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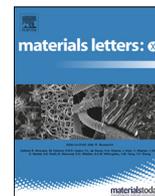
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Quantitative chemical analysis of perovskite deposition using spin coating

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ABSTRACT

Lead and halide ion compositions of spin coated organo-lead halide perovskite films have been quantified using ion chromatography (IC) and atomic absorption spectroscopy (AAS) using perovskite films manufactured by 5 different researchers (3 replicates per treatment) to monitor variability between researchers and individual researcher reproducibility. Planar and mesoporous TiO_2-coated glass substrates have been studied along with tribromide ($CH_3NH_3PbBr_{3)}$, triiodide ($CH_3NH_3PbI_3$) and mixed halide ($CH_3NH_3PbI_{3-x}Cl_x$) perovskite films. The data show low yields of spin coated perovskite material (*ca.* 1%) and preferential deposition of I^- over Cl^- in mixed halide films.

Since 2012 [1], organolead halide perovskites have generated huge interest in new solid-state photovoltaic devices (e.g. [2]). Various researchers have reported how absorber stoichiometry can be varied using different ions substituted into the RMX_3 formula (R = organic cation, M = metal cation, X = halide). Methyl amine,[1–2] formamidinium [3] and Cs [4] have been used for R, whilst Sn [5] is currently the most viable alternative to Pb for M. Various halides (Cl^-, Br^- and I^-) have also been used in single [1] or mixed devices [6]. Solution processing by spin coating [1] is the most common manufacturing procedure whilst device efficiencies have increased from 12% [1] to 23.3% [7].

Efforts to understand how device processing affects performance have used thermal analysis to study residual solvent [8], X-ray powder diffraction (XRPD) to study structure [9] and electron microscopy/EDAX to study morphology and composition [10,11]. However, XRPD provides "averaged" data and EDAX uses high accelerating voltages (>15 kV) so data arises from a "pear-drop" shaped depth profile [12] which is problematic for thin film samples. XRPD and EDAX also have poor limits of detection (approx. few weight %). Here, we address this by reporting quantitative analysis of deposited perovskite thin films by measuring metal ions by atomic absorption spectroscopy (AAS) and halide anions by ion chromatography (IC).

1. Experimental

Perovskite solutions were prepared in anhydrous dimethyl formamide (DMF) using the quantities in Table 1 using methylamine halides (Dyenamo) and lead halides (Sigma). Perovskite solutions were filtered through PTFE syringe filters (0.45 µm). Perovskite deposition methods are described in the ESI.

Halide ions were measured using an ICS-2100 ion chromatograph (Thermo Dionex) with an IonPac® AS11 (4 mm) column and AG11 (4 mm) guard column with a $KOH_{(aq)}$ mobile phase (0.38 ml min^{-1}). Lead ions were measured using a Varian SpectrAA 220FS atomic absorption spectrometer (AAS) at 283.3 nm in an acetylene flame. The IC and AAS were calibrated using certified standards (purity >99.99%) in H_2O to give $R^2 > 0.99$ (see ESI).

2. Results and discussion

Spin coating produces, consistent thin films on flat substrates from solution. For organolead halide perovskite solar cell manufacturing, an organic solvent containing metal, organic amine and halide ions is dropped onto a pre-heated substrate which is spun at increasing speeds to drive off excess solvent and create a "wet film". Heat then produces the perovskite (Fig. 1).

Firstly, considering perovskite yield, Table 1 shows the mass of halide ions in the 100 µl of tribromide, triiodide and mixed halide DMF solutions used in these experiments. The perovskite yield here is defined as the mass of halide recovered from the substrate compared to the mass of halide in the original perovskite solution

Table 1
Organolead perovskite deposition solutions.

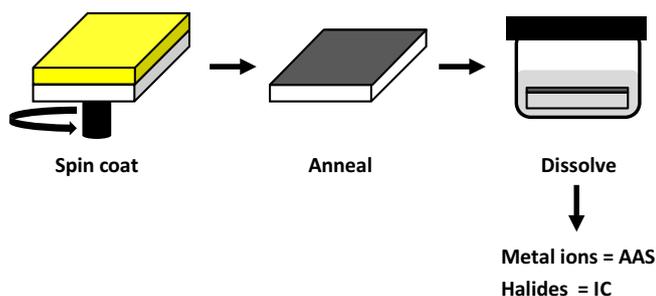| Perovskite	Methylamine Halide (g)	Lead Halide (g)	DMF volume (ml)	Mass of ions in 100 μl (mg)			
				I^-	Br^-	Cl^-	Pb^{2+}
Tribromide	0.4575 g CH_3NH_3Br	0.5 g $PbBr_2$	1.5	0.0	36.3	0.0	18.9
Triiodide	0.5074 g CH_3NH_3I	0.5 g PbI_2	1.6	42.5	0.0	0.0	14.0
Mixed Halide	0.8395 g CH_3NH_3I	0.5 g $PbCl_2$	2.1	31.9	0.0	3.0	17.7

Fig. 1. Procedure to deposit, anneal and analyse perovskite films.

as listed in Table 1. For tribromide, this contains 36.3 mg of Br^- whilst, in the deposited films, the mass of Br^- ranges from 353 to 553 μg (Table 2). This yield ranges from 1.0 to 1.5% so 99.0 to 98.5% of the bromide is spun off the substrate. For the triiodide perovskite (initial $I^- = 42.5$ mg), the deposited masses range from 302 to 460 μg which represents a yield of 0.7–1.1%. For the mixed halide (initial solution contains 31.9 mg iodide and 3 mg chloride), the deposited masses of I^- range from 219 to 357 μg and the chloride from 8 to 10 μg. Hence, the yields based on iodide range from 0.7 to 1.1% and, for chloride, are *ca.* 0.3%. So, for the more prevalent halides, the yields are *ca.* 1% but for lower abundancy ions (such as Cl^-) even more is lost (99.7%). The yield has been examined further by studying the tribromide perovskite deposited at room temperature (RT) on planar or mesoscopic TiO_2 substrates (ESI Figs. 4 and 5). The data show lower Br^- concentrations for 2×2 cm planar and mesoscopic substrates at RT (115 and 437 μg, respectively) which shows the importance of pre-heating the substrates to 110 °C. The effect of substrate area was also studied by using 5×5 cm substrates. For RT deposition, planar and mesoscopic substrates still showed low Br^- yields when the additional substrate area is considered (324 and 563 μg, respectively). However, preheated (110 °C) 5×5 cm planar and mesoscopic substrates did show increased Br^- deposition (1276 and 2236 μg, respectively)

which represents a bromide yield of 3.5% and 6.2%, respectively. Looking at the range of Br^- yields from Table 1 (353–553 μg), whilst these data do not show the proportional increase in Br^- yield that might be expected in increasing the substrate area from 4 cm^2 to 25 cm^2 substrates, it does suggest that increased perovskite yields are possible with larger substrates. Nonetheless, the low yields of perovskite do raise issues for scaling perovskites unless waste material can be recycled during processing, whilst the preferential loss of low abundancy ions raises issues for compositional consistency.

Table 2 also shows the presence of trace amounts of other halides (particularly chloride) in deposited perovskites which should be purely tribromide or triiodide. This suggests that there are trace impurities in the precursors. At the trace levels observed here, these impurities might not be identified by XRD or EDAX analysis, but they could still influence device performance and so should be considered when reporting high efficiency devices.

To study spin coating repeatability, five researchers repeated the same spin coating procedure (3 replicates per condition). Taking individual errors first, the three largest values are ±11–13% for R1 and R5 for triiodide and mixed halide perovskites. However, most individual researcher errors are <5% showing consistency for each person repeating their own method. The second level of variation is between researchers. Here a larger compositional range is observed; e.g. R1 and R4 generally have larger halide masses than R2, R3 and R5 as evidenced by the tribromide data (534–578 μg of Br^- for R1 and R4) *versus* 308–385 μg of Br^- for R2, R3 and R5; this is a 50–70% variance. This suggests that how the solution is deposited onto the substrate (e.g. how clean and dry the substrate is, where the droplet is located and how it wets the surface) and the timings involved (e.g. how long after deposition the spin coater starts) make significant differences to the perovskite mass formed.

Another observation is the consistently higher loadings of halides in the mesoscopic *versus* planar TiO_2 substrates. This is expected because the mesoscopic films are a network of sintered

Table 2
Mass (μg) of bromide, iodide and chloride found in spin coated tribromide ($CH_3NH_3PbBr_3$), triiodide ($CH_3NH_3PbI_3$) and mixed halide ($CH_3NH_3PbI_{3-x}Cl_x$) perovskite films from 5 researchers (R1–R5). Errors on the final digit are shown in brackets.

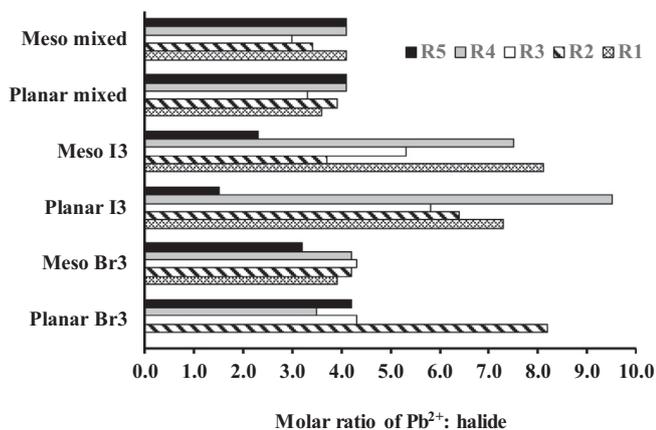|	Ion	Tribromide		Triiodide		Mixed halide	
		Planar	Meso	Planar	Meso	Planar	Meso
R1	Br^-	553 (9)	559 (25)	0 (0)	0 (0)	0 (0)	0 (0)
	I^-	0 (0)	0 (0)	407 (46)	455 (14)	299 (15)	378 (10)
	Cl^-	3 (1)	7 (1)	3 (0)	1 (1)	8 (1)	10 (0)
R2	Br^-	353 (39)	445 (9)	0 (0)	0 (0)	0 (0)	0 (0)
	I^-	0 (0)	0 (0)	312 (12)	352 (1)	232 (2)	269 (4)
	Cl^-	4 (2)	0 (0)	6 (3)	2 (1)	10 (1)	9 (1)
R3	Br^-	376 (38)	441 (30)	0 (0)	0 (0)	0 (0)	4 (4)
	I^-	0 (0)	0 (0)	302 (12)	344 (29)	219 (12)	275 (11)
	Cl^-	0 (0)	0 (0)	0 (0)	2 (1)	5 (1)	8 (1)
R4	Br^-	534 (40)	578 (47)	0 (0)	0 (0)	1 (0)	2 (0)
	I^-	0 (0)	0 (0)	460 (13)	485 (25)	357 (17)	366 (9)
	Cl^-	1 (0)	1 (0)	1 (0)	3 (3)	9 (2)	10 (0)
R5	Br^-	385 (21)	308 (21)	0 (0)	0 (0)	0 (0)	0 (0)
	I^-	0 (0)	0 (0)	344 (5)	418 (50)	251 (20)	271 (36)
	Cl^-	7 (3)	0 (0)	0 (0)	1 (1)	8 (1)	10 (1)

Fig. 2. Molar ratios of Pb^{2+} to halide ions for tribromide, triiodide and mixed halide perovskite films spin coated onto either planar or mesoscopic TiO_2 coated glass substrates by 5 different researchers (R1–R5).

TiO_2 nanoparticles. Hence, as the DMF solution reaches the substrate, it penetrates into the mesoscopic film and wets the TiO_2 nanoparticles. Hence, less solution is expected to be thrown off during spin coating.

Finally, we have considered the ratio of ions in the perovskite films. Snaith's first report of solid-state perovskite devices[1], used a 3:1 mixture of $CH_3NH_3I:PbCl_2$. This should have resulted in a $CH_3NH_3Pb(I_xCl_y)_3$ with x:y = 3:2 (i.e. $CH_3NH_3PbI_{1.8}Cl_{1.2}$). However, EDAX showed the product to have an I:Cl ration of 2:1. Effectively, the final material was chloride deficient.

Our data agree with Snaith et al. because we observe less chloride in the mixed halide perovskite film than is present in the precursor solution (Table 2). We have studied the molar ratios further by calculating the molar ratio of Pb^{2+} to the total halide concentration (Fig. 2, raw data in ESI Table 2). Firstly, for all the perovskites studied, the ratio of Pb^{2+}:halide should be 1:3. Fig. 2 shows that, in general, the Pb^{2+} composition is lower than predicted which probably reflects lower Pb^{2+} solubility relative to Cl^-, Br^- or I^- so, when the perovskite films are dissolved in water prior to analysis, the halides dissolve preferentially. This is likely to be exaggerated in less stable perovskite films which is reflected in the higher ratios observed for the triiodide. Interestingly, the mixed halide perovskites produce the most consistent ratios which are closest to the theoretical value suggesting these ions dissolve in a more evenly way.

3. Conclusions

The data confirm low yields of perovskite (*ca.* 1%) from spin coating and the difficulty in maintaining composition from precursor solution to deposited film especially in mixed halide systems.

The data do suggest that individual researchers can reduce compositional errors to ±5% but researcher-to-researcher variation is higher (50–70%) suggesting that alternatives to spin coating are required to scale this technology.

Conflicts of interest

There are no conflicts of interest related to this paper for the authors.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mlblux.2019.100011.

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