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Supporting Information

Impact of Processing Conditions on the Film Formation of Lead-Free Halide Double Perovskite $Cs_2AgBiBr_6$

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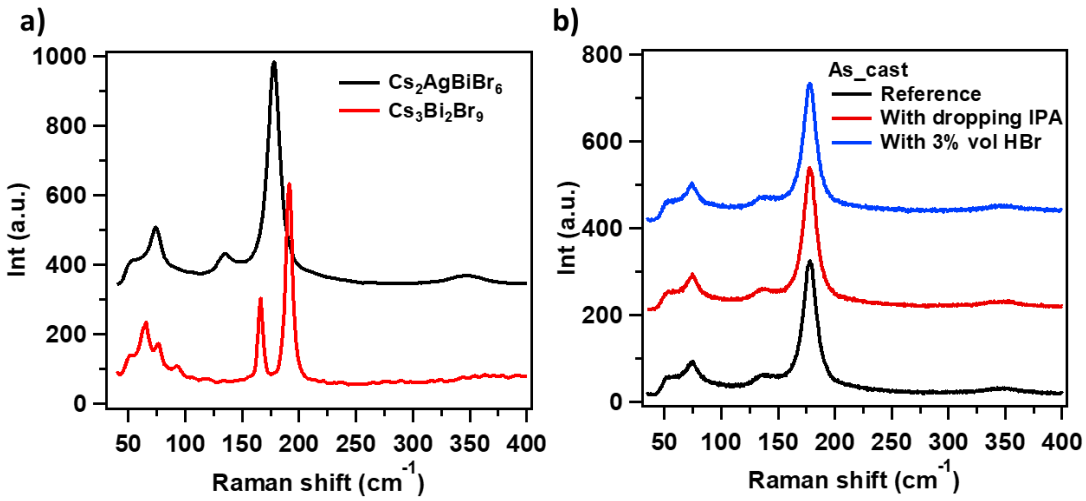

Figure S1 (a) Raman spectra of annealed $Cs_2AgBiBr_6$ (black) and $Cs_3Bi_2Br_9$ films (red). The Raman features in these spectra agree with previously reported spectra for $Cs_2AgBiBr_6$ films and $Cs_3Bi_2Br_9$ phases.[1] (b) Raman spectra of the as-cast $Cs_2AgBiBr_6$ films prepared with different 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.

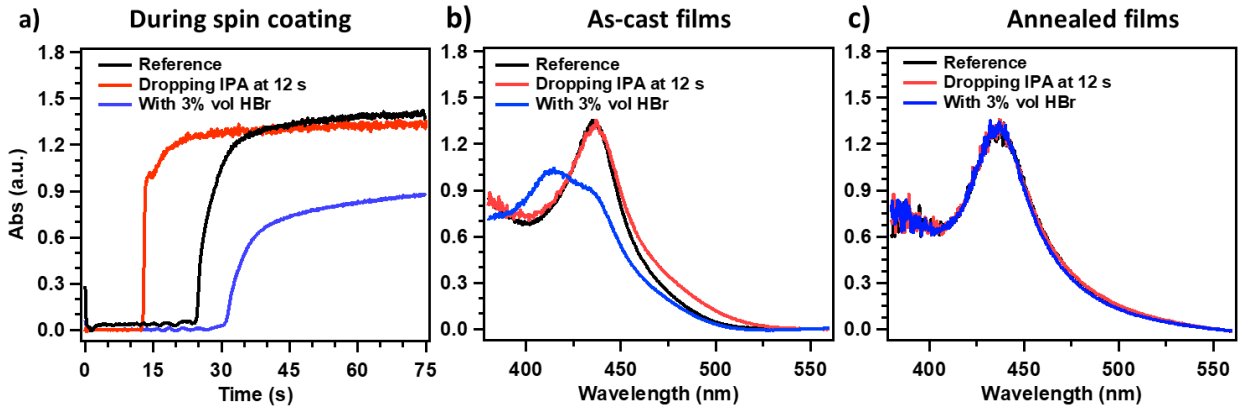

Figure S2 (a) Time-evolution of absorbance at 439 nm extracted from in situ absorption measurements during spin coating of $Cs_2AgBiBr_6$ precursor solution. (b-c) Absorbance spectra of $Cs_2AgBiBr_6$: (b) as-cast films and (c) annealed films.

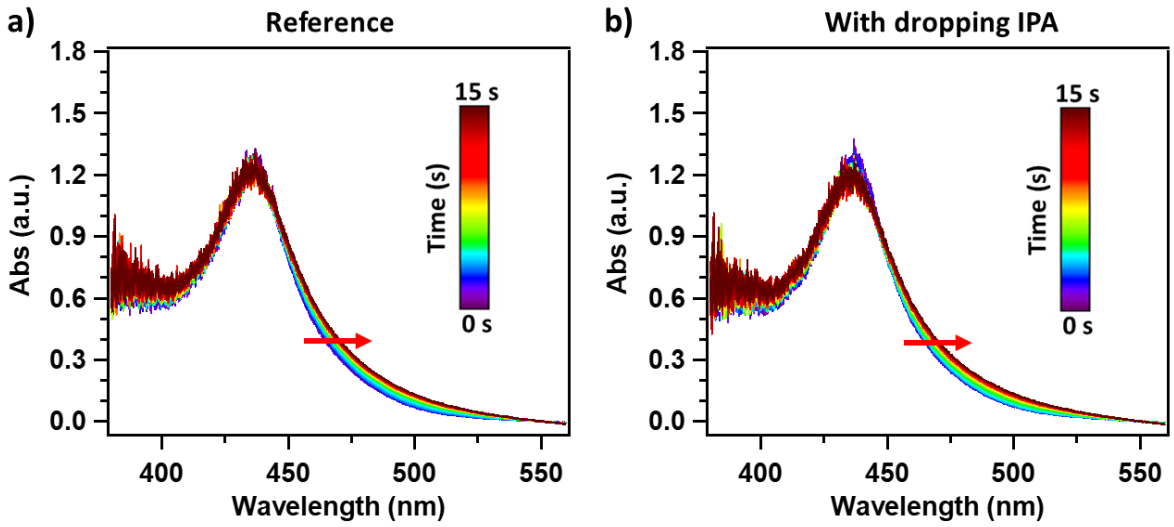

Figure S3 Time-resolved absorbance spectra during the initial 15 s of thermal annealing of $Cs_2AgBiBr_6$ at 285 °C; reference sample in (a) and sample prepared with dropping IPA at 12 s from the starting spin coating at 5000 rpms in (b).

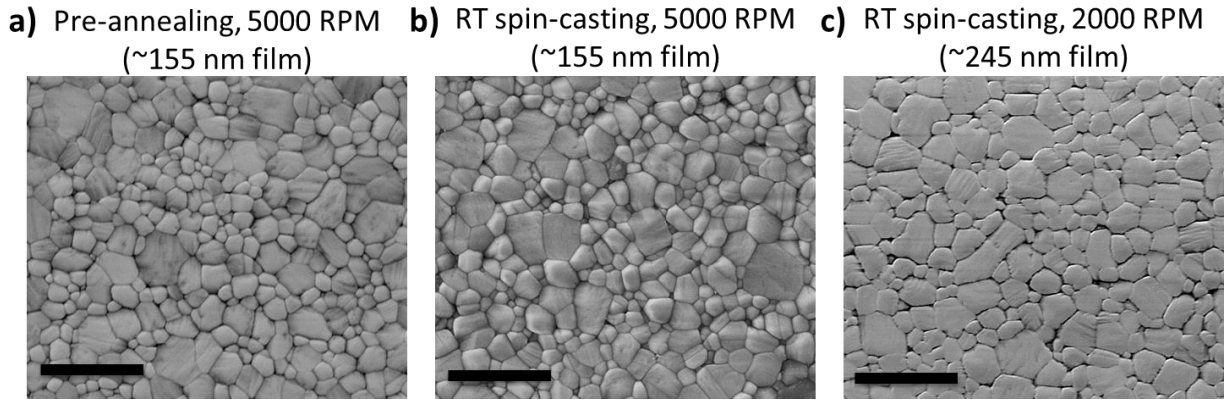

Figure S4 (a-c) SEM images of $Cs_2AgBiBr_6$ thin films prepared with the addition of 3% vol HBr to the precursor solution using different coating conditions: (a) prepared with pre-annealing (hot-casting) at 80 ^{o}C and spin coating at 5000 RPM, (b) room-temperature (RT) spin-coating at 5000 RPM, and (c) RT spin-coating at 2000 RPM. The scale bar is 2 µm.

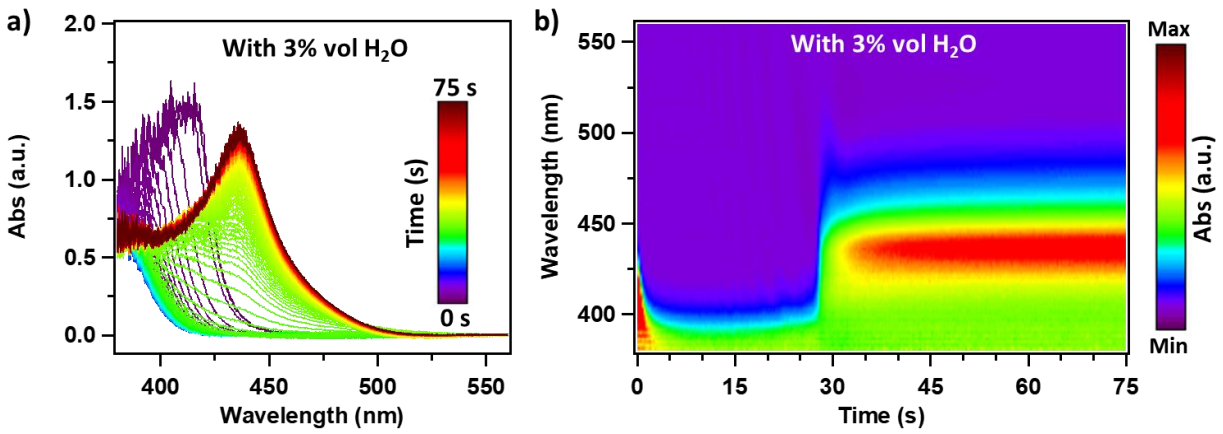

Figure S5 (a) Time-resolved absorbance spectra during spin coating of a $Cs_2AgBiBr_6$ precursor solution with the addition of 3%vol H_2O. (b) 2D color plots of *in situ* absorption measurements for the experiments shown in (a).

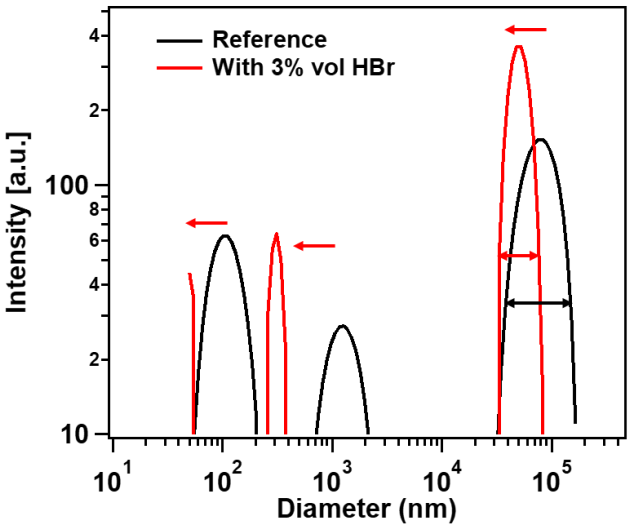

Figure S6 Colloidal hydrodynamic size distribution via dynamic light scattering (DLS) of $Cs_2AgBiBr_6$ precursor solution without HBr (reference) and with the addition of 3% vol HBr; shown in black and red lines, respectively.

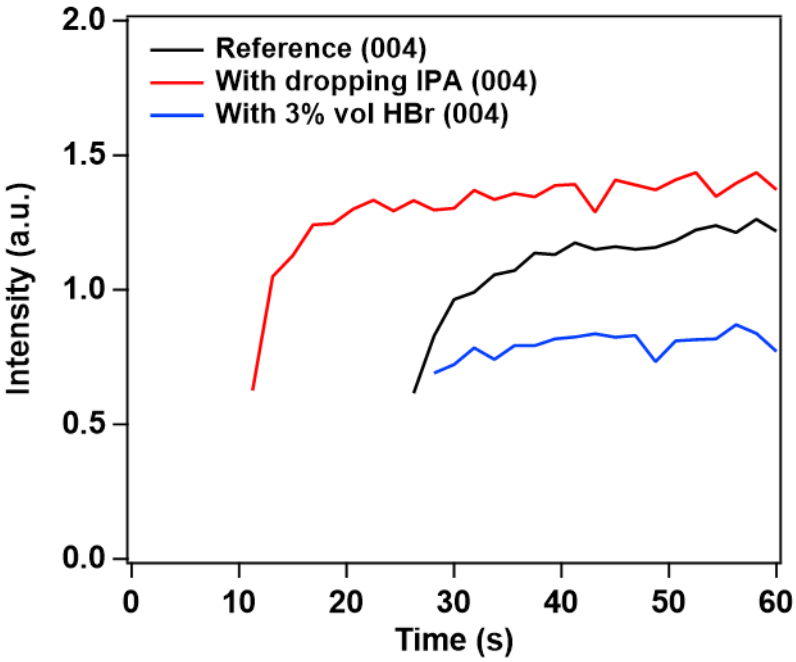

Figure S7 Time evolution of the scattering intensities at selected q-value corresponding to the (004) scattering peak during spin-coating of $Cs_2AgBiBr_6$; prepared without solution engineering (reference sample), with dropping IPA at 12 s, and with adding 3%vol HBr to the precursor solution.

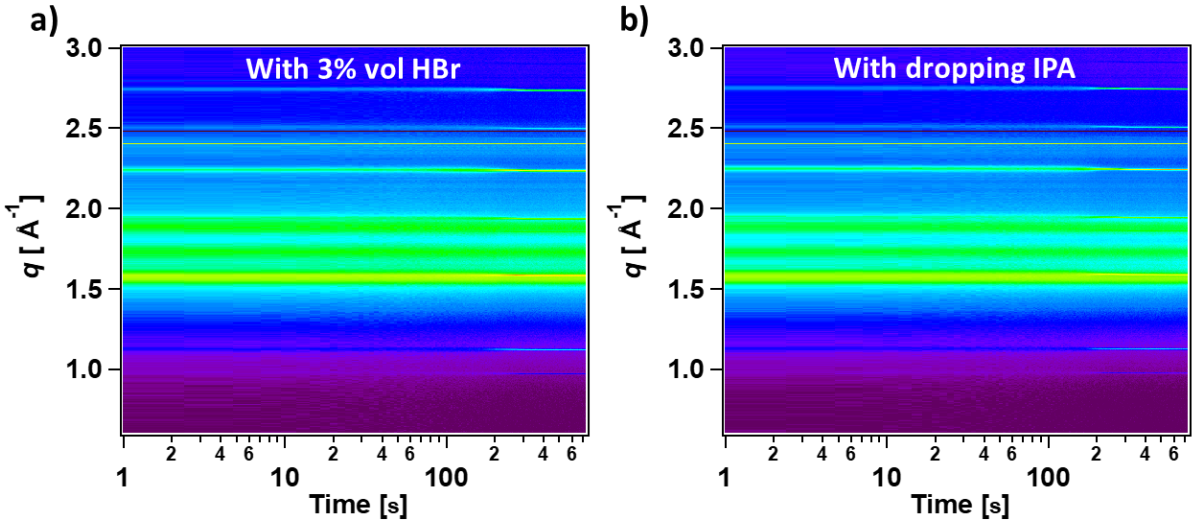

Figure S8 (a-b) False-color plots of in situ GIWAXS during thermal annealing of spin-coated $Cs_2AgBiBr_6$ thin films; prepared with (a) adding HBr to precursor solution and (b) dropping IPA at 12 s from the start of the spin coating.

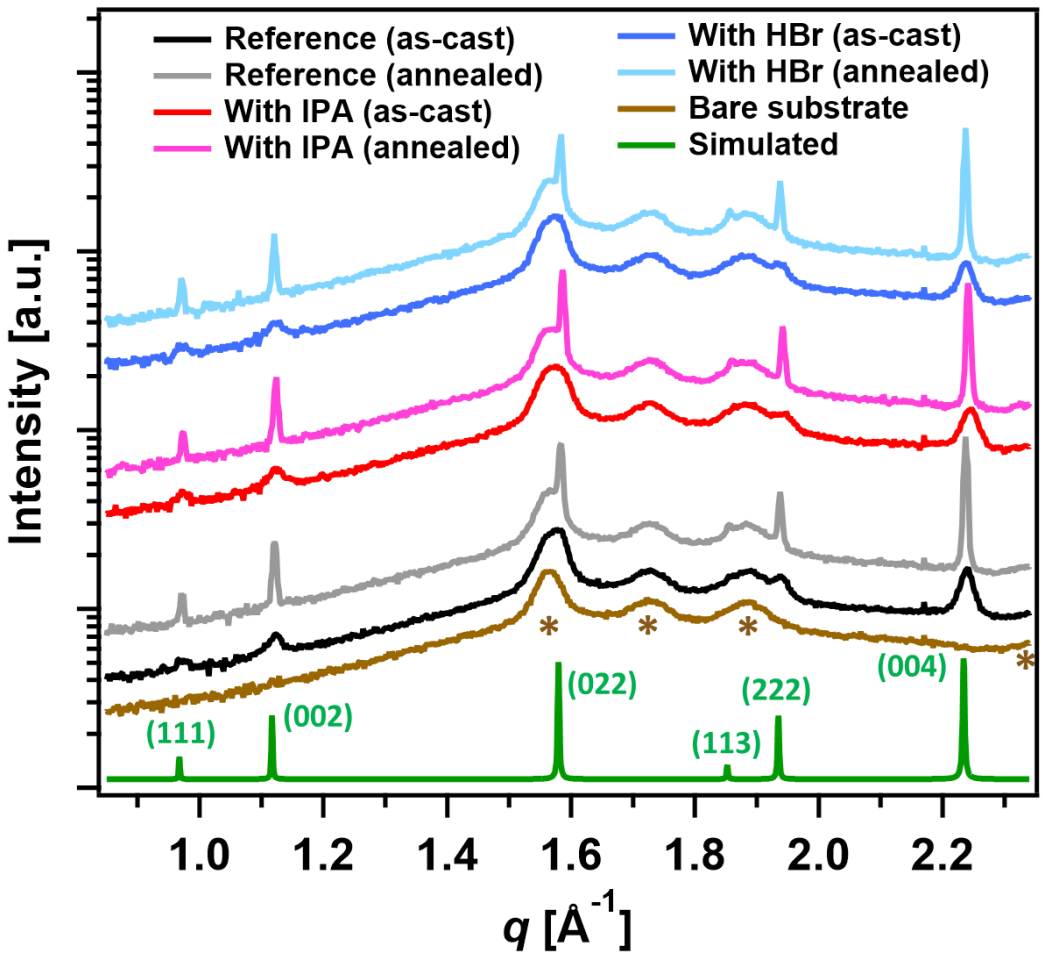

Figure S9 Integrated scattering intensity of GIWAXS measurements of the as cast and annealed $Cs_2AgBiBr_6$ films prepared without IPA/HBr, with dropping IPA at 12 s during spin coating, and with the addition of HBr to precursor solution. The brown line shows scattering of the bare substrate and from 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 $Å^{-1}$ (marked as asterisks). The simulated $Cs_2AgBiBr_6$ perovskite peaks are shown and labeled in green.

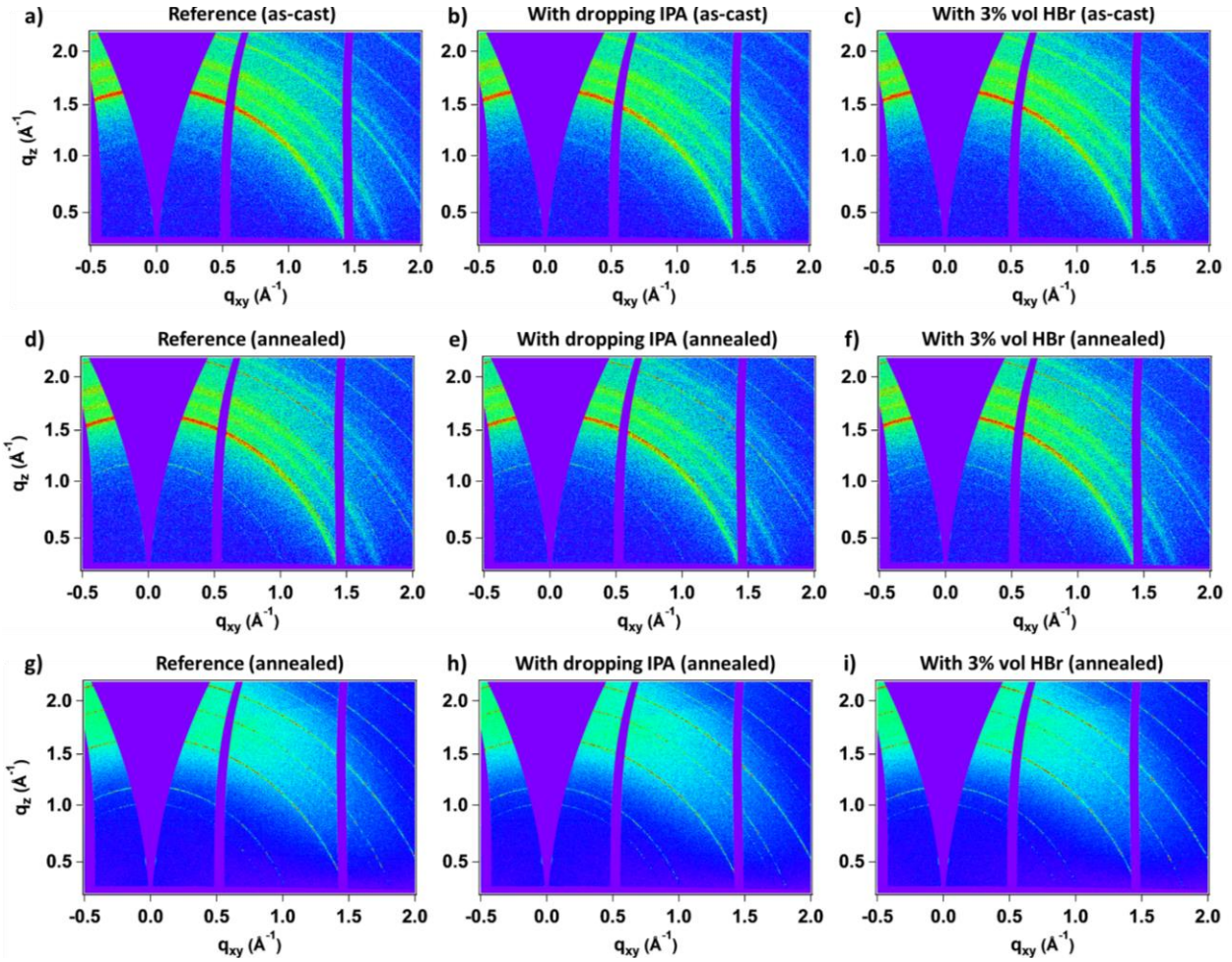

Figure S10 2D GIWAXS images of the as cast (a-c) and annealed (d-f) $Cs_2AgBiBr_6$ thin films; (a, d) reference sample, (b, e) prepared with dropping IPA at 12 s during spin coating, and (c, f) prepared with the addition of HBr to the precursor solution. Samples in (a-f) were prepared by annealing in a custom-made inert N_2-chamber at the beamline during *in situ* GIWAXS measurements. (g-h) 2D GIWAXS images of $Cs_2AgBiBr_6$ 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.

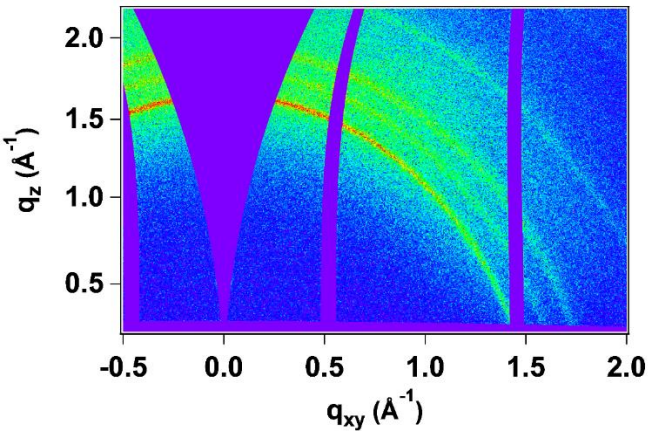

Figure S11 2D GIWAXS images of bare substrate, showing the scattering from the PEEK dome used for the inert chamber during *in situ* GIWAXS measurements. The scattering from the PEEK dome gives rise to the broad peaks centered around ~ 1.57, 1.73, 1.89, and 2.4 Å^{-1}.

Table S1 Thickness measurements of the as cast and annealed $Cs_2AgBiBr_6$ 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

References

(1) Pistor, P.; Meyns, M.; Guc, M.; Wang, H.-C.; Marques, M. A. L.; Alcobé, X.; Cabot, A.; Izquierdo-Roca, V. Advanced Raman Spectroscopy of Cs2AgBiBr6 Double Perovskites and Identification of Cs3Bi2Br9 Secondary Phases. *Scr. Mater.* **2020**, *184*, 24–29. https://doi.org/10.1016/j.scriptamat.2020.03.040.