

Synthesis of  $\text{CH}_3\text{NH}_3\text{SnI}_3$  perovskite films by reaction of Sn metallic film with  $\text{CH}_3\text{NH}_3\text{I}$  vapor

Said Kazaoui\* and Ivan Turkevych

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan,  
\*e-mail address: s-kazaoui@aist.go.jp

Sn-based perovskite thin films and solar cells (PSCs) are of great interest to overcome the toxicity issue posed by Pb-based perovskite. Several methods to synthesize Sn-based perovskite by solution and vacuum processes were already reported [1, 2]. For instance,  $\text{CH}_3\text{NH}_3\text{SnI}_3$  ( $\text{MASnI}_3$ ) are often synthesized by the reaction of  $\text{SnI}_2$  and  $\text{CH}_3\text{NH}_3\text{I}$  (MAI) dissolved in organic solutions including various additives to control the growth and to prevent the oxidation of  $\text{Sn}^{2+}$  into  $\text{Sn}^{4+}$ , which are known to hamper the performance of the solar cells. Note that very few reports have also demonstrated that  $\text{CH}_3\text{NH}_3\text{SnI}_3$  thin films can be produced by the reaction of Sn thin metallic films in the presence of MAI in a solution or in a gas phase [3, 4]. Based on this information and on our previous experience on the synthesis of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  ( $\text{MAPbI}_3$ ) by reaction of Pb thin film in presence of  $\text{CH}_3\text{NH}_3\text{I} + \text{I}_2$  [5], we address the synthesis of  $\text{CH}_3\text{NH}_3\text{SnI}_3$  from the layers of metallic Sn.

Here, we report that  $\text{CH}_3\text{NH}_3\text{SnI}_3$  thin film can be spontaneous formed by heating  $\text{CH}_3\text{NH}_3\text{I}$  powder source (at around 145 °C, 0.1 Atm) placed near a Sn thin film pre-deposited on glass substrate (at around 90 °C), as shown in the figure 1a. We observed that the synthesis of  $\text{CH}_3\text{NH}_3\text{SnI}_3$  thin films occurs by one-step chemical vapor reaction of Sn thin film in the presence of  $\text{CH}_3\text{NH}_3\text{I}$  vapor and/or its byproducts due to thermal decomposition, without the formation of  $\text{SnI}_2$  intermediate compound. Based on the x-ray diffraction study (Fig. 1b,c) and the thermogravimetry/mass spectroscopy data, we will discuss several reaction mechanisms such as in eq. (1). Note that the chemical nature of the intermediate and byproducts is still highly debated.



In the course of this study, we noticed that the synthesis of  $\text{CH}_3\text{NH}_3\text{SnI}_3$  thin films does not require exposure to  $\text{I}_2$  vapor. Indeed, if we perform the reaction as shown in eq. (2) in the very similar way as described in ref. 5, we observed that the reaction mainly leads to  $(\text{CH}_3\text{NH}_3)_2\text{SnI}_6$  and  $\text{SnI}_4$  (only containing  $\text{Sn}^{4+}$ ) rather than the expected  $\text{CH}_3\text{NH}_3\text{SnI}_3$  (only containing  $\text{Sn}^{2+}$ ), because  $\text{I}_2$  is a very strong oxidant.



In conclusion, we have developed a one-step chemical vapor reaction process to synthesize  $\text{CH}_3\text{NH}_3\text{SnI}_3$  by directly converting Sn thin films in the presence of  $\text{CH}_3\text{NH}_3\text{I}$  vapor at moderated temperature, which also can be applied to synthesize various type of Sn-based perovskite such as  $\text{FASnI}_3$ .

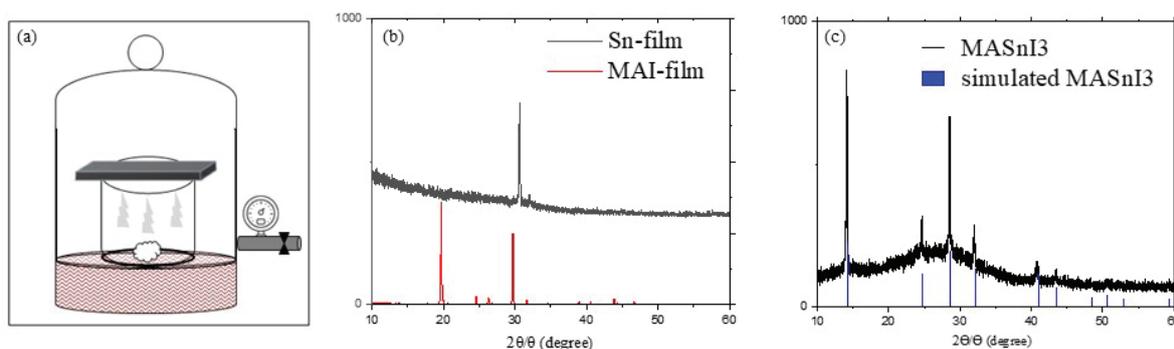


Figure 1: (a) experimental setup. (b) XRD spectra of Sn and MAI films. (c) XRD spectrum of  $\text{MASnI}_3$  film.

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Sub area: Perovskite photovoltaics and related technologies

Degradation kinetics of Perovskite solar cells exposed to H<sub>2</sub>O or O<sub>2</sub>

Said Kazaoui\* and Ivan Turkevych

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan,  
\*e-mail address: s-kazaoui@aist.go.jp

The degradation kinetics of the perovskite solar cells (PSCs) upon exposure to air are still unelucidated, mainly because H<sub>2</sub>O and O<sub>2</sub> impact the properties of the perovskite differently, and their concomitant effects obstruct the analysis. To solve this problem, we experimentally investigated the evolution of the figure-of-merits of unencapsulated PSCs exposed in situ to specific gases (Ar, H<sub>2</sub>O, O<sub>2</sub>) while performing current-voltage (I-V) scan and maximum power point tracking (MPPT) under 1-sun continuous illumination.

Here, we investigated PSCs consisting of Cs<sub>0.10</sub>(NH=CHNH<sub>2</sub>)<sub>0.83</sub>(CH<sub>3</sub>NH<sub>3</sub>)<sub>0.17</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> perovskite (hereafter APbX<sub>3</sub>) embedded in the Glass/FTO/ETL/APbX<sub>3</sub>/HTL/Au device architecture, because they exhibit relatively high efficiency and stability (note that FTO, ETL and HTL stand for fluorine doped tin oxide, compact and mesoporous TiO<sub>2</sub>, and spiro-OMeTAD, respectively).

Interestingly, we observed that the figure-of-merits of PSCs exhibit different behavior upon exposure to either H<sub>2</sub>O or O<sub>2</sub> (Figure 1a, 1c), and their recovery in inert atmosphere (such as Ar) is almost reversible for H<sub>2</sub>O, but irreversible for O<sub>2</sub>. In addition, the analysis of the temporal and gas concentration evolution of the figure-of-merits of PSCs, within the framework of the Langmuir model, unveiled that the degradation kinetic constants are relatively higher in H<sub>2</sub>O compared to O<sub>2</sub> (Figure 1b, 1d). Our new results allow us to clarify the degradation mechanisms upon exposure to either H<sub>2</sub>O or O<sub>2</sub>, and to rationalize the puzzling results observed upon exposure to air. At this conference, we will discuss these results, the degradation mechanisms, and the strategies to mitigate these harmful effects in order to achieve the long-term environmental stability.

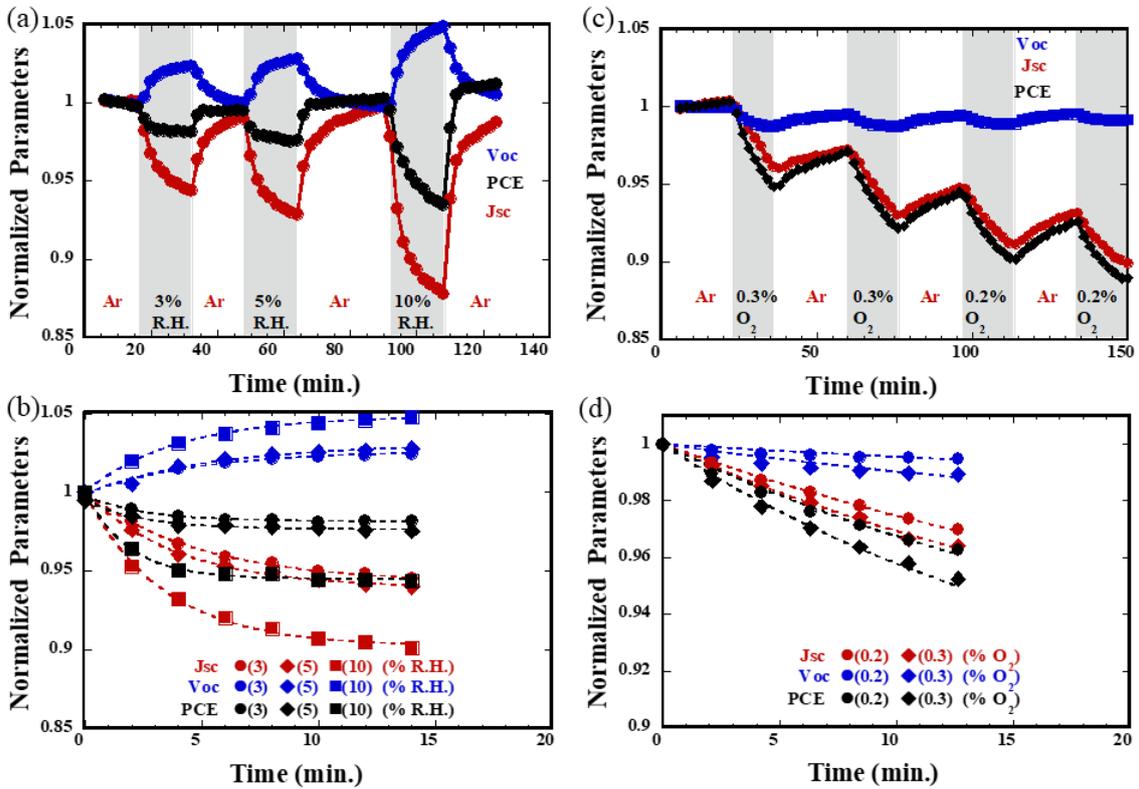


Figure 1: (a) the temporal evolution of the normalized Jsc, Voc and PCE (derived from I-V scan) of PSCs sequentially exposed to Ar and to H<sub>2</sub>O (at various relative humidity, R.H.) under 1-sun at 35~40°C; (b) the corresponding degradation kinetics at various R.H., where symbols are experimental data and dashed lines are the fitting curves based on the Langmuir model. (c, d) similar legend for O<sub>2</sub>.