Experimental report

17/10/2016

Proposal: 5-24-567 **Council:** 4/2015

Title: Hydration and dehydration of photovoltaic methylammonium lead iodide

Research area: Materials

This proposal is a new proposal

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Samples: Methylammonium lead iodide
CsPbI3

Instrument	Requested days	Allocated days	From	To
D20	4	4	13/11/2015	17/11/2015

Abstract:

Methylammonium lead iodide (MAPI) perovskite has generated frenzied interest in the field of alternative photovoltaics as a promising material for achieving the paradigm of the technology: simplicity of processing combined with outstanding optoelectronic properties. MAPI is sensitive to moisture, which may have both detrimental and beneficial effects depending on the context. We have recently studied this hydration behavior using powder X-ray diffraction and observed the formation of the monohydrate phase CH3NH3PbI3H2O but much of the process occurring takes place at the grain boundaries inside the bulk and film materials and is not observed via X-ray diffraction methods . This experiment will study the key phases found and produced in the MAPI-water reaction, initially as the bulk material (to fully elucidate structures including H-positions and bonding) and then to investigate the hydration/ dehydration of these materials both as bulk phases and then in situ as typical PV films. Crystallographic experiments will employ D20 in higher resolution mode and in situ experiments will use high flux mode to milligram quantities of these heavy metal iodide phases on thin film plates.

Introduction

Methylammonium lead iodide (MAPI) perovskite has generated frenzied interest in the field of alternative photovoltaics as a promising material for achieving the paradigm of the technology: simplicity of processing combined with outstanding optoelectronic properties. MAPI is sensitive to moisture, which may have detrimental or beneficial effects depending on the context. The presence of humidity during film processing has been shown to significantly influence thin film morphology and was claimed to lead to an improvement of the performance of solar cells. The aim of this experiment was to study the key phases found and produced in the MAPI-water reaction, initially as the bulk material (to fully elucidate structures including H-positions and bonding) and then to investigate the hydration/ dehydration of these materials both as bulk phases and then *in situ* as typical PV films**.**

Experiment

The experiment was undertaken as described in the submitted proposal. This included *in situ* work involving controlled humidity atmospheres and reactions. Preliminary results from parts of the experiment are summarized here.

1. ***Thermal decomposition of $(CH_3NH_3)_4PbI_6.2H_2O$ to MAPI.***

Diffraction patterns of $(CH_3NH_3)_4PbI_6.2H_2O$ (P21/n 10.42 11.33 10.67 Å 91.73°) were collected to refine structural parameters including hydrogen atom positions. The sample was loaded into an 8 mm Vanadium can. Initial measurements were carried out at room temperature (Figure 1). This sample was then heated to 350 K to induce dehydration and the kinetics of the response followed, with dehydration to $CH_3NH_3PbI_3$ observed (Figure 1).

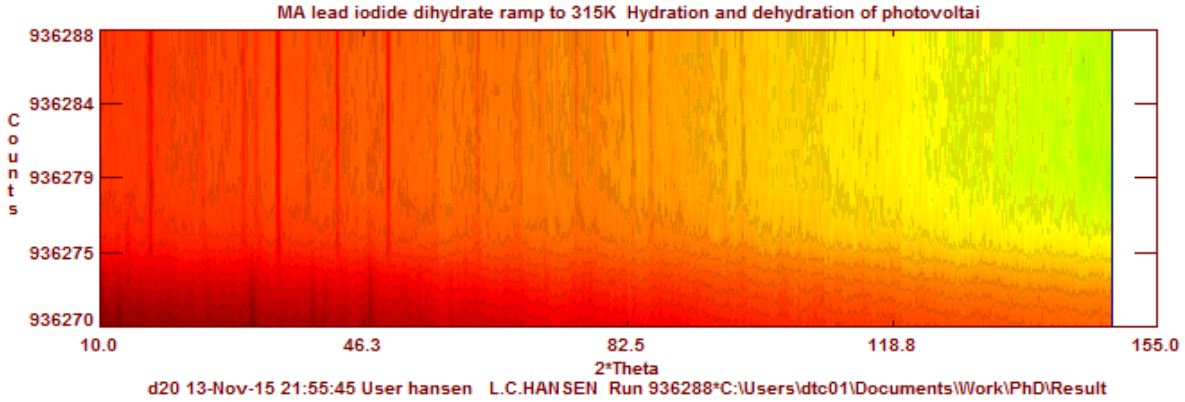

Figure 1. Stacked plot showing the thermal decomposition of $(CH_3NH_3)_4PbI_6.2H_2O$ to MAPI between 315 and 350 K

2. Structure and thermal decomposition of the monohydrate, $CH_3NH_3PbI_3.H_2O$

The monohydrate $CH_3NH_3PbI_3.H_2O$ was synthesised at the ILL and loaded into an 8 mm Vanadium can for measurement at 165 K, Figure 2, before ramping the temperature to 350 K to observe dehydration. Peaks of $MAPbI_3$ were clearly seen growing in by 315 K, Figure 3.

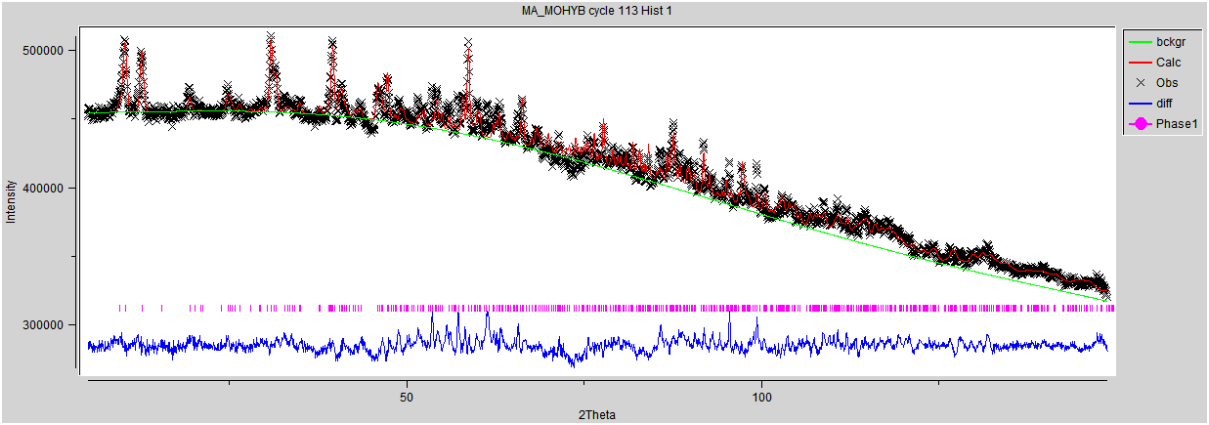

Figure 2 Rietveld refinement profile, in GSAS, for the monohydrate $CH_3NH_3PbI_3.H_2O$ using data collected at 165 K.

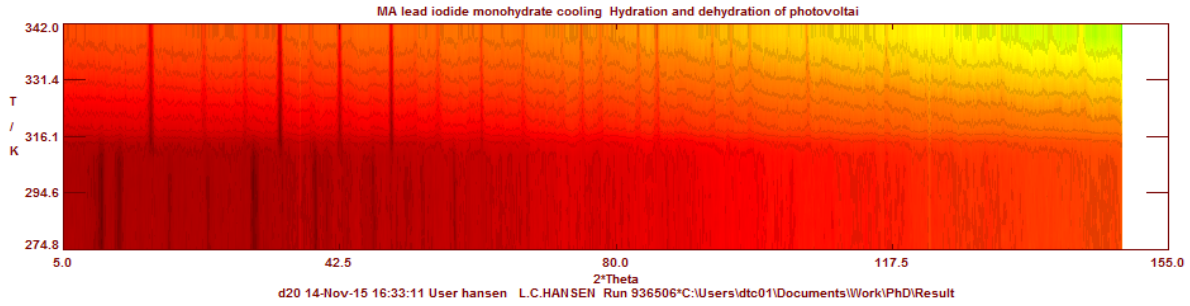

Figure 3. Stacked plot of heating MAPI monohydrate to 350 K at 10 K/min. MAPI peaks can be observed growing in as dehydration starts to occur near 316 K (43°C)

Summary

The experiment was successfully undertaken, following the proposal. Further analysis of the results is ongoing and will form the basis of future publications