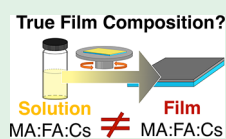# On the True Composition of Mixed-Cation Perovskite Films

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S *Supporting Information*

True Film Composition?

Solution MA:FA:Cs ≠ Film MA:FA:Cs

ABSTRACT: Herein we show that mixed-cation perovskite films made by spin-coating do not necessarily have the same stoichiometry as the precursor solution from which they are made and propose a simple method to quantify the true composition of such films.

Lead-based perovskites, with general formula APbI$_3$ (A = CH$_3$NH$_3$+, CH(NH$_2$)$_2$+, or Cs) have disrupted the field of optoelectronics and have shown remarkable performance in solar cells with efficiencies of up to 23.3%.[1] While early devices relied on materials with one A-site cation (most notably MAPbI$_3$; MA = CH$_3$NH$_3$+), the advantages of mixing A-site cations quickly became apparent in terms of device performance and stability.[2,3] In fact, almost of all today's high-efficiency (>20%) devices are made from a combination of two, three, or even four A-site cations.[3,4]

The most common film fabrication technique for perovskite-based solar cells is spin-coating. This method is convenient and affordable but is also highly sensitive to deposition conditions such as temperature, spin velocity, and casting solvent(s).[5] In fact, it has been shown that the composition of mixed-halide perovskites can change significantly depending the synthesis method.[6−8] To date, most studies assume that the stoichiometry of the starting precursor solution is equal to the composition of the final film, but little to no attention has been paid to actually determining the composition of such films. Herein, we show that this assumption can be erroneous and propose a simple method to determine the true composition of double- and triple-cation films made by spin-coating.

Determination of the true composition of mixed-cation perovskite films is challenging for several reasons. First, technologically relevant films are a few hundred nanometers thick, yielding a few milligrams of material at best, depending on film area. Second, relevant cations include formamidinium (FA) and methylammonium (MA), which limits the ability of common techniques, such as X-ray diffraction, X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spec-troscopy (EDX), or inductively coupled plasma (ICP), all of which are insensitive to light atoms (such as C, H, or N). Third, the effects of cation mixing on the properties of the materials (i.e., absorption or photoluminescence) are not always linear,[9] and it is therefore challenging to estimate the relative concentration of cations by simple extrapolation and even more so when three or more cations are present. Given these challenges, we employed quantitative nuclear magnetic resonance (qNMR) to determine the actual composition of the films. Solution-state ^{1}H qNMR is a widely accessible and affordable technique that can also be very sensitive and precise (precision and accuracy are both approximately 1%).[10]

To quantify A-site cations in perovskite samples (Scheme 1), we prepared films using standard spin-coating procedures for

Scheme 1. Schematic Representation of Our Method to Quantify Cations in Mixed-Cation Perovskites by qNMR

Solution MA : FA : Cs — Spin-coating — Scraping — ^{1}H NMR Spectrum — Integration — Film MA : FA : Cs
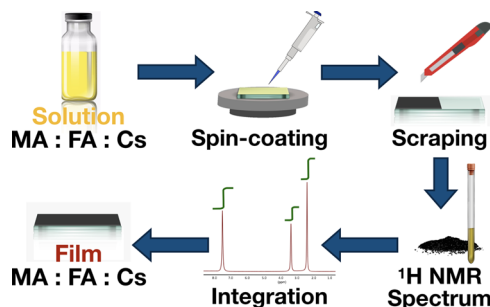
two double- and three triple-cation perovskites (see SI).[11] We then scraped off several films made by the exact same procedure, carefully weighing the resulting powders and dissolving them in a known volume of deuterated DMSO with a known amount of internal standard. Finally, an ^{1}H NMR spectrum was measured, and the signals from the nonlabile carbon-bound protons of MA and FA were integrated and normalized using the signal from the internal standard. As the integrated peak of each signal is directly proportional to the number of protons, these results allowed us
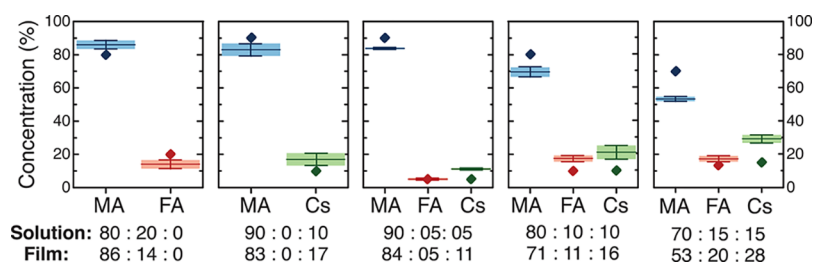
Figure 1. Average concentration and MA:FA:Cs ratios of perovskites films made from solutions with different stoichiometries. The filled boxes show average concentration values with error, while the diamond markers show the precursor solution (or nominal) concentration.

to determine the absolute mass of FA and MA and, by inference, the mass of Cs (Figure 1).

The composition determined for MA:FA perovskites showed decent agreement with the precursor solution stoichiometry (Figure 1 and Table S2) in accordance with previous results.[12] The films that contained cesium, however, showed significant discrepancies between the stoichiometries of the precursor solutions and that of the obtained films, with MA concentrations up to 24% smaller than that of the solution concentration and FA and Cs concentrations up to 33 and 220% higher, respectively, than their nominal compositions (Figure 1 and Table S2). The lower than expected MA concentration across all triple-cation films can presumably be explained by the lower solubility and higher volatility of FA and Cs cations with respect to MA. We note that the compositions obtained from our method are an average value of the composition of the films obtained from the specific method used and do not consider local inhomogeneities and assume that our films are phase-pure, both of which are not always true, as previously demonstrated using NMR methods by Vela[6] and Emsley[7] (for further discussion on the assumptions and limitations of our technique, please refer to the SI).

To verify the validity of our results, we performed EDX to determine approximate Cs:Pb ratios in our Cs-containing films. EDX results (Figure S5) are consistent with the results obtained by our qNMR protocol: the films consistently showed higher than expected Cs/Pb ratios.

The discrepancy between the solution and film compositions is remarkable and indicates that the precursor solution and films obtained from them do not necessarily possess the same stoichiometry. While the quantitative results obtained in this study pertain only to the particular film preparation conditions and the solution compositions used herein, our method is a simple option to enable others to precisely determine the stoichiometry of films fabricated under the specific conditions and compositions that best suit their work, which is important because film compositions will likely be extremely sensitive to the specific deposition conditions. Significantly, this method is not limited to films made by spin-coating of the cations used in this study nor is it even limited to three-dimensional (3D) perovskites. This method is applicable to numerous types of perovskite materials and compositions. In particular, 2D perovskites,[13] 2D/3D perovskites,[14] and even passivated films[15] could be studied using this procedure because it can be easily adapted to detect virtually any other organic molecule incorporated in perovskite films and complemented, if necessary, with other methods.

In conclusion, we have developed a simple, yet precise, method to determine the formula of double- and triple-cation perovskite films. Knowing the true composition of films used in the state-of-the-art perovskite solar cells is of fundamental importance for understanding and improving these materials, and we hope this method will enable such studies in the near future.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergy-lett.8b01577.

Detailed experimental procedures (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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