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Impact of Processing Conditions on the Film Formation of Lead-Free Halide Double Perovskite $\text{Cs}_2\text{AgBiBr}_6$

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Abstract:

Lead-Free halide double perovskites with enhanced stability have gained attention as a promising environmentally friendly alternative to lead-based halide perovskites. Amongst different halide double perovskites, $\text{Cs}_2\text{AgBiBr}_6$ has shown attractive optoelectronic properties and stability, making it a promising candidate for stable high-efficiency optoelectronic devices. Motivated by a data mining effort, we present here the effects of different processing strategies on the microstructure and thin-film formation dynamics of $\text{Cs}_2\text{AgBiBr}_6$. We apply some of the most successfully used solvent engineering approaches from the halide perovskite research to halide double perovskites, namely antisolvent- and additive-assisted synthesis. Using in situ spectroscopy and diffraction, the film formation of $\text{Cs}_2\text{AgBiBr}_6$ is investigated during spin coating, and the subsequent post-deposition thermal annealing. Dropping antisolvents during spin coating induces immediate supersaturation and crystallization of the wet film, whereas the time of dropping the antisolvent has implications on the film formation dynamics and the final microstructure. For additive (HBr)-assisted synthesis, we show how the addition of HBr affects colloid formation in solution and thus influences the crystallization pathway during thin-film processing.

Finally, HBr additive simplifies synthesis in that it doesn't require solution and substrate preheating to obtain pinhole-free films even with higher thickness.

1. Introduction

As an alternative to typically lead-based halide perovskites with structure ABX_3 ($A = CH_3NH_3, CH(NH_2)_2, Cs, Rb$; $B = Pb, Sn, Ge$; $X = I, Br, Cl$), lead-free halide double perovskites have emerged as environmentally friendly candidates for optoelectronic applications. They are not only of interest for perovskite solar cells (PSCs) but also for other optoelectronic applications such as photodetectors, X-ray detectors, lasers and light-emitting diodes (LEDs) due to their intrinsic thermodynamic stability, suitable band gaps, small carrier effective masses, and low exciton binding energies.¹⁻³ These halide double perovskites adopt a crystal lattice with general formula $A_2B^+B'^{3+}X_6$ or $A_2B^{4+}X_6$ (A is a monovalent cation, B^+ , B'^{3+} , and B^{4+} are monovalent, trivalent, and tetravalent metal cations, respectively, and X is a halide anion), corresponding to mixed mono- plus trivalent-metal double perovskites or tetravalent-metal vacancy ordered double perovskites, respectively.^{3,4} Amongst different halide double perovskites, $Cs_2AgBiBr_6$ has shown attractive optoelectronic properties and stability, making it a promising candidate for stable high-efficiency optoelectronic devices.⁵⁻¹⁰ Although the synthesis of $Cs_2AgBiBr_6$ has been successfully demonstrated via solution processing methods,⁵⁻¹⁰ mechanistic insights on the thin film formation process are lacking. Understanding the effects of synthetic parameters on the film formation kinetics and its microstructure are of crucial importance since the film quality significantly influences the device performance.¹⁰

The processing window for high performance devices is narrow and many experimental parameters make it a time-consuming effort to optimize film quality. A plethora of solution engineering approaches has been successfully

developed in the lead-based ABX_3 halide perovskite field to improve film quality, stability, charge carrier transport, and performance.¹¹ Although solution engineering is essential in making high quality ABX_3 films, only a few of these approaches have been applied and optimized for halide double perovskites. Additive processing for example, is commonly used for lead-based perovskites to tune the microstructure and reduce the processing temperature.¹²⁻¹⁵ It has been proposed to control the solubility of precursor solutes, coordinate with solutes, act as sites for heterogeneous nucleation, control the kinetics of crystal growth, form crystallized intermediate phases, and facilitate dissolution of intermediate phases.¹⁴⁻¹⁶ Despite its success, additive processing hasn't been applied to halide double perovskites (beyond its use as a solvent). A second example and possibly the most successful solution engineering approaches for ABX_3 perovskites was the introduction of antisolvent-assisted synthesis.^{17,18} Dropping a nonpolar antisolvent which does not dissolve the perovskite during the spin coating of the precursor film accelerates supersaturation by aiding the solvent removal and reducing precursor solubility in the solvent-antisolvent mixture.¹⁹⁻²² Despite the great success of solution engineering approaches to ABX_3 perovskites, application and systematic optimization via real time process insights to halide double perovskites is rare as evidenced by a text mining effort presented below.

Here we synthesized $Cs_2BiAgBr_6$ thin films via different solution engineering strategies and used *in situ* absorption spectroscopy and grazing incidence wide angle X-ray scattering (GIWAXS) to obtain a fundamental understanding on the film formation pathways. These complementary *in situ* techniques play a critical role in providing time-resolved information on the evolution of structural and optical properties under various synthetic conditions.²³⁻²⁵ We use this mechanistic understanding of how processing strategies impact film formation pathways to tailor crystallization and microstructure of $Cs_2BiAgBr_6$.

2. Experimental section

Text mining to extract halide double perovskite synthesis publications: Statistics on the body of synthesized halide double perovskites were extracted through a combination of automated and manual text processing techniques, similar to the methods for text mining discussed in Zhao et al.⁴ To facilitate automated text extraction, we leveraged article data from a collection of full-text papers mined by the Ceder Group (with years ranging from 2000-2020) and abstracts from MatScholar (with years ranging from 1900-2018).^{26,27} Articles from these databases were filtered through a keyword search for “perovskite(s)”. From these articles, any material entities were extracted using Chemical Named Entity Recognition (CNER).²⁸ Any material entity which contained a formula was analyzed using Pymatgen.²⁹ Articles containing material formulae with a character length greater than or equal to 7 and with a halide element whose stoichiometry was equal to 6 (corresponding to the $A_2BB'X_6$ double perovskite structure) were accepted. All accepted articles were inspected manually to determine which articles were related to experimental syntheses. We used Clarivate Analytics’ Web of Science literature search tool to search for articles from 2020-present and to account for any articles missing either of the databases mentioned above. Any halide double perovskite material synthesized under any method within a given article was recorded.

$Cs_2AgBiBr_6$ synthesis extraction: Halide double perovskite synthesis methods were delineated into four categories: crystal synthesis using (1) a solution or (2) a solid-state route, and thin film synthesis using (3) solution or (4) vapor deposition, similar to the text-mined synthesis breakdown in Zhao et. al.⁴ In addition to all of the $Cs_2AgBiBr_6$ synthesis articles extracted through the methods above, all remaining relevant publications were found by querying Clarivate Web of Science for articles containing the topic “ $Cs_2AgBiBr_6$ ”. The synthesis method used in each article was determined manually. An article could contain multiple syntheses for the same material.

Cs₂AgBiBr₆ thin film solution-deposition synthesis extraction: The yield of publications on Cs₂AgBiBr₆ thin film solution-deposition syntheses using the automated techniques above was low (only 4 were extracted from the Ceder group or MatScholar databases), so the details for the 48 thin film syntheses were extracted manually from the text. From each synthesis, we extracted the solvent, coating technique, deposition environment, any antisolvents or additives used, the way the precursors were deposited, and whether the solution and substrate were baked prior to final annealing.

Film Fabrication: The precursor solution was prepared by dissolving 224.35 mg BiBr₃ (≥99%, Sigma Aldrich), 93.9 mg of AgBr (≥99.9%, Alfa Aesar), and 212.81 mg CsBr (≥99.9%, Alfa Aesar) in 1 mL dimethylsulfoxide [DMSO] (anhydrous, 99.9%, Sigma-Aldrich). After complete dissolution of the precursors at 75 °C, both the solution and the substrate were either preheated to 75 °C or coated at room temperature. Spin coating was performed for 75 s at 5000 rpm if not stated differently. For samples prepared with dropping an antisolvent, the antisolvents (isopropyl alcohol (IPA) or toluene) were applied at different times during the spin coating. For additive-assisted synthesis, a small amount of hydrobromic acid (HBr) in aqueous solution (48 wt. % in H₂O, ≥99.99%, Acros Organics) was added to the precursor solution and heated at 75 °C for 10 min. After spin coating, the substrates were subsequently annealed at 285 °C for 5 min. All film preparation steps were performed in inert (N₂) environment.

In situ UV-Vis transmission measurements: Transmission measurements were collected using a fiber coupled Ocean Optics spectrometer (Flame) with an integration time of 0.1 s per spectrum. The equation [$A_\lambda = -\log_{10}(T_\lambda)$] was used to calculate the UV-Vis absorbance (A_λ) from the transmission spectra (T_λ). The *in situ* UV-Vis transmission measurements during spin coating and thermal annealing were performed

using a set-up described in a previous work³⁰ and a custom-built heating stage³¹, respectively.

In situ synchrotron X-ray diffraction (XRD): Synchrotron diffraction measurements during spin coating and thermal annealing were conducted at beamline 12.3.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory. For diffraction measurements during spin coating, the detector (DECTRIS Pilatus 1 M) was located at 35° with respect to the direct beam and \approx 226 mm from the sample. For diffraction measurements during thermal annealing, the detector was located at 40° with respect to the direct beam and \approx 191 mm from the sample. A finely ground Al₂O₃ reference sample was used to calibrate the detector geometry. Measurements were performed at wavelength 1.2398 Å with an incident angle of 1-2°. For diffraction measurements during thermal annealing, the samples were spin-coated in N₂-glove-box then heated to 285 °C at the beamline, with an average rate of 50 °C. s⁻¹, and were held at 285 °C for 5 min. The heating stage used for X-ray diffraction during thermal annealing is a ANTON-PAAR DHS900 stage adapted to fit onto the beamline sample stage. The samples were enclosed inside a N₂-filled dome made of a high-performance polymer (poly(ether-ether-ketone), known as PEEK). The dome is cooled by air flow when the heater reached a temperature of 200 °C.

Scanning electron microscopy (SEM): SEM images were collected using a Quanta FEG 250 instrument at an electron beam acceleration of 10 kV.

Dynamic light scattering (DLS): DLS measurements were performed using a NanoPlus-3 instrument. The measurements were done with a quartz cuvette at 80 °C.

Raman spectroscopy: Raman spectra were collected using a confocal Raman microscope (LabRAM HR, Horiba Yvon Jobin) with an excitation wavelength of 532 nm. The typical acquisition time for each spectrum was 10 s.

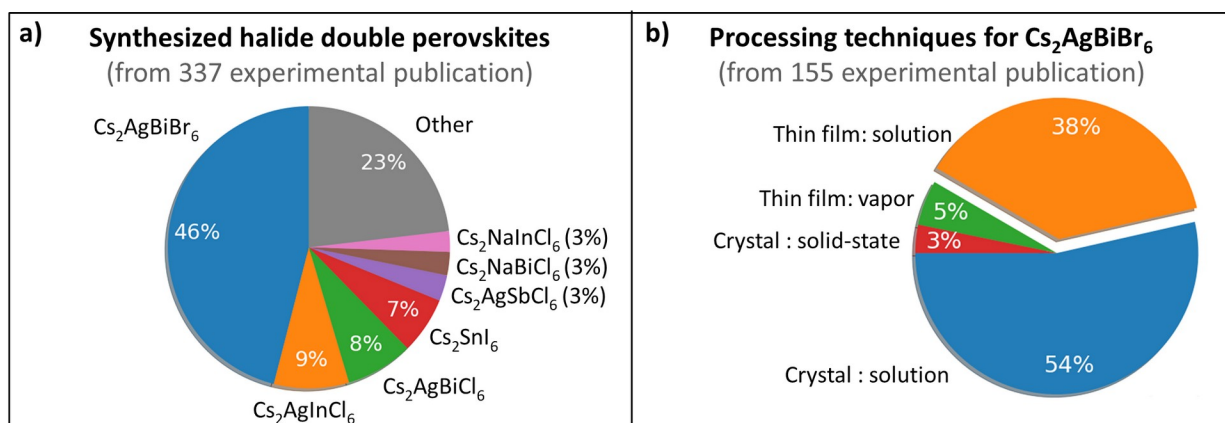
Spectroscopic ellipsometry: A variable-angle infrared spectroscopic ellipsometer IR-VASE from J.A. Woollam Co. Inc was used to extract the thickness of Cs₂AgBiBr₆ films.

3. Results and discussion

3. 1. Data mining of Cs₂AgBiBr₆ synthesis recipes

Text-mining was employed to generate an overview of synthesis processes used to fabricate Cs₂AgBiBr₆ from the existing literature body. Figure 1a illustrates the distribution of synthesized halide double perovskite materials out of 337 experimental publications, with Cs₂AgBiBr₆ having the highest share (43%) of experimental publications among halide double perovskites. Apart from Cs₂AgBiBr₆, other halide double perovskites have been synthesized, including Cs₂AgInCl₆, Cs₂AgBiCl₆, Cs₂SnI₆, Cs₂AgSbCl₆, Cs₂NaBiCl₆, Cs₂NaInCl₆, Cs₂SnBr₆, Cs₂SnCl₆, Cs₂AgInBr₆, Rb₂AgInBr₆, and Rb₂CuInCl₆. The large share of Cs₂AgBiBr₆ in experimental publications is probably due to the ease of processability of Cs₂AgBiBr₆ from solutions due to the relatively good solubility of Cs₂AgBiBr₆ precursors as compared to other halide double perovskite compounds.^{3,4} Figure 1b shows the distribution of the most used processing techniques to synthesize Cs₂AgBiBr₆ out of 155 experimental publications. Solution synthesis is dominant for both crystal synthesis (54%) and thin film synthesis (38%), whereas thin film vapor deposition and solid-state crystal synthesis have a smaller share (5% and 3%, respectively). In Figure 1c-h, we show an overview of synthetic approaches/parameters to fabricate Cs₂AgBiBr₆ thin films via solution synthesis, including deposition environment, coating technique, solvent, application of pre-annealing, and the use of antisolvents or additives for a total of 56 experimental Cs₂AgBiBr₆ solution-based thin film syntheses. As shown in Figure 1c, a wide range of deposition environments have been reported including inert glovebox (either N₂ or Ar or not specified) and ambient atmosphere. Nevertheless, the deposition environment wasn't

mentioned in 58% of the publications. Spin coating is by far the most used solution coating technique for $\text{Cs}_2\text{AgBiBr}_6$ thin films (98% of the publications) whereas drop casting has been used otherwise (Figure 1d). Due to the limited solubility of precursor materials, only few solvents have been used to synthesize $\text{Cs}_2\text{AgBiBr}_6$ thin films. DMSO is the most common used solvent followed by mixed DMSO and dimethylformamide (DMF), see Figure 1e. Pre-annealing (or also called hot-casting) approaches, where both the solution and substrate are pre-heated prior to casting, is widely used to obtain high-quality $\text{Cs}_2\text{AgBiBr}_6$ thin films. As shown in Figure 1f, the pre-annealing approach has been used in 60% of the publications. While antisolvent-processing is the most successful route for lead-based halide perovskites, the majority, 61%, of $\text{Cs}_2\text{AgBiBr}_6$ solution-based thin film syntheses did not report on any antisolvent treatment. From the remaining 39%, chlorobenzene was the most used followed by isopropanol (Figure 1g). Finally, regarding additive-assisted processing, only 4% of reported syntheses have relied on additives such as tetrabutylammonium bromide (TBAB), Figure 1h.



Distribution of synthetic variables used for solution processed $\text{Cs}_2\text{AgBiBr}_6$ thin films

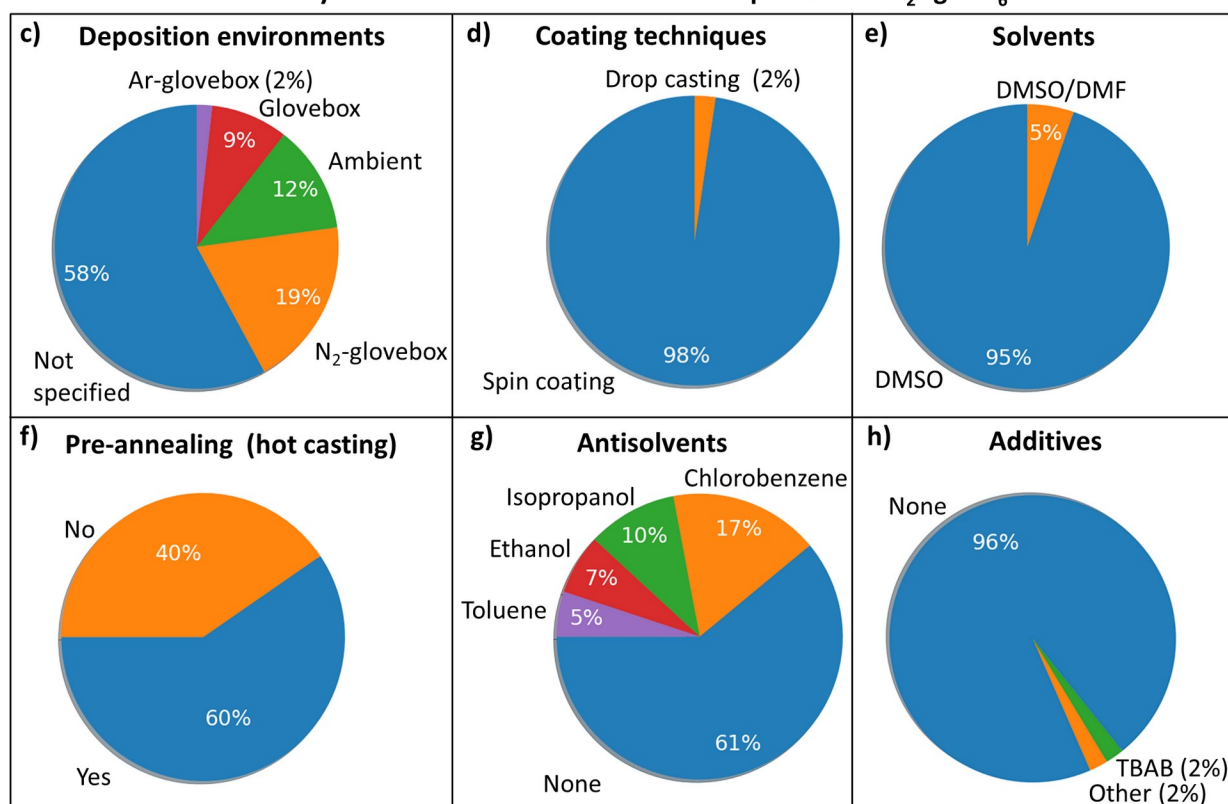


Figure 1 (a, b) Pie-charts of data mining of the distribution of synthesized halide double perovskites from 337 experimental publications and the distribution of processing techniques for $\text{Cs}_2\text{AgBiBr}_6$ from 155 experimental publications, respectively. (c-h) Detailed distribution of synthetic approaches and parameters used for thin-film solution processing of $\text{Cs}_2\text{AgBiBr}_6$ from 56 experimental publications: (c) deposition environments, (d) coating techniques, (e) solvents, (f) the use of pre-annealing (hot-casting), (g) antisolvent treatment, and (h) additive-processing.

3. 2. Effects of solvent engineering on Cs₂AgBiBr₆ thin film microstructure

We first show that smooth, pinhole-free and homogeneous microstructures can be obtained by antisolvent dropping and via additives in precursor solutions in contrast to films containing pinholes in the absence of solution engineering. We first show that smooth, pinhole-free and homogeneous microstructures can be obtained by antisolvent dropping and via additives in precursor solutions in contrast to films containing pinholes in the absence of solution engineering. We first show that smooth, pinhole-free and homogeneous microstructures can be obtained by antisolvent dropping and via additives in precursor solutions in contrast to films containing pinholes in the absence of solution engineering. Figure 2a-c show scanning electron microscopy (SEM) images of Cs₂AgBiBr₆ films when prepared without treatment (reference sample), via antisolvent-treatment, or via additive (HBr)-assisted synthesis. The reference sample appears with pinholes across the film, but pinhole-free films can be obtained by dropping an antisolvent or the addition of HBr to the precursor solution. Integrated scattering intensity from GIWAXS measurements of the annealed films reveal the formation of phase pure Cs₂AgBiBr₆ for all three conditions (Figure 2d) and confirmed by Raman spectroscopy (Figure 2e). The latter shows distinct characteristics of Cs₂AgBiBr₆ in the absence of secondary phases such as Cs₃Bi₂Br₉ (compare Raman spectra in Figure S1a). a-c show scanning electron microscopy (SEM) images of Cs₂AgBiBr₆ films when prepared without treatment (reference sample), via antisolvent-treatment, or via additive (HBr)-assisted synthesis. The reference sample appears with pinholes across the film, but pinhole-free films can be obtained by dropping an antisolvent or the addition of HBr to the precursor solution. Integrated scattering intensity from GIWAXS measurements of the annealed films reveal the formation of phase pure Cs₂AgBiBr₆ for all three conditions (We first show that smooth, pinhole-free and homogeneous microstructures can be

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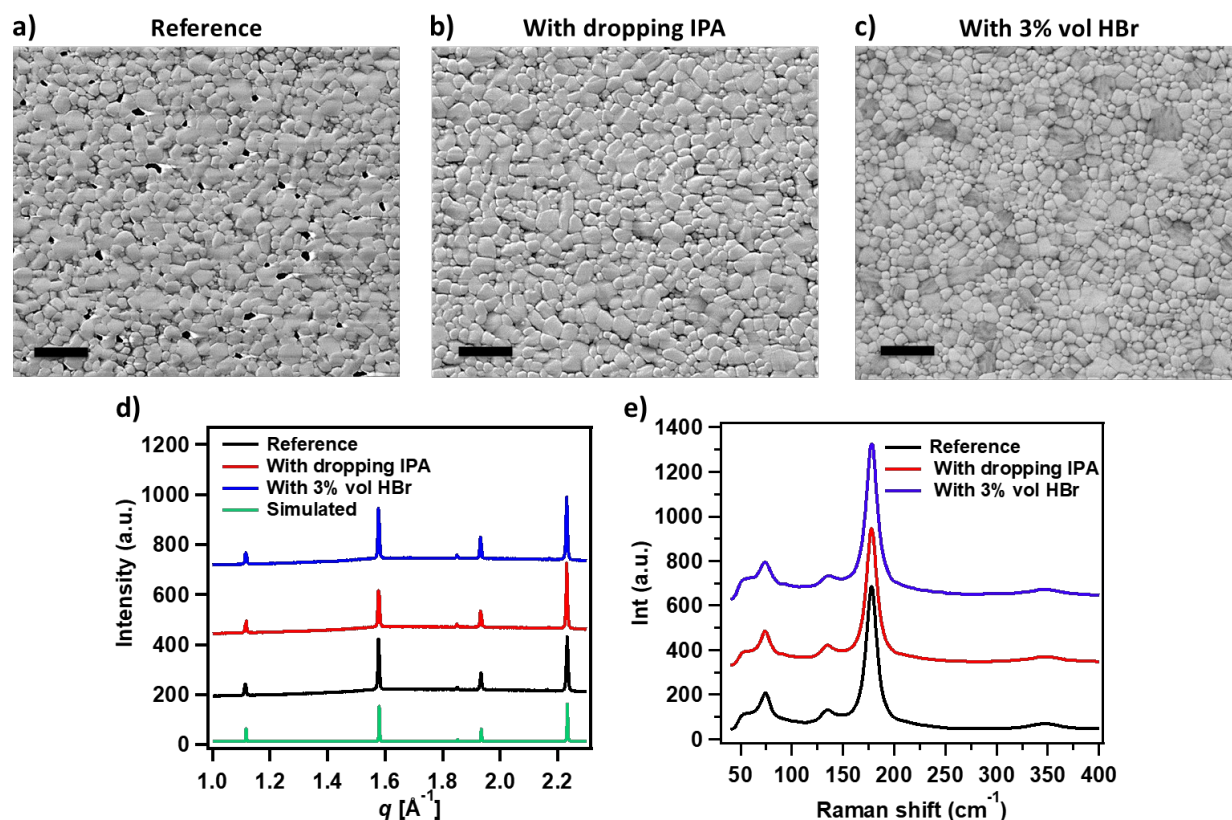


Figure 2 (a-c) SEM images of Cs₂AgBiBr₆ thin films; (a) reference sample, (b) prepared with dropping IPA at 12 s from the start of spin coating, and (c) prepared with adding 3% vol HBr to precursor solution. The scale bar for samples in (a-c) is 2 μm. (d) Integrated scattering intensity from GIWAXS measurements and (e) Raman spectra of samples shown in (a-c). The simulated diffraction pattern of Cs₂AgBiBr₆ is shown in green in (d); calculated using a CIF file from a previous work.⁵

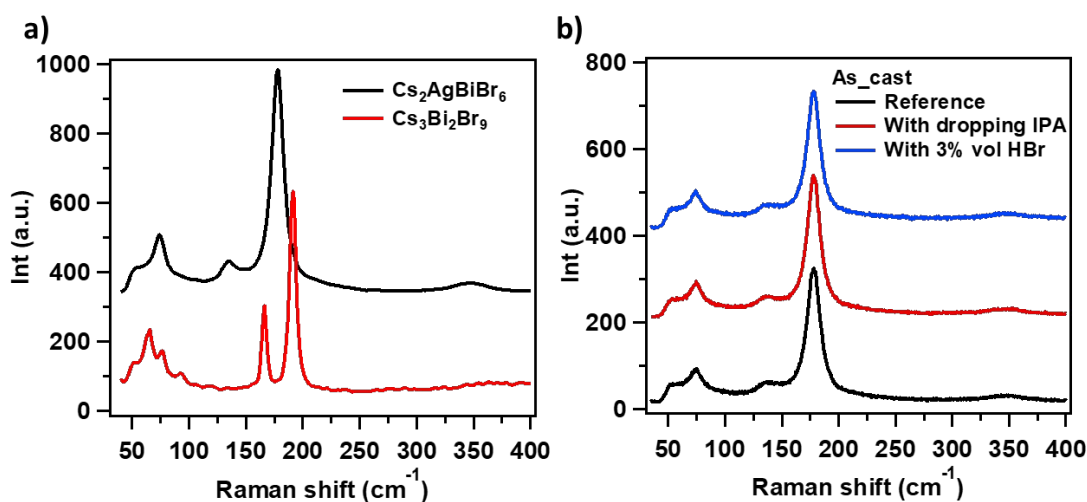


Figure S1 (a) Raman spectra of annealed Cs₂AgBiBr₆ (black) and Cs₃Bi₂Br₉ films (red). The Raman features in these spectra agree with previously

reported spectra for $\text{Cs}_2\text{AgBiBr}_6$ films and $\text{Cs}_3\text{Bi}_2\text{Br}_9$ phases.³² (b) Raman spectra of the as-cast $\text{Cs}_2\text{AgBiBr}_6$ films prepared with different conditions; reference sample, with dropping IPA at 12 s from the start of spin coating, and with adding 3% vol HBr to precursor solution are shown as black, red, and blue lines, respectively.

3. 3. In situ UV-Vis absorption during spin coating and thermal annealing

Next, we conducted *in situ* UV-Vis absorption spectroscopy during spin coating and subsequent thermal annealing of $\text{Cs}_2\text{AgBiBr}_6$ films to investigate the film formation kinetics. The UV-Vis spectra for the reference sample are shown in Figure 3. During the initial few seconds of spin coating, we observe a reduction in absorbance of the precursor solution mostly around 400 nm (marked by a violet arrow) which can be explained by loss of precursor materials due to solution spinning off (Figure 3a-b). This is followed by a step where no significant changes in absorbance are observed where the solvent evaporates but supersaturation is likely not reached yet, thus crystallization from solutes hasn't started. Upon reaching supersaturation, nucleation and film formation starts signified by a red-shift and an increase in the absorbance peak near 439 nm (marked by a red arrow in Figure 3a). It is worth noting that the absorbance peak near $\sim 420\text{-}440$ nm can be due to either $\text{Cs}_3\text{Bi}_2\text{Br}_9$ or $\text{Cs}_2\text{AgBiBr}_6$ phases. Due to the overlap of the absorption features between the two phases, we performed Raman spectroscopy measurements on the as-cast spin-coated films. Raman spectra support the presence of $\text{Cs}_2\text{AgBiBr}_6$ phase rather than $\text{Cs}_3\text{Bi}_2\text{Br}_9$ phase in the as-cast films (see **Figure S1b**). Thus, we attribute the absorbance near 439 nm to the $\text{Cs}_2\text{AgBiBr}_6$ phase. The evolution of the absorbance peak near 439 nm can be used to determine the film formation dynamics during spin coating which dominantly occur from ~ 25 s to ~ 37 s revealed by the gradual increase of the absorbance peak (**Figure S2a**). During the subsequent thermal annealing (Figure 3c and **Figure S3a**), the changes in absorption spectra are dominated by a red shift of the absorption edge during the initial 15-20 s, followed by constant characteristics.

It is known from the ABX_3 perovskites that the ideal antisolvent dropping time is crucial and depends on solvent, precursor concentration, spin-speed, as well as subtle variations in deposition environment.^{11,33,34} Under ideal conditions, dropping an antisolvent results in pinhole-free films (We first show that smooth, pinhole-free and homogeneous microstructures can be obtained by antisolvent dropping and via additives in precursor solutions in contrast to films containing pinholes in the absence of solution engineering. We first show that smooth, pinhole-free and homogeneous microstructures can be obtained by antisolvent dropping and via additives in precursor solutions in contrast to films containing pinholes in the absence of solution engineering. Figure 2a-c show scanning electron microscopy (SEM) images of $Cs_2AgBiBr_6$ films when prepared without treatment (reference sample), via antisolvent-treatment, or via additive (HBr)-assisted synthesis. The reference sample appears with pinholes across the film, but pinhole-free films can be obtained by dropping an antisolvent or the addition of HBr to the precursor solution. Integrated scattering intensity from GIWAXS measurements of the annealed films reveal the formation of phase pure $Cs_2AgBiBr_6$ for all three conditions (Figure 2d) and confirmed by Raman spectroscopy (Figure 2e). The latter shows distinct characteristics of $Cs_2AgBiBr_6$ in the absence of secondary phases such as $Cs_3Bi_2Br_9$ (compare Raman spectra in Figure S1a). a-c show scanning electron microscopy (SEM) images of $Cs_2AgBiBr_6$ films when prepared without treatment (reference sample), via antisolvent-treatment, or via additive (HBr)-assisted synthesis. The reference sample appears with pinholes across the film, but pinhole-free films can be obtained by dropping an antisolvent or the addition of HBr to the precursor solution. Integrated scattering intensity from GIWAXS measurements of the annealed films reveal the formation of phase pure $Cs_2AgBiBr_6$ for all three conditions (We first show that smooth, pinhole-free and homogeneous microstructures can be obtained by antisolvent dropping and via additives in precursor solutions in contrast to films containing pinholes in the absence of solution engineering. Figure 2a-c show scanning electron microscopy (SEM) images of

Cs₂AgBiBr₆ films when prepared without treatment (reference sample), via antisolvent-treatment, or via additive (HBr)-assisted synthesis. The reference sample appears with pinholes across the film, but pinhole-free films can be obtained by dropping an antisolvent or the addition of HBr to the precursor solution. Integrated scattering intensity from GIWAXS measurements of the annealed films reveal the formation of phase pure Cs₂AgBiBr₆ for all three conditions (Figure 2d) and confirmed by Raman spectroscopy (Figure 2e). The latter shows distinct characteristics of Cs₂AgBiBr₆ in the absence of secondary phases such as Cs₃Bi₂Br₉ (compare Raman spectra in Figure S1a). d) and confirmed by Raman spectroscopy (We first show that smooth, pinhole-free and homogeneous microstructures can be obtained by antisolvent dropping and via additives in precursor solutions in contrast to films containing pinholes in the absence of solution engineering. Figure 2a-c show scanning electron microscopy (SEM) images of Cs₂AgBiBr₆ films when prepared without treatment (reference sample), via antisolvent-treatment, or via additive (HBr)-assisted synthesis. The reference sample appears with pinholes across the film, but pinhole-free films can be obtained by dropping an antisolvent or the addition of HBr to the precursor solution. Integrated scattering intensity from GIWAXS measurements of the annealed films reveal the formation of phase pure Cs₂AgBiBr₆ for all three conditions (Figure 2d) and confirmed by Raman spectroscopy (Figure 2e). The latter shows distinct characteristics of Cs₂AgBiBr₆ in the absence of secondary phases such as Cs₃Bi₂Br₉ (compare Raman spectra in Figure S1a). e). The latter shows distinct characteristics of Cs₂AgBiBr₆ in the absence of secondary phases such as Cs₃Bi₂Br₉ (compare Raman spectra in Figure S1a). b). The SEM images in Figure 4a-c reveal that the dripping time has significant effects on the film microstructure. For early dripping times (≤ 10 s from the start of the spin coating), the films appear with more and larger pinholes as compared to the reference film. When the antisolvent is dropped too late (≥ 15 s), the antisolvent treatment is not effective in eliminating pinholes from Cs₂AgBiBr₆ films as shown in Figure 4b. The optimum dripping time leading to pinhole-

free films was found to be ~ 12 s for the given chemistry and synthesis conditions (Figure 4c).

In situ absorption measurements during synthesis with antisolvent reveal the effects of different dripping times on film formation dynamics (Figure 4d-f). Upon dropping the antisolvent a red shift is observed and a sharp increase in absorbance near 439 nm irrespective of the drop time. As shown in Figure 4d, when the antisolvent is dropped early (≤ 10 s), an initial sharp increase in absorbance is followed by a sharp decrease and then a gradual increase in absorbance near 439 nm. These three stages can be explained as dropping IPA induces immediate crystallization, followed by redissolution of the formed crystals due to the high amount of DMSO at this early stage of spin coating, then the crystallization develops gradually with solvent removal.³⁵ When the antisolvent IPA is dropped too late (≥ 15 s), most of the solvent is ejected and film formation occurs quickly within 2 s (Figure 4e). We attribute this behavior to the quick removal of the remaining DMSO by the antisolvent inducing immediate supersaturation and film formation. For films prepared with dropping IPA at the ideal time (~ 12 s), when reaching the gelation point, there is a sharp initial increase in absorbance, followed by a gradual increase near 439 nm (Figure 4f). The initial immediate film formation upon dropping the antisolvent can be explained by the quick initial wash out of DMSO, while the second film formation step (with slower rate) can be attributed to the slower DMSO removal via evaporation (see Figure 4f and **Figure S2a**). Next, we performed *in situ* absorption measurements during subsequent thermal annealing (**Figure S3b**). Similarly, to the films prepared without IPA, we observe a red shift in absorption edge during the initial 15-20 s, followed by steady absorption characteristics as shown in **Figure S3b**. While dropping IPA at 12 s was effective to obtain pinhole-free films, using another antisolvent such as toluene wasn't as effective as IPA and requires its own optimization with respect to dripping time. This behavior was

reported previously and IPA was shown to obtain smoother, and pinhole free films as compared to toluene.³⁶

Although the antisolvent treatment helps to obtain pinhole-free $\text{Cs}_2\text{AgBiBr}_6$ films, there is an optimum processing window which requires optimization for each individual chemistry. Additionally, a combination of hot-casting and antisolvent treatment is required to obtain pinhole-free films.³⁶ Therefore, we have looked for alternative and simplified processing strategies to obtain pinhole-free films and found that additive-processing using HBr fulfills these criteria (SEM images in We first show that smooth, pinhole-free and homogeneous microstructures can be obtained by antisolvent dropping and via additives in precursor solutions in contrast to films containing pinholes in the absence of solution engineering. We first show that smooth, pinhole-free and homogeneous microstructures can be obtained by antisolvent dropping and via additives in precursor solutions in contrast to films containing pinholes in the absence of solution engineering. Figure 2a-c show scanning electron microscopy (SEM) images of $\text{Cs}_2\text{AgBiBr}_6$ films when prepared without treatment (reference sample), via antisolvent-treatment, or via additive (HBr)-assisted synthesis. The reference sample appears with pinholes across the film, but pinhole-free films can be obtained by dropping an antisolvent or the addition of HBr to the precursor solution. Integrated scattering intensity from GIWAXS measurements of the annealed films reveal the formation of phase pure $\text{Cs}_2\text{AgBiBr}_6$ for all three conditions (Figure 2d) and confirmed by Raman spectroscopy (Figure 2e). The latter shows distinct characteristics of $\text{Cs}_2\text{AgBiBr}_6$ in the absence of secondary phases such as $\text{Cs}_3\text{Bi}_2\text{Br}_9$ (compare Raman spectra in Figure S1a). a-c show scanning electron microscopy (SEM) images of $\text{Cs}_2\text{AgBiBr}_6$ films when prepared without treatment (reference sample), via antisolvent-treatment, or via additive (HBr)-assisted synthesis. The reference sample appears with pinholes across the film, but pinhole-free films can be obtained by dropping an antisolvent or the addition of HBr to the precursor solution. Integrated

scattering intensity from GIWAXS measurements of the annealed films reveal the formation of phase pure Cs₂AgBiBr₆ for all three conditions (We first show that smooth, pinhole-free and homogeneous microstructures can be obtained by antisolvent dropping and via additives in precursor solutions in contrast to films containing pinholes in the absence of solution engineering. Figure 2a-c show scanning electron microscopy (SEM) images of Cs₂AgBiBr₆ films when prepared without treatment (reference sample), via antisolvent-treatment, or via additive (HBr)-assisted synthesis. The reference sample appears with pinholes across the film, but pinhole-free films can be obtained by dropping an antisolvent or the addition of HBr to the precursor solution. Integrated scattering intensity from GIWAXS measurements of the annealed films reveal the formation of phase pure Cs₂AgBiBr₆ for all three conditions (Figure 2d) and confirmed by Raman spectroscopy (Figure 2e). The latter shows distinct characteristics of Cs₂AgBiBr₆ in the absence of secondary phases such as Cs₃Bi₂Br₉ (compare Raman spectra in Figure S1a). d) and confirmed by Raman spectroscopy (We first show that smooth, pinhole-free and homogeneous microstructures can be obtained by antisolvent dropping and via additives in precursor solutions in contrast to films containing pinholes in the absence of solution engineering. Figure 2a-c show scanning electron microscopy (SEM) images of Cs₂AgBiBr₆ films when prepared without treatment (reference sample), via antisolvent-treatment, or via additive (HBr)-assisted synthesis. The reference sample appears with pinholes across the film, but pinhole-free films can be obtained by dropping an antisolvent or the addition of HBr to the precursor solution. Integrated scattering intensity from GIWAXS measurements of the annealed films reveal the formation of phase pure Cs₂AgBiBr₆ for all three conditions (Figure 2d) and confirmed by Raman spectroscopy (Figure 2e). The latter shows distinct characteristics of Cs₂AgBiBr₆ in the absence of secondary phases such as Cs₃Bi₂Br₉ (compare Raman spectra in Figure S1a). e). The latter shows distinct characteristics of Cs₂AgBiBr₆ in the absence of secondary phases such as Cs₃Bi₂Br₉ (compare Raman spectra in Figure S1a). c and **Figure**

S4). To reveal the effects of HBr additive on film formation, we have again performed *in situ* UV-Vis absorption measurements during spin coating (Figure 5a-b) and the subsequent thermal annealing (Figure 5c-d) with 3% vol HBr in solution. *In situ* UV-Vis absorption measurements during spin coating reveal significant differences not only in the dynamics of the film formation but also in the spectral features for films prepared with HBr (Figure 5a-b) as compared to the reference film (Figure 3a-b). Evolution of an additional absorbance peak near 410 nm is observed together with the peak near 439 nm (Figure 5a-b), suggesting the evolution of a secondary phase during spin coating. **Figure S2b** shows a comparison of absorbance spectra of the as-cast reference film, the film prepared with dropping IPA, and with HBr additive. All spectra exhibit peaks near 439 nm, but the as-cast films prepared with HBr exhibit a second peak near 410 nm. Furthermore, the evolution of the absorbance peak near 439 nm is delayed in the presence of HBr and film formation dominantly occurs from ~ 30 s to ~ 39 s (**Figure S2a**). Since HBr is an aqueous solution (48 wt. % in H₂O), and to exclude the effect of water, we have performed *in situ* UV-vis absorption measurements during spin coating of a Cs₂AgBiBr₆ precursor solution with the addition of 3% vol H₂O. It is confirmed that the additional peak near 410 nm is associated with HBr and not with H₂O as visible in **Figure S5** showing only the peak near 439 nm.

It was reported that addition of hydrohalic acids to ABX₃ precursor solutions can alter colloid size and dispersion.³⁶ To further evaluate the effect of HBr, we have performed dynamic light scattering (DLS) of Cs₂AgBiBr₆ precursor solutions without and with the addition of 3% vol HBr, as shown in **Figure S6**. The reference precursor solution exhibits three different colloidal size distributions centered around ~ 100 nm, ~ 1.2 μ m, and ~ 75.5 μ m. In the presence of HBr, these three colloidal size distributions are shifted to smaller sizes centered around < 50 nm, ~ 0.3 μ m, and ~ 50 μ m. The addition of HBr to the precursor solution not only reduces the colloidal size of species in

solution but also leads to a narrower size distribution. Notably, part of the lowest size distribution (i.e. < 50 nm) is outside the feasible measurement range thus, only a portion of it is measured. These results indicate that HBr increases the solubility of halides in the precursor solution which can explain the delayed film formation during spin coating.

During the subsequent thermal annealing of samples prepared with HBr, we observe growth of the absorbance peak near 439 nm at the expense of absorbance peak near 410 nm, followed by a red shifting of the absorbance edge as shown in Figure 5c-d. Upon thermal annealing, the absorbance spectra of films prepared with HBr appear identical to absorbance spectra of the reference film and films prepared with IPA, as shown in **Figure S2c**.

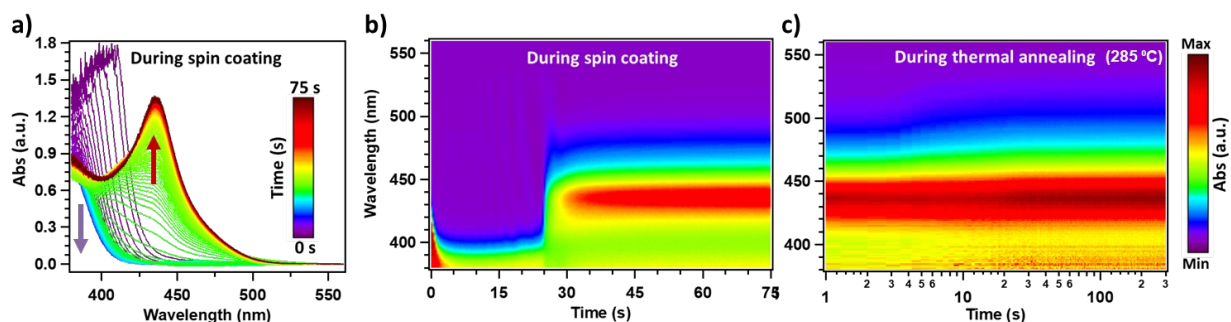


Figure 3 (a) Time-resolved absorbance spectra during spin coating of $\text{Cs}_2\text{AgBiBr}_6$ precursor solutions. (b-c) 2D color plots of *in situ* absorption measurements: (b) during spin coating of $\text{Cs}_2\text{AgBiBr}_6$ precursor solution and (c) during the subsequent thermal annealing at 285 °C.

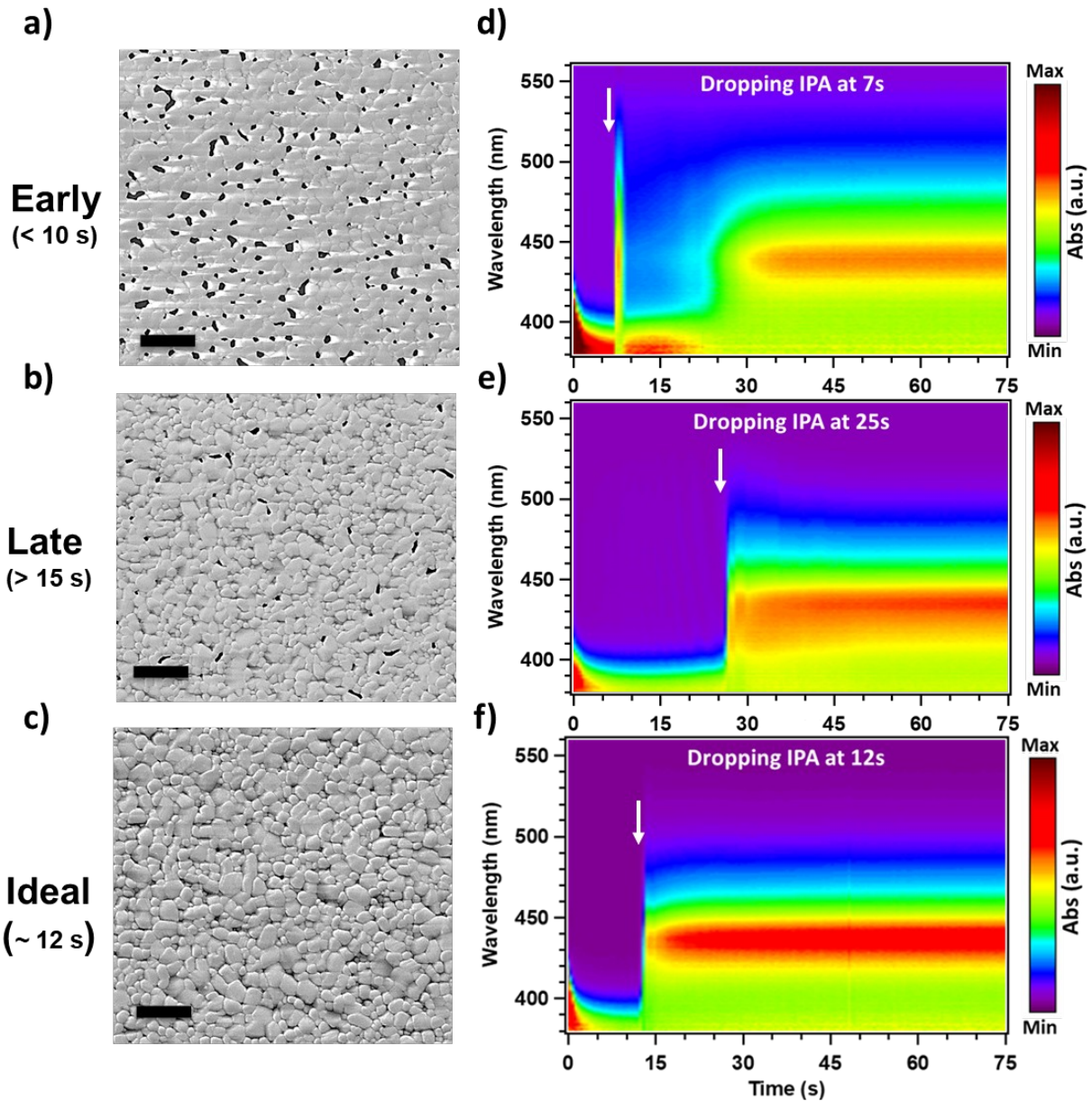


Figure 4 (a-c) SEM images of $\text{Cs}_2\text{AgBiBr}_6$ thin films prepared with dropping the antisolvent IPA at different dropping times; (a) at 7 s, (b) at 25 s, and (c) at 12 s from the starting of spin-coating. (d-f) 2D color plots of *in situ* absorption measurements during spin coating of $\text{Cs}_2\text{AgBiBr}_6$ precursor solution with dropping the antisolvent IPA at different dropping times; (d) at 7 s, (e) at 25 s, and (f) at 12 s from the starting of spin-coating. The time for dropping IPA is marked by a white arrow in (d-f). The scale bar is 2 μm for samples in (a-c).

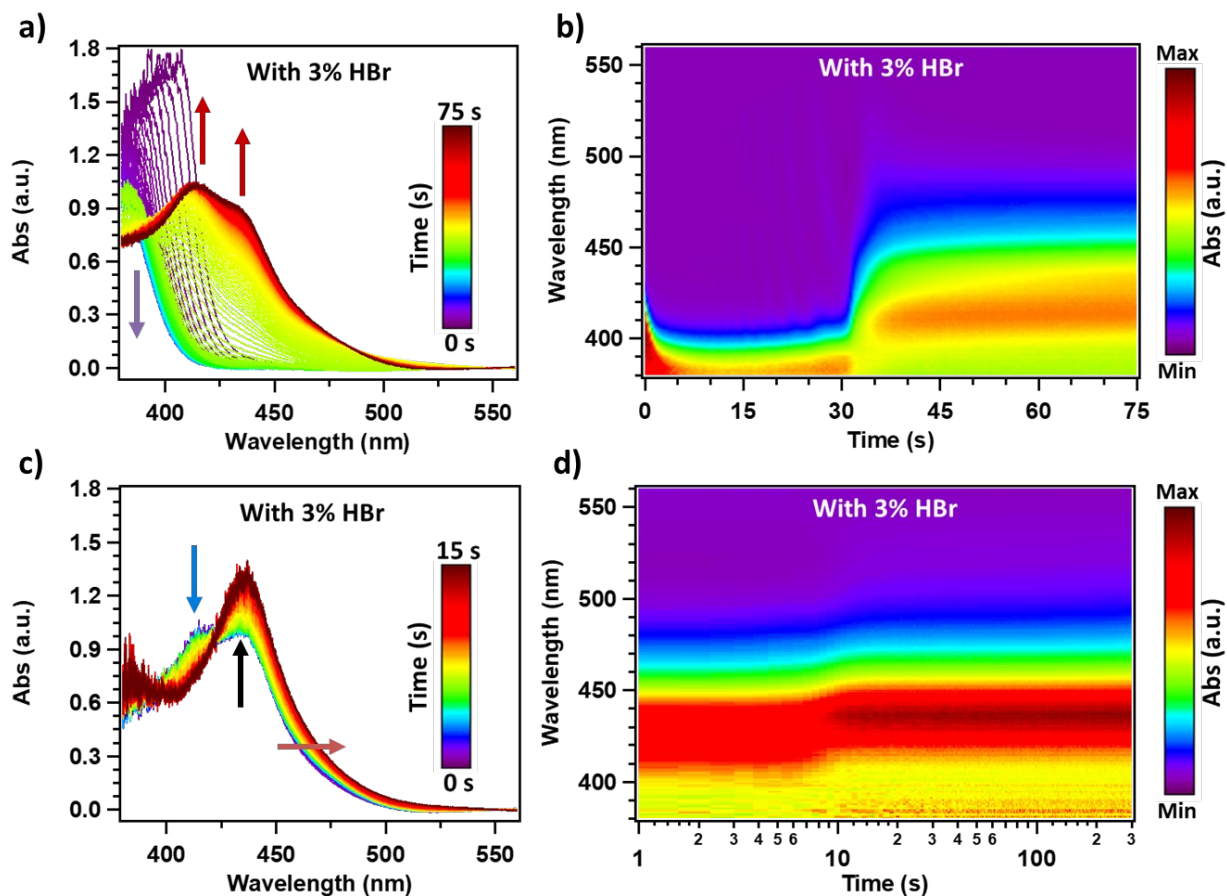


Figure 5 (a&c) Time-resolved absorbance spectra of additive-processing of $\text{Cs}_2\text{AgBiBr}_6$ using the addition of 3% HBr to precursor solution: (a) during spin coating and (c) during the subsequent thermal annealing. (b) and (d) 2D color plots of in situ absorption measurements for the experiments shown in (a) and (c) respectively.

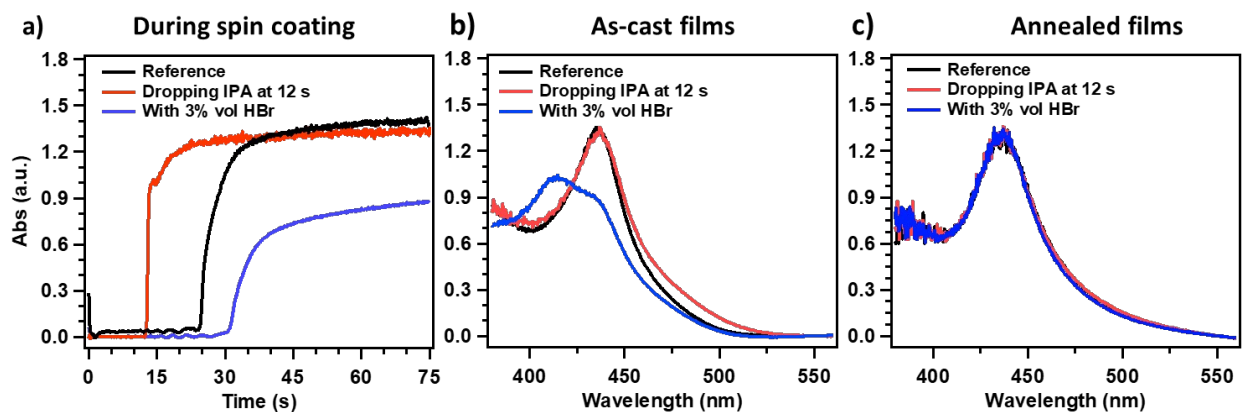


Figure S2 (a) Time-evolution of absorbance at 439 nm extracted from in situ absorption measurements during spin coating of $\text{Cs}_2\text{AgBiBr}_6$ precursor

solution. (b-c) Absorbance spectra of $\text{Cs}_2\text{AgBiBr}_6$: (b) as-cast films and (c) annealed films.

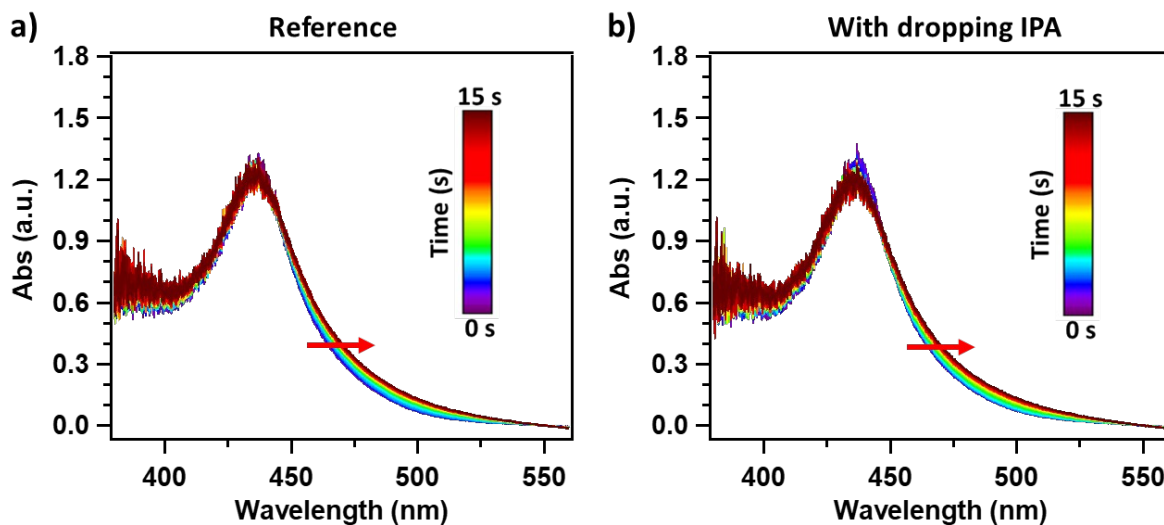


Figure S3 Time-resolved absorbance spectra during the initial 15 s of thermal annealing of $\text{Cs}_2\text{AgBiBr}_6$ at 285 °C; reference sample in (a) and sample prepared with dropping IPA at 12 s from the starting spin coating at 5000 rpms in (b).

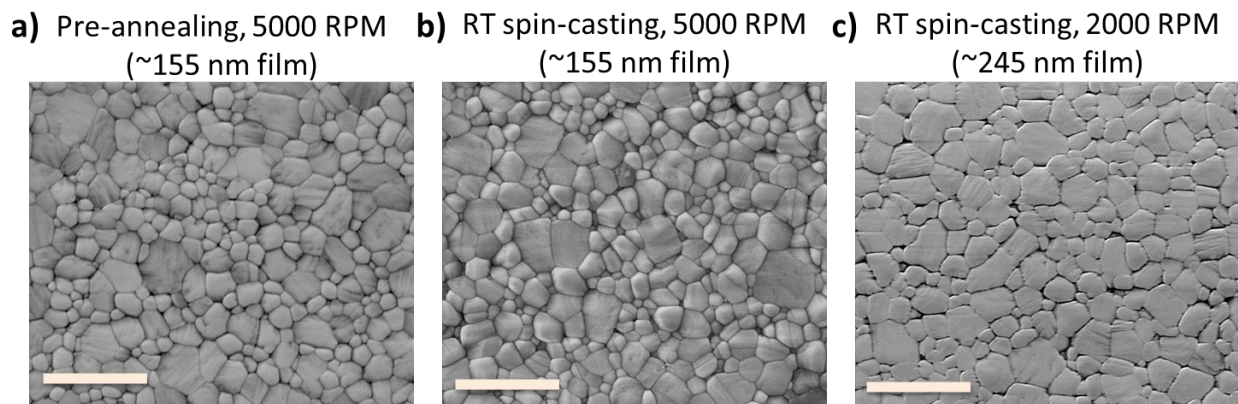


Figure S4 (a-c) SEM images of $\text{Cs}_2\text{AgBiBr}_6$ thin films prepared with the addition of 3% vol HBr to the precursor solution using different coating conditions: (a) prepared with pre-annealing (hot-casting) at 80 °C and spin coating at 5000 RPM, (b) room-temperature (RT) spin-coating at 5000 RPM, and (c) RT spin-coating at 2000 RPM. The scale bar is 2 μm.

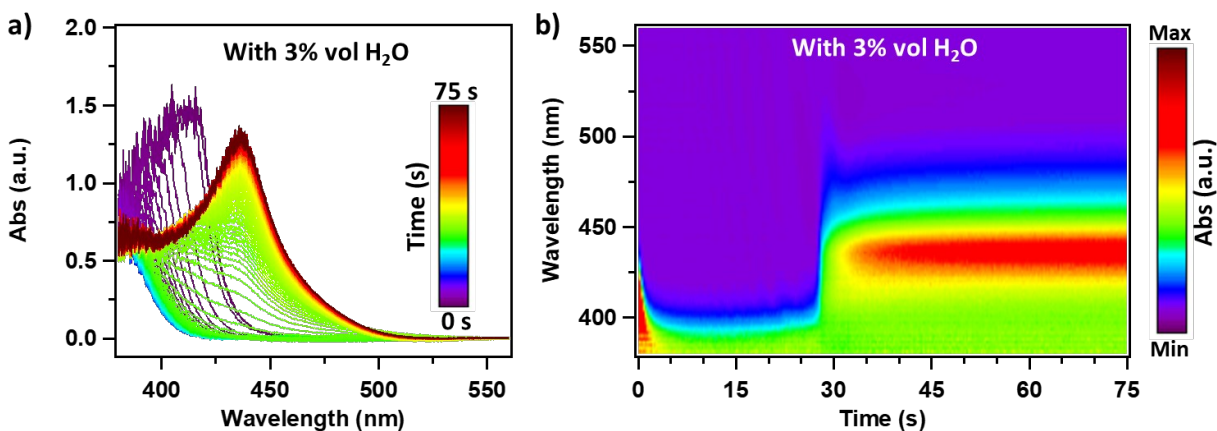


Figure S5 (a) Time-resolved absorbance spectra during spin coating of a $\text{Cs}_2\text{AgBiBr}_6$ precursor solution with the addition of 3%vol H_2O . (b) 2D color plots of *in situ* absorption measurements for the experiments shown in (a).

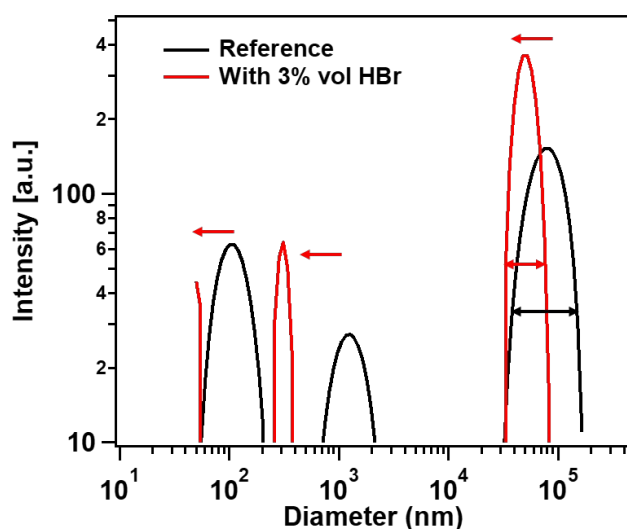


Figure S6 Colloidal hydrodynamic size distribution via dynamic light scattering (DLS) of $\text{Cs}_2\text{AgBiBr}_6$ precursor solution without HBr (reference) and with the addition of 3% vol HBr; shown in black and red lines, respectively.

3. 4. In situ GIWAXS during spin coating and thermal annealing

To investigate the effects of processing on crystallization dynamics during spin coating and thermal annealing, we have performed *in situ* GIWAXS. False-color plots of *in situ* GIWAXS and time evolution of the (004) scattering peak during spin coating of $\text{Cs}_2\text{AgBiBr}_6$ are shown in Figure 6 and **Figure S7**. For the reference sample, only broad scattering from 1.2 \AA^{-1} to 2.2 \AA^{-1} is

observed during the initial steps of spin coating (i.e. solution ejection and solvent evaporation). Upon reaching supersaturation, nucleation and growth of $\text{Cs}_2\text{AgBiBr}_6$ crystals occur as revealed by the appearance of $\text{Cs}_2\text{AgBiBr}_6$ diffraction peaks (see Figure 6a). The onset of crystallization occurs after ~ 26 s from the start of spin coating (see the evolution of scattering intensity of the (004) peak in **Figure S7**). For samples prepared with dropping IPA, supersaturation and crystallization occur immediately upon dropping IPA as observed by the emergence of $\text{Cs}_2\text{AgBiBr}_6$ diffraction peaks (Figure 6b). For samples prepared with HBr, we observe a short delay in the onset of crystallization which occurs after ~ 28 s from the start of spin coating (Figure 6c and **Figure S7**). This observation of delayed crystallization for HBr-samples matches with the in-situ UV-Vis absorption results as discussed previously (Figure 3 and Figure 5). Nevertheless, no crystalline secondary phases were observed for HBr-samples, unlike the in-situ UV-Vis absorption results that showed an additional phase which we attribute to HBr-complexes. Possibly, these HBr-precursor complexes are amorphous due to the absence of any extra diffraction peaks in the GIWAXS data (Figure 6c and **Figure S9**) for the as-cast samples prepared with HBr. This is also supported by the lack of any additional features in their Raman spectra (**Figure S1**) other than $\text{Cs}_2\text{AgBiBr}_6$ phase. In all cases for as-cast films, we observe diffraction from the $\text{Cs}_2\text{AgBiBr}_6$ perovskite phase only with no detectable scattering from any crystalline secondary phases as illustrated by the integrated scattering intensity versus q as shown in **Figures S9** and **S10**. It is worth noting that there are slight differences in the onset of $\text{Cs}_2\text{AgBiBr}_6$ film formation measured by in-situ GIWAXS and in-situ UV-vis absorption spectroscopy but the overall trend is similar. This can be due to differences in the environment of the in situ GIWAXS and in situ UV-Vis absorption measurements (i.e. at the beamline vs in the glovebox).

False-color plots of in situ GIWAXS and time evolution of the (004) scattering peak during thermal annealing of spin-coated $\text{Cs}_2\text{AgBiBr}_6$ thin films

are shown in Figure 7Error: Reference source not found and **Figure S8**. Upon thermal annealing, we observe an increase in the scattering intensity of the $\text{Cs}_2\text{AgBiBr}_6$ diffraction peaks indicating an improvement in crystallinity. Hence, the as-cast films likely consist of seeds of $\text{Cs}_2\text{AgBiBr}_6$ perovskite phase and an amorphous complex phase, while thermal annealing leads to growth of the $\text{Cs}_2\text{AgBiBr}_6$ perovskite phase at the expense of the amorphous complex phase. Notably, the broad peaks centered around ~ 1.57 , 1.73 , and 1.89 \AA^{-1} correspond to scattering from the PEEK dome (used for the enclosure to create an inert chamber), see **Figures S9** and **S11** which includes a GIWAXS measurement of the bare glass substrate.

During heating from RT to $285 \text{ }^\circ\text{C}$, the scattering intensity remains constant till a threshold temperature is reached at which the scattering intensity starts to increase, see the evolution of the (004) scattering peak in Figure 7Error: Reference source not foundb. Such threshold temperatures (marked by arrows in Figure 7Error: Reference source not foundb) depend on the solvent engineering strategy hinting that the as-cast films possibly have initially either different microstructure and/or different precursor complexes induced by different processing treatments. For the reference sample, we observed a sharp increase in the scattering intensity of the (004) peak upon reaching a heating temperature of $\sim 160 \text{ }^\circ\text{C}$. This can possibly be attributed to crystallization of $\text{Cs}_2\text{AgBiBr}_6$ perovskite phase from amorphous DMSO-precursor complexes. For samples prepared with dropping IPA, the sharp increase occurs earlier upon reaching a heating temperature of $\sim 140 \text{ }^\circ\text{C}$. As revealed by thickness measurements (see **Table S1**), the samples prepared with dropping IPA have less retained volatiles (i.e. DMSO) in the as-cast film, perhaps leading to a reduction in the temperature required for crystallization. For samples prepared with HBr, the increase in scattering intensity of the (004) peak starts $\sim 120 \text{ }^\circ\text{C}$ and develops with a slower rate, then a sharp increase in scattering intensity occurs at $\sim 160 \text{ }^\circ\text{C}$. We hypothesize that the initial crystallization step for samples prepared with HBr

can be attributed to the crystallization from HBr-precursor complexes, while the second crystallization step can be attributed to crystallization from DMSO-precursor amorphous complexes. For both samples prepared with IPA or HBr, we observe an additional crystallization step with slower rate after the sharp crystallization step. On the other hand, the reference sample reaches saturation upon the sharp crystallization step.

2D GIWAXS images of the as cast and annealed films measured during in situ annealing are shown in **Figure S10a-f**. The scattering peaks of $\text{Cs}_2\text{AgBiBr}_6$ crystals appear as isotropic scattering rings indicating homogenous crystallization. This observation can be attributed to crystallization from mainly amorphous phase (with no preferred orientation for crystal growth). Notably, homogeneous nucleation becomes often dominant if it occurs in the interior of an amorphous phase.^{37,38} To confirm that the samples prepared at the beamline during in situ measurements have similar microstructure as samples prepared in glovebox, we have measured GIWAXS of samples prepared in glovebox, shown in **Figure S10g-i**. The GIWAXS patterns of samples prepared in glovebox appears very similar to these prepared at the beamline confirming that they have similar crystal structure, compare **Figure S10d-f** and **Figure S10g-i**.

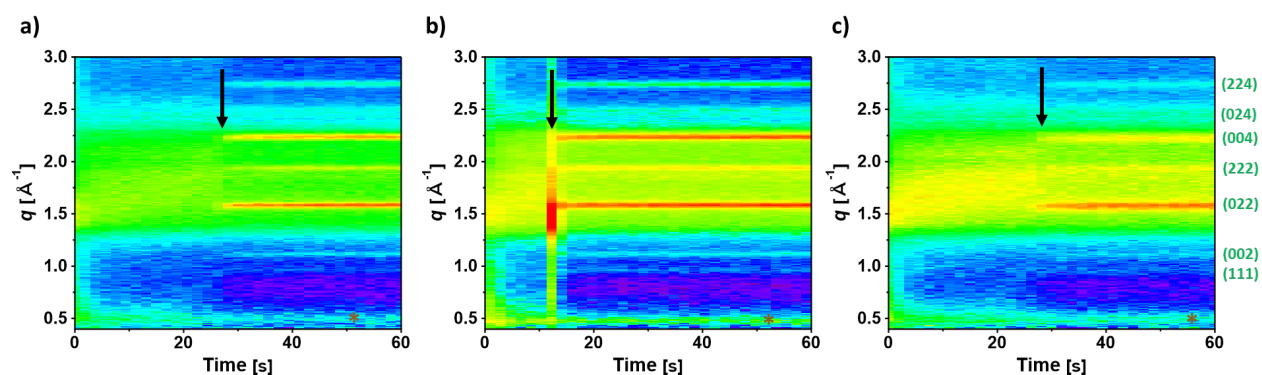


Figure 6 False-color plots of in situ GIWAXS during spin-coating of $\text{Cs}_2\text{AgBiBr}_6$; (a) prepared without solution engineering (reference sample), (b) with dropping IPA at 12 s from the start of spin coating, and (c) with adding 3% vol HBr to the precursor solution. The onset of crystallization is marked

by black arrows. The scattering near $\sim 0.5 \text{ \AA}^{-1}$ (marked as asterisks) is due artifacts.

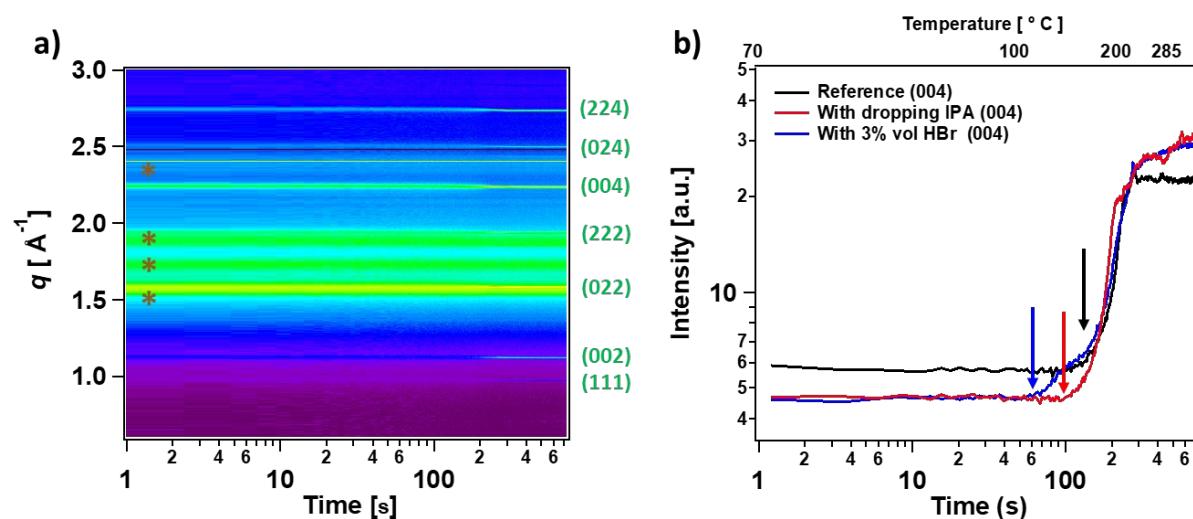


Figure 7 (a) False-color plot of in situ GIWAXS during thermal annealing of spin-coated $\text{Cs}_2\text{AgBiBr}_6$ thin films prepared without solution engineering (reference sample). (b) Time evolution of the scattering intensities at selected q -value corresponding to the (004) scattering peak; the spin-coated films were prepared without adding HBr or dropping IPA (reference, black line), with dropping IPA at 12 s from the start of spin coating (red line), and with adding HBr to precursor solution (blue line). The $\text{Cs}_2\text{AgBiBr}_6$ perovskite peaks are labeled on the right of Figure 7a. The onset of crystallization is marked in Figure 7b by arrows with the same corresponding color as figure curves. The scattering from the PEEK dome gives rise to the broad peaks centered around $\sim 1.57, 1.73, 1.89$ and 2.4 \AA^{-1} (marked as asterisks).



Figure S7 Time evolution of the scattering intensities at selected q-value corresponding to the (004) scattering peak during spin-coating of $\text{Cs}_2\text{AgBiBr}_6$; prepared without solution engineering (reference sample), with dropping IPA at 12 s, and with adding 3%vol HBr to the precursor solution.

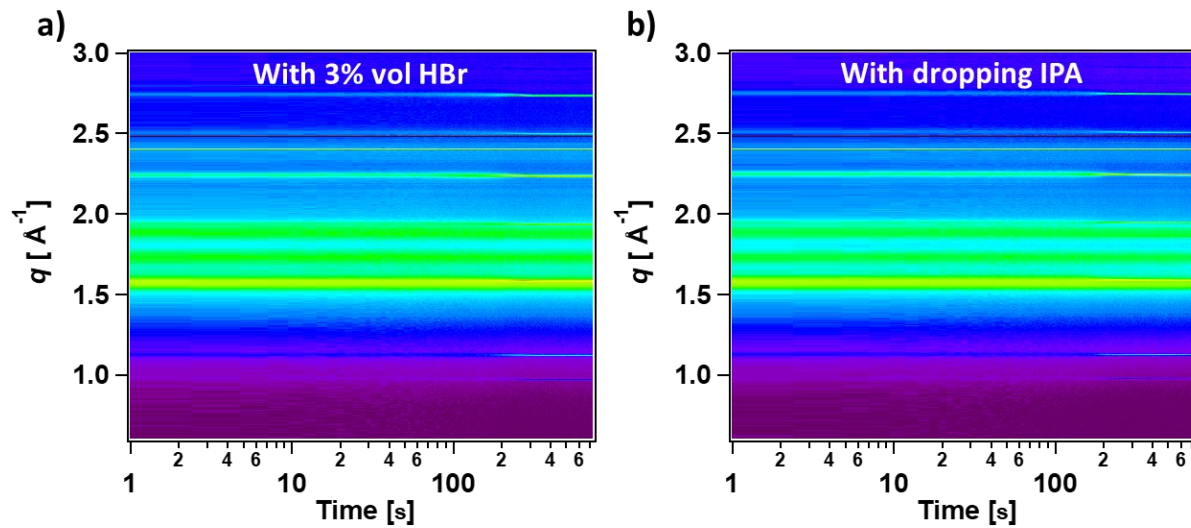


Figure S8 (a-b) False-color plots of in situ GIWAXS during thermal annealing of spin-coated $\text{Cs}_2\text{AgBiBr}_6$ thin films; prepared with (a) adding HBr to precursor solution and (b) dropping IPA at 12 s from the start of the spin coating.

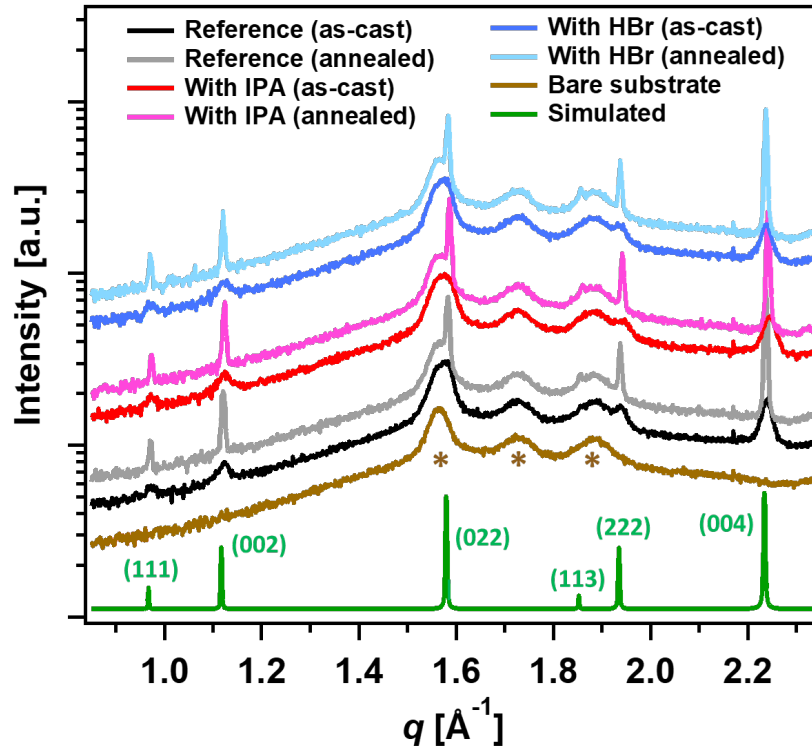


Figure S9 Integrated scattering intensity of GIWAXS measurements of the as cast and annealed $\text{Cs}_2\text{AgBiBr}_6$ films prepared without IPA/HBr, with dropping IPA at 12 s during spin coating, and with the addition of HBr to precursor solution. The brown line shows scattering of the bare substrate and from the PEEK dome used for the closed chamber during *in situ* GIWAXS measurements. The scattering from the PEEK dome gives rise to the broad peaks centered around ~ 1.57 , 1.73 , 1.89 , and 2.4 \AA^{-1} (marked as asterisks). The simulated $\text{Cs}_2\text{AgBiBr}_6$ perovskite peaks are shown and labeled in green.

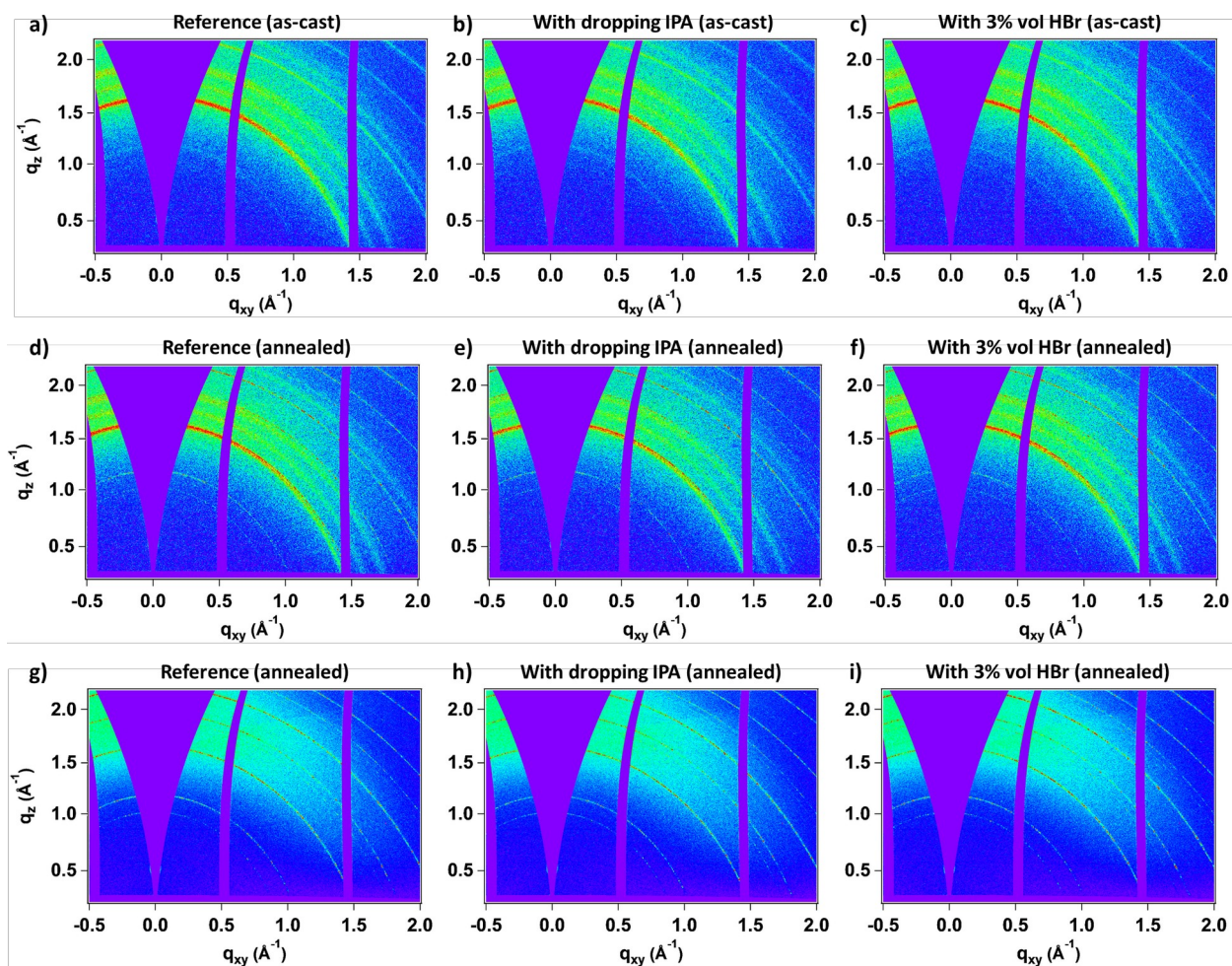


Figure S10 2D GIWAXS images of the as cast (a-c) and annealed (d-f) $\text{Cs}_2\text{AgBiBr}_6$ thin films; (a, d) reference sample, (b, e) prepared with dropping IPA at 12 s during spin coating, and (c, f) prepared with the addition of HBr to the precursor solution. Samples in (a-f) were prepared by annealing in a custom-made inert N_2 -chamber at the beamline during *in situ* GIWAXS measurements. (g-h) 2D GIWAXS images of $\text{Cs}_2\text{AgBiBr}_6$ thin films annealed in an inert glovebox (N_2); (g) reference sample, (h) prepared with dropping IPA at 12 s during spin coating, and (i) prepared with the addition of HBr to the precursor solution. It is worth noting that samples in (a-f) and samples in (g-h) were measured with and without the PEEK dome, respectively.

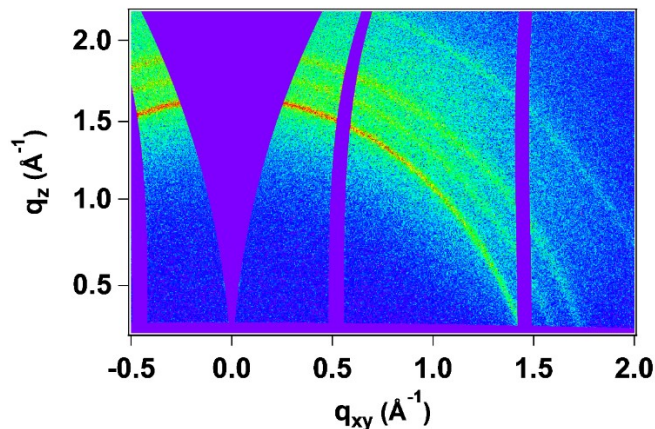


Figure S11 2D GIWAXS images of bare substrate, showing the scattering from the PEEK dome used for the inert chamber during *in situ* GIWAXS measurements. The scattering from the PEEK dome gives rise to the broad peaks centered around $\sim 1.57, 1.73, 1.89,$ and 2.4 \AA^{-1} .

Table S1 Thickness measurements of the as cast and annealed $\text{Cs}_2\text{AgBiBr}_6$ thin films

Samples	As-cast Thickness (nm)	Annealed Thickness (nm)	Retained volatiles (vol% per unit area)
Reference	184.6	157.4	14.7
Dropping IPA at 12 s	166.3	155.4	6.6
With 3% vol HBr	189.1	160.2	15.3

3. 5. Summary of the film formation mechanisms

Based on the above presented results we propose the following explanation of the observed solution engineering effects (antisolvent and additive-assisted synthesis) on the film formation of $\text{Cs}_2\text{AgBiBr}_6$ (illustrated in Figure 8). For all synthesis conditions, the as-cast films are predominantly

amorphous with seeds of $\text{Cs}_2\text{AgBiBr}_6$ crystals. The amorphous phase is likely different for the different solution engineering approaches and is speculated to include DMSO-precursor complexes. Thermal annealing facilitates the evaporation of volatiles and the growth of $\text{Cs}_2\text{AgBiBr}_6$ crystals at the expense of the amorphous phases. It was found that the solution engineering treatments have additional effects on the crystallization pathways during spin coating and subsequent thermal annealing. Dropping antisolvent induces immediate crystallization during spin coating and reduces the amount of retained volatiles (i.e., DMSO) in the as-cast films most efficiently. We hypothesize that the reduction of retained DMSO in the as-cast film (Figure 8b and **Table S1**) leads to a reduction in the activation energy for the crystallization during thermal annealing as evidenced by the reduced crystallization onset temperature (**Figure 7**Error: Reference source not foundb). One drawback however, for the antisolvent treatment is the narrow time window for dropping the antisolvent.

The addition of HBr to the precursor solution has effects on the colloidal formation in solution giving rise to the formation of smaller colloids with narrower distribution of their sizes. During spin coating, HBr induces the formation of an additional phase (possibly HBr-related precursor complexes) besides the amorphous DMSO-precursor and $\text{Cs}_2\text{AgBiBr}_6$ crystalline phase (Figure 8c). Notably, the amount of retained volatiles (HBr and DMSO) in the as-cast films prepared with HBr is similar to the reference samples. However, we hypothesize that the HBr-related precursor complexes are less stable than in the reference sample and therefore, the activation energy for crystallization is reduced as evidenced by the lower crystallization onset temperature (**Figure 7b**). HBr has a positive effect on the precursor solution and film processing resulting in more facile fabrication of pinhole-free $\text{Cs}_2\text{AgBiBr}_6$ films, and in particular without the need for hot-casting. Furthermore, pinhole-free $\text{Cs}_2\text{AgBiBr}_6$ films can be obtained from HBr-containing precursor solutions aged for a day without stirring or heating.