Wide-bandgap (WBG) mixed-halide perovskites as the front cell absorber are accomplishing perovskite-based tandem solar cells with over 29% power conversion efficiency. However, their large voltage deficits limit their ultimate performance. Only a handful of studies probe the fundamental mechanisms underlying the voltage deficits, which remain an unsolved challenge in the field. In this study, we investigate the formation dynamics and defect physics of WBG mixed-halide perovskites in contrast with their corresponding triiodide-based perovskites. Our results show that the inclusion of bromide introduced a halide homogenization process that occurs during the perovskite growth stage from an initial bromide-rich phase toward the final target stoichiometry. We further elucidated a physical model that correlates the role of bromide with the formation dynamics, defect physics, and eventual optoelectronic properties of the film. This work provides a fundamental and unique perspective toward understanding the performance-limiting factors affecting WBG mixed-halide perovskites.
that brings the lattice composition to the eventual target stoichiometry. This homogenization process inadvertently altered the formation dynamics of mixed-halide perovskites and promoted defect formation, which consequently led to increased nonradiative recombination losses in the final perovskite film. In other words, Br affected the perovskite formation dynamics, which may have contributed to the large voltage deficits in high Br%-containing compositions.

RESULTS
We specifically focused on the triple cation mixed-halide WBG perovskite FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$, as it is one of the most widely reported compositions with a good resistance against light-induced halide segregation and also high PV performance. The triiodide reference with the same triple cations, FAMACsPbl$_3$, will serve as the reference to investigate the effects of Br inclusion on the perovskite formation dynamics. As shown in both the digital photographs (Fig. 1A) and absorption spectra (Fig. 1B) of the two perovskites, the as-cast FAMACsPbl$_3$ film already exhibited strong band edge absorption, indicating that the α-phase perovskite has partially formed. In contrast, the as-cast FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ film was more transparent and showed negligible absorption associated with its perovskite phase near its target bandgap of approximately 1.67 eV (745 nm). After annealing, the band edge absorptions and absorption coefficients for both compositions were similar (but displaced in wavelength), hinting that the formation dynamics during crystalization have been altered by the inclusion of Br. We further investigated the films using x-ray diffraction (XRD). Both as-cast films exhibited an α-phase perovskite (001) peak. Upon annealing, the (001) peak position for FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ underwent a notably larger shift toward lower 2θ (Fig. 1C and fig. S1), whereas the peak position for FAMACsPbl$_3$ changed negligibly in comparison. Decreasing Br content in the perovskite lattice would increase the lattice constant (smaller 2θ); therefore, the XRD results perhaps suggest that a Br-rich phase nucleated initially, and the lattice Br ratio is decreasing during the growth stage due to gradual iodide incorporation into the perovskite nuclei during crystallization [the FACs (MA-free) system was also explored in detail; see figs. S2 to S3]. Furthermore, although the cation composition is fixed as a constant for the above-discussed perovskite films, we further analyzed the XRD patterns of MAPb(I$_{1-x}$Br$_{x}$)$_3$, FAPb(I$_{1-x}$Br$_{x}$)$_3$ (with or without MACl additive), FAMACsPb(I$_{1-x}$Br$_{x}$)$_3$, and FACsPb(I$_{1-x}$Br$_{x}$)$_3$ films to rule out any possible contribution by the cations and the MACl additive (figs. S5 to S9; detailed discussion in Supplementary Text), and the observations from these “single cation” and the “MACl-free” films were consistent with the triple-cation system with MACl that delivered the champion performance. Therefore, we hypothesized that the initial nucleation was most likely dominated by a Br-rich phase, which is followed by slower iodide incorporation during the growth stage. We also observed that PbI$_2$ formed more readily in FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$, and the film crystallinity during the growth stage was poorer than FAMACsPbl$_3$ (fig. S1; detailed discussion in Supplementary Text).

To investigate such a hypothesis, we used in situ photoluminescence (PL) to monitor the perovskite crystallization process in real time. In contrast to diffraction methods, in situ PL provides direct proof of the bandgap evolution during growth, which is dominated mainly by the halide ratio in halide perovskites and thus is valuable to probe the formation dynamics related to the halide elements in real time. A 532-nm laser diode, coupled with a visible range spectrometer, was mounted in an N$_2$ glove box to track the film photoemission during nucleation and growth. As shown in Fig. 2A, the experiment was designed to collect the PL signal during the approximately 1 min of spin-coating step, followed by annealing at 65°C for 5 min. Figure 2 (B and C) depicts the PL spectra evolution during the formation of the mixed-halide FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ and triiodide FACsPbI$_3$ films; data displayed on the left initiates from antisolvent dripping during spin coating. Figure S10 exemplifies the Gaussian fitting of the in situ PL spectra to extract the PL peak position, intensity, and full width at half maximum (FWHM), as plotted in Fig. 2 (D to F). It was observed that, for both formulations, their respective PL signals initiated at much higher energy levels [1.88 eV for FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ and 1.67 eV for FACsPbI$_3$] compared with the final bandgap of the bulk perovskite films (approximately 1.67 and 1.57 eV, respectively, from their PL maxima). For FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$, the energy shifted by 0.115 eV during the spin-coating stage (ΔE$\lambda$) and 0.051 eV upon annealing (ΔE$_f$). The corresponding values were 0.072 and 0.011 eV for FACsPbI$_3$, much less than the mixed-halide composition. We speculated that the emission peak shifting during the perovskite formation, especially during the early growth period, could be attributed to a combination of two effects: (i) The quantum confinement of the nanograins, in which case a larger initial crystal size would show smaller energy

![Image](https://www.science.org/doi/10.1126/sciadv.abbj1799)
shifting; and (ii) a compositional evolution during perovskite formation dominated by an initial higher bandgap species (15–17). Therefore, the larger $\Delta E$ in FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ is most likely due to the formation of an initial Br-rich nuclei, complementing the XRD analysis discussed.

On the other hand, the FAMACsPbI$_3$ film took only ~54 s to reach its stable emission peak position during annealing, while for FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$, the emission peak shifting lasted for over 150 s. Therefore, the growth stage has been retarded in FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$, likely associated with an increased activation energy barrier for perovskite growth (18). The emission peak transition during annealing for FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ underwent two separate stages (denoted as $t_1$ beginning at 42.3 s and $t_2$ beginning at 109.8 s) before its stabilization. We further compared the growth evolution with different amounts of Br incorporation of 20, 10, 5, and 0% (fig. S11), observing that the growth stage successively retarded further with increasing Br%. The PL intensity (Fig. 2E) observed during the spin-coating stage, while it continued to increase to a maximum in tens of seconds, and then decreases before the signal stabilizes during the annealing stage. We speculate that the formation of illuminating perovskite crystals dominated the PL intensity during spin coating, while during annealing, the time required to reach the intensity maximum serves as an indicator of the crystal growth rate (i.e., the earlier it reaches the intensity maximum, the faster is the growth rate). For FAMACsPbI$_3$, we observed that the signal quickly “saturated” after 28.1 s upon casting the antisolvent, while the intensity of FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ continued to increase during spin coating (Fig. 2E, left slab). During the annealing stage, these two compositions reached their maximum intensities at 33.5 and 19.9 s, respectively. Analyzing the FWHM (Fig. 2F), the signal from FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ achieved a much sharper peak during spin coating and stabilized slower than that of the FAMACsPbI$_3$. For the fully annealed films shown in fig. S12, both compositions exhibited clear and monopeak PL, indicating that both films eventually reached their target stoichiometry with good phase homogeneity, and matched well with their absorption cutoffs. The bandgaps were determined to be approximately 1.56 and 1.67 eV for the as prepared FAMACsPbI$_3$ and FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ films, respectively. This indicates that a halide homogenization process must have occurred during the growth stage to achieve the target stoichiometry from the initial Br-rich phase. Such a homogenization process occurs by diffusion of iodide to incorporate into the initial
Br-rich phase, which introduces an activation energy barrier and is consistent with a retardation of the perovskite growth (19). We further explored the FACs (MA-free) composition, which has also been reported to be highly resistant to halide segregation and delivers high PCE. The trends were consistent with the triple-cation system (figs. S13 and S14; for detailed discussion, see Supplementary Text), supporting our hypothesis and demonstrating the universal role of Br.

In addition to changing the perovskite lattice constant and bandgap, our above analyses suggest that bromide affected the perovskite formation dynamics. Bromide and iodide have different solubility with the coordinating solvents used for perovskite deposition, such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and gamma-Butyrolactone (GBL). We further used density functional theory (DFT) to calculate the interaction energies of PbXX’ (X and X’ denote either I or Br) species with DMSO. DMSO is partially removed by the antisolvent during spin coating, but the remaining residuals would form an adduct phase with PbXX’ and FAX to assist with the formation of the α-phase perovskite (20, 21). From the optimized molecular configurations and bond distances shown in Fig. 3A and the interaction energies summarized in Fig. 3B, DMSO bonds most strongly with PbI2 (0.84 eV), followed by PbIBr (0.79 eV), and has the weakest bond with PbBr2 (0.77 eV), indicating that Br-rich species have lower solubility and therefore potentially nucleate first during supersaturation. Moreover, the formation energies for the PbXX’:DMSO adduct crystals were also calculated (fig. S16 includes the optimized crystal structures). The formation energies decreased as I was gradually replaced by Br (−0.18 eV for PbI2:DMSO, −1.10 eV for PbBr2:DMSO, and −1.32 eV for PbBr2:DMSO), suggesting that bromide-containing intermediate adduct phases are more thermodynamically favored to form. The surface energies between the triiodide perovskites with various A-site cations were also calculated to be much higher than that of the tribromide perovskites, regardless of

Fig. 3. First-principle calculations and characterizations of the fully annealed perovskite films. (A) Molecular configuration and interaction distance of coordinating solvent DMSO and PbXX’ molecules. (B) Interaction energy between DMSO and PbXX’ molecule and formation energy of DMSO:PbXX’ adduct phase. (C) Time-resolved PL spectra of the as-prepared CsFAMAPb(I0.8Br0.2)3 and CsFAMAPbI3 films. (D) Quasi-Fermi level splitting (qFL) results quantified by a calibrated laser intensity and (E) the as-extracted Voc,SQ (Voc,SQ = qFLs) for perovskite films with Br% of 20, 10, 5, and 0%. (F) The extracted values of emission peak position from 60-s PL tracking. (G) PAS depth profiling of CsFAMAPbI3 and CsFAMAPbBr3 films. Solid lines are fitted plots. Green/orange shaded areas indicate the top surface/bulk region of the films. (H) Shape parameters from PAS extracted for the surface/bulk regions.
calculations that show $V_{FA}$ and $FA_i$ were thermodynamically more favored with higher Br% incorporation, which is supported by further theoretical organic A-site cations were less stable and decompose more readily negligible for the FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ film due to its highly optimized composition, as seen by its stable emission peak positions retained during continuous PL measurements (Fig. 3F).

Positron annihilation spectroscopy (PAS) uses positively charged positrons that annihilate with negatively charged/neutral defects, capable of nondestructively probing the density and spatial distribution of defects in semiconductor thin films, and has been reported to be compatible with halide perovskite materials (29, 30). Compared with admittance spectroscopy that also provides information about trap density, PAS could be carried out directly on bare perovskite films and is therefore independent of experimental variables that affect admittance spectroscopy results, such as the bandgap of the materials (which affects the device built-in potential) and the properties of the contacting transport materials (31). By controlling the kinetic energy of the incident positron beam and extracting the shape parameter from the gamma ray annihilation spectra (where a stronger gamma ray signal from positron annihilation could derive a larger shape parameter, indicating a higher density of negatively charged/neutral defects), a depth-resolved spectrum was obtained in Fig. 3G for the FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ and FAMACsPbI$_3$ films. We observed that the shape parameter for FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ was clearly higher throughout the entire perovskite film, indicating a higher overall trap density. The surface region (shaded in green, 0 to 50 nm, Fig. 3G) contained a much higher density of surface defects, which will be detrimental to both the device performance and stability. FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ also had a higher shape parameter in the perovskite bulk region (shaded in orange, 150 to 500 nm, Fig. 3G), indicating a higher trap density throughout the entire film. Crucially, this indicates that the defects formed through intrinsic processes (i.e., during perovskite formation and growth). In contrast, extrinsic processes (e.g., degradation) would have initiated from the film surface, preserving the bulk trap density of the film (32, 33). Statistical analysis of the shape parameters comparing the surface and bulk regions is displayed in Fig. 3H. The eventual performance of the solar cell devices is a reflective consequence of the distinct defect physics and dynamics of the films. As shown in Fig. 4A, devices based on both compositions exhibited $>79%$ fill factor (FF), while the $J_{SC}$ of FAMACsPbI$_3$ (23.1 mA/cm$^2$) was distinctly lower than that of FAMACsPbI$_3$ (25.1 mA/cm$^2$) due to the larger bandgap of the former. The external quantum efficiency (EQE) cutoffs (Fig. 4B) of the devices also matched well with the bandgaps estimated by the ultraviolet-visible absorption and PL measurements. The $V_{OC}$ gain of FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ over FAMACsPbI$_3$, however, was insufficient to compensate for the bandgap increase, with $V_{OC}$ values of 1.16 and 1.19 V ($V_{OC,SO} − V_{OC}$ of 0.13 and 0.20 V, $gE_g − V_{OC}$ of 0.40 and 0.48 V), respectively. The solar cell performance results coincided with the film characterization results, where nonradiative recombination losses were more severe for the FAMACsPb(I$_{0.8}$Br$_{0.2}$)$_3$ perovskite. A stability test was also carried out, from which the FAMACsPbI$_3$ devices exhibited a much better long-term stability under illumination than FAMACsPbI$_3$ devices after encapsulation (Fig. 4C). However, we found that the nonencapsulated devices of FAMACsPbI$_3$ decayed at a much faster rate, which is consistent with our observation during the PL quantum yield (PLQY) tests regarding the fatal extrinsic instability (most likely due to moisture-induced phase transformation) of the FAMACsPbI$_3$ perovskite. Detailed discussion on stability test is available in Supplementary Text.

**DISCUSSION**

On the basis of all our experimental and theoretical observations and results, we summarize the physical model of the formation dynamics of WBG mixed-halide perovskites in Fig. 4C. The inclusion of bromide in the composition altered the perovskite crystallization pathway. A bromide-rich phase was more thermodynamically stable and thus nucleates first from solution during supersaturation. To attain the final target stoichiometry, during the growth stage, a halide...
homogenization process by diffusion gradually incorporates iodine into the expanding perovskite lattice. However, intrinsic defects formed readily during the homogenization process, and consequently, the final film had a higher defect density across the entire film depth, compared to the corresponding triiodide composition. Consequently, the WBG composition suffered from more severe nonradiative recombination losses and thus inferior optoelectronic properties and device performance. In this work, we correlated the complex perovskite formation dynamics with the defect physics and charge carrier dynamics of the resulting film. This study will guide the community to rethink the significance of precursor engineering and crystallization control for WBG mixed-halide perovskites toward more efficient and stable PVs based on these materials.

**MATERIALS AND METHODS**

**Materials**

DMF (99.8%), DMSO (99.7%), isopropanol (IPA; 99.7%), chlorobenzene (CB; 99.8%), acetonitrile (ACN; 99.8%), 4-tert-butyl pyridine (98%), lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI; 99.95%), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine) cobalt(III) tri[bis(trifluoromethane)sulfonimide] [FK 209 Co(III) TFSI salt], and PbI2 (99.999%, perovskite grade) were purchased from Sigma-Aldrich. PbBr2 (99.999%), CsI (99.99%), deionized water, and SnO2 colloidal solution (15% in water) were purchased from Alfa Aesar. Formamidine iodide (FAI), formamidine bromide (FABr), methylammonium iodide (MAI), methylammonium bromide (MABr), and n-octylammonium iodide (OAI) were purchased from GreatCell Solar Materials (Australia). Methylammonium chloride (MACl) and Spiro-OMeTAD (99.8%) were purchased from Xi’an Polymer Light Technology (China). All the materials were used without further purification.

**Perovskite precursor preparation**

**FAMACs-based perovskites**

CsI (35.8 mg/ml), FAI (192.6 mg/ml), MAI (22.3 mg/ml), and PbI2 (645.4 mg/ml) were dissolved in a DMF/DMSO = 80:20 solvent for the FAMACsPbI3 precursor. For FAMACsPb(10.8Br0.2)3 precursor, CsI (35.8 mg/ml), FAI (168.6 mg/ml), PbI2 (516.3 mg/ml), MABr (31.4 mg/ml), and PbBr2 (102.8 mg/ml) were used. The final stoichiometries were (CsPbI3)0.1(FAPbI3)0.8(MAPbI3)0.1 and (CsPbI3)0.10(FAPbI3)0.7(MAPbBr3)0.2, respectively. Five to 50% Br...
precursors were prepared by partially or fully substitute MAPbI$_3$ in the triiodide precursor by MAPbBr$_3$ correspondingly. **FACs-based perovskites**

CsI (71.7 mg/ml), FAI (192.6 mg/ml), and PbI$_2$ (645.4 mg/ml) were dissolved in a DMF/DMSO = 80:20 solvent for the FACsPbI$_3$ precursor. For FACsPb$_3$Br$_{0.83}$I$_{0.17}$ precursor, CsI (71.7 mg/ml), FAI (192.6 mg/ml), PbI$_2$ (480.8 mg/ml), and PbBr$_2$ (115.6 mg/ml) were used. The final stoichiometries were FA$_{0.8}$Cs$_{0.2}$PbI$_3$ and FA$_{0.8}$Cs$_{0.2}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$. The perovskite layers were prepared on top of the SnO$_2$ layer at 3000 rpm for 30 s followed with 30 min ambient annealing at 150°C. The perovskite layers were prepared on top of the SnO$_2$ layer.

For solar cell fabrication, SnO$_2$ layer was prepared by spin coating a diluted SnO$_2$ colloidal solution on precleaned glass/ITO substrates at 3000 rpm for 30 s followed with 30 min ambient annealing at 150°C. The perovskite layers were prepared on top of the SnO$_2$ layer. For the best device performance, the passivation layer was done by spin-coating OAI (10 mM in IPA) at 5000 rpm followed with 1 min of annealing at 100°C. Twenty-five microliters of Spiro-OMeTAD in CB was spin coated at 3500 rpm on the perovskite surface. After aging in dry air overnight, 120-nm gold was then evaporated to form the metal electrodes.

**Thin films and device characterizations**

For in situ PL measurement, a homebuilt platform consists of a 532-nm laser diode and an Ocean Optics Spectrometer (Flame) coupled with optical fibers, optical filters, and several planoconvex lenses described in our previous reports were used (34, 35). The power density of the laser was approximately 100 mW/cm$^2$ as the intensity reaching the sample could vary as adjusting the setup. Integration time of each spectra was 100 ms during the measurement. Calibrated measurements for qFLs were carried out in another homebuilt PL setup also with 532-nm excitation. The laser beam is quantified by a charge-coupled device camera and a power meter to calculate the equivalent number of suns from the photon flux. The wavelength dependence of the spectrometer and the collection optics is corrected using a commercial calibration lamp with known spectrum. For the TRPL measurement, a PicoHarp 300 with time-correlated single-photon counting capabilities excited by the 640-nm pulse laser diode (PLD 800B, PicoQuant) with a repetition frequency of 200 kHz. A biexponential decay fitting model was used to extract the charge carrier lifetime. For the XRD measurement, an x-ray diffractometer (PANalytical) with Cu K$_\alpha$ radiation at a scan rate of 3° min$^{-1}$ was used, and the contact angle was obtained by VCA optima 100. All XRD measurements were carried out in ambient environment after transferring the samples out from the N$_2$-filled glove box. Scanning electron microscopy was captured by a Nova Nano 230 system. PAS measurement was carried out at the Washington State University positron beam. Experimental details and spectra analysis methods have been fully discussed in our previous publication (27). An empirical formula of $d = \frac{40 E_{\text{kin}}}{\rho} \left( \frac{\text{nm} \cdot \text{g}}{\text{cm}^3 \cdot \text{keV}^{1/4}} \right)$ was used to convert the kinetic energy of incident positron ($E_{\text{kin}}$) into depth profile. The fraction of the annihilated gamma ray signal in a narrow central region that increase in relative intensity at positron trap sites was determined as the shape parameter. The J-V characteristics were measured with a Keithley 2401 meter under the illumination of an Oriel Sol3A class AAA solar simulator (Newport) that simulated AM 1.5 G spectrum (100 mW/cm$^2$) calibrated with an NREL-certified Si photodiode with KG-5 filter. The EQE was measured by an Enlitel designed system under AC mode without bias light.

**DFT calculations**

All quantum chemical calculations of interaction energies between DMSO and PbXX$^\text{′}$ were performed using Gaussian 16.1 (36). The initial structures used in computations were constructed using GaussView 6.0.16. PbXX$^\text{′}$ was positioned at various locations around the DMSO, and the geometry of each resulting DMSO:PbXX$^\text{′}$ complex was optimized with the wb97X-D density functional and the 6-31+G(d,p) basis set for C, H, O, S, and Br atoms and LANL2DZ basis set for Pb and I atoms. Optimized geometries were verified as minima (zero imaginary frequencies) by frequency calculations at the same level of theory. Interaction energies were computed using the same level of theory and using the following equation: $\Delta E_{\text{int}} = E_{\text{DMSO + PbXX}} - [E_{\text{DMSO}} + E_{\text{PbXX}}]$. Molecular structures were visualized and rendered using Mercury 4.3.1 (Build 273956). (37-39)

All first-principle calculations for bulk and slab systems are carried out using the Vienna Ab initio Simulation Package (VASP) code (40, 41). A revised Perdew-Burke-Ernzerhof generalized gradient approximation (PBEsol) (42, 43) was used for the exchange correlation including a dispersion correction using Grimme’s DFT-D3 scheme (44, 45). PBEsol functional has been introduced to improve the equilibrium properties of solids and surfaces (46). Valence-core interactions were described by projector augmented wave pseudo-potentials (47). Plane wave expansions with kinetic energies up to 300 eV were chosen as the basis set for all geometry optimization and energy calculations. Both atomic positions and cell dimensions were optimized using a conjugate gradient algorithm until all Hellman-Feynman forces are smaller than 0.02 eV/Å. Γ-center $k$-point mesh ($4 \times 4 \times 4$ and $4 \times 4 \times 1$) was adopted for Brillouin zone sampling in bulk and surface calculations, respectively.

For formation energies of DMSO:PbXX$^\text{′}$ adduct crystals, we used the following expression: $\Delta H(\text{DMSO : PbXX}) = \Delta H(\text{DMSO : PbXX}) - [\Delta H(\text{DMSO}) + \Delta H(\text{PbXX})]$, where the first, second, and third terms in the right hand side are the energies of DMSO:PbXX$^\text{′}$, DMSO, and PbXX$^\text{′}$, respectively. We considered XX$^\text{′} = $I$_2$, IBr, and Br$_2$ and used the monoclinic DMSO in all cases, and the crystal structures of DMSO:PbXX$^\text{′}$ and PbXX$^\text{′}$ are based on orthorhombic DMSO:PbI$_2$ and hexagonal PbI$_2$ crystals, respectively.

For surface energy calculations, the 2 $\times$ 2 $\times$ L surfaces were formed along (001) by periodic slabs including 9 to 11 atomic layers for a surface separated by 10 to 15 Å of vacuum. To characterize the formation and stability of the ABX$_3$ surfaces, we use surface energies...
described as follows: we first calculate the cleavage energy of the clean surface
\[
\sigma_{clv} = \frac{1}{2} \left[ E_{slab}^{unrel} - N E_{bulk} + \sum_i n_i \mu_i \right]
\]
where the first term is the energy of the unrelaxed slab, \( \mu_i \) is the chemical potentials, \( n_i \) is the number of \( i \)th unit removed, and \( E_{bulk} = \mu_A + 3 \mu_B \) is the energy per formula unit of the bulk perovskite. The relaxation energy is then calculated from
\[
\sigma_{rel} = E_{slab}^{rel} - E_{slab}^{unrel}
\]
where the first and second terms are the total energy of the relaxed and unrelaxed slabs, respectively. The surface energy is calculated by
\[
\gamma = (\sigma_{clv} + \sigma_{rel})/A,
\]
where \( A \) is the area of the surface. For the APbX3 perovskite, \( A = \text{FA}, \text{MA}, \text{or Cs} \) and \( X = \text{Br} \) or \( I \) were calculated independently. For this study, we considered PbX2-terminated slabs.

Formation energies of the defects in FAPb(I\(_{1-x}\)Br\(_x\))3 in a charge-state \( q \) is calculated from
\[
\Delta H_q(q) = E_d(q) - E_{pr} + \sum_i n_i \mu_i \cdot q(E_B + E_{VBM})
\]
where \( E_d(q) \) is the total energy of the system with defect and \( E_{pr} \) is the pristine system. \( \mu_i \cdot q \) is the chemical potential, which includes intrinsic \( \mu_0 \) and growth condition–dependent term \( \mu_i \); \( n_i \) is the number of \( i \)th unit (i.e., atom or molecule) exchanged with the reservoir to form the defect. \( E_B \) is the Fermi energy, and \( E_{VBM} \) is the energy at the valence band maximum. Following Freysoldt’s correction scheme, the energy corrections arising from the spurious interactions due to the finite-size are included in Eq. 3.

To determine the chemical potentials required for formation energy of a FAPb(I\(_x\)Br\(_{1-x}\))3
\[
\mu_{FA} + \mu_{PB} + 3 \left[ x \mu_{I} + (1 - x) \mu_{Br} \right] = \Delta H_1
\]
should be satisfied under thermodynamic equilibrium growth conditions, where \( \Delta H_1 \) is the formation energy of FAPb(I\(_{1-x}\)Br\(_x\))3. In this study, we considered \( x = 1, 0.8, \) and \( 0.5 \). To avoid the formation of undesired phases
\[
\mu_{FA} + \mu_{PB} + 3 \left[ x \mu_{I} + (1 - x) \mu_{Br} \right] = \Delta H_1
\]
conditions should also be satisfied where appropriate. The formation energies in the right hand sides of Eqs. 5 and 6 are calculated from
\[
\Delta H_1 = H(FAI) - H(FA) - \frac{1}{2} H(Br_2),
\]
\[
\Delta H_2 = H(FAI) - H(FA) + \frac{1}{2} H(Br_2).
\]

\[
\Delta H_Br_1 = H(PbI_2) - H(PbI) + \frac{1}{2} H(I_2),
\]
\[
\Delta H_Br_2 = H(PbBr_2) - H(PbBr).
\]
Here, to calculate each energy term, we used the respective structures: FABr and FAI in the rock-salt phases, PbI2 and PbBr2 in the hexagonal phases, FA in the body-centered cubic phase, Pb in the cubic phase, and I2 and Br2 in the gas phase. We considered the Pb-rich growth conditions in all chemical potential calculations.

### Supplementary Materials

Supplementary material for this article is available at https://science.org/doi/10.1126/sciadv.abj1799


Performance-limiting formation dynamics in mixed-halide perovskites
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