Monitoring Chlorine by X-ray Absorption Spectroscopy of $PbCl_2$-Derived Perovskite Films

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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]. Preparation from $PbCl_2$ has also demonstrated improved surface coverage and film uniformity as compared to films derived from PbI_2 [2], and it has been suggested that residual chlorine may have an effect on perovskite device electronics [3].

We have investigated the amount of chlorine 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) at the chlorine K-edge. A 1:3 mix of $PbCl_2$:MAI in DMF was spin-coated on FTO/c-TiO_2 in a nitrogen glovebox; in-situ XANES measurements were then performed while the films were annealed in a helium environment. The films were never exposed to ambient air.

We have previously reported that chlorine leaves the film during annealing through sublimation of MACl [4]. Through in-situ XANES, we observe the chlorine content decline consistently throughout the anneal before plateauing above zero. The amount of residual chlorine is estimated by comparison of chlorine and lead absorption edges. $CH_3NH_3PbI_{3-x}Cl_x$ films annealed at a range of temperatures are seen to plateau with a residual amount of chlorine ~x=0.05.

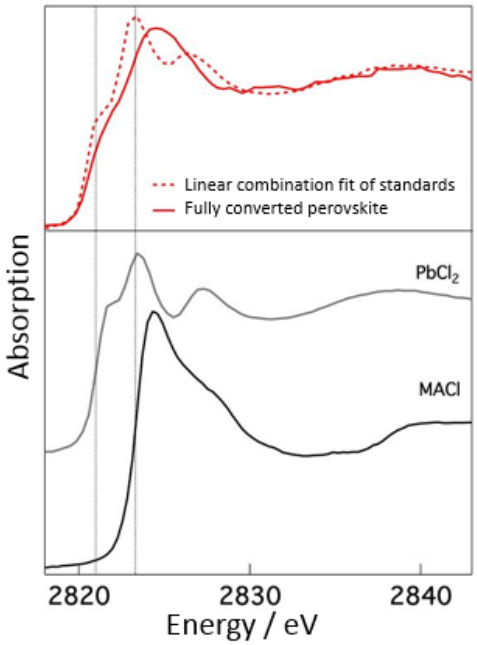

Figure 1: Linear combination fit of the standards MACl and $PbCl_2$ cannot express perovskite XANES

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 chlorine 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 chlorine in perovskite is not exclusively $PbCl_2$ and MACl (Figure 1).

References

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