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Supporting Information for

Two-Step Spin-Coating of Vacancy-Ordered Double Perovskites Enables Growth of Thin Films for Electronic Devices

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TeBr4 Reaction Mechanism

The reaction between TeBr₄ and CsBr is understood to proceed through a polar solventcoordinated intermediate. In its solid form, TeBr₄ has a cubane-like structure of isolated Te₄Br₁₆ tetramers.¹ IR spectroscopy has demonstrated that polar solvents will dissolve TeBr₄ clusters by coordinating to form [L₂TeBr₃]⁺Br⁻ complexes (L is a solvent molecule).² This is further supported by the observation that the reaction between TeBr₄ and CsBr proceeds faster as the solvent's Lewis basicity increases.³ The formation of Cs₂TeBr₆ therefore follows the below reaction equations.

 $2L + TeBr_4 \rightarrow [L_2TeBr_3]^+Br^ [L_2TeBr_3]^+Br^- + 2CsBr \rightarrow Cs_2TeBr_6 + 2L$



Cross-Sectional SEM Images of Cs₂TeBr₆ Film

Figure S1. Cross-sectional images of a Cs_2TeBr_6 film made by spinning TeBr₄ at 4000 rpm followed by CsBr at 2000 rpm. The film was grown on a silicon substrate which was broken in half to view the cross-section at the middle of the film. The approximate thickness matches what was measured with a profilometer and reported in **Figure 2c** (approximately 3.2 μ m).

In-Situ Photoluminescence



Figure S2. Time evolution of emission from CsPbBr₃ (top) and Cs₂TeCl₆ (bottom) films made via a two-step deposition process. CsX solution was deposited at t = 0 s. Additional emission features centered around 2.75 eV and 1.60 eV are likely a measurement artifact intensified because of the relatively low PL emission intensity.

The evolution of optical properties during the film growth process was investigated with *in-situ* capabilities in the Sutter-Fella lab at the Molecular Foundry. Specifically, the photoluminescence of Cs₂TeCl₆ and CsPbBr₃ was probed in the time following deposition of CsCl and CsBr at approximately 20 seconds to form Cs₂TeCl₆ and CsPbBr₃, respectively. The two-step deposition procedure was adapted for CsPbBr₃, where PbBr₂ was deposited initially from a 1M DMF solution followed by CsBr in ethylene glycol. Samples were excited with a 405 nm laser and the resulting photoluminescence peak intensity and position were measured for approximately 40 seconds following CsCl/CsBr deposition. CsPbBr₃ shows characteristic emission starting at around 2.40 eV, which then continuously red shifts to around 2.37 eV during film growth. This shift in energy is possibly attributed to quantum confinement effects as CsPbBr₃ crystallites increase in size⁴. However, no significant shift in energy is observed in the Cs₂TeCl₆ photoluminescence. This is attributed to the molecular nature of zero-dimensional perovskites given the isolated octahedra. This localizes the wavefunction and thus emission energy is not sensitive to crystallite size.

GIWAXS 2D Diffraction Patterns



Figure S3. GIWAXS images of Cs₂TeBr₆ films made with 0.5 M (left), 1 M (middle), and 1.5 M (right) CsBr solution.



Grazing Angle Dependence of Cs₂TeBr₆

Figure S4. Azimuthally integrated GIWAXS data of Cs₂TeBr₆ films acquired with varying grazing-incidence angle. The pink shaded region marks the most prominent TeBr₄ reflection. Films were made by spinning 50 uL of 1 M TeBr₄ at 2000 rpm followed by 50 uL of 1 M CsBr deposited dynamically at 2000 rpm.

Incidence Angle	Penetration Depth (nm)
0.2°	93.70
0.5°	234.18
1°	468.36
2°	936.71

Table S1. Calculated GIWAXS penetration depth for varying incidence angle.

Estimate of CsBr Liquid Layer Thickness

Conclusions made regarding processing conditions support estimates for the quantity of CsBr reacted to form Cs₂TeBr₆ during spin-coating. At 2000 rpm, the initial TeBr₄ film has a thickness of approximately 3 μ m. Using the molar mass (*MM* = 447.2 g mol⁻¹) and density (ρ = 4.3 g cm⁻³) of TeBr₄, the number of moles per substrate area can be roughly estimated with the following equation:

$$\frac{mol_{TeBr_4}}{cm^2} = \frac{thickness * \rho_{TeBr_4}}{MM_{TeBr_4}} \approx 2.9 * 10^{-6} mol \ cm^{-2}$$

Given the stoichiometry of the reaction, twice as many CsBr molecules per cm² are required to convert all TeBr₄. Additionally, since GIWAXS experiments indicated very little remaining TeBr₄ when depositing 1.5 M CsBr solution, we can assume 100% yield at this concentration to estimate the thickness of the liquid second layer when spinning at 2000 rpm. We set up the following equation:

$$2 * 2.9 * 10^{-6} mol \ cm^{-2} = C_{CsBr} * thickness$$

Using 1.5 M, this gives a liquid layer thickness of roughly 38.5 μ m when spinning at 2000 rpm. This estimate informs the conditions required to induce full conversion in the film, which we've shown to be highly dependent on the thickness of the CsBr liquid layer controlled with spin speed.

XPS of Cs₂TeBr₆ Films



Figure S5. XPS scans of a Cs₂TeBr₆ film in binding energy regions for cesium, tellurium, and bromide. The film was made by spin-coating 1 M TeBr₄ at 2000 rpm followed by 1 M CsBr at 2000 rpm.

Core Level	Peak BE (eV)	FWHM (eV)	Area (CPS*eV)	Atomic %
Cs 3d5/2	722.82	2.48	291903.99	6.14
Te 3d5/2	575.13	2.33	1161916.84	26.02
Br 3d/2	67.76	2.67	420990.45	67.84

Table S2. Quantification results for XPS scans.

In a pure sample of Cs₂TeBr₆, cesium, tellurium, and bromine would have theoretical atomic percentages of 22.2, 11.1, and 66.7%, respectively. We acquired an XPS spectra of pure TeBr₄ to assess the uncertainty in instrumental factors, such as the relative atomic sensitivity factor, and find that using the standard instrument parameters, the ratio of the atomic percentages of Te/Br is 0.29 vs. a theoretical value of 0.25 (~15% difference) (**Figure 6**, **Table S3**). We do not have an appropriate reference material for Cs for comparison with Te and Br. Determination of the exact

amount of each phase in the 2-step coated sample of Cs₂TeBr₆, depends on how the phases are distributed across the surface of the sample laterally and into the depth of the sample, which is relatively rough compared to the electron escape depth.⁵ Despite the uncertainty, the higher tellurium percentage than expected and lower cesium percentage in the 2-step film of Cs₂TeBr₆ indicates that unreacted TeBr₄ exists at the surface within the escape depth of the photogenerated electrons (~1 nm) consistent with GIWAXS.

XPS of TeBr₄ Film



Figure S6. XPS scans of a TeBr₄ film in binding energy regions for tellurium and bromide.

Core Level	Peak BE (eV)	FWHM (eV)	Area (CPS*eV)	Atomic %
Te 3d5/2	574.94	2.28	1136452.69	22.61
Br 3d/2	67.79	2.59	540536.36	77.39

Table S3. Quantification results for XPS scans.

CsX (X = Cl, Br, I) ICSD Reference Data



Figure S7. Reference PXRD spectra for CsCl, CsBr, and CsI from ICSD.

Residual TeBr₄ in Films Made at Higher Spin Speeds



Figure S8. Azimuthally integrated GIWAXS data collected at a 3° incidence angle of Cs₂TeBr₆ film made by depositing both layers at 6000 rpm.

Varying TeBr₄ and CsBr Spin Speed



Figure S9. SEM images of films made by varying the spin speed of both the first TeBr₄ layer and the second CsBr layer.

Cs₂TeCl₆ and Cs₂TeI₆ Formed via Two-Step Deposition



Figure S10. PXRD patterns for Cs₂TeCl₆ and Cs₂TeI₆ formed via two-step spin-coating and reference ICSD spectra. The strong reflection at q = 3.50 Å⁻¹ in the Cs₂TeI₆ pattern is from the quartz substrate.

XPS of Film Made with TeBr₄ and CsCl



Figure S11. XPS scan of a film made by spin-coating 1 M TeBr₄ and 1 M CsCl in the binding energy region for chlorine. There are no photoemission peaks in the spectrum.

Cs₂TeI₆ in Mixed-Phase Films



Figure S12. Azimuthally integrated GIWAXS data collected at a 3° incidence angle of a film made by depositing CsI on top of TeBr₄ via a two-step deposition.

DFT Calculations for Formation of TeCl₄

The following reaction is proposed to explain the formation of TeCl₄ when CsCl is deposited onto a TeBr₄ film during spin-coating:

$3 TeBr_4 + 4 CsCl \rightarrow 2 Cs_2TeBr_6 + TeCl_4$

The internal energy of this reaction was found to be -1.934 eV. This was calculated from total energies determined using density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) v5.4.4.^{6–8} The calculations used the VASP-recommended projector-augmented wave potentials and Perdew-Burke-Ernzerhof (PBE) functionals. D3 van der Waals corrections with Becke-Johnson damping (IVDW = 12) were additionally included.^{9,10} An energy convergence criterion of 10–6 eV was applied for all calculations, with a plane-wave energy cut-off of 500 eV. Automatic k-mesh generation was used with the length parameter l set to 50. Materials Project structures with energy-above-hull of 0 eV were employed as starting structures, and all crystal structures were fully relaxed.^{11,12} Elemental reference state energies were also determined to allow for the calculation of compound formation energies.

Compounds	TOTEN	Formation Energy (eV)	Formation Energy (eV/atom)
TeBr ₄	-12.738635	-3.08463853	-0.616927706
CsCl	-6.94437257	-4.211767035	-2.105883518
Cs ₂ TeBr ₆	-26.7329452	-12.15640813	-1.350712015
TeCl ₄	-14.46198281	-3.722645405	-0.744529081

Table S4. Summary of results from DFT calculations described above.

Ultraviolet Photoelectron Spectroscopy of Cs₂TeBr₆ Films



Figure S13: UPS spectrum of Cs2TeBr6 film with fitted energy onset and cutoff.

The energy onset position of the valence band was determined from a logarithmic plot and linear fitting of the top of the valence band; this is a common technique for MHPs due to the low density of states at the valence band maximum (VBM).^{13,14} The energy cutoff was determined through a linear fitting of the bottom of the valence band. From these two values, the position of the fermi level (E_F) and VBM can be determined with respect to the vacuum energy (E_{vac}). E_F is equal to the excitation energy (He I = 21.22 eV) subtracted from the valence band cutoff, while the VBM is equal to the excitation energy subtracted from the difference between the onset and the cutoff.





Figure S14. XPS scans of a Cs₂TeBr₆ device in binding energy regions for cesium, tellurium, and bromide. The film was made by spin-coating 1 M TeBr₄ at 4000 rpm followed by 1.5 M CsBr at 2000 rpm.

Core Level	Peak BE (eV)	FWHM (eV)	Area (CPS*eV)	Atomic %
Cs 3d5/2	723.09	2.40	1019740.16	17.67
Te 3d5/2	575.20	2.43	838055.93	15.46
Br 3d/2	67.72	2.55	503550.95	66.67

Table S5. Quantification results for XPS scans.

In a pure sample of Cs₂TeBr₆, cesium, tellurium, and bromine would have theoretical atomic percents of 22.2, 11.1, and 66.7%, respectively. If we correct the instrumental sensitivity factors for Te and Br, based on our experimental XPS spectra for TeBr₄, we obtain a Te/Br ratio of \approx 0.2 for the 2-step film of Cs₂TeBr₆, which is close to the theoretical value of 0.17.

Space-Charge-Limited Current Model



Figure S15. (a) Shunt leakage current observed at low bias and fit to Ohm's law to extract shunt resistance value. (b) *J-V* curve for Cs₂TeBr₆ SCLC diode held at 280 K with Mott-Gurney SCLC model used to fit the data and extract hole mobility value.

In non-ideal devices, current can bypass active layers of a device through defects. This is referred to as shunt leakage current and dominates measured current at low bias.¹⁵ We fit *J*-*V* data between 0 V and 0.5 V to Ohm's law and determine the shunt current. This is then subtracted from the total measured current across the full bias range, isolating the current that flows strictly through the active layer.

Corrected J-V curves were fit with the Mott-Gurney law for SCLC printed below:

$$J = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{V^2}{L^3}$$

Devices were made by spinning the initial TeBr₄ layer at 4000 rpm, so 3.2 μ m was used for *L*. 3.8 was reported as the static dielectric constant for Cs₂TeBr₆ in a recent theory paper and therefore used for ε_0 in this model.¹⁶ The below Arrhenius equation is used to fit the linear region in the mobility plot:

$$\mu_h = \mu_0 * \exp\left(\frac{-E_a}{RT}\right)$$

 μ_0 is a pre-factor that can be interpreted as the upper limit for hole mobility in Cs₂TeBr₆. We determine $\mu_0 = 0.35$ cm² V⁻¹ s⁻¹ based on the exponential fitting.



Figure S16. *J-V* curves for Cs₂TeBr₆ SCLC diode acquired at various temperatures, corrected for Shunt resistance, and fit with Mott-Gurney SCLC model to extract hole mobility value.

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