



Hydrate Formation and Loss on the Hybrid Perovskite Methyl Ammonium Lead Iodide (MAPI)

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Hydration states of the hybrid perovskite methyl ammonium lead iodide (MAPI) is investigated using water vapour sorption and desorption measurements. Accurate water vapour sorption isotherms would play an important role in developing and protecting MAPI devices from moisture-induced damage.

Introduction

Hybrid perovskite methyl ammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$), are attracting an increasing interest due to their potential application in devices used for converting solar energy into direct current electricity. However, the real challenge is to develop devices, which work under different environmental conditions because MAPI may form monohydrate ($\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$) or dihydrate ($(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$) crystalline phases and the charge transport properties of MAPI devices would depend on the network of methylammonium ions and water molecules in these phases[1]. MAPI crystals in aqueous solution at temperatures below 40°C form the colorless monohydrated methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$). Pale yellow dihydrate crystals result when MAPI is cooled to below 40°C in a mother liquor of aqueous $\text{Pb}(\text{NO}_3)_2$ and methylammonium iodide solution. The presence of humidity has been shown to significantly influence the morphology and was claimed to lead to an improvement of the

performance of solar cells. However, the presence of water has also been suggested to catalyse the irreversible decomposition of MAPI into aqueous HI, solid PbI_2 , and CH_3NH_2 either released as gas or dissolved in water [2]. Consequently, the exposure of MAPI solar cells to a relative humidity greater than $\sim 50\%$ has rapid detrimental effects on device performances.

This paper describes how dynamic vapour sorption can be used to detect and characterize these hydrated phases as a function of environment relative humidity.

Method

Dynamic vapour sorption (DVS) is a well-established method for the determination of vapour sorption isotherms. The DVS instrument used for these studies measures the uptake and loss of vapour gravimetrically using a SMS ultra-balance with a mass resolution of $\pm 0.1 \mu\text{g}$. The high mass resolution and excellent baseline stability allow the instrument to measure the adsorption and desorption of very small amounts



of probe molecule. The vapour partial pressure around the sample is controlled by mixing saturated and dry carrier gas streams using electronic mass flow controllers. The temperature is maintained constant $\pm 0.1^\circ\text{C}$, by enclosing the entire system in a temperature-controlled incubator.

MAPI was prepared at Imperial College of London by Piers et al [1], using the procedures described in reference [3]. For the DVS experiments, 39mg of the sample was placed in the pan and initially dried at 0% RH for 5 h at 25°C to remove any residual moisture and then exposed to a series of stepped relative humidities ($\pm 0.5\%$). The experiment proceeded to the next RH step when the rate of change of sample mass fell below $\sim 0.002\%/\text{min}$ or ~ 3 h. The humidity was increased to 95% RH and then decreased in a similar manner for the desorption process. The experiment was repeated at 50°C .

Results

The moisture sorption kinetics for the MAPI sample over the 0 to 95% RH range at 25°C is displayed in Figure 1. The red line traces the percentage change in mass (based on the dry value) as a function of time, while the blue line traces the relative humidity as a function of time. The corresponding isotherm is shown in Figure 2, where the red line follows the sorption branch and the blue trace follows the desorption branch.

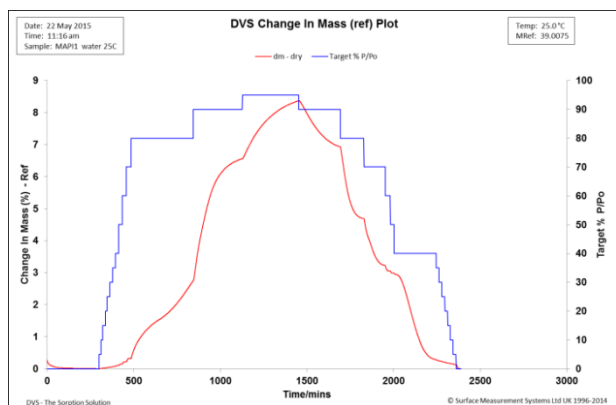


Figure 1. Water sorption kinetics for a MAPI dihydrate sample at 25°C .

During the initial drying stage, the mass loss is not significant indicating the starting material was the anhydrous form. MAPI monohydrate has a molecular weight of 637.9 amu and loss of one water molecule would represent a 3% weight loss (based on dry value, 619.9 amu). Considering that there is no mass loss during the initial drying stage the DVS data indicates that the starting sample is not in the hydrated state. From Figure 1, as the relative humidity increases to above 70% the moisture uptake increases significantly and reaches $\sim 8.3\%$ at 95% RH. During the desorption phase the sample mass decreases to 3.2% of the original mass at 70% RH step. There is almost no change in mass from 70% to 50% RH after which the mass decreases to $\sim 0.2\%$ mass change and then to 0.0% at RH = 0%, indicating a reversible process.

According to the below chemical equation, we can calculate that a transformation from MAPI to the monohydrate should result in a 3% increase in the sample mass.

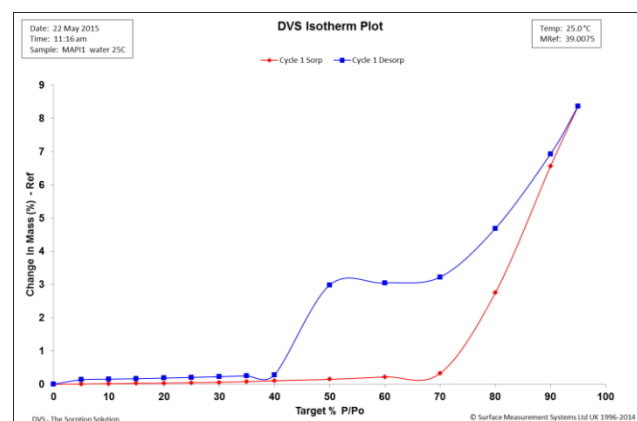
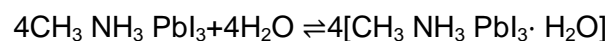


Figure 2. Water sorption (red) and desorption (blue) isotherms for a MAPI dihydrate sample at 25°C .

The isotherms in Figure 2 show a wide hysteresis gap between 50 and 70% RH. This is often indicative of hydrate formation, where the sample will lose the water molecules at a lower RH than it gains them. Based on the uptakes we can estimate the stoichiometry of the hydrated species. At the 50% RH desorption step, the sample retains approximately 3% of its dry weight

in water. Using Equation 1 we can estimate the stoichiometry of this hydrated species:

$$S = \frac{3.0\%}{100\%} \times \frac{619.9 \text{amu}}{18.01 \text{amu} / \text{watermolecule}} = 1.0(1)$$

As Equation 1 indicates, the stoichiometry of the hydrated species at the desorption 50% RH step is 1.0, suggesting a monohydrate species. The difference in uptake between the sorption and desorption isotherms at 50 or 60% RH may be taken as 3.0%, which corresponds to the uptake without the surface sorption contribution.

The MAPI sample upon exposure to water vapour takes up relatively significant amount of water to change to the monohydrate phase over the 60% to 80% RH range. During the desorption phase, the sample maintains a monohydrate stoichiometry until below 50% RH where it again loses one water molecule.

From Figure 1, the sample uptakes a relatively large amount of water at the 80% - 90% RH step where there is a sharp increase in mass. The mass uptake is completed by the end of the 90% RH step, as the mass has approached equilibrium and resulted in a further 3.5% increase in the sample mass, which corresponds to the formation of a dihydrate species. However, at 90% and 95% RH the sample mass did not reach equilibrium and any hydrate formation would not be complete.

During the desorption phase, there is 3.2% mass decrease as the humidity decreases from 90% to 70% RH, indicating the sample returns to the monohydrate form.

The correlation between the DVS experimental results and the theoretical values together with the published XRD of MAPI crystals exposed to 70% RH by Leguy et al's [2] suggest that the monohydrate phase remains stable between 70% and 50% RH. However, the change in the hydration state is kinetically limited and longer exposure to higher % RH values may result in the formation of dihydrate species.

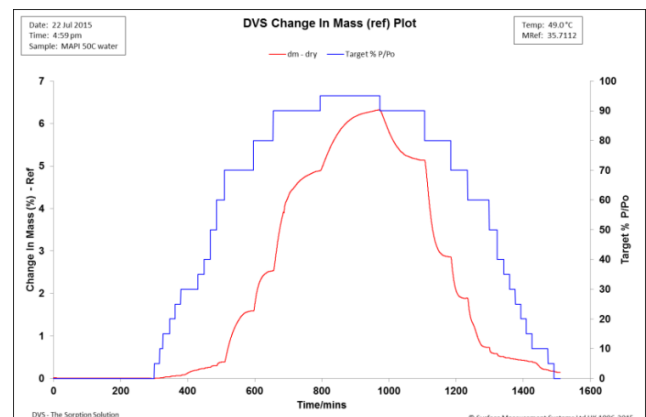


Figure 3. Water sorption kinetics for a MAPI dihydrate sample at 50°C.

The effect of temperature on the hydrate species was investigated by performing the experiment at 50°C. From Figure 3 the sample mass increases initially at around 25% RH and then at above 60% RH after each %RH increase. However, the amount of moisture uptake is relatively smaller compared to the corresponding %RH values at 25°C. This is due to the greater molecular mobility at higher temperatures which would result in faster kinetics as well.

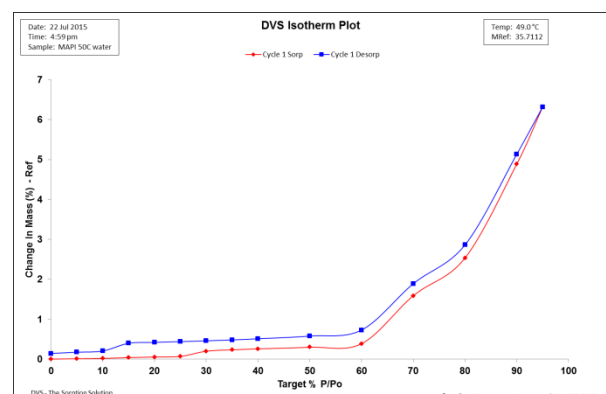


Figure 4. Water sorption (red) and desorption (blue) isotherms a MAPI dihydrate sample at 50°C.

Figure 4 shows a hysteresis loop during the entire %RH range, which remains open at 0% RH. The smaller hysteresis gap, relative to the experiment at 25°C (Figure 2) confirms that the formation of the hydrated states occurs reversibly with significantly less kinetic limitations at 50°C.



Conclusion

Hydrate formation and loss were studied on the hybrid perovskite methyl ammonium lead iodide (MAPI). The stoichiometry of the hydrated species were determined by the corresponding weight increases as a function of relative humidity at two temperatures. The DVS experiments suggest that at room temperature the reversible transition to the hydrated species is kinetically limited which results in hysteresis in the uptake and release of water from the material. At higher temperature the transition occurs without hysteresis and kinetics are faster.

Previous studies and direct synthesis of the dihydrate and its subsequent drying have also indicated recovery of the original monohydrate and MAPI structures, confirming the DVS results in terms of the reversibility of these reactions.

References

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- [1] Barnes, P. R. F. et al. The hydration of organic-inorganic hybrid perovskites: theory and experiment. In press.
[2] Leguy, A. et al. The reversible hydration of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in films, single crystals and solar cells. *Chem. Mater.* 150405140636003 (2015).
[3] Im, J.-H., Lee, C.-R., Lee, J.-W., Park, S.-W. & Park, N.-G. 6.5% Efficient Perovskite Quantum-Dot-Sensitized Solar Cell. *Nanoscale* 3, 4088 (2011).

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