

Controlling Pbl₂ Stoichiometry during Synthesis to Improve the Performance of Perovskite Photovoltaics

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ABSTRACT: Over the past decade, remarkable progress has advanced the field of perovskite solar cells to the forefront of thin film solar technologies. The stoichiometry of the perovskite material is of paramount importance as it determines the optoelectronic properties of the absorber and hence the device performance. However, little published work has focused on the synthesis of fully stoichiometric precursor materials of high purity and at high yield. Here, we report a low-cost, energy-efficient, and solvent-free synthesis of the lead iodide precursor by planetary ball milling. With our synthetic approach, we produce low-oxygen, single or multiple polytypic phase PbI₂ with tunable stoichiometry. We determine the stoichiometry and the



polytypes present in our synthesized materials and further compare them to commercially available materials, using X-ray diffraction, X-ray photoelectron spectroscopy, and Rutherford backscattering spectroscopy. Both the stoichiometric PbI₂ we synthesized and a substoichiometric commercially available PbI_2 (where the iodide content is below the optimum Pb:I atomic ratio of 1:2) were used to grow methylammonium lead iodide microcrystals (which corrects the iodide content). Perovskite solar cells were then produced using stoichiometric and substoichiometric PbI₂ mixed with an equimolar amount of methylammonium iodide and compared to devices produced from re-dissolved microcrystals. The photoactive perovskite layer deposition was processed in air, enabled by the use of a single low-toxicity solvent (dimethyl sulfoxide) combined with vacuum-assisted solvent evaporation. We find that the device performance is strongly dependent upon the stoichiometry of the lead iodide precursor, reaching champion efficiencies over 17%, with no obvious correlation with its polytypic phases. This work highlights the critical role of PbI₂ stoichiometry in hybrid perovskites as well as demonstrating synthesis methods and perovskite layer fabrication protocols suitable for low-cost solar energy harvesting.

INTRODUCTION

Immense academic and commercial research efforts are being undertaken into perovskite solar cells (PSCs), tapping into their potential as the next low-cost solar power technology. The improvement in photovoltaic performance for the most ubiquitous hybrid organic-inorganic halide perovskite absorber (methylammonium lead iodide, CH₃NH₃PbI₃) has been prodigious, with power conversion efficiencies (PCEs) increasing from 3.8% to 21.2% in a decade.^{1,2} Mixtures of organic and inorganic cations, predominantly methylammonium, formamidinium, and cesium (MA+/FA+/Cs+) with various halogen anions, such as chloride, bromide, and iodide $(Cl^{-}/Br^{-}/I^{-})$ have been used to improve the performance and stability of PSC devices. However, the long-term stability and durability of PSCs have remained barriers to their commercialization. These effects might be related to either deficiency or excess of lead iodide (PbI_2) in the synthesized perovskite and a tolerance factor closer to unity that corresponds to the cubic crystal structure.³⁻⁷ This degradation occurs regardless of the device architecture utilized (p-i-n or n-i-p).8 Controlling the stoichiometry of the precursor materials used may help to reduce the presence of impurities and improve the stability of

PSC devices. In parallel to the challenge of stability is that of scalability, where the possibility for air processing offers the potentially lowest-cost approach to perovskite fabrication. This necessitates the development of fabrication methods for materials and devices under ambient conditions using less toxic solvents.

Whilst various researchers have demonstrated the importance of perovskite phase purity and stoichiometry,⁹⁻¹¹ few have covered the role of the precursor materials PbI2 and methylammonium iodide (CH₃NH₃I), $^{5,12-14}$ in particular, the stoichiometry of PbI2 and its polytypic behavior. Previous reports have described more stoichiometrically correct CH₃NH₃PbI₃ thin films, synthesized using CH₃NH₃PbI₃ single crystals, in comparison with the nominally equimolar intermixed powders of PbI₂ with CH₃NH₃I.^{15,1}

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PbI₂ is an intrinsic semiconducting material with a wide energy band gap (E_{σ}) of 2.3–2.4 eV.¹⁷ Its crystalline structure is hexagonally close-packed with the space group $P\overline{3}m1$, consisting of three alternating layers of lead and iodide atoms (I–Pb–I) within the basic unit cell, which is a near-octahedron $[PbI_6]^{4-}$. For the most stable at room temperature (RT) 2H polytypic phase, the unit cell's dimensions are a = b = 0.4557nm and c = 0.6979 nm.¹⁸ However, the stacking sequence of the $(I-Pb-I)_n$ layers can vary significantly due to the weak van der Waals interactions between those sequential lavers. This results in the crystallochemical phenomenon of polytypism, in which different polytypes with variable *c*-axis dimensions are formed. These variations in the *c* axis also result in minor changes to *a* and *b* axes.^{19–21} Polytype formation can also be dependent on the synthetic process used, for example, cosolvent,²² modified gel,²³ sublimation,²⁴ epitaxial,²⁵ or vertical Bridgman–Stockbarger²⁶ synthesis. During the synthesis, the formation of multiple polytypic phases may occur. Moreover, reversible and irreversible transitions between different polytypic phases might be responsible for the coexistence of several energy states in $PbI_{22}^{21,27,28}$ in a way that is analogous to the polytypism in silicon carbide.²⁹ Despite the identification of more than 40 polytypic phases of $\overline{P}bI_2$ over the last 60 years, primarily using X-ray diffraction techniques, the exact mechanism of their formation and diversity remains poorly understood. Further details regarding the theory of polytypism are provided in Supporting Information Section 1.

Here, we report the use of a planetary ball milling (PBM) process to synthesize PbI2, which permits control of the stoichiometry and the degree of polytypism. PBM utilizes high kinetic energy, inelastic impacts between stainless steel spheres surrounded by the reactant powders (lead(II) nitrate and potassium iodide), and the walls of the ball milling jar. This approach provides a controllable and energy efficient way (~31.3 watts per hour per gram) to produce moderate quantities at the lab scale (\geq 40 grams per run and yield of ~96 \pm 0.5%) of PbI₂, without using solvents. By avoiding the use of solvent during the PbI₂ synthesis, less waste is produced and a potential route for impurities is removed. We then tested the PSC performance of devices fabricated in air using a single-step deposition method with vacuum-assisted evaporation^{30,31} of the solvent (dimethyl sulfoxide) and without the use of any additional anti-solvent rinsing step. This fabrication method permits the formation of high-quality perovskite thin films without using the highly toxic and widely used solvent dimethyl formamide (DMF).³² PSC devices fabricated using equimolar amounts of substoichiometric PbI₂ and CH₃NH₃I precursors exhibited inferior performance due to the presence of unreacted PbI₂ in the resultant perovskite thin film. Meanwhile, the polytypic phase of PbI2 had no profound effect on the device performance. Our results indicate that the precise control over the stoichiometry of the precursor materials may be a route toward more efficient perovskite solar cells.

RESULTS AND DISCUSSION

Hydrothermal and Mechanochemical Synthesis of Pbl₂. In order to vary both stoichiometry and polytypism, two methods of synthesis of PbI₂ have been considered in this work: (1) the conventional hydrothermal (HT) reaction that requires the dissolution of reactants (lead(II) nitrate and potassium iodide) in water and (2) the water-free mechanochemical (MC) process using PBM, which allows

the solid-state reaction of the same reactants. The HT synthesis of PbI_2 results in the formation of continuous layers of hexagonal PbI_2 platelets decorated with needle-shaped crystal formations, as shown in Figure 1a. In these needles,



Figure 1. Scanning electron microscopy (SEM) images of lead iodide powders as synthesized by (a) hydrothermal (HT) and (b) mechanochemical (MC) routes or commercially available from (c) Sigma-Aldrich (SA) and (d) Tokyo Chemical Industries (TCI); scale bars represent 10 μ m. Background and hexagonal shaped formations correspond to PbI₂, while needle-shaped crystal formations correspond to oxyiodide and lead iodide hydroxide compounds in image (a).

incorporation of oxygen was detected by energy-dispersive spectroscopy (EDS) point analysis, as can be seen in Table S1. We believe that autoionization of water molecules occurs during the HT synthesis of PbI₂ (Figure 1a and Figure S1a), caused by the strong Coulomb interactions between the ions (Pb²⁺, K⁺, I⁻, and NO₃⁻) and water molecules. This may result in the formation of a mixture of lead oxyiodide and lead iodide hydroxide compounds, with general chemical formulas Pb- $(I_{1-x}O_x)_2$ and Pb $(I_{1-y}(OH)_y)_2$, respectively.^{33–35}

In contrast, the PBM synthesis of PbI₂ causes extensive deformation and fragmentation of the platelets, with reduced particle size (average size of <4 μ m), as illustrated in Figure 1b and Figure S1b. No oxygen was detected in the MC powder, as determined by EDS and shown in Table S1, presumably due to the absence of water during the synthesis. Also, for the commercially available PbI₂ powders from Sigma-Aldrich with a purity of 99.999% (SA) and Tokyo Chemical Industries with a purity of 99.999% (TCI), the particles (as shown in Figures 1 1dc and, respectively) are considerably larger than the MC sample shown in Figure 1b.

PbI₂ powders synthesized by the HT method and the PBM method under three different conditions with respect to the rotation and duration (MC1: (200 rpm for 2 h), MC2: (400 rpm for 1 h), and MC3: (400 rpm for 4 h)) were characterized by X-ray diffraction (XRD), alongside the two commercially available PbI₂ powders from Sigma-Aldrich (SA) and from Tokyo Chemical Industries (TCI), as shown in Figure 2. Differences in the XRD patterns were observed between the mechanochemical (MC1 to MC3), HT, and commercial SA and TCI materials. The observed XRD peaks were qualitatively labeled based on the corresponding Miller index and the associated polytypic phases. Also, the crystallographic planes and their corresponding Miller indices for each polytypic phase with respect to the diffraction 2θ angle are summarized in



Figure 2. X-ray diffraction (XRD) patterns of commercial (SA and TCI), hydrothermal (HT), and mechanochemical (made under different conditions: MC1, MC2, and MC3) PbI_2 powders. Normalization was applied with respect to the intensity of the peak that corresponds to the (001) crystallographic plane for 2H PbI_2 . All peaks are labeled based on the polytypic phases 2H, 4H, 14H, and 20H, which can contribute to scattering at that angle as outlined in Supporting Information Table S2.

Table S2. Based on the International Centre for Diffraction Database, XRD peaks of crystallographic planes with Miller indices (001), (011), and (003) correspond to the 2H polytypic phase of PbI₂ with code 01-071-6147, which is the most stable PbI₂ phase at RT, while all the other XRD peaks correspond mostly to a mixture of 4H (04-017-4470), 14H (04-007-2277), and 20H (04-007-2278) polytypic phases, with characteristic *c*-axis unit cell dimensions 1.3962, 4.8853, and 6.979 nm, respectively. Further quantitative analysis of the polytypic phases present was not possible due to complications associated with overlapping of the XRD peaks that correspond to the 2H with those of 4H, 14H, and 20H, respectively. There may also be undetected minor fractions of PbI₂, which have crystallized in a rhombohedral structure.

The MC1 sample (200 rpm for 2 h) did not show strong diffraction at the secondary XRD peak positions, indicating that it has mostly crystallized in a single polytypic phase, closely resembling that of the SA sample. Mechanochemically prepared PbI₂ powders MC2 and MC3 show enhanced intensity at the secondary XRD peaks as a result of the increased rotation speed (400 rpm) and duration (4 h) of the PBM process. The formation of more than one polytypic phase in the mechanochemical powders (MC2 and MC3) makes them more comparable with the TCI PbI₂ sample. The presence of additional polytypic phases in MC2 and MC3 is attributed to the increased energy given via the inelastic collisions occurring at the higher rotation speed between the stainless steel spheres surrounded by the reactant powders during the mechanochemical synthesis.

Stoichiometry of the PbI₂ Samples. Three different methods ((1) X-ray photoelectron spectroscopy (XPS), (2) Rutherford backscattering (RBS), and (3) X-ray diffraction (XRD) studies of perovskite microcrystals made from PbI₂) have been utilized to determine the stoichiometry of the PbI₂ samples.

XPS characterization of the commercial and synthesized PbI₂ samples was conducted to determine the lead to iodide

ratio and the amount of oxygen contained in PbI_2 . The stoichiometric variations between the lead and iodide measured and the amount of oxygen are summarized in Table 1. It should be noted that these results are averaged

Table 1. Stoichiometric Ratios of Different Lead Iodide Samples and Their Oxygen Content Percentage from XPS Measurements a

lead iodide sample	synthesis conditions/ sample information	ratio of Pb:I	amount of oxygen (%)
MC3	mechanochemical (400 rpm, 4 h)	1:2.1 (± 0.1)	2.91 (± 0.01)
MC2	mechanochemical (400 rpm, 1 h)	1:2 (± 0.1)	3.97 (± 0.16)
MC1	mechanochemical (200 rpm, 2 h)	1:2.1 (± 0.1)	5.21 (± 0.76)
HT	hydrothermal (in water)	$1:2.1 (\pm 0.1)$	7.15 (± 0.21)
TCI	Tokyo Chemical Industries, 99.99%	1:2.3 (± 0.1)	4.46 (± 0.14)
SA	Sigma-Aldrich, 99.999%	1:1.70(+0.1)	4.90(+0.02)

^aThe samples include commercial (SA and TCI), hydrothermal (HT), and mechanochemically synthesized under different conditions (MC1 to MC3) PbI₂ powders. The data was determined by two high-resolution XPS scans (a survey scan followed by high-resolution scans were used for all samples).

values and do not reveal potential localized deviations as a result of polytypism, which may be present in inhomogeneous materials. X-ray-induced photolysis of PbI_2 may also occur during the XPS measurement process; therefore, only the general trends in the Pb:I ratio are considered here. Further discussion of inhomogeneity in XPS data and X-ray-induced photolysis of PbI_2 is available in Supporting Information Section 2.

In the SA material, the lead to iodide ratio was less than the expected 1:2. Meanwhile, for the HT, MC, and TCI samples, the ratio varied significantly, with values for HT, MC1, MC3, and TCI above the stoichiometric 1:2 ratio and for MC2 being almost stoichiometric, as shown in Table 1. This variation in MC samples is attributed to the different conditions used during the PBM process. Rotation speed was found to be the dominant factor in the process followed by duration.³⁶ Understanding the influence of using overstoichiometric (TCI, MC1, and MC3) materials as compared to almost stoichiometric MC2 PbI₂ is of great future research interest. The presence of excess iodide within the perovskite grains or at grain boundaries caused by the use of overstoichiometric PbI₂³⁷ could have detrimental effects on PSC performance. These may vary with environmental conditions (such as oxygen/inert gas/moisture),^{38,39} or diffusion of excess iodide could lead to secondary chemical reactions and degradation of the other incorporated layers in a functioning solar cell device (hole/electron transporting layers or metallic contacts).⁴⁰⁻⁴²

Rutherford backscattering spectroscopy (RBS) characterization was also conducted to determine the lead to iodide ratio of the commercial and synthesized PbI₂ samples. RBS spectra with normalized yield of lead to iodide in each PbI₂ sample are shown in Figure S3. Moreover, the extracted stoichiometric ratio between the lead and iodide measured are summarized in Table S3. Uncertainties are given for statistical error, while a 4% systematic error due to uncertainty in the stopping power of the beam of ions was considered. In the SA material, the lead to iodide ratio was 1:1.9 (\pm 0.008), while in the mechanochemical MC2, it was 1:2.002 (\pm 0.008).



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Figure 3. XRD patterns of $CH_3NH_3PbI_3$ microcrystals synthesized at different temperatures (asterisks represent the XRD peaks of the lead iodide): (a) mechanochemical MC2 and CH_3NH_3I , with a 1:1 molar ratio, (b) mechanochemical MC2 and CH_3NH_3I , with a 1:1 molar ratio plus 30% by weight of CH_3NH_3I , (c) commercial SA and CH_3NH_3I , with a 1:1 molar ratio, and (d) commercial SA and CH_3NH_3I , with a 1:1 molar ratio plus 30% by weight of CH_3NH_3I . Normalization of XRD patterns was with respect to the peak that corresponds to plane with Miller indices (110) for tetragonal $CH_3NH_3PbI_3$ in all patterns, except for (c) commercial SA and CH_3NH_3I , with a 1:1 molar ratio at 20 °C, which is normalized with respect to the peak of the 2H lead iodide with Miller indices (001).

However, for the TCI, MC1, and MC3 samples, the ratio shows an excess of iodide to be present.

The different PbI₂ materials prepared, shown to have a range of Pb:I ratios and a number of polytypic phases as previously discussed, were used to synthesize CH₃NH₃PbI₃ microcrystals. The system of alcohol/PbI₂/CH₃NH₃I, similar to Acik et al.,⁴³ was used to prepare the perovskite microcrystals which were subsequently characterized by X-ray diffraction (XRD). Two groups of perovskite microcrystals were prepared as a function of PbI₂ used and the corresponding amount of CH₂NH₃I at a range of temperatures (20, 50, 70, and 90 °C). In the first group, the almost stoichiometric MC2 was reacted either with (a) an equimolar amount of CH₃NH₃I or (b) an excess of CH₃NH₃I (30% more CH₃NH₃I by weight), as shown in Figures 3a and3b, respectively. While, in the second group, substoichiometric SA was reacted either with (c) an equimolar amount of CH₃NH₃I or (d) an excess of CH₃NH₃I (30% more CH₃NH₃I by weight), as shown in Figures 3c and 3d,

respectively. Each reaction was permitted to proceed for 24 h at a constant temperature of 20, 50, 70, or 90 $^{\circ}$ C.

Considering the experiments where equimolar amounts of reactants were used to prepare the CH₃NH₃PbI₃ microcrystals, less unreacted PbI2 was detected when MC2 was used, as compared to SA. The XRD peaks that correspond to the unreacted PbI₂ are identified with asterisks in Figure 3 and are more prevalent in the SA sample (Figure 3c). The percentage of the unreacted PbI₂ after each reaction at each temperature was found by integrating the area under the primary XRD peaks and comparing the ratio of (001) PbI₂ to CH₃NH₃PbI₃ with Miller indices (002)/(110) that corresponds to the perovskite with a tetragonal crystal structure. The results are summarized in Table S4. In contrast, when an excess of CH₃NH₃I was introduced (30% more CH₃NH₃I by weight) at the most, only traces of or zero unreacted PbI₂ was detected in all the CH₃NH₃PbI₃ microcrystals synthesized, regardless of the PbI₂ source (either MC2 or SA), as shown in Figures 33db

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and , respectively. We believe that methylammonium cations $(CH_3NH_3^+)$ and iodide anions (I^-) from CH_3NH_3I , primarily react with the substoichiometric PbI₂, fulfilling the formation of $CH_3NH_3PbI_3$ and resulting in some unreacted PbI₂ (yellow in color), as shown in Figure S4 during filtering of the $CH_3NH_3PbI_3$ microcrystals. Consequently, using substoichiometric PbI₂, partially depleted of iodide, during the fabrication of perovskite thin films, results in unreacted PbI₂. This could provide a possible explanation for the improved device performance noted in the literature when hydroiodic acid (HI) is used as an additive during the $CH_3NH_3PbI_3$ formation, a correction of the iodide content when the substoichiometric PbI₂ is used, thus reducing undercoordinated Pb.⁴⁴

The same system of alcohol/PbI2/CH3NH3I was used to synthesize CH₃NH₃PbI₃ microcrystals with a controlled excess of CH₃NH₃I by weight to determine quantitatively the amount of iodide missing from PbI₂. These microcrystal samples were obtained by reacting either substoichiometric SA with 10%, 15%, 20%, and 25% excess of CH₃NH₃I by weight or the almost stoichiometrically correct MC2 with 2%, 4%, and 6% excess CH₃NH₃I by weight for 24 h at a constant temperature of 90 °C. The synthesized CH₃NH₃PbI₃ microcrystals were characterized by XRD, as shown in Figure S5. By gradually increasing the amount of excess CH₃NH₃I, the amount of unreacted PbI₂ was reduced, as indicated in the XRD patterns shown in Figure S5a,c. We found that when 20% excess CH₃NH₃I was reacted with the substoichiometric SA, the weak XRD peak that corresponds to unreacted PbI₂, as shown in Figure S5b, had almost entirely disappeared. This indicates that the required excess of CH₃NH₃I should be slightly greater than 20% to achieve the complete elimination of unreacted PbI2 during the synthesis of CH3NH3PbI3 microcrystals when the substoichiometric SA material is used. This value of 20% excess of CH₃NH₃I by weight is consistent with the value of 10% excess PbI₂ in the PbI₂/CH₃NH₃I mixture used for the formation of perovskite as reported by Nazeeruddin et al.45 In both cases, the iodine deficiency is corrected, by iodine originating from either the 20% excess of CH₃NH₃I or the 10% excess of PbI₂ used, to achieve the required stoichiometry in the final product of CH₃NH₃PbI₃. Meanwhile, when 4% excess CH₃NH₃I was reacted with the almost stoichiometric MC2, this resulted in an even weaker PbI₂ XRD peak, as shown in Figure S5d. The stoichiometric ratios for SA and MC2 were calculated based on the need for either the 20% more CH₃NH₃I reacting with substoichiometric SA or the 4% more CH₃NH₃I reacting with the almost stoichiometric MC2 to eliminate any signal that corresponds to PbI₂ in the XRD data. We found after analysis that the initial (Pb:I) ratio for SA is approximately 1:1.80 and that for MC2 is approximately 1:1.96, as presented in Supporting Information Section 3. Also, based on all the above XRD analysis of CH₃NH₃PbI₃ microcrystals, a theory about the formation of unreacted PbI₂ was developed, as presented in Supporting Information Section 4, accompanied by several examples, as shown in Table S5.

The results from the XPS and RBS characterization techniques used to determine the lead to iodide ratio in the commercial (SA) and mechanochemical (MC2) PbI₂ samples are considered alongside the ratios derived from the synthesis of CH₃NH₃PbI₃ microcrystals with controlled excess CH₃NH₃I and their subsequent XRD characterization (further analysis is provided in Supporting Information Section 3). The results from all three techniques show consistent trends; less

iodide was detected in the SA sample as compared to the MC2 sample, as shown in Figure 4. The large experimental error in



Figure 4. Number of iodide atoms in lead iodide (commercial (SA) and mechanochemical (MC2)) as function of the characterization technique (XPS correspond to white columns, $CH_3NH_3PbI_3$ microcrystals correspond to red columns, and RBS correspond to blue columns).

the XPS data could be related to X-ray-induced photolysis of PbI₂ (further discussion is available in Supporting Information Section 2) and the penetration depth of photons that correspond to X-rays (typically 2–5 nm). Meanwhile, in RBS with a typical ⁴He⁺ ion penetration depth of ~100 nm, the acquired signal might be affected by the number of polytypic phases present and their structural density (2H ρ str. = 6.214 g·cm⁻³, 4H ρ str. = 5.452 g·cm⁻³, 14H ρ str. = 6.098 g·cm⁻³, and 20H ρ str. = 6.1 g·cm⁻³), as provided by the International Centre for Diffraction Database.

Impact of Stoichiometry of Pbl₂ on Device Perform**ance.** Fabrication of PSC devices with the n-i-p (regular) architecture of glass/ITO/SnO₂/CH₃NH₃PbI₃/spiro-OMe-TAD/Au was performed, where nanoparticle tin oxide (SnO_2) served as the electron transporting layer (ETL) and spiro-OMeTAD as the hole transporting layer (HTL), to determine how the variable stoichiometry affects the device performance. Comparisons were made between devices fabricated using two varieties of PbI2: SA, which is depleted in iodide, and mechanochemical MC2, which is almost stoichiometrically correct. PSC devices were made by dissolving either the SA or MC2 powders with an equimolar amount of CH₃NH₃I in dimethyl sulfoxide (DMSO) to produce photoactive thin films with thicknesses \sim 550 nm (± 50 nm) and \sim 380 nm (\pm 70 nm) as shown in cross-sectional SEM images, Figures S6a and S6b, respectively, after correcting for the 45° sample angle. A second set of PSC devices was also made by re-dissolving CH₃NH₃PbI₃ microcrystals in DMSO. The same two PbI₂ materials (either SA or MC2) were used in the reaction with a 30% excess of CH₃NH₃I by weight. Minor morphological differences of CH₃NH₃PbI₃ microcrystals synthesized at a temperature of 90 °C, using the two varieties of PbI₂ (either SA or MC2), are shown in Figure S7a,b. The formation of the microcrystals made with an excess of CH₃NH₃I helped to correct for any deficiency of iodide within PbI₂. The PSC devices, with the photoactive layer made by re-dissolving the CH₃NH₃PbI₃ microcrystals (made using



Figure 5. Variation of FF, J_{SC} , PCE, and V_{OC} of the solar cell devices as a function of the synthesis route/materials used. Their structure was glass/ITO/SnO₂/CH₃NH₃PbI₃/spiro-OMeTAD/Au. The devices using the CH₃NH₃PbI₃ microcrystal synthesis involved a stoichiometry correction step for iodide by the addition of CH₃NH₃I. The devices using equimolar amounts of PbI₂ and CH₃NH₃I powders did not include this step.

Table 2. Performance Parameters of Solar Cell Devices with the Structure Glass ITO/SnO₂/CH₃NH₃PbI₃/spiro-OMeTAD/ Au, as a Function of the Starting Materials Used and the Synthesized CH₃NH₃PbI₃ Microcrystals^{*a*}

		FF (%)	$J_{\rm SC}~({\rm mA/cm^2})$	$V_{\rm OC}$ (V)	PCE (%)			
dissolution of $CH_3NH_3PbI_3$ microcrystals in DMSO	CH ₃ NH ₃ PbI ₃ microcrystals (synthesized using MC2)	68.19 (73.66)	20.98 (21.61)	1.03 (1.04)	14.69 (16.55)			
	CH ₃ NH ₃ PbI ₃ microcrystals (synthesized using SA)	72.08 (75.82)	20.8 7 (21.65)	1.06 (1.06)	16.02 (17.40)			
dissolution of equimolar PbI_2/CH_3NH_3I in	MC2/CH ₃ NH ₃ I (equimolar)	71.75 (75.29)	21.09 (21.60)	1.04 (1.05)	15.77 (17.07)			
DMSO	SA/CH ₃ NH ₃ I (equimolar)	34.18 (41.01)	13.06 (14.96)	1.02 (1.02)	4.58 (6.26)			
a The photovoltaic parameters of the average values from 20 devices in bold and champion devices in parentheses.								

either SA or MC2) in DMSO, had photoactive thin film thicknesses of ~460 nm (\pm 50 nm) and ~440 nm (\pm 40 nm), as shown in cross-sectional SEM images, Figures S6c and S6d, respectively, after correcting for the 45° sample angle. The deposition of the photoactive thin films was performed in ambient air, and the black/brown perovskite phase formation was accomplished using a vacuum-assisted method that promotes the extraction of solvent in a single step (without an anti-solvent rinsing process),^{46,47} as shown in Figure S8a (before annealing) and Figure S8b (after annealing), respectively.

The average and champion photovoltaic parameters: fill factor (FF), short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), and power conversion efficiency (PCE), as measured during a reverse ($V_{OC} \rightarrow 0$) scan with a scan step of 10 mV s⁻¹, are illustrated in Figure 5. Additionally, the

photovoltaic parameters for all the devices are summarized in Table 2.

Notably, the photovoltaic parameters are significantly enhanced in PSC devices made from either CH₃NH₃PbI₃ microcrystals, where the iodide content was corrected by the processing regardless of the number of polytypic phases in PbI₂ used (SA or MC2), or when equimolar amounts of almost stoichiometric MC2 with CH₃NH₃I were used. In comparison, the device performance parameters (FF, J_{SC} and PCE) of PSC devices fabricated using equimolar amounts of the SA with CH₃NH₃I were notably inferior. This reduction in device performance is attributed to the presence of a significant amount of unreacted PbI₂ between, covering or possibly within the grains of CH₃NH₃PbI₃.^{48–50} Also, the characteristic current density–voltage (J-V) curves in forward ($0 \rightarrow V_{OC}$) and reverse ($V_{OC} \rightarrow 0$) scans of PSC devices were compared as a function of the photoactive layer fabricated using either

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Figure 6. (a) IPCE and (b) electron current of perovskite solar cells and electron-only devices, respectively, using $CH_3NH_3PbI_3$ microcrystals (using MC2) (black curves), $CH_3NH_3PbI_3$ microcrystals (using SA) (orange curves), equimolar amounts of $MC2/CH_3NH_3I$ (red curves), and equimolar amounts of SA/CH_3NH_3I (blue curves).



Figure 7. (a) Visible-infrared (Vis-IR) absorbance, (b) steady-state photoluminescence (PL) spectra, and (c, d) TRPL decay curves of perovskite thin films synthesized using $CH_3NH_3PbI_3$ microcrystals (using MC2) (black curves), $CH_3NH_3PbI_3$ microcrystals (using SA) (orange curves), equimolar amounts of $MC2/CH_3NH_3I$ (red curves), and equimolar amounts of SA/CH_3NH_3I (blue curves) (from five different measured points only in (a)). Absorbance due to the presence of unreacted lead iodide is indicated with black arrow in (a).

 $CH_3NH_3PbI_3$ microcrystals or equimolar amounts of different PbI_2 with CH_3NH_3I , as shown in Figure S9. In all the plots, black curves correspond to the average from all J-V curves recorded and the error bars represent the deviation across all the devices. Hysteresis was observed between the J-V curves

for the forward $(0 \rightarrow V_{OC})$ and reverse $(V_{OC} \rightarrow 0)$ scans for all devices, and that of the higher performing conditions was worst in the case for the equimolar of reactants used. All the *J*-*V* curves (either in reverse or forward scans) of PSC devices fabricated using equimolar amounts of substoichiometric PbI₂

(SA) with CH₃NH₃I were notably inferior in performance, as shown in Figure S9d.

Less hysteresis was observed between forward and reverse scans of PSC devices fabricated using equimolar amounts of the substoichiometric PbI₂ (SA) with CH₃NH₃I. The hysteresis could be related to ion migration originating from unreacted PbI₂ likely present between the grain boundaries and also possibly within the grains themselves, affecting the diffusion lengths of charge carriers. It may be masked in the SA sample because of the considerably lower current observed. We believe that the amount of iodide present in the substoichiometric SA is insufficient to form the exact composition of CH₃NH₃PbI₃, but this can be corrected by using the above method for the preparation of microcrystals to adjust the stoichiometry.

In order to shed light on the differences in the device performance, the internal photon-to-electron-conversion efficiencies (IPCE) of the fabricated PSC devices were measured. The results are shown in Figure 6a and clearly demonstrate that the photon-to-electron conversion process is more efficient for the devices based on perovskite absorbers synthesized from the close to perfectly stoichiometric precursors. Furthermore, electron-only devices with the structure FTO/SnO₂/CH₃NH₃PbI₃/PCBM/Ag were fabricated and their I-V characteristics were measured under dark conditions, as shown in Figure 6b. These results indicate that the electron injection is inferior in the device when the substoichiometric PbI2 with an equimolar amount of CH₃NH₃I were used. This can be explained by the presence of a large excess of unreacted PbI₂ within the perovskite synthesized from the substoichiometric precursor material.

The presence of unreacted PbI₂ in the perovskite films obtained when using equimolar amounts of SA/CH₃NH₃I was also confirmed by the short wavelength shoulder present in the visible infrared (Vis-IR) absorption spectra shown in Figure 7a. The experimentally calculated optical band gap values (E_{obg}) for PbI₂ ($E_{obg} = 2.53 \text{ eV} (\pm 0.01 \text{ eV})$) and CH₃NH₃PbI₃ ($E_{obg} = 1.48 \text{ eV}$), as determined by Tauc plots, support the hypothesis that unreacted PbI₂ might also form within the perovskite grains because they show a deviation from the optical band gap values that correspond to neat PbI₂ ($E_{obg} = 2.36 \text{ eV}$) and CH₃NH₃PbI₃ ($E_{obg} = 2.36 \text{ eV}$) and CH₃NH₃PbI₃ ($E_{obg} = 1.51 \text{ eV}$),⁵¹ as presented in Figures S10a and S10b, respectively.

Also, the presence of unreacted PbI_2 in the perovskite films obtained when equimolar amounts of SA and CH₃NH₃I were used results in a binary mixture of CH₃NH₃PbI₃ and PbI₂ (with CH₃NH₃PbI₃ as the major phase and PbI₂ as the minor phase) with $E_{obg} = 1.48$ eV and a similar binary mixture (with PbI_2 as the major phase and $CH_3NH_3PbI_3$ as the minor phase) with $E_{\rm obg} = 2.53$ eV (± 0.01 eV). Consequently, when equimolar amounts of SA and CH₃NH₃I are used, the formation of those binary mixtures, which are neither pure CH₃NH₃PbI₃ nor pure PbI₂, may lead to materials with absorption coefficients different than their absolute values.⁵² Wang et al., and Cui et al. reported that different precursor ratios of PbI2:CH3NH3I affect the optoelectronic properties of the resulting CH₃NH₃PbI₃ formed, such as the Fermi level, charge carrier mobilities, carrier concentrations, and recombination rates.^{53,54} Further details of how this can result in unreacted PbI₂ in the resulting perovskite film are given in Supporting Information Section 4. Steady-state photoluminescence (PL) spectra of the different perovskite samples deposited on SnO₂/ITO substrates were also measured

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(Figure 7b). The PL intensities varied significantly and were much lower for the perovskite films fabricated from the stoichiometric precursors or for those where the stoichiometry has been adjusted through processing (microcrystals). While it is difficult to disentangle the effects of interface recombination and carrier extraction, this difference could be due to either fewer defects in the samples fabricated using microcrystals or efficient blocking in samples based on the presence of unreacted PbI₂. However, in light of the PSC device data, we attribute this difference to suppressed electron injection into the ETL in the SA/CH₃NH₃I sample leading to increased bulk radiative recombination. Upon perovskite photoexcitation in the SnO₂/perovskite samples, electrons are transferred from its conduction band (lying at about -3.9 eV) to the lower conduction band of SnO_2 (lying about -4.1 eV), hence suppressing the PL signal. In the PbI2-rich samples, this electron transfer pathway is blocked due to the insulating properties of PbI₂.

This was further corroborated by the transient PL (TRPL) measurements taken on the same samples (detection at 770 nm) (Figure 7c,d and Table S6), which indicated faster electron transfer from the excited perovskite toward SnO_2 in the equimolar $MC2/CH_3NH_3I$ sample compared to the SA/ CH_3NH_3I counterpart. We note that the small difference in the decay kinetics between equimolar and microcrystal samples may be due to the differences in morphology.

The above results indicate that the perovskite samples derived from substoichiometric precursors are enriched in insulating PbI₂, which is formed between the grains or combined within consecutive layers of (CH₃NH₃PbI₃/PbI₂) likely formed within the grains of CH₃NH₃PbI₃. The formation of CH₃NH₃PbI₃ ferroelastic domains, regardless of the stoichiometry in PbI2, has also been noted in the literature⁵⁵⁻⁵⁷ and is confirmed here by AFM (Figure S11). This phenomenon may also explain the spatial variability of the J_{SC} within individual CH₃NH₃PbI₃ grains, as reported by Kutes et al.⁵⁸ The measured roughness of all fabricated CH₃NH₃PbI₃ thin films using the vacuum-assisted method was less than 16 nm, as measured by AFM. Also, an increased concentration of larger pinholes formed in the CH₃NH₃PbI₃ thin films fabricated from the CH₃NH₃PbI₃ microcrystals regardless of PbI₂ used (either substoichiometric SA or almost stoichiometric MC2) as observed in LV-SEM images, Figure S12a,b. This might suggest that, with further process development, such as by further modifying the 1.13 M concentration of the perovskite ink using the CH₃NH₃PbI₃ microcrystals, even better photovoltaic performance is achievable by this route. For all the LV-SEM images in Figure S12, grain size distribution calculations were conducted and are summarized in Figure S13. Specifically, the majority of grains on CH₃NH₃PbI₃ thin films when microcrystals were employed and fabricated using the almost stoichiometric MC2 PbI₂ had an average size of 110 ± 10 nm. Meanwhile, the majority of grains had an average size of 90 \pm 10 nm when microcrystals were prepared using the substoichiometric SA PbI₂. Also, equimolar amounts of the almost stoichiometric MC 2 PbI₂/ CH₃NH₃I resulted in thin films with the maximum average grain size of 175 ± 25 nm. Meanwhile, for thin films of perovskite made using equimolar amounts of substoichiometric SA PbI₂/CH₃NH₃I, the average grain size was 130 ± 10 nm. The smaller grain sizes observed when using the microcrystal processing route may be due to slightly different growth mechanisms occurring in the perovskite thin films

made from $CH_3NH_3PbI_3$ microcrystals and equimolar amounts of reactants, which requires further investigation.

CONCLUSIONS

In conclusion, planetary ball milling is a low-cost, energyefficient pathway to produce PbI2 with reduced oxygen content, whereby it is possible to control both the stoichiometry and polytype of the resulting PbI₂ by varying the mechanochemical parameters of synthesis (revolutions per minute and duration). The absence of water during the PbI₂ production via planetary ball milling allows for a significant reduction in the oxygen content present as determined by XPS analysis. Although the polytypism of the PbI₂ precursor had no profound effect on the solar cell performance, its stoichiometry was proven to exhibit serious implications for the device performances. PSC devices with a photoactive layer manufactured using substoichiometric PbI2 showed reduced performance due to the large excess of PbI2 in the perovskite film, unless an excess of CH₃NH₃I was used via the fabrication of CH₃NH₃PbI₃ microcrystals. If PbI₂ was stoichiometrically correct, an excess of CH₃NH₃I was not necessary. Using stoichiometrically corrected PbI2, in combination with the single-step vacuum-assisted method, which is free of any antisolvent rinse step and does not use other toxic solvents, promotes the formation of CH₃NH₃PbI₃ with close to no detectable unreacted PbI₂. This processing route can help enable a low-cost and air-processable fabrication route for PSC devices with repeatably high performance. This work highlights the importance of proper material control and synthesis procedures to achieve enhanced quality of PSC devices.

EXPERIMENTAL DETAILS

Methylammonium lodide Synthesis. Methylammonium iodide (CH₃NH₃I) was synthesized by adding dropwise 38 mL of hydroiodic acid (57% w/w in water, Alfa Aesar) in 30 mL of methylamine (40% w/w in water, Sigma-Aldrich) in a 250 mL round-bottom flask at 0 °C (ice bath) and constant stirring (400 rpm) for 2 h. The round-bottom flask was transferred into an oil bath at a temperature of 90 °C to evaporate water for 6–7 h. The resulting yellow/white precipitate was further purified by recrystallizing two times from pure anhydrous ethanol. The white/transparent crystallized flakes were collected by vacuum filtration (Whatman filter paper grade 5 with a pore size of 2.5 μ m) and dried in a vacuum oven at 50 °C for 24 h before storage in dark conditions. The same methylammonium iodide was used for both the synthesis of the CH₃NH₃PbI₃ microcrystals and perovskite solutions.

Hydrothermal Pbl₂ Synthesis. Hydrothermal PbI₂ was synthesized by dissolving 1 g of lead(II) nitrate (Pb(NO₃)₂, Sigma-Aldrich) with a purity of \geq 99% and 1.01 g of potassium iodide (KI, Honeywell Fluka) with a purity of \geq 99% (both precursors as received) in a 1 L volume round-bottom flask filled with 1 L of boiled (100 °C) ultrapure deionized water (Sigma-Aldrich) with a resistivity of 18.2 MΩ. The round-bottom flask was covered with towel made of fiber glass and left to cool down slowly to room temperature for 24 h. An excess of potassium iodide was used, to complete the reaction of the Pb(NO₃)₂ based on the chemical reaction: Pb(NO₃)₂ + 2KI \rightarrow PbI₂ + 2KNO₃. The golden colored crystalline flakes of PbI₂ were collected after vacuum filtration (Whatman filter paper grade 5 with a pore size of 2.5 μ m) and dried in a vacuum oven at 50 °C for 24 h before further characterization.

Mechanochemical Pbl₂ **Synthesis.** Mechanochemical Pbl₂ powder was synthesized using a planetary ball milling machine (PM 100 Retsch) at variable revolutions per minute and time duration. Thirty grams of Pb(NO₃)₂ with a purity of \geq 99%, 30.07 g of KI with a purity of \geq 99%, and 160 stainless steel spheres with a diameter of 6 mm were mixed in a ball milling jar with a capacity of 500 mL.

Oxygen reduction inside the ball milling jar was conducted by displacing the air with argon gas (purity: 99%). This oxygen reduction was only applied for the mechanochemical sample MC3 (400 rpm, 4 h), leading to oxygen reduction by $\sim 36 (\pm 10)\%$, in comparison with the mechanochemical samples MC1/MC2 synthesized without the introduction of argon gas. We expect that further oxygen reduction in the mechanochemical PbI2 powders might be achievable by careful drying the reactants used and by displacing the air with ultra-pure argon gas (>99.99%) inside the ball milling jar. The yellow colored PbI₂ powder was separated from the stainless steel spheres and washed five times with 70-80 mL (each time) of deionized water during vacuum filtration (Whatman filter paper grade 5 with a pore size of 2.5 μ m) to remove any potassium nitrate byproduct. Finally, PbI₂ was dried in a vacuum oven at 50 °C for 24 hours, before storage in dark conditions and further characterization. The yield of the produced PbI₂ (MC2) was defined by the relative number of product/reactant moles between PbI_2 and $Pb(NO_3)_2$ (considering the ideal molecular weight for PbI_2 to be 461.01 g/mol), resulting ((40.32) $g/461.01 \text{ g}\cdot\text{mol}^{-1})/(30 \text{ g}/(331.21 \text{ g}\cdot\text{mol}^{-1})) \times 100\% \approx 96.5\%.$

CH₃NH₃Pbl₃ Microcrystal Synthesis. CH₃NH₃PbI₃ microcrystals were synthesized by reacting 0.7 g of the almost stoichiometric MC2 or substoichiometric SA PbI₂ (used as received and stored in dark conditions) with an equimolar amount of CH₃NH₃I (0.2414 g) or an equimolar amount plus 30% excess by weight of CH_3NH_3I (0.2414 g + 0.0724 g = 0.3138 g) in 15 mL of 1pentanol at variable temperatures (20, 50, 70, and 90 °C) for 24 h (in an oil bath). In this process, 1-pentanol, which is a polar protic nontoxic alcohol, was used to selectively dissolve only the methylammonium iodide but not the $\ensuremath{\text{PbI}}_2$ powder and the final product of the CH₃NH₃PbI₃ microcrystals. The black powder of CH₃NH₃PbI₃ microcrystals was collected by vacuum filtration (Whatman filter paper grade 5 with a pore size of 2.5 $\mu m)$ and washed with 5 mL of chlorobenzene (Alfa Aesar) during the filtration step followed by drying in a vacuum oven for 30 min at room temperature before further characterization.

After completion of the chemical reaction, the 1-pentanol/PbI₂/ CH_3NH_3I solution must be kept warm and filtrated as fast as possible (<2 s). Recrystallization of the excess CH_3NH_3I dissolved in the 1-pentanol during the vacuum filtration process (to separate out the $CH_3NH_3PbI_3$ microcrystals) was prevented by the use of a large volume of 1-pentanol, which reduces the probability of the dissolved ions ($CH_3NH_3^+$ and I^-) interacting. Unreacted $CH_3NH_3^+$ and I^- ions remain dissolved in warm 1-pentanol and are therefore removed from the microcrystals upon filtration.

Dry Dimethyl Sulfoxide Preparation. Dry dimethyl sulfoxide (DMSO, Sigma-Aldrich) was prepared by intermixing 150 mL of asreceived dimethyl sulfoxide (DMSO) with a purity of \geq 99.5% and 20 g of magnesium sulfate (MgSO₄, Fisher Chemical) in a 250 mL round-bottom flask. The round-bottom flask was capped and left in a fume hood at room temperature for at least 2 weeks before extracting crystal clear dry DMSO.

Perovskite Solution Preparations. Perovskite solutions were prepared either by dissolving 0.4 g of the almost stoichiometric MC 2 or substoichiometric SA PbI2 directly with an equimolar amount of CH₃NH₃I (0.1379 g) in 0.620 mL of dry DMSO with a final concentration of 2.8 M or by dissolving 0.4 g of the CH₃NH₃PbI₃ microcrystals synthesized using the almost stoichiometric MC 2 or substoichiometric SA $\ensuremath{\text{PbI}}_2$ in 0.571 mL of dry DMSO with a final concentration of 1.13 M. Additionally, all perovskite solutions were kept on a hot plate at a temperature of 100 °C for 10 min to ensure complete dissolution of the reactants in DMSO before being filtered through a PTFE filter (pore size of 0.45 μ m) and kept under constant stirring (~300 rpm) and temperature (65–70 $^\circ\text{C})$ in a custom-made aluminum block (see Figure S14) before deposition. The block helped to reduce condensation of DMSO on the inside of the vial walls, thereby preventing premature perovskite crystallization. In all our experiments with CH₃NH₃PbI₃ microcrystals, the solution concentrations were calculated based on the assumption of perfect CH₃NH₃PbI₃ microcrystals with a molecular weight of 619.98 gmol⁻¹, as defined by the atomic mass units of each element in

 $CH_3NH_3PbI_3$ and prepared for 24 h after their synthesis. Also, in all our experiments with either commercial SA or mechanochemical MC2, solution concentrations were calculated based on the false assumption of stoichiometrically perfect PbI₂ (Pb:I = 1:2, atom ratio), with a molecular weight of 461.01 g·mol⁻¹.

Device Fabrication. Glass substrates pre-patterned with six ITO (indium tin oxide) pixels (20 Ω /square, Ossila) were first sonicated for 10 min in a solution made of 1 mL of detergent (Hellmanex III) and 250 mL of boiled deionized water (100 °C). Any residual detergent was subsequently washed off by rinsing the substrates three times with 100 mL (each time) of deionized water. The glass/ITO substrates were further sonicated two more times for 10 min (each time) in 250 mL of acetone and then 250 mL of isopropanol. The cleaned substrates were then treated with oxygen plasma for 10 min to remove organic contaminants. Clean glass/ITO substrates were transferred into a cleanroom (class 1000) with a constant temperature of 20 °C and humidity of 30% for deposition of the electron transporting layer and perovskite thin film. A colloidal dispersion of tin(IV) oxide (SnO₂) in deionized water (15%, Alfa Aesar, diluted to 3%) was spin coated at 3000 rpm for 30 s followed by removal of SnO₂ from part of the substrate using a cotton bud, re-exposing the \sim 4–5 mm ITO electrode. The coated substrates were then annealed at 150 °C for 30 min and cooled down to 20 °C, without any further treatment.⁵⁹ Fifty microliters of the perovskite solutions made of either CH₃NH₃PbI₃ microcrystals in DMSO with a concentration of 1.13 M or solutions of (almost stoichiometric MC2 or substoichiometric SA) PbI₂ reacted with equimolar amounts of CH₃NH₃I in DMSO with a concentration of 2.8 M was statically dispersed onto the glass/ITO/SnO₂ samples followed by spin coating at 2500 or 3100 rpm for 10 s, respectively. Each substrate was placed in a custom-made vacuum chamber for 120 s and a pressure of ~0.02 mbar, as shown in Figure S15. Then, each substrate was annealed on a hot plate at 100 °C for 30 s. All glass/ITO/SnO₂/CH₂NH₂PbI₂ samples were then transferred inside a nitrogen-filled glove box for the synthesis and deposition of the doped hole transporting layer of 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD, ≥99.5%, Ossila). An 86.6 mg solution of spiro-OMeTAD powder was dissolved in 1 mL of chlorobenzene. The solution was then doped with lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI, ≥99%, Sigma-Aldrich), 4-tert-butylpyridine (TBP 96.6%, Sigma-Aldrich), and FK209 (FK 209 Co(II) PF6, Greatcell). The quantity of dopants used in 1 mL of the spiro-OMeTAD/ chlorobenzene solution was as follows: 20 µL of Li-TFSI (500 mg· mL⁻¹ in acetonitrile), 34 μ L of TBP, and 11 μ L of FK209 (300 mg· mL^{-1} in acetonitrile). The solution was filtered with a PTFE filter (pore size of 0.2 μ m), and then 50 μ L was spin coated on each sample dynamically at 4000 rpm for 30 s. Devices were left overnight in dry air to allow for spiro-OMeTAD to be oxidized. Finally, 80 nm of gold was deposited in an Edwards thermal evaporator, with a deposition rate of 0.1 Å s⁻¹ for the first 2 nm and then 1 Å s⁻¹ for the remaining thickness.⁶⁰ All un-encapsulated PSCs devices were immediately characterized electrically.

Photocurrent Density–Voltage (*J–V***) Measurements.** Photocurrent density–voltage (*J–V*) characteristics were measured under an AM 1.5G light (1000 W m⁻²) produced by a xenon lamp (Newport solar simulator). The light intensity was calibrated using a silicon reference cell (Newport). Each solar cell device was mounted and covered with a six-pixelated cell shadow mask, with an aperture area of 0.0256 cm² per cell. Cells were scanned from -0.2 to 1.2 V and then back to -0.2 V at a scan step of 0.01 V·s⁻¹ using a Keithley 237 source measure unit.

Powder X-ray Diffraction Measurements. X-ray diffraction patterns of all (commercial (used as received and stored in dark conditions), hydrothermal, and mechanochemical) lead iodide powders and CH₃NH₃PbI₃ microcrystals were obtained using a D2 Phaser (Bruker) diffractometer under monochromatic Cu K α radiation ($\lambda = 1.54184$ Å) and step size $2\theta = 0.020273^{\circ}$ over the 2θ range from 9° to 52°. X-ray diffraction patterns of CH₃NH₃PbI₃ microcrystals with different amounts of excess CH₃NH₃I were obtained at double acquisition time for higher accuracy. Also, all

measurements of powders were taken using a zero-background holder made of monocrystalline silicon.

SEM Images and EDS Analysis. Scanning electron microscopy (SEM) images and energy-dispersive spectroscopy (point or full image) elemental analysis were obtained using a JSM-6010LA (JEOL) at accelerating voltages 12 and 15 kV, respectively. Low-voltage scanning electron microscopy images were obtained using a FEI Helios NanoLab G3 UC SEM at an accelerating voltage of 2 kV using a through-lens detector (TLD) at a working distance of 4.2 mm and with a beam current of 13 pA.

Visible–Infrared (Vis-IR) Spectroscopy Measurements. Absorption spectra of all $CH_3NH_3PbI_3$ thin films were obtained using a spectrometer (USB2000 + UV–VIS-ES) equipped with a deuterium halogen light source (UV–VIS-NIR_DT-MINI-2-GS), both from Ocean Optics.

Time-Resolved Photoluminescence (TRPL) Measurements. The time-resolved photoluminescence measurements were performed using the time-correlated single photon counting (TCSPC) method (FluoTime 200, Picoquant) under magic-angle conditions. Excitation was performed by a pulsed diode laser at 470 nm, and the instrument's response function (IRF) was ~80 ps. Multi-exponential functions convoluted with the IRF were used for the fitting taking into account that the χ^2 factor should be smaller than 1.1.

X-ray Photoelectron Spectroscopy (XPS) Measurements. Each powder was mounted for analysis by pushing the powder into indium foil. The indium foil was then mounted directly onto the sample holder using double-sided conducting carbon tape. The analyses were carried out using a Kratos Supra instrument with a monochromatic aluminum source and an energy of 1486.69 eV. Survey scans were collected between binding energies from 1200 to 0 eV at 1 eV intervals with an acquisition time of 10 min (per point) from two analysis points per sample. High-resolution scans were also collected for the I 3d, O 1s, C 1s, and Pb 4f core levels at 0.1 eV intervals with an acquisition time of 5 min for each point. The data collected were calibrated in intensity using a transmission function characteristic of the instrument to make the values instrumentindependent. The data was then quantified using the CasaXPS software, determining the transmission functions as provided by the National Physical Laboratory (NPL). Binding energy calibrations for all survey or high-resolution scans were conducted with respect to the Pb 4f 7/2 core level at 138.0 eV. No selected option as an escape depth correction was applied at each survey or high-resolution scan before starting any further quantification analysis.⁶¹ For the compositional analysis of the core level spectra of I 3d 5/2, O 1s, C 1s, and Pb 4f 7/2, the Scofield relative sensitivity factors of 16, 2.52, 1, and 13.7 were used, respectively. The binding energy regions used for analysis were kept constant with respect to each element at each survey or high-resolution scan. Also, for each binding energy region, a Shirley type background function was used.

Rutherford Backscattering Spectroscopy (RBS) Measurements. Two commercial and four synthesized PbI_2 samples in the form of pellets with a diameter of ~13 mm and thickness of ~1.5 mm were prepared using a press under an applied mass of 9 tons. For the RBS measurements, a 1.7 MV Tandetron RBS linear type tandem ion beam accelerator was used, which is located in the Laboratory of Ion Beam Physics at the ETH Zurich facilities in Switzerland. PbI₂ pellets were bombarded with accelerated ions of ⁴He⁺ at 2 MeV, while a PIN diode detector was placed at an angle of 168°, with respect to the beam of incident ions. The resulted data were plotted using the RUMP simulation software.

Atomic Force Microscopy (AFM) Measurements. Atomic force microscopy of the CH₃NH₃PbI₃ thin films was performed using a Dimension icon with ScanAsyst AFM (Bruker) with a cantilever consisting of a silicon tip on a silicon nitride lever (Bruker) (f = 70 kHz, $k = 0.4 \text{ N} \cdot \text{m}^{-1}$).

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c03517.

(Section 1) Discussion of polytypism in PbI₂; SEM-EDS data; photograph of HT and MC PbI2 samples, completed films, sample preparation, and the vacuumassisted drying setup; XRD peak positons for different PbI₂ polytypes; (Section 2) XPS discussion and results; RBS data and calculated stoichiometric ratios; percentage unreacted PbI₂ as determined from XRD; photograph of residual PbI₂ in perovskite microcrystal powder; microcrystal XRD data; (Section 3) description of method to determine stoichiometry from crystallization XRD; (Section 4) iodine deficiency discussion including example calculations; SEM images: cross-sectional SEM of SA and MC films, SA and MC microcrystals, film coverage for SA, MC, SA(microcrystal), and MC-(microcrystal) films plus grain size distributions; device I(V) plots; Tauc plots for SA and MC samples; TRPL fitting parameters; and AFM images of SA and MC samples (PDF)

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Notes

The authors declare the following competing financial interest(s): D. G. Lidzey is a co-director of the company Ossila Ltd., that retail materials and equipment used in perovskite photovoltaic device research and development.

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REFERENCES

(1) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* **2009**, *131*, 6050–6051.

(2) Shin, S. S.; Yeom, E. J.; Yang, W. S.; Hur, S.; Kim, M. G.; Im, J.; Seo, J.; Noh, J. H.; Seok, S. I. Colloidally prepared La-doped BaSnO₃ electrodes for efficient, photostable perovskite solar cells. *Science* **2017**, 356, 167–171.

(3) Wang, R.; Mujahid, M.; Duan, Y.; Wang, Z.-K.; Xue, J.; Yang, Y. A Review of Perovskites Solar Cell Stability. *Adv. Funct. Mater.* **2019**, 1808843.

(4) Huang, F.; Li, M.; Siffalovic, P.; Cao, G.; Tian, J. From scalable solution fabrication of perovskite films towards commercialization of solar cells. *Energy Environ. Sci.* **2019**, *12*, 518–549.

(5) Jacobsson, T. J.; Correa-Baena, J.-P.; Anaraki, E. H.; Philippe, B.; Stranks, S. D.; Bouduban, M. E. F.; Tress, W.; Schenk, K.; Teuscher, J.; Moser, J.-E.; Rensmo, H.; Hagfeldt, A. Unreacted PbI₂ as a Double-Edged Sword for Enhancing the Performance of Perovskite Solar Cells. J. Am. Chem. Soc. **2016**, 138, 10331–10343.

(6) Saliba, M.; Matsui, T.; Seo, J.-Y.; Domanski, K.; Correa-Baena, J.-P.; Nazeeruddin, M. K.; Zakeeruddin, S. M.; Tress, W.; Abate, A.; Hagfeldt, A.; Grätzel, M. Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. *Energy Environ. Sci.* **2016**, *9*, 1989.

(7) Roose, B.; Dey, K.; Chiang, Y.-H.; Friend, R. H.; Stranks, S. D. Critical assessment of the use of excess lead iodide in lead halide perovskite solar cells. *J. Phys. Chem. Lett.* **2020**, *11*, 6505–6512.

(8) Song, Z.; Watthage, S. C.; Phillips, A. B.; Heben, M. J. Pathways toward high-performance perovskite solar cells: review of recent advances in organo-metal halide perovskites for photovoltaic applications. *J. Photonics Energy* **2016**, *6*, No. 022001.

(9) Chang, J.; Zhu, H.; Li, B.; Isikgor, F. H.; Hao, Y.; Xu, Q.; Ouyang, J. Boosting the performance of planar heterojunction perovskite solar cell by controlling the precursor purity of perovskite materials. *J. Mater. Chem. A* **2016**, *4*, 887–893.

(10) Yao, J.; Yang, L.; Cai, F.; Yan, Y.; Gurney, R. S.; Liu, D.; Wang, T. The impacts of PbI_2 purity on the morphology and device performance of one-step spray-coated planar heterojunction perovskite solar cells. *Sustainable Energy Fuels* **2018**, *2*, 436–443.

(11) Kumar, V.; Barbé, J.; Schmidt, W. L.; Tsevas, K.; Ozkan, B.; Handley, C. M.; Freeman, C. L.; Sinclair, D. C.; Reaney, I. M.; Tsoi, W. C.; Dunbar, A.; Rodenburg, C. Stoichiometry-dependent local instability in MAPbI₃ perovskite materials and devices. *J. Mater. Chem. A* **2018**, *6*, 23578–23586.

(12) Zhang, Y.; Lv, H.; Cui, C.; Xu, L.; Wang, P.; Wang, H.; Yu, X.; Xie, J.; Huang, J.; Tang, Z.; Yang, D. Enhanced optoelectronic quality of perovskite films with excess CH₃NH₃I for high-efficiency solar cells in ambient air. *Nanotechnology* **2017**, *28*, 205401.

(13) Mastroianni, S.; Heinz, F. D.; Im, J.-H.; Veurman, W.; Padilla, M.; Schubert, M. C.; Würfel, U.; Grätzel, M.; Park, N.-G.; Hinsch, A. Analysing the effect of crystal size and structure in highly efficient CH₃NH₃PbI₃ perovskite solar cells by spatially resolved photo- and electroluminescence imaging. *Nanoscale* **2015**, *7*, 19653–19662.

(14) Song, Z.; Watthage, S. C.; Phillips, A. B.; Tompkins, B. L.; Ellingson, R. J.; Heben, M. J. Impact of Processing Temperature and Composition on the Formation of Methylammonium Lead Iodide Perovskites. *Chem. Mater.* **2015**, *27*, 4612–4619.

(15) Chen, Z.; Dong, Q.; Liu, Y.; Bao, C.; Fang, Y.; Lin, Y.; Tang, S.; Wang, Q.; Xiao, X.; Bai, Y.; Deng, Y.; Huang, J. Thin single crystal perovskite solar cells to harvest below-bandgap light absorption. *Nat. Commun.* **2017**, *8*, 1890.

(16) Yen, H. J.; Liang, P.-W.; Chueh, C.-C.; Yang, Z.; Jen, A. K.-Y.; Wang, H.-L. Large Grained Perovskite Solar Cells Derived from Single-Crystal Perovskite Powders with Enhanced Ambient Stability. *ACS Appl. Mater. Interfaces* **2016**, *8*, 14513–14520.

(17) Ferreira Da Silva, A.; Veissid, N.; An, C. Y.; Pepe, I.; Barros De Oliveira, N.; Batista Da Silva, A. V. Optical determination of the direct bandgap energy of lead iodide crystals. *Appl. Phys. Lett.* **1996**, *69*, 1930–1932.

(18) Shah, K. S.; Olschner, F.; Moy, L. P.; Bennett, P.; Misra, M.; Zhang, J.; Squillante, M. R.; Lund, J. C. Lead iodide X-ray detection systems. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1996**, 380, 266– 270.

(19) Beckmann, P. A. A review of polytypism in lead iodide. *Cryst. Res. Technol.* **2010**, *45*, 455–460.

(20) Trigunayat, G. C. A survey of the phenomenon of polytypism in crystals. *Solid State Ionics* **1991**, *48*, 3–70.

(21) Palosz, B.; Steurer, W.; Schulz, H. The structure of PbI_2 polytypes 2H and 4H: a study of the 2H-4H transition. *J. Phys.: Condens. Matter* **1990**, *2*, 5285–5295.

(22) Wei, Q.; Shen, B.; Chen, Y.; Xu, B.; Xia, Y.; Yin, J.; Liu, Z. Large-sized PbI_2 single crystal grown by co-solvent method for visiblelight photo-detector application. *Mater. Lett.* **2017**, *193*, 101–104.

(23) Patel, A. R.; Rao, A. V. An improved design to grow larger and more perfect single crystals in gels. *J. Cryst. Growth* **1980**, *49*, 589–590.

(24) Street, R. A.; Ready, S. E.; Lemmi, F.; Shah, K. S.; Bennett, P.; Dmitriyev, Y. Electronic transport in polycrystalline Pbl₂ films. *J. Appl. Phys.* **1999**, *86*, 2660–2667.

(25) Zheng, Z.; Liu, A.; Wang, S.; Wang, Y.; Li, Z.; Lau, W. M.; Zhang, L. In situ growth of epitaxial lead iodide films composed of hexagonal single crystals. *J. Mater. Chem.* **2005**, *15*, 4555–4559.

(26) Zhu, X. H.; Wei, Z. R.; Jin, Y. R.; Xiang, A. P. Growth and characterization of a PbI_2 single crystal used for gamma ray detectors. *Cryst. Res. Technol.* **2007**, *42*, 456–459.

(27) Hassan, M. A.; Jafar, M. M.; Matuchova, M.; Bulos, B. N. An experimental evidence of some lead iodide polytypes compatible with the dielectric functions model. *J. Appl. Sci.* **2010**, *10*, 3367–3373.

(28) Salje, E.; Palosz, B.; Wruck, B. In situ observation of the polytypic phase transition 2H-12R in PbI₂: investigations of the thermodynamic structural and dielectric properties. *J. Phys. C: Solid State Phys.* **1987**, *20*, 4077–4096.

(29) Falk, A. L.; Buckley, B. B.; Calusine, G.; Koehl, W. F.; Dobrovitski, V. V.; Politi, A.; Zorman, C. A.; Feng, P. X. L.; Awschalom, D. D. Polytype control of spin qubits in silicon carbide. *Nat. Commun.* **2013**, *4*, 1819.

(30) Li, X.; Bi, D.; Yi, C.; Décoppet, J.-D.; Luo, J.; Zakeeruddin, S. M.; Hagfeldt, A.; Grätzel, M. A vacuum flash-assisted solution process for high-efficiency large-area perovskite solar cells. *Science* **2016**, *353*, 58–62.

(31) Wu, C.; Zhang, Q.; Liu, Y.; Luo, W.; Guo, X.; Huang, Z.; Ting, H.; Sun, W.; Zhong, X.; Wei, S.; Wang, S.; Chen, Z.; Xiao, L. The Dawn of Lead-Free Perovskite Solar Cell: Highly Stable Double Perovskite Cs₂AgBiBr₆ Film. *Adv. Sci.* **2017**, 1700759.

(32) Konstantakou, M.; Perganti, D.; Falaras, P.; Stergiopoulos, T. Anti-Solvent Crystallization Strategies for Highly Efficient Perovskite Solar Cells. *Crystals* **2017**, *7*, 291.

(33) Bredig, M. A.; Bamberger, C. E.; Richardson, D. M. A mixed-valency lead oxyiodide. J. Inorg. Nucl. Chem. 1978, 40, 1497–1500.

(34) Berry, F. J.; Jones, C. H. W.; Dombsky, M. An Iodine Mössbauer Study of Lead(II) Iodide and Lead Oxyiodide. *J. Solid State Chem.* **1983**, *46*, 41–45.

(35) Tavakoli, F.; Salavati-Niasari, M.; Mohandes, F. Sonochemical Synthesis and Characterization of Lead Iodide Hydroxide Micro / nanostructures. *Ultrason. Sonochem.* **2014**, *21*, 234–241.

(36) Butyagin, P. Y.; Streletskii, A. N. The Kinetics and Energy Balance of Mechanochemical Transformations. *Phys. Solid State* 2005, 47, 856–862.

(37) Wang, S.; Jiang, Y.; Juarez-Perez, E. J.; Ono, L. K.; Qi, Y. Accelerated degradation of methylammonium lead iodide perovskites induced by exposure to iodine vapour. *Nat. Energy* **201**7, *2*, 16195.

(38) Brenes, R.; Eames, C.; Bulović, V.; Islam, M. S.; Stranks, S. D. The Impact of Atmosphere on the Local Luminescence Properties of Metal Halide Perovskite Grains. *Adv. Mater.* **2018**, *30*, 1706208.

(39) Wang, Q.; Chen, B.; Liu, Y.; Deng, Y.; Bai, Y.; Dong, Q.; Huang, J. Scaling behavior of moisture-induced grain degradation in polycrystalline hybrid perovskite thin films. *Energy Environ. Sci.* 2017, *10*, 516–522.

(40) Kim, S.; Bae, S.; Lee, S.-W.; Cho, K.; Lee, K. D.; Kim, H.; Park, S.; Kwon, G.; Ahn, S.-W.; Lee, H.-M.; Kang, Y.; Lee, H.-S.; Kim, D. Relationship between ion migration and interfacial degradation of $CH_3NH_3PbI_3$ perovskite solar cells under thermal conditions. *Sci. Rep.* **2017**, *7*, 1200.

(41) Besleaga, C.; Abramiuc, L. E.; Stancu, V.; Tomulescu, A. G.; Sima, M.; Trinca, L.; Plugaru, N.; Pintilie, L.; Nemmes, G. A.; Iliescu, M.; Svavarsson, H. G.; Manolescu, A.; Pintilie, I. Iodine Migration and Degradation of Perovskite Solar Cells Enhanced by Metallic Electrodes. J. Phys. Chem. Lett. **2016**, *7*, 5168–5175.

(42) Wong-Stringer, M.; Game, O. S.; Smith, J. A.; Routledge, T. J.; Alqurashy, B. A.; Freestone, B. G.; Parnell, A. J.; Vaenas, N.; Kumar, V.; Alawad, M. O. A.; Iraqi, A.; Rodenburg, C.; Lidzey, D. G. High-Performance Multilayer Encapsulation for Perovskite Photovoltaics. *Adv. Energy Mater.* **2018**, *8*, 1801234.

(43) Acik, M.; Alam, T. M.; Guo, F.; Ren, Y.; Lee, B.; Rosenberg, R. A.; Mitchell, J. F.; Park, I. K.; Lee, G.; Darling, S. B. Substitutional Growth of Methylammonium Lead Iodide Perovskites in Alcohols. *Adv. Energy Mater.* **2018**, *8*, 1701726.

(44) Heo, J. H.; Song, D. H.; Han, H. J.; Kim, S. Y.; Kim, J. H.; Kim, D.; Shin, H. W.; Ahn, T. K.; Wolf, C.; Lee, T. W.; Im, S. H. Planar CH₃NH₃PbI₃ Perovskite Solar Cells with Constant 17.2% Average Power Conversion Efficiency Irrespective of the Scan Rate. *Adv. Mater.* **2015**, *27*, 3424–3430.

(45) Roldán-Carmona, C.; Gratia, P.; Zimmermann, I.; Grancini, G.; Gao, P.; Graetzel, M.; Nazeeruddin, M. K. High efficiency methylammonium lead triiodide perovskite solar cells: the relevance of non-stoichiometric precursors. *Energy Environ. Sci.* **2015**, *8*, 3550–3556.

(46) Jeon, N. J.; Noh, J. H.; Kim, Y. C.; Yang, W. S.; Ryu, S.; Seok, S. I. Solvent engineering for high-performance inorganic-organic hybrid perovskite solar cells. *Nat. Mater.* **2014**, *13*, 897–903.

(47) Xiao, M.; Huang, F.; Huang, W.; Dkhissi, Y.; Zhu, Y.; Etheridge, J.; Gray-Weale, A.; Bach, U.; Cheng, Y.-B.; Spiccia, L. A Fast Deposition-Crystallization Procedure for Highly Efficient Lead Iodide Perovskite Thin-Film Solar Cells. *Angew. Chem., Int. Ed.* **2014**, *53*, 9898–9903.

(48) Ummadisingu, A.; Grätzel, M. Revealing the detailed path of sequential deposition for metal halide perovskite formation. *Sci. Adv.* **2018**, *4*, No. e1701402.

(49) Philippe, B.; Saliba, M.; Correa-Baena, J. P.; Cappel, U. B.; Turren-Cruz, S. H.; Grätzel, M.; Hagfeldt, A.; Rensmo, H. Chemical Distribution of Multiple Cation (Rb⁺, Cs⁺, MA⁺, and FA⁺) Perovskite Materials by Photoelectron Spectroscopy. *Chem. Mater.* **2017**, *29*, 3589–3596.

(50) Du, T.; Burgess, C. H.; Kim, J.; Zhang, J.; Durrant, J. R.; McLachlan, M. A. Formation, location and beneficial role of PbI_2 in lead halide perovskite solar cells. *Sustainable Energy Fuels* **2017**, *1*, 119–126.

(51) Da Silva Filho, J. M. C.; Ermakov, V. A.; Marques, F. C. Perovskite Thin Film Synthesised from Sputtered Lead Sulphide. *Sci. Rep.* **2018**, *8*, 1563.

(52) Mayerhöfer, T. G.; Popp, J. Beyond Beer's Law: Spectral Mixing Rules. *Appl. Spectrosc.* **2020**, *74*, 1287–1294.

(53) Wang, Q.; Shao, Y.; Xie, H.; Lyu, L.; Liu, X.; Gao, Y.; Huang, J. Qualifying composition dependent p and n self-doping in CH₃NH₃PbI₃. *Appl. Phys. Lett.* **2014**, *105*, 163508.

(54) Cui, P.; Wei, D.; Ji, J.; Huang, H.; Jia, E.; Dou, S.; Wang, T.; Wang, W.; Li, M. Planar p-n homojunction perovskite solar cells with efficiency exceeding 21.3%. *Nat. Energy* **2019**, *4*, 150–159.

(55) Rothmann, M. U.; Li, W.; Zhu, Y.; Bach, U.; Spiccia, L.; Etheridge, J.; Cheng, Y. B. Direct observation of intrinsic twin domains in tetragonal CH₃NH₃PbI₃. *Nat. Commun.* **2017**, *8*, 14547.

(56) Liu, Y.; Collins, L.; Proksch, R.; Kim, S.; Watson, B. R.; Doughty, B.; Calhoun, T. R.; Ahmadi, M.; Ievlev, A. V.; Jesse, S.; Retterer, S. T.; Belianinov, A.; Xiao, K.; Huang, J.; Sumpter, B. G.; Kalinin, S. V.; Hu, B.; Ovchinnikova, O. S. Chemical nature of ferroelastic twin domains in CH₃NH₃PbI₃ perovskite. *Nat. Mater.* **2018**, *17*, 1013–1019.

(57) Lan, C.; Zhou, Z.; Wei, R.; Ho, J. C. Two-dimensional perovskite materials: From synthesis to energy-related applications. *Mater. Today Energy* **2019**, *11*, 61–82.

(58) Kutes, Y.; Zhou, Y.; Bosse, J. L.; Steffes, J.; Padture, N. P.; Huey, B. D. Mapping the Photoresponse of CH₃NH₃PbI₃ Hybrid Perovskite Thin Films at the Nanoscale. *Nano Lett.* **2016**, *16*, 3434– 3441.

(59) Jiang, Q.; Zhang, L.; Wang, H.; Yang, X.; Meng, J.; Liu, H.; Yin, Z.; Wu, J.; Zhang, X.; You, J. Enhanced electron extraction using SnO_2 for high-efficiency planar-structure $HC(NH_2)_2PbI_3$ -based perovskite solar cells. *Nat. Energy* **2017**, *2*, 16177.

(60) Saliba, M.; Correa-Baena, J.-P.; Wolff, C. M.; Stolterfoht, M.; Phung, N.; Albrecht, S.; Neher, D.; Abate, A. How to Make over 20% Efficient Perovskite Solar Cells in Regular (n-i-p) and Inverted (p-i-n) Architectures. *Chem. Mater.* **2018**, *30*, 4193–4201.

(61) Powell, C. J.; Jablonski, A. Electron effective attenuation lengths for applications in Auger electron spectroscopy and x-ray photoelectron spectroscopy. *Surf. Interface Anal.* **2002**, *33*, 211–229.