Bismuth-based Perovskite-Inspired Solar Cells: *In situ* Diagnostics Reveal Similarities and Differences in the Film Formation of Bismuth- and Lead-based Films

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Abstract

Organic-inorganic lead-based halide perovskite compounds have recently been utilized in solar cells with power conversion efficiency (PCE) of >23%. However, replacing the lead with less-toxic elements while maintaining high device performance remains a challenge. For this reason, significant effort has been directed toward the development of Pb-free compounds, including bismuth (Bi)-based methylammonium bismuth iodide (MA₃Bi₂I₉), but such systems continue to severely underperform when compared to the prototypical Pb-based methylammonium lead iodide (MAPbI₃) perovskite. For the latter, and other Pb-based systems, it is known that Pb²⁺ complexes with polar solvents, such as DMSO and DMF, and solution-processed MAPbI₃ and PbI₂, form intermediate ordered precursor phases that incorporate these solvents into co-crystals during solution processing. Here, we compare and contrast the solidification and growth behaviors of Bi and Pb precursor inks based on the same solvents using multi-probe characterization methods. In both instances, we see evidence of a sol-gel process whereby solvent-metal complexes form and lead to a colloidal solution which solidifies. We show that the Bi-based compound crystallizes directly and rapidly into a textured polycrystalline microstructure from a precursor solution without evolving through intermediate crystalline solvated phases, in contrast to MAPbI₃. This solidification process produces isolated crystals and challenges the growth of continuous and crystalline films required for application in solar cells. We reveal that solvent engineering in combination with antisolvent dripping are necessary to address this limitation and enable the formation of continuous polycrystalline films of Pb-free

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MA₃Bi₂I₉ and functional solar cells. The work provides valuable insights linking the solid-state microstructure of the film and solar cell performance to the ink formulation and the solidification pathway.

Introduction

Organic-inorganic hybrid perovskite-based solar cells have been attracting enormous attention in recent years because of their exceptionally high power conversion efficiency (PCE) that has lately surpassed 23%.¹⁻⁷ In addition to the high PCE, hybrid perovskite materials offer a unique combination of advantageous characteristics that include low exciton binding energy, earth-abundant elements, and solution processability, hence making them particularly attractive amongst emerging photovoltaic technologies.⁸⁻¹³ Hybrid perovskite compounds based on metal halides are represented as AMX₃ perovskite composition, where A is an organic or inorganic cation, most often methylammonium (CH₃NH₃⁺, MA⁺) or formamidinium (HC(NH₂)₂⁺, FA⁺), M is a metal cation, such as Pb²⁺ or Sn²⁺, and X is a monovalent anion (halide ion Cl⁻, Br⁻, or I⁻).^{11, 14-16} However, one major disadvantage of the MAPbX₃ perovskite is the presence of lead (Pb), which is rather toxic.¹⁷ An important task is, therefore, to replace Pb with the less toxic element(s) while preserving the perovskite structure and its functionality. It has previously been shown that tin (Sn) can be used to replace Pb to form the less toxic MASnI₃ perovskite as an active layer for solar cells.¹⁸⁻²⁰ However, the assumed lower toxicity of the Sn-based compound has recently been challenged by Conings *et al.*, which claimed that the Sn compound exhibits similar toxicity levels to Pb-based systems.²¹ Alternative non-toxic elements, such as bismuth (Bi), is now widely viewed as a potential candidate to replace Pb. For this reason, significant recent effort has been focused on the development of lead-free compounds^{22, 23}, including Bi-based systems and their application in functional optoelectronic devices. Unfortunately, most of the Bi-based systems continue to severely underperform when employed in solar cells as compared to their Pb-based counterparts.²⁴⁻²⁷ Bismuth-based hybrid metal halide compounds have shown excellent stability in ambient air, but their solar cell device performance is comparatively low. This may be attributed to a number of factors, including higher exciton binding energy (around 400 meV), low and anisotropic carrier mobility, large optical band gap, lower absorption and an energy level mismatch between the lead-free MA₃Bi₂I₉ and hole/electron extraction layers, as well as to thin film microstructure and morphology.^{25, 28,29} One

of the solutions proposed has been to replace the organic cation (MA^+) with Ag^+ (AgBi_2I_7), which has yielded a more promising PCE of 1.2 %.³⁰ This successful employment of monovalent metal cation (Ag^+) in the bismuth halide may open up future directions. Nevertheless, a potential current limitation to the development of these materials is that solution-processing approaches used to fabricate Bi-based films have typically relied on the same formulations and coating approaches and conditions optimized for Pb-based perovskites in an Edisonian fashion. We take the view that understanding the differences and similarities between Pb-based and Bi-based compounds in terms of their solidification and crystallization pathways from similar ink formulations (solvent, halide, cation) and processing conditions will expand our understanding of metal halide thin film formation and point the community toward the most suitable and successful processing routes for making high quality Bi-based hybrid metal halide semiconductor films and devices.

A wide range of thin film deposition techniques are available to make MAPbI_3 hybrid perovskite films, including spin coating¹⁵, dip coating³¹, blade coating³², and vacuum deposition³³ and different protocols have been developed for many of these techniques. To date, the one-step spin coating process incorporating an antisolvent drip remains the most popular and facile implementation for fabricating high-quality MAPbI_3 hybrid perovskite thin films on the laboratory scale³⁴ and has been used for a wide range of other lead-based perovskite formulations.³⁵ In recent years, *in situ* time-resolved grazing incidence wide-angle X-ray scattering (GIWAXS) has emerged as an effective method to monitor solid-state thin film formation and microstructure evolution during solution casting of ink-based semiconductors.³⁶⁻⁴¹ More recently, it has also been used successfully to investigate crystallization behavior for 3D and reduced dimensional perovskites solution-cast using spin-coating and blade-coating.^{16, 32, 42-52} Chen *et al.* found the coexistence of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) in the intermediate phase of MAPbI_3 perovskite and accordingly fine-tuned the quality of films by adjusting DMSO concentration to further improve solar cell performance.⁴⁷ We previously reported that solution-processed MAPbI_3 and PbI_2 have a propensity to form intermediate ordered precursor phases¹⁶, which can fully solidify into solvate co-crystals during solution processing, as revealed by *in situ* diagnostics.^{32, 42, 44-46} By contrast, the addition of significant amounts of Br and Cl significantly inhibited solvate co-crystallization, pointing to the importance of halide-mediation in Pb-solvent complexation.⁴⁴ While Pb-based perovskites have

been studied intensively, lead-free methylammonium bismuth iodide ($\text{MA}_3\text{Bi}_2\text{I}_9$) ink solidification has not been investigated *in situ*. Therefore, the impact of substituting Pb with Bi on the solidification pathway of these hybrid metal halides is not well understood. Furthermore, it is not known whether processing routes developed for lead-based perovskites inks work well with bismuth-based compounds to produce high-quality compact films.

Herein, we compare and contrast the solidification and growth behavior of Pb-based and Bi-based inks (cation: MA^+ ; halide: I^-) using complimentary multi-probe *in situ* diagnostics and *ex situ* characterization techniques. We show the hexagonal ($\text{P6}_3/\text{mmc}$) $\text{MA}_3\text{Bi}_2\text{I}_9$ compound forms directly from the solution phase without the presence of intermediate crystalline solvated phases typically formed in DMSO-based inks of MAPbI_3 . Using these early studies as a guide and with the aid of *in situ* thickness, thermogravimetric and fourier transform infrared spectroscopy measurements, we show that the solvent choice for $\text{MA}_3\text{Bi}_2\text{I}_9$ also plays a critical role. In particular, we show that DMSO solvent retention within $\text{MA}_3\text{Bi}_2\text{I}_9$ layers during processing is significantly higher compared to GBL, a behavior also noted in MAPbI_3 and linked to solvent-metal interaction strengths.⁵³ Use of DMSO:GBL solvent blends is then exploited to better control the crystallization and growth dynamics of the $\text{MA}_3\text{Bi}_2\text{I}_9$ layer, albeit with limited success. Additional control is achieved by using an antisolvent dripping step in combination with an optimized DMSO:GBL solvent mixture. With the aid of the *in situ* diagnostic tools, we show that dripping at the appropriate time can help nucleate crystalline $\text{MA}_3\text{Bi}_2\text{I}_9$ as well as change its crystalline texture, leading to a dramatically enhanced light absorbance and improved solar cell power conversion efficiency. The present work provides unique insights into the inner workings of the solvent engineering approach that is widely used to address the limitation of layer morphology and help optimize the performance of the bismuth-based $\text{MA}_3\text{Bi}_2\text{I}_9$ layers and solar cells.

Results and discussion

In situ time-resolved grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were performed during spin-coating using a custom-built miniature spin-coating stage controlled by a PC located outside the D1 beam station at the Cornell High Energy Synchrotron Source (CHESS).^{37, 39, 44} All the GIWAXS experiments were performed in ambient atmosphere at $T \approx 25$

°C with relative humidity (RH) between 30-40 %. The impact of the processing atmosphere, i.e., ambient environment vs. inert N₂ atmosphere (glove box), upon MA₃Bi₂I₉ microstructure will be discussed later. A measurement repetition rate of 5 Hz and a measurement duration of 120 s were deemed sufficient to monitor all relevant processes. We begin by monitoring the time-evolution of different ink formulations ranging from classical MAPbI₃ ink to MA₃Bi₂I₉ ink in two solvents, namely dimethyl sulfoxide (DMSO) and γ -butyrolactone (GBL). Representative 2D GIWAXS snapshots taken at various stages of spin coating of MA₃Bi₂I₉ inks are shown in **Figure 1**.

Figure 1 *In situ* GIWAXS 2D snapshots taken during spin coating at 10, 60, and 120 s of the perovskite-inspired MA₃Bi₂I₉ precursor inks without any antisolvent dripping. (a, d, g) show the snapshots taken for DMSO, (b, e, h) for GBL, and (c, f, i) for GBL:DMSO solvent mixture (6:4).

In the early stages of spin coating (≈ 10 s; **Figure 1 a-c**), two halo rings dominate the scattering features for all three solvent formulations: the halo at high q is associated with the liquid solvent;³⁸ the halo at low q is associated with the colloidal sol-gel precursor.⁵⁴ This indicates that at ≈ 10 s the as-cast film is still in a wet, colloidal state. The peak position at low q indicates the dominant spacing between precursor colloids is approximately 1.25 nm at ≈ 10 s. It is noteworthy that the DMSO solution is still in a wet colloidal state after 60 s, with a colloidal spacing reduced to around 0.9 nm, whereas the other formulations have already dried and solidified entirely or nearly so at ≈ 60 s (**Figure 1 d-f**). We will later ascribe this to the stronger DMSO-Bi interactions, which retains the solvent longer, delays crystallization and frustrates the crystallization process of the Bi-based compound.

Reasonably well-defined diffraction features can be seen in the pure GBL and GBL:DMSO (6:4) mixture cases at ≈ 60 s (**Figure 1 e, f**) and later in the DMSO case (**Figure 1 g**). All the patterns show the diffraction features at $q \approx 5.8$ and 11.5 nm^{-1} in q_z direction, related to Bi-based compound, and several in-plane peaks. The perovskite-inspired $\text{MA}_3\text{Bi}_2\text{I}_9$ compound is known to form into the Laue class $6/mmm$ with $P6_3/mmc$ space group ($a = 8.5821(3) \text{ \AA}$ and $c = 21.7678(8) \text{ \AA}$).²⁴ The indexing of the patterns in **Figure S5** indicates a 2D powder texture formation, whereby the a (and b) axes of the hexagonal phase crystals are randomly oriented in-plane but their c axis is perpendicular to the substrate plane. It is noteworthy that the formation of these two peaks is accompanied by additional in-plane diffraction features indexed to the same phase. The sharp diffraction features are consistent with a 2D powder texture (recalling that the sample is spinning 16.7 revolutions per GIWAXS snapshot). The 2D powder texture of Bi-based compound is in stark contrast with the 3D powder usually formed with lead-based perovskite films, including MAPbI_3 , as indicated by the appearance of isotropic rings rather than peaks.^{15, 32, 46} To this end, we note that the presence of DMSO in the ink formulation (i.e. DMSO only or DMSO:GBL blend) introduces broader in-plane diffraction peaks in the angular direction, which suggests an increase in the film's mosaicity and suppression of the growth of the oriented crystallites.

Figure 2 shows the integrated 2D maps of scattering intensity with respect to time (abscissa; $0 < t < 120$ s) and q (ordinate; $4 < q < 12 \text{ nm}^{-1}$) for spin coating of bismuth- or lead-

based inks ($\text{MA}_3\text{Bi}_2\text{I}_9$ and MAPbI_3 , respectively) prepared in GBL and DMSO. The length of the scattering vector (q) was determined using: $q = \sqrt{q_z^2 + q_{xy}^2}$, where $q_z = \frac{4\pi \sin \alpha_f}{\lambda}$, $q_{xy} = \frac{4\pi \sin \theta_f}{\lambda}$, and λ is the wavelength.³⁸ The emerging waves with momentum can be described by the in-plane exit angle α_f and the out-of-plane angle θ_f (with respect to the scattering plane).⁵⁵ Solution-casting was performed onto TiO_2 -coated glass substrates using the same processing conditions, namely the common one-step recipe used for the fabrication of lead-based hybrid perovskite solar cells (1000 rpm for 10 s followed by 5000 rpm for 110 s) at room temperature.

Figure 2 *In situ* 2D GIWAXS intensity map of the various precursor inks showing ink-to-solid transformation during spin coating up to 120 s. $\text{MA}_3\text{Bi}_2\text{I}_9$ in DMSO (a), and GBL (b). MAPbI_3 in DMSO (c), and GBL (d). Time evolution of the diffraction intensities related to $\text{MA}_3\text{Bi}_2\text{I}_9$ ($q \approx 8.50$ and 8.68 nm^{-1}) (e), and MAPbI_3 ($q = 10$ nm^{-1}) (g), for GBL and DMSO based inks. Scattering vector q versus intensity distribution of these inks at the final stage of spin coating (120 s) for (f) $\text{MA}_3\text{Bi}_2\text{I}_9$, and (h) MAPbI_3 .

Figures 2a and 2b summarize the time-evolution of scattering for $\text{MA}_3\text{Bi}_2\text{I}_9$ inks using DMSO and GBL, respectively. A hexagonal $\text{MA}_3\text{Bi}_2\text{I}_9$ phase emerges in layer processed from GBL inks as indicated by the presence of sharp diffraction features at $q \approx 5.91$, 8.50 and 9.41 nm^{-1} .

¹, respectively. For the case of DMSO, the diffraction features appear at $q \approx 5.86, 8.68$ and 9.94 nm^{-1} , respectively. The observed shift from the theoretical positions is most likely attributed to the fact that all GIWAXS measurements were performed in ambient atmosphere at $T \approx 25 \text{ }^{\circ}\text{C}$ with RH between 30-40 %, and not under inert atmosphere. As a result there is a possibility for bismuth metal cation (Bi^{+3}) to form crystallites and solvated complexes with both DMSO and water similar to those reported previously (i.e. $[\text{Bi}(\text{DMSO})_8(\text{ClO}_4)_3]$, $[\text{Bi}(\text{H}_2\text{O})_9](\text{CF}_3\text{SO}_3)_3$, $\text{BiI}_3(\text{DMSO})_3$).^{56, 57} Our hypothesis is partly supported by the solvent retention seen in the TGA data in **Figure 3e**, indicating that a substantial volume of volatile species (DMSO) is entrapped within the as-cast film and gradually released as evident by the decrease in mass with increasing temperature.

Figure 2e compares the time evolution of the diffraction feature related to Bi-based compound in both solvents. The longevity of the colloidal scattering features at low q in 2a and 2b is significantly more extended in DMSO ($\approx 80\text{-}90 \text{ s}$) compared to GBL ($\approx 30\text{-}35 \text{ s}$), delaying the onset of crystallization (**2e**) in DMSO ($\approx 70 \text{ s}$) and GBL ($\approx 30 \text{ s}$) based inks. The crystallization of Bi-based compound completed within $\approx 30 \text{ s}$ for GBL, whereas it needed $\approx 70 \text{ s}$ for DMSO case (based on the *in situ* experiments). Conversion of the colloidal ink into the 2D powder-textured polycrystalline phase is direct, as indicated by the commensurate disappearance of the colloidal scattering halo^{32, 44} and appearance of the diffraction features of the crystalline phase. The texture of the 2D powder-textured polycrystalline films was determined by indexing the GIWAXS data in **Figure 1**, indicating Bi-based grains predominantly grow along the c axis perpendicular to the substrate. The kinetics of film formation are counterintuitive from the perspective of solvent evaporation rates, as the boiling point/vapor pressure ($20 \text{ }^{\circ}\text{C}$) of GBL and DMSO are $204^{\circ}\text{C}/2.0\text{hPa}$ and $189^{\circ}\text{C}/0.56\text{hPa}$, respectively, very much in favour of faster drying and solidification of the DMSO-based ink as compared to GBL-based one. Instead, the effective evaporation rate appears to be linked to other aspects of the solvent, such as the strength of complexation bonds between the solvents and Bi ions, which appears to be very much in favour of DMSO retention, just like the case of lead.⁵³

Figure 2f compares the diffraction features of the as-cast DMSO and GBL inks. The data show that; (i) the various diffraction peaks are not located at exactly the same q values for GBL and DMSO, and (ii) the intensity distribution of the peaks is not identical, pointing to potential

differences in texture, structure, or stoichiometry. In line with our discussion above, earlier studies have demonstrated the tendency of the bismuth cation (Bi^{+3}) to form crystalline complexes [i.e. $\text{Bi}(\text{DMSO})_8(\text{ClO}_4)_3$, $[\text{Bi}(\text{H}_2\text{O})_9](\text{CF}_3\text{SO}_3)_3$ and $\text{BiI}_3(\text{DMSO})_3$] with various solvents, including water, DMSO and DMF, in which the molecules were coordinating through the oxygen.^{56, 57}

To study the possible influence of the humid atmosphere under which the GIWAXS measurements being conducted, we measured the XRD patterns of $\text{MA}_3\text{Bi}_2\text{I}_9$ films prepared in ambient air ($\text{RH} \approx 50\text{-}60\%$) and inside a nitrogen-filled glove box ($\text{H}_2\text{O} < 1\text{ ppm}$), and compared them against the simulated diffraction data (**Figure S6**). Interestingly, for $\text{MA}_3\text{Bi}_2\text{I}_9$ layers processed in humid air a new peak at $\approx 10.2^\circ$ emerges irrespective of the solvent employed. Although preliminary, the findings correlate with results reported in the literature which show that bismuth complexes with water to form an ordered phase.⁵⁶ This new peak is absent from all samples prepared inside the glovebox, suggesting that the presence of water in ambient air affects the structure of $\text{MA}_3\text{Bi}_2\text{I}_9$ through the formation of crystalline solvates between bismuth and water e.g. $[\text{Bi}(\text{H}_2\text{O})_9](\text{CF}_3\text{SO}_3)_3$.⁵⁶ Importantly, thermal annealing of ambient air-processed layers in nitrogen at 110°C for 1 h causes the (002) diffraction peak to shift back to its expected position for $\text{MA}_3\text{Bi}_2\text{I}_9$, while the new peak at $\approx 10.2^\circ$, completely vanishes. We attribute this to dissociation of the Bi-metal/water complex and its removal from the $\text{MA}_3\text{Bi}_2\text{I}_9$ lattice. Besides, the XRD data in **Figure S7** shows that the crystal structure of $\text{MA}_3\text{Bi}_2\text{I}_9$ films deposited inside the glove box using CB antisolvent (at 40 s), remain the same before and after thermal annealing in nitrogen. These findings highlights that the *in-situ* GIWAXS measurements in ambient air is more complicated to interpret especially in the context of probing the microstructure evolution, mosaicity, crystal orientation, and layer texture, but nevertheless provide highly valuable insights on the materials selections (solvents) and processing conditions (atmosphere) for the synthesis of $\text{MA}_3\text{Bi}_2\text{I}_9$. To this end, the *ex-situ* XRD measurements performed inside and outside the glovebox help to bridge the gap between the real device processing conditions and the *in-situ* GIWAXS data.

On the basis of the experimental evidence and discussion above, the plausible reasons for causing a smaller in-plane lattice constant ($a = b$) in as-cast films prepared from different solvents (with a difference on the order of $0.5\text{ \AA}$), include strong coordination of Bi with DMSO

and complex formation of Bi^{+3} cations with water. Indeed, the incorporation of solvent and water molecules into the as-cast film structure is in line with the TGA (**Figures 3e**) and XRD (**Figure S6**) analyses which will be discussed later. To summarize, the deformation of the Bi-based compound seen in the *in-situ* GIWAXS measurements is most likely attributed to the complexation of DMSO and water with the Bi^{+3} cation.

Figure 2c illustrates the representative time evolution of the scattering features during spin coating with respect to the scattering vector q and time for the MAPbI_3 ink in DMSO. During the first 50 s, we observe a wet, gel-like precursor indicated by the formation of a scattering halo at low q values ($4\text{--}5\text{ nm}^{-1}$) which is assigned to the disordered precursor colloidal gel.⁴⁶ The features of PbI_2 crystals located at $q = 9.0\text{ nm}^{-1}$ and intermediate $\text{MAPbI}_3\cdot\text{DMSO}$ solvate situated at $q = 4.4, 4.8, 6.3,$ and 8.1 nm^{-1} are observed after around 50 s without the formation of perovskite phase during spin coating. Interestingly, the MAPbI_3 ink prepared using GBL exhibit an initial broad scattering halo at low q range followed by the formation of the MAPbI_3 phase after approximately 20 s without being mediated by any solvate phase (**Figure 2d**). It is worth noting that once the MAPbI_3 precursor ink forms the stable and ordered $\text{MAPbI}_3\cdot\text{DMSO}$ solvate phase, it is hard to be converted to the perovskite phase during spin coating. Thus, if the intermediate ordered $\text{MAPbI}_3\cdot\text{DMSO}$ solvate phase could be removed via simple ink engineering (*e.g.*, by replacing DMSO with GBL), then it should be straightforward to form the MAPbI_3 perovskite phase directly even during spin coating. Indeed, **Figure 2g** (black line) reveals that MAPbI_3 layers processed from GBL exhibit characteristic diffraction ($q \approx 10\text{ nm}^{-1}$) associated with the MAPbI_3 perovskite phase that forms at around 20 s. In contrast, no such diffraction feature is observed in MAPbI_3 layers spin cast from DMSO (**Figure 2 g**, red line).

At the final stage of the spin coating ($\approx 120\text{ s}$) step from DMSO (**Figure 2h**, red line), both the ordered precursor solvate ($q = 4.4, 4.8, 6.3,$ and 8.1 nm^{-1}) and the crystalline PbI_2 phases ($q = 9.0\text{ nm}^{-1}$) are present without any traces of the perovskite phase. The latter phase is only found in layers processed from GBL (**Figure 2h**, black line) after 120 s. Therefore, it is evident that in the case of MAPbI_3 the choice of the solvent plays a significant role as it determines whether the solvate phases or the perovskite phase forms. This is not the case for the Bi-based precursor ink for which the Bi-compound phase is found to form directly without being

mediated by a crystalline solvate phase. To conclude, the *in situ* GIWAXS study (**Table 1**) revealed that the $\text{MA}_3\text{Bi}_2\text{I}_9$ precursor ink tends to convert from an initially disordered solvate state directly to a highly textured Bi-compound phase during the spin coating from both DMSO and GBL. In contrast, for DMSO-based MAPbI_3 precursor inks, a transformation from disordered colloids to ordered solvate co-crystal phase and crystalline PbI_2 phase occurs without the perovskite phase being present. Only when DMSO is replaced with GBL, the MAPbI_3 inks appear to undergo a direct transformation from the disordered colloids phase to the desired perovskite phase without any traces of the PbI_2 phase.

	$\text{MA}_3\text{Bi}_2\text{I}_9$		MAPbI_3	
	DMSO	GBL	DMSO	GBL
Solvate co-crystal	Disordered	Disordered	Ordered	Disordered
PbI_2	n/a	n/a	√	×
Bi-compound/ MAPbI_3	√	√	×	√

Table 1 Summary of the phases formed in as-cast films prepared by spin coating $\text{MA}_3\text{Bi}_2\text{I}_9$ and conventional lead-based MAPbI_3 in DMSO and GBL.

Figure 3 (a-b) Layer thinning behaviors of spin-cast MA₃Bi₂I₉ inks based on GBL and DMSO as the solvents, respectively. The thinning behavior of the blank GBL and DMSO solvents are also shown for comparison. (c-d) Thinning behavior of spin-cast MAPbI₃ inks based on GBL and DMSO, respectively. The thinning behavior of the blank GBL and DMSO solvents are also shown for comparison. (e) TGA measurements of mass loss during heating of as-cast films of lead-free MA₃Bi₂I₉ in GBL and DMSO. (f) Infrared spectral showing substantial solvent retention by as-cast films especially in DMSO. FTIR absorption spectra of DMSO and GBL solvents and powders from as-cast films for different lead-free MA₃Bi₂I₉ ink.

We have conducted *in situ* time-resolved optical reflectometry measurements to monitor the ink thinning behavior for both Bi and Pb-based inks in DMSO and GBL, and shed more light into the comparative roles of evaporation and complexation with the metal ions. These experiments were performed under inert nitrogen atmosphere. **Figure 3a and 3b** reveal rapid thinning behavior for the blank GBL and DMSO solvent from an initial thickness of ≈ 20 μm

within ≈ 15 s. The time needed for the $\text{MA}_3\text{Bi}_2\text{I}_9$ ink in GBL to dry is significantly longer (≈ 25 s) and leaves a 5-6 μm solvated film on the surface. When $\text{MA}_3\text{Bi}_2\text{I}_9$ is cast from DMSO, the solvent retention appears to be significantly exacerbated. The initial thickness of the solution is considerably higher than the blank solvent, likely due to differences in the viscosity of the solution due to the presence of significant solvent-solute interactions.³² The time it takes the blank DMSO to dry is similar to GBL (15 s), but the DMSO-based ink thins much slower with a highly solvated layer $\approx 10 \mu\text{m}$ thick remaining after 25 s. This explains why the crystallization of the Bi-based compound is not detected in DMSO even after 60 s (**Figure 3b**). The differences in the strength of solvent-metal interactions evident in bismuth-based inks is also observed in lead-based inks. DMSO-based inks dry slower than GBL-based ones, as demonstrated in **Figures 3c and d**. Comparing between $\text{MA}_3\text{Bi}_2\text{I}_9$ and MAPbI_3 inks, either in DMSO or in GBL, the major difference in thinning behavior is Bi-based precursors take more time to dry, indicating the presence of stronger solvent-solute interactions in the Bi-based inks, which leads to higher solvent retention in the as-cast films.

We further confirm the differences in solvent retention by performing thermogravimetric analysis (TGA) on as-cast films scraped from the sample substrate (**Figure 3e**). A much smaller overall amount of solvent is removed from the as-cast $\text{MA}_3\text{Bi}_2\text{I}_9$ film spun from GBL when compared to layers spun from DMSO. Specifically, the sample exhibits a total loss of ≈ 5 wt % when GBL was used, whereas layers spun from DMSO lose ≈ 18 wt % in total when heated to 110°C . Overall, the TGA analysis demonstrates that a substantial volume of volatile species is entrapped in the as-cast film, which can be attributed to the significantly higher retention of DMSO as compared to GBL.

The entrapment of DMSO and GBL molecules in as-cast films is further confirmed by Fourier transform infrared (FTIR) absorption spectroscopy performed on the same samples, as shown in **Figure 3f**. The FTIR spectra of the liquid solvents DMSO and GBL are also shown at the bottom of **Figure 3f** for reference. In the $600\text{--}1800 \text{ cm}^{-1}$ spectral region, the FTIR spectrum of DMSO exhibits several different absorption bands at 1309 cm^{-1} (DMSO1), 1042 cm^{-1} (DMSO2), and 952 cm^{-1} (DMSO3) that could be assigned, respectively, to symmetric deformation of CH_3 ($\delta_s \text{ CH}_3$) group, and S=O stretching (νSO) modes.⁵⁸ These characteristic bands are also present in the as-cast layer spun from DMSO. However, a detailed comparison of

the absorbance bands of liquid DMSO with the as-cast films reveals significant frequency shifts. In particular, some of the absorption bands redshift (DMSO2, DMSO3), a phenomenon that could be attributed to the interaction and coordination of the DMSO molecule with the $\text{MA}_3\text{Bi}_2\text{I}_9$ structure. Similar behavior was also found by the interaction of DMF with lead in MAPbI_3 and in PbI_2 .⁵⁹ For the spun layers of $\text{MA}_3\text{Bi}_2\text{I}_9$ prepared from GBL inks, these characteristic absorption bands are significantly weaker, indicating the presence of substantially less GBL within the as-cast film, hence further supporting our earlier findings.

A commonly used procedure in one-step processing of lead-based perovskites is the dripping of a so-called antisolvent at an optimized time during spin coating of the ink.^{35, 60} The schematic representation of the one-step spin coating $\text{MA}_3\text{Bi}_2\text{I}_9$ inks is shown in **Figure S1**. We have investigated via *in situ* GIWAXS the impact of antisolvent dripping during spin coating of a Bi-based ink using the DMSO:GBL (6:4) solvent mixture. **Figure 4** summarizes the time evolutions of *in situ* GIWAXS data in ambient air and *in situ* time-resolved UV-Vis absorbance measurements in inert glove box without and with (at 40 s) CB dripping. Just as in the cases of pure DMSO and GBL, the ink in GBL:DMSO mixture also transforms directly from the colloidal sol-gel state to the Bi-compound phase (**Figure 4a**). The onset of crystallization occurs at an intermediate time (≈ 50 s) in DMSO:GBL mixture, *i.e.* later than pure GBL but earlier than pure DMSO. Based on the *in situ* GIWAXS snapshots of $\text{MA}_3\text{Bi}_2\text{I}_9$ inks with CB drip at 40 s (**Figure 4g-i**), Bi-based compound tends to form 3D powder films from pure DMSO solvent and DMSO:GBL mixture, rather than 2D powder texture from pure GBL solvent. Antisolvent dripping at 40 s initiates the early nucleation and growth of the Bi-compound phase, as shown in **Figure 4b**. These results indicate that antisolvent dripping at 40 s not only pre-nucleate the solid-state Bi-compound phase but also changes the overall texture of the Bi-compound crystallites in the film. The static XRD measurements also confirmed that CB dripping at 20 s changes the dominant $\text{MA}_3\text{Bi}_2\text{I}_9$ growth direction from (002) diffraction plane to (011) diffraction plane in all three solvent systems (**Figure S3**). The change in texture from 2D powder to 3D powder may be due to differences in the growth mechanism; as-cast films are likely to nucleation and grow from the substrate, whereas CB dripping from the top changes nucleation position toward the bulk and the surface of the sol-gel film, reducing the templating benefits of the substrate in the cases of pure DMSO and DMSO:GBL mixture. To conclude, the CB dripping triggers the nucleation of the Bi-compound phase. Antisolvent dripping, which extracts the solvent from the film during

spinning within seconds, can induce rapid and uniform nucleation of the grains, hence preventing large grains from forming.⁶¹ In GBL solvent, the textured film has started to form before dripping at 40s. Thus, dripping at this specific time does not alter the crystalline texture. However, in DMSO and mixed solvent cases, the phase transition has not started prior to dripping. Therefore, the CB drip triggers the nucleation and crystallization much earlier, promotes their formation from the top and results in the loss of crystalline texture in the film.

The evolution of the UV-Vis absorbance spectra during spin coating of the inks without (**Figure 4d**) and with (**Figure 4e**) antisolvent CB drip, were measured *in situ* and shown in **Figure 4d-e**. The results reveal a significant increase in absorbance upon antisolvent dripping consistent with very rapid transformation of the ink to the crystalline MA₃Bi₂I₉ phase. The transition is slower and the absorbance weaker for the no drip case, as confirmed by comparing the absorbance vs. time at 590 nm **Figure 4f**. Based on these results, we conclude that the major effect of CB dripping is to induce the nucleation of the MA₃Bi₂I₉ phase directly from the ink, which in turn solidifies the MA₃Bi₂I₉ layer during solution casting. This has been shown to be due to the solubility of GBL and DMSO solvents in CB, which helps their rapid extraction from the solution-cast film.⁶² In contrast, the as-cast film remains partially solvated with DMSO and GBL, which take much longer to leave, thanks in part to interactions with the solute and their low vapour pressure.

Figure 4 *In situ* 2D GIWAXS intensity map of the lead-free $\text{MA}_3\text{Bi}_2\text{I}_9$ precursor inks in GBL:DMSO (6:4), showing ink-to-solid transformation with (a), and without (b), CB drip at 40 s during spin coating up to 120 s. (c) Diffraction intensity distribution comparison between w/o and w/ CB drip at final state (at 120 s) for lead-free $\text{MA}_3\text{Bi}_2\text{I}_9$ precursor inks. *In situ* 2D absorbance intensity map of the lead-free $\text{MA}_3\text{Bi}_2\text{I}_9$ precursor inks in GBL:DMSO (6:4), during spin coating (d) without, and (e) with CB antisolvent drip. (f) Time evolution of absorbance at 590 nm during spin coating w/ and w/o CB antisolvent drip for $\text{MA}_3\text{Bi}_2\text{I}_9$ ink. *In situ* GIWAXS

2D snapshots taken during spin coating of Bi-based precursor inks at 120 s in DMSO (g), in GBL (h), and in the GBL:DMSO (6:4) blend (i), with dripping CB antisolvent applied at 40 s.

To gain more insights of the relationship between dripping time and $\text{MA}_3\text{Bi}_2\text{I}_9$ layer morphology evolution, we conducted scanning electron microscope (SEM) measurements on as-cast films from $\text{MA}_3\text{Bi}_2\text{I}_9$ inks in GBL, DMSO, and GBL:DMSO (6:4) and films subjected to antisolvent drip at 40 s (regular dripping), and after 70 s (late dripping). Obtained results are shown in **Figure 5**.

Figure 5 SEM images of as-cast, CB drip at 40 s, and 70 s drip thin films for lead-free $\text{MA}_3\text{Bi}_2\text{I}_9$ precursor dissolved in (a, d, g) GBL, (b, e, h) DMSO, and (c, f, i) mixture of GBL and DMSO (6:4).

In the natural evolution behavior (no dripping), the $\text{MA}_3\text{Bi}_2\text{I}_9$ inks in all different solvents, form isolated large hexagonal crystals (signature of textured growth with c-axis normal to the substrate plane, in agreement with GIWAXS analysis) distributed on the surface of the layer

(**Figure 5a-c**). The effect of antisolvent dripping, on the other hand, is dramatic, especially if timed correctly, and for GBL-based inks (**Figure 5d**) results in a smoother layer the surface of which contains hexagonal-shaped domains with similarly shaped cracks. $\text{MA}_3\text{Bi}_2\text{I}_9$ layers processed from DMSO (**Figure 5e**), on the other hand, exhibit much smaller grain size with insufficient surface coverage manifested as large pinholes. Interestingly, the surface of $\text{MA}_3\text{Bi}_2\text{I}_9$ layers processed from GBL:DMSO (6:4) solvent mixtures (**Figure 5f**) appears more continuous and smooth without apparent pinholes. The impact of CB dripping time on morphology as seen through SEM images indicates morphology evolution from isolated crystals to pinhole-free thin films is very sensitive to the timing of CB dripping during spin coating $\text{MA}_3\text{Bi}_2\text{I}_9$ ink (**Figure S4**). These results also demonstrate that significant kinetic quenching is needed to achieve continuous and pinhole-free films by suppressing the thermodynamically preferred state of large, isolated crystals formed on the substrate surface. The change in texture is commensurate with the nucleation and growth of a much finer microstructure of the $\text{MA}_3\text{Bi}_2\text{I}_9$ phase due to the drip.

To understand the relationship between dripping time and morphology, we have also obtained SEM images for the $\text{MA}_3\text{Bi}_2\text{I}_9$ layers where the antisolvent dripping step has been applied after 70 s (late dripping) during spin coating. From the *in situ* GIWAXS data shown in **Figures 2 and 4**, it is known that in the absence of antisolvent dripping the solid-state $\text{MA}_3\text{Bi}_2\text{I}_9$ phase forms before 70 s. For this reason, we have chosen to apply the late dripping step in combination with all these three inks investigated in order to study its effect. Indeed, the surface of the films prepared using GBL and late dripping exhibit isolated sizeable hexagonal crystals with non-uniform surfaces (**Figure 5g**), features quite similar to as-cast layers shown in **Figure 5a**. We attribute this to the existence of an already formed $\text{MA}_3\text{Bi}_2\text{I}_9$ layer where the application of the antisolvent dripping step has hardly any effect. In the case of DMSO-based inks (**Figure 5h**), the resulting layers exhibit similar surface characteristics with those produced by regular dripping shown in **Figure 5e**. The main features of such layers include significantly smaller size grains and incomplete surface coverage that is manifested as large pinholes. Finally, **Figure 5i** shows the surface morphology of the $\text{MA}_3\text{Bi}_2\text{I}_9$ layers processed from the solvent mixtures in combination with the late dripping step. As can be seen, the resulting layers are featuring numerous non-ideal characteristics the most prominent of which include the small size grains and the presence of large cracks.

Using the knowledge gained by the *in situ* and *ex situ* studies, we fabricated planar n-i-p type $\text{MA}_3\text{Bi}_2\text{I}_9$ solar cells using the solvent mixture and following layer configuration (**Figure 6a**): glass/ fluorine-doped tin oxide (FTO)/ titanium dioxide (TiO_2)/ $\text{MA}_3\text{Bi}_2\text{I}_9$ / 2,2',7,7'-tetrakis-(*N,N*-di-pmethoxyphenylamine) 9,9'-spirobifluorene (Sprio-MeOTAD)/ gold (Au)/ silver (Ag). Dripping of the CB antisolvent during $\text{MA}_3\text{Bi}_2\text{I}_9$ deposition was performed at the optimized time of 40 s. **Figure 6a** shows the energy levels of the various materials employed and include the conductive transparent electrode FTO, the electron transport layer TiO_2 , the lead-free $\text{MA}_3\text{Bi}_2\text{I}_9$, and the hole transport material Spiro-MeOTAD, as determined by UV-Vis absorbance and ultraviolet photoelectron spectroscopy (UPS).^{6, 22, 23, 35} The valence bands of lead-free $\text{MA}_3\text{Bi}_2\text{I}_9$ prepared from different inks demonstrate similar results (6.0 eV) in **Figure S2c**. In this particular device configuration, the bottom TiO_2 layer combines a suitable conduction band (4.0 eV) with a large valence band (6.9 eV). These features are expected to facilitate efficient electron transfer from the $\text{MA}_3\text{Bi}_2\text{I}_9$ later to TiO_2 while blocking any hole transfer to FTO electrode.

Figure 6 (a) Energy diagram and photovoltaic structure of relevant materials used in n-i-p solar cell devices. (b) J-V curves of devices based on glass/ TiO_2 / $\text{MA}_3\text{Bi}_2\text{I}_9$ / Sprio-MeOTAD/ Au/ Ag (reverse and forward scan). Stability of $\text{MA}_3\text{Bi}_2\text{I}_9$ solar cells performance for (c) normalized PCE (d) FF (e) V_{OC} (f) J_{SC} versus time (day) in ambient condition.

Figure 6b displays representative current density (J) versus voltage (V) characteristics (forward and reverse sweeps) for the resulting cells. Applying the CB antisolvent dripping step at 40 s during spin coating of the ink [GBL:DMSO (6:4 ratio)], is found to yield cells with the maximum power conversion efficiency (PCE) of 0.14 %, and the highest short circuit current (J_{SC}) of 0.5 mA/cm². The open-circuit voltage (V_{OC}) and fill factor (FF) of the cells are both low and on the order of 0.59 V and 57.2 %, respectively. Under reverse bias scan direction, the PCE is found to increase to 0.17 %. MA₃Bi₂I₉-based solar cells severely underperform as compared to their Pb-based counterparts may be attributed to non-uniform Bi and I components distributed across the MA₃Bi₂I₉ thin films and I to Bi ratio is higher than theoretical value through the measurements of energy-dispersive X-ray spectroscopy in **Figure S2**.

Finally, the stability of the MA₃Bi₂I₉ solar cell has also been studied by monitoring the variation of cells' performance during storage in ambient condition ($T = 22\text{ }^{\circ}\text{C}$, $\text{RH} \approx 60\%$) for 21 days. As can be seen in **Figure 6c**, the normalized PCE gradually drops after 6 days of storage and remains over 77 % of its initial value after 13 days, followed by faster degradation. A similar trend is observed in the FF as shown in **Figure 6d**. In contrast, both J_{SC} and V_{OC} remain almost constant during the entire period of storage. The latter observation suggests that the main factor responsible for the PCE degradation is the deterioration of the cell's FF (**Figure 3d**). The latter is most likely attributed to the decomposition of the MA₃Bi₂I₉ layer during storage in ambient air without any encapsulation. Further work is currently under way to elucidate the impact of the environmental conditions on the MA₃Bi₂I₉ layer. Moreover, the thin films stability comparison between MA₃Bi₂I₉ and MAPbI₃ in ambient condition is shown in **Figure S2a**, indicating MAPbI₃ decomposes much faster than MA₃Bi₂I₉. The features and onsets of MA₃Bi₂I₉ static UV-Vis absorbance do not evolve much during 12 days in the ambient environment, meaning the MA₃Bi₂I₉ thin films are reasonably stable (**Figure S2b**).

Conclusion

We studied the microstructure evolution of the lead-free MA₃Bi₂I₉ compound from precursor inks to solid-state thin films using *in situ* time-resolved GIWAXS and UV-Vis absorption spectroscopy and compared it against the prototypical lead-based MAPbI₃ system using the same solvents and characterization techniques. Contrary to MAPbI₃, which tends to form ordered

solvates in DMSO or direct MAPbI₃ phase in GBL, the MA₃Bi₂I₉ phase tends to form directly from the precursor solution without any intermediate ordered phases, irrespective of the solvent used. This unusual behavior makes the deposition of uniform and pinhole-free MA₃Bi₂I₉ layers extremely challenging and requires the use of quenching intervention, such as antisolvent dripping. The latter was successfully applied at 40 s and triggered the immediate and rapid nucleation of the crystals from the surface and the bulk. Instead of its purpose of preventing solvate formation in DMF or DMSO-based inks of MAPbI₃, the antisolvent drip fulfilled a different purpose: to promote the formation of compact and pinhole-free MA₃Bi₂I₉ layers. This comes at the cost of the [001] preferential texture, which becomes a 3D powder texture. Nevertheless, the films were used to fabricate functional MA₃Bi₂I₉-based solar cells. Although the achieved PCE is low, our microstructure evolution studies provide new and unique insights into the layer formation and the role of antisolvent dripping. Moreover, our results highlight the important role of the environmental conditions under which MA₃Bi₂I₉ processing is taking place and particularly the role of humid air. The present work highlights how simple solvent engineering can be adjusted to help optimize the quality of MA₃Bi₂I₉ layers and the performance of the resulting solar cells.

Experimental Section

Raw materials and Substrate Preparation: All the chemicals are purchased from Sigma–Aldrich unless stated otherwise. All the GIWAXS experiments were performed on a TiO₂ coated glass substrate. Substrates cleaning procedures and TiO₂ is coated according to the published recipe.⁵⁴ The TiO₂ precursor solution was spin-coated on a glass substrate and annealed on a hot plate at a temperature of 100 °C for 10 min and then annealed at 500 °C for 30 min and was allowed to cool down naturally in the ambient air. The thickness of TiO₂ is about 50 nm. For solar cell devices, glass was taken replaced by pre-patterned FTO (FTO: 15 ohm sq⁻¹ bought from Xinyan Technologies) glass substrate and residue procedure keep the same.

MA₃Bi₂I₉ Solution Preparation and Deposition: Precursor (0.825M) solution was prepared by dissolving methylammonium iodide (MAI), purchased from Dyesol, and bismuth iodide (BiI₃) (3:2 ratio) in dimethyl sulfoxide (DMSO) or γ -butyrolactone (GBL) or mixed solvent (GBL: DMSO) (6:4 ratio) and kept precursors overnight at 60 °C with stirring. Thin

films were deposited by spin coating at 1000 rpm for 10 s and 5000 rpm for 40 s while dripping CB antisolvent at different timing to optimize the device performance.

Grazing-Incidence Wide-Angle X-ray Scattering: GIWAXS measurements were conducted on D1 beamline at Cornell High Energy Synchrotron Source (CHESS). The monochromated x-ray with the wavelength of 1.17Å shone on the spin-coating films with the incident angle of 0.5°. The spin-coating experiments were conducted at a custom-built spin-coating stage with Kapton windows and controlled from the computer outside the hutch. There was a delay of ≈ 15 s between solution dropping and the start of spinning/measuring. A Pilatus 200K detector was placed at 170 mm away from the sample and each spin-coating process was continuously recorded for 120s with the frame rate of 5 images/s. The solutions were prepared in an N₂ glove box with moisture levels below 0.1 ppm and were taken out in the ambient environment right before the experiment. All the experiments were conducted in an ambient atmosphere where the relative humidity was ≈ 20 –25 %. The data analysis was performed by Fit2D and indexing via indexGIXS.

Solar Cell Device Preparation: The solar-cell devices were fabricated using the same TiO₂ thin-film procedure on the patterned FTO-coated glass. MA₃Bi₂I₉ solutions were spin-coated on top of the TiO₂ layer at 1000 rpm for 10 s and 5000 rpm for 40 s. Chlorobenzene (0.25 ml) was dropped on the spinning substrate during the second spin-coating step at 10s before the end of the procedure. The films were then annealed at 100 °C for 10 min. After cooling down to room temperature, the hole-transporting layer was then deposited on top of the MA₃Bi₂I₉ film via spin-coating at 2000 rpm for 30 s using a chlorobenzene of a 80 mg/ml solution of 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine) 9,9'-spirobifluorene (spiro-MeOTAD), with additives of lithium bis(trifluoromethanesulfonyl) imide and 4-*tert*-butylpyridine. Finally, 20 nm of gold and 80 nm of silver thick electrodes were deposited by thermal evaporation using an Angstrom evaporator. The current-density–voltage (*J*–*V*) curves were measured using a solar simulator (Newport, Oriel Class A, 91195A) with a source meter (Keithley 2420) at 100 mA cm⁻² illumination (AM 1.5G) and a calibrated Si-reference cell certificated by NREL. All the solar cells were masked during the *J*–*V* measurements to define the active area of about 0.1 cm².

Attenuated Total Reflectance–Fourier Transform Infrared Spectroscopy: MA₃Bi₂I₉ solutions were dropped cast on the substrates, which left to dry for 45 min followed by nitrogen

flow for $\approx 2\text{--}4$ min until a solid powder was obtained. The resulting films were scratched out through a blade in a vial for both as-cast materials measurement. Powders were pressed tightly in the FTIR spectrometer to obtain spectra for all. A Bruker Tensor 27 FTIR spectrometer using the attenuated total reflectance (ATR) configuration was used.

In situ UV-Vis Transmission Measurements during Spin Coating: UV-vis transmission/reflection measurements were performed using an F20-UVX spectrometer with a tungsten halogen light source (Filmetrics, Inc.) with a repetition rate of 10 Hz and an integration time of 0.1 s for each spectrum during spinning. These measurements were conducted in an N₂ glove box with moisture level below 0.1 ppm.

Thermogravimetric Analysis: A Netzsch thermogravimetric analyzer (TG 209 F1) was used to track the mass loss of the solvates. Processing was the same as for FTIR measurements. An alumina crucible was used to contain the powder. A constant nitrogen flow was maintained during the whole process. As-cast films were prepared in an N₂ glove box with moisture level below 0.1 ppm and then scraped off.

Scanning Electron Microscopy: A Quanta 200FEG scanning electron microscope from FEI was used to observe the morphology of annealed films.

X-ray Powder Diffraction: XRD patterns via Bruker D8 advance A25 diffractometer in the Bragg-Brentano geometry equipped with a Cu tube (Cu K α ; $\lambda = 0.15418$ nm) operating at 40 kV and 40 mA using a linear position sensitive detector (opening 2.9°).

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The formation of lead-free $\text{MA}_3\text{Bi}_2\text{I}_9$ films is investigated *in situ* during spin-coating by x-ray scattering and optical spectroscopy and contrasted to the case of MAPbI_3 . Using similar solvent engineering approaches the Bi-based compound crystallizes directly from solution while the Pb-based formulation forms a solvated crystalline phase requiring annealing. Nevertheless, both materials benefit from anti-solvent dripping timed during the disordered sol-gel state.