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Origin of Sn(II) oxidation in tin halide perovskites†

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Tin-halide perovskites have great potential as photovoltaic materials, but their performance is hampered by undesirable oxidation of Sn(II) to Sn(IV). In this work, we use nuclear magnetic resonance spectroscopy (NMR) to identify and describe the origins of Sn(IV) in Sn-based perovskites, mainly focusing on direct measurements of Sn oxidation states with ¹¹⁹Sn-NMR in solid-state and solution. We find that dimethylsulfoxide (DMSO), a typical solvent for Sn-based perovskites, oxidizes Sn(II) in acidic conditions under temperatures used for film annealing. We propose a redox reaction between DMSO and Sn(II), catalyzed by hydroiodic acid, with iododimethylsulfonium iodide intermediate. We find that lower temperatures and less acidic conditions abate this reaction, and we assess a range of compositions and solution components for this instability. These results suggest the need for strategies to prevent this reaction and shed light on other solution instabilities beyond Sn(IV) that must be mitigated to achieve high-performance lead-free perovskites.

Tin halide perovskite materials have recently gained the attention of the photovoltaic community due to their advantages over lead-based perovskites, such as their close-to ideal bandgap,¹ lower environmental toxicity² and potential to be the bottom cell in all-perovskite tandem solar cells.³ However, the efficiency of tin-based perovskite solar cells has only recently surpassed 10%,⁴ mainly due to the instability of the Sn(II) oxidation state, easily oxidised to Sn(IV).⁵ Although the presence of Sn(IV) in the

films has been proven, it has not yet been fully explained how, and at which stage of the material and device processing, Sn(II) can be oxidised in the absence of any oxidant species, assuming that these materials are processed in inert atmospheres of shallow O₂ content (*i.e.* <0.1 ppm).⁶

Several reports have attempted to quantify the Sn(IV) content in perovskite films utilising X-ray photoelectron spectroscopy (XPS) measurements. This technique is highly surface sensitive, probing depths usually below 10 nm. Therefore values obtained with XPS can be misleading and inaccurately represent the real Sn(IV) content in the film. Besides, the influence on Sn(IV) formation from ultra-high vacuum and X-rays, which are claimed to induce degradation in lead-based perovskite films,⁷ has not yet been studied in detail. While precisely measuring the proportion of these two oxidation states in perovskite thin films can be tricky, there are other facile and available techniques to investigate the origins of Sn(II) oxidation directly. Considering that the electronic environment of different oxidation states markedly differs, we should explore methods that are sensitive to changes in this property. In this regard, nuclear magnetic resonance (NMR) is an ideal technique with excellent capability to differentiate between chemical environments of each element. Mainly used in materials science for the characterisation of organic molecules, NMR has proven its utility for characterising organometallic systems.⁸ Although there are steadily increasing reports on its application for metal halide perovskites,^{9,10} its full potential remains underexplored.

In this work, we present the use of a range of NMR techniques as a straightforward and versatile tool for quantifying Sn(IV) content in Sn-based precursors and solutions. By making use of ¹¹⁹Sn-NMR, we identify and describe the origin of Sn(IV) formation from the reaction between DMSO, which is the most commonly used solvent to prepared devices, and Sn(II) at high temperature in acidic conditions, quantifying the amount of oxidised Sn(IV) being generated. This study aims to be a reproducible guideline for rapid and facile use of NMR for characterising the properties and chemical processes occurring in tin halide perovskite materials.

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Fig. 1 (a) Steps of tin-based perovskite material preparation studied in this work as possible sources of Sn(II) oxidation; (b) solid-state ^{119}Sn -NMR spectra of SnI_2 precursor with and without air exposure.

Intending to find when Sn(IV) is formed during the processing of perovskite, we identified three possible sources of oxidation: precursors, solutions and annealing (Fig. 1a). The versatility of NMR allowed for different experiments appropriate for each processing step. We first used solid-state ^{119}Sn -NMR for characterising the content of the different oxidation states in SnI_2 , the precursor generally used for perovskite solution preparation. For the as-received material, Sn(II) signal appears at -529 ppm (Fig. 1b), but no Sn(IV) signal was detected. Consequently, the molar content of any Sn(IV) in the precursor was below the detection limit of the measurement, which we estimate to be ~ 1.5 wt% from the signal-to-noise ratio. Exposure of the powder to air led to increasing Sn(IV) content with time, indicating that oxidised Sn(IV) from SnI_2 shows up between -1740 and -1745 ppm. These results confirm that there is not a significant contribution from the precursor to the final Sn(IV) content into the perovskite.

Our next hypothesis involved the potential oxidation of Sn(II) through the preparation of the tin halide perovskite solution. In this step, we studied DMF and DMSO (both deuterated), the most common solvents in literature for these materials, as well as formamidinium iodide (FAI) as the organic salt for the

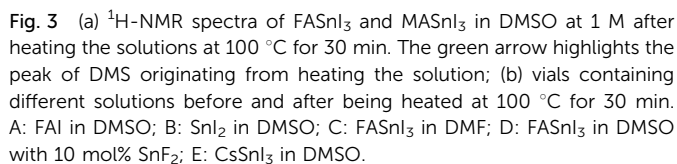


Fig. 2 (a) ^{119}Sn -NMR Sn(II) signals for SnI_2 in DMF (green) and DMSO (red), FASnI_3 in DMF (turquoise) and DMSO (yellow) and Sn(IV) signal for SnI_4 in DMSO (purple); (b) dependence of the ^{119}Sn -NMR Sn(II) signal chemical shift of SnI_2 in DMSO and DMF with solution concentration; (c) FASnI_3 (left) and FASnI_3 in DMSO heated at 100°C for 30 min (right); (d) ^{119}Sn -NMR spectra in the Sn(IV) range of FASnI_3 solutions in DMSO heated at 80°C and 100°C for 30 min.

preparation of FASnI_3 perovskite. For this purpose, we measured freshly prepared solutions (no heating was applied unless stated otherwise) using liquid-state ^{119}Sn -NMR (Fig. 2a) and found no Sn(IV) for either SnI_2 or FASnI_3 in both solvents. This finding agrees with the results from solid-state NMR. A 1.0 M sample of SnI_4 in DMSO was measured to know the approximate expected shift, with Sn(IV) signal found at -2023 ppm (Fig. 2a). We found that the chemical shift of the SnI_2 can vary significantly. Firstly, we found lower chemical shifts in DMSO than in DMF, which agrees with the more effective donation of electron density from DMSO to SnI_2 and, to a lesser extent, between SnI_2 and FASnI_3 (Fig. 2a). In the latter case, the introduction of FAI can have an electron-withdrawing effect on SnI_2 adducts, as NMR has already proven its complexing ability in solution.¹¹ Interestingly, Fig. 2b shows that there is a strong dependence of the SnI_2 chemical shift with its solution concentration in DMSO, which is less



To have insights into the Sn(II) oxidation reaction, we also investigated the state of the organic parts (*i.e.* DMSO and FAI/MAI) by ^1H - and ^{13}C -NMR. As we can see from the ^1H spectra in Fig. 3a, a signal is found in the 1.89–1.92 ppm range for both MA and FA containing solution. This trend fits the expected shift for dimethyl sulfide (DMS), that we determined by adding 1 equivalent of DMS to a FASnI_3 sample (Fig. S5 and S6, ESI †). This was also confirmed with a ^{13}C -NMR experiment, where we

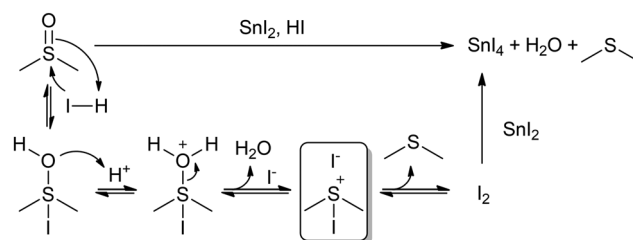


found the signal of the methyl groups from DMS at 17 ppm (Fig. S7, ESI[†]). In this respect, ¹³C-NMR is a more reliable method than ¹H-NMR for monitoring DMS formation, considering that using DMSO-d₆ leads to deuterated DMS. These results are in explicit agreement with the recent work on DMS formation, where the authors establish a relationship between the decomposition of DMSO and the emergence of the signal from DMS by ¹H-NMR in Sn-based perovskite solutions, which they indirectly link to the oxidation of Sn(II).¹³ However, this correlation might present some drawbacks. At the same time, the authors also found traces of DMS for MAPbI₃ solutions, as we did for unheated SnI₂ or FASnI₃ samples (Fig. S8, ESI[†]), which is reasonable considering that DMS is one of the main impurities found in DMSO.¹⁴ Also, DMS has such a low boiling point (37.3 °C) that it could potentially be lost during sample preparation. We see no longer an increase in the intensity of the DMS signal after heating at 100 °C for 2 or 4 days (Fig. S9, ESI[†]). We believe the direct

$$2\text{SnI}_2 + 2(\text{CH}_3)_2\text{SO} \rightarrow \text{SnO}_2 \text{ (s)} + \text{SnI}_4 + 2(\text{CH}_3)_2\text{S}$$

The results obtained so far point towards a redox reaction between DMSO and Sn(II) that is favoured in acidic conditions. The oxidation of many different types of organic compounds in DMSO in the presence of hydrogen halides has been widely studied.^{18–21} Through the *in situ* generation of halodimethylsulfonium halides¹⁹ it is possible to carry out oxidative halogenations on olefins²⁰ or aromatic compounds,²¹ among others. In this sense, any I₂ generated would also be able to oxidise SnI₂ to SnI₄. We confirmed this by adding I₂ beads to a FASnI₃ solution and found both Sn(II) and Sn(IV) presence (Fig. S11, ESI†).

Characterisation by NMR can also shed light on the decomposition of the organic components of the perovskite. As mentioned earlier, we heated FASnI₃ solutions at 100 °C for 2 and 4 days. In contrast to the previous experiments, no signal was found for Sn(IV) in this case. Interestingly, we began to observe a precipitate, eliciting that extended heating can potentially lead to the precipitation of all Sn(IV) as SnO₂. Additionally, we found a new group of signals in ¹H spectra with shifts in the range of 6.80–7.20 ppm, which were increasing in intensity over time (Fig. S9, ESI[†]), suggesting that they belong to compounds forming during decomposition of the solution. At this point, we performed 2D-NMR experiments to understand the nature of these products. The ¹H–¹H correlation spectroscopy (COSY) (Fig. S12, ESI[†]) and rotating frame Overhauser effect spectroscopy (ROESY) results (Fig. S13, ESI[†]) confirmed that the signals are not coupled with each other. Still, they showed chemical exchange in between them and with the amine protons of FA (Fig. S13, ESI[†]), indicating that they have exchangeable protons. Therefore, these new signals might belong to decomposition products of FA that has only amine protons, meaning that these signals must belong to the ammonium ion. These signals have been previously assigned to



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NH_4^+ in the study on DMS generation,¹³ and are one of the decomposition products described by Clay Hamill *et al.* in perovskite solutions in DMSO.¹⁶ Other decomposition processes of DMSO such as its degradation to sulfate ion should always be considered, although, to the best of our knowledge, we believe our system does not provide the required conditions for this process to happen.

Currently FASnI_3 -based devices achieve V_{oc} values between 0.4 and 0.6 V (with SnF_2 , Fig. S14, ESI†), while the material has potential for much higher values. This fact points out that there is a limiting factor, which would be strongly influenced by the so reviewed Sn^{4+} content.⁵ The oxidising effect of DMSO could be behind it, therefore alternative strategies that avoid the use of this solvent have to be discovered in order to improve the performance of these devices.

Conclusions

In conclusion, we have presented solid- and liquid-state ^{119}Sn -NMR as a simple and straightforward technique for identifying Sn(II) oxidation and described its redox reaction with DMSO. Other methods traditionally used for oxidation state quantification in Sn-based perovskite materials show clear limitations. For instance, XPS not only requires extended measurement, ultra-high vacuum and X-rays, all of which may damage samples but also only gives information about the sample surface. At the same time, XANES depends on synchrotron facilities, making it a less available technique. These results also present NMR as a useful and accessible tool, with clear underexplored potential for understanding perovskite solutions, and point out the necessity of finding new solvents for Sn perovskites to substitute DMSO or otherwise suppressing its decomposition.

Author contribution

A. A. supervised the project. R. A. and A. D. supervised the solid-state and liquid-state NMR measurements, respectively. J. P., M. H. A., J. A. S., M. F. and N. P. prepared the NMR samples. G. N. coordinated the solid-state NMR measurements. J. P., D. D. G. and A. A. designed the experimental plan. D. D. G., S.-H. T.-C. and M. L. helped with the coordination of the work. J. P. wrote the manuscript with the help of the rest of the authors. All authors discussed the results and contributed to the manuscript.

Conflicts of interest

There are no conflicts to declare.

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