics to the formation of the perovskite crystal. This combination of measurements reveals new insights about the formation of $MAPbI_3$ from the $PbCl_2$-derived precursor solution.

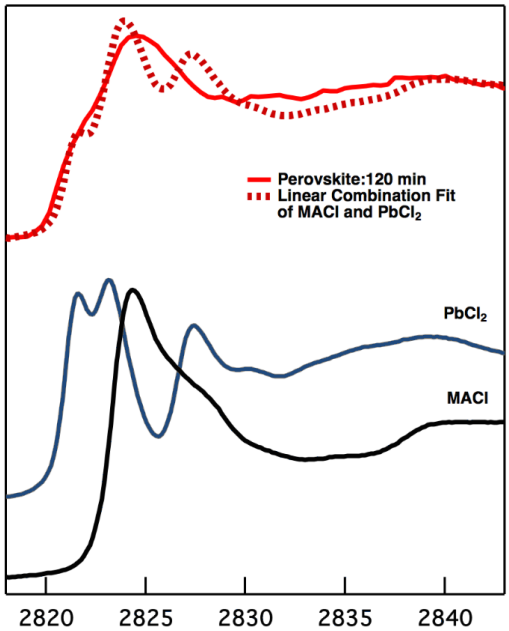

Figure 1: Linear combination fit of the standards MACl and $PbCl_2$ cannot express perovskite XANES

Linear combination fitting of XANES spectra can be used to determine whether an element in a sample matches a set of standards. It has been suggested that residual Cl may be unconverted $PbCl_2$ or unevaporated MACl. We have compared the XANES of fully converted perovskite to the standards $PbCl_2$ and MACl and have found that a linear combination of the standards is unable to express the perovskite XANES. Thus, the residual Cl in perovskite is not exclusively $PbCl_2$ and MACl (Figure 1).

References

[1] S. Stranks *et al*. *Science* (2013), 342, 341-344.
[2] E. Unger *et al*., *Chem. Mater.* (2014), 26, 7158-7165.
[3] Pool, Vanessa L., et al. *Chem Mater* (2015), 27, 7240-7243.