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Growth-Controlled Broad Emission in Phase-Pure Two-Dimensional Hybrid Perovskite Films

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ABSTRACT.

Two-dimensional hybrid metal halide perovskites (2D perovskites) are attractive for light emitting devices, and other applications, because their emission is tunable across the visible spectrum. The emission profile of 2D perovskites can be broadened via a variety of mechanisms, and is further complicated by the presence of impurities. Here, the challenge of making phase-pure films in Ruddlesden-Popper phases ($(A')_2(A)_{n-1}B_nX_{3n+1}$ structure) is overcome by using a single A/A'-site cation, ethylammonium (EA), whose optimal size also prohibits formation of off-target phases. In the $(EA)_2(EA)_{n-1}Pb_nBr_{3n+1}$ family, the low-energy, broad emission observed in bulk crystals is reduced in spin-cast, polycrystalline films. This decrease in broad emission, attributed to phonon-mediated processes, is correlated with strain in polycrystalline films that is observed by X-ray scattering. Photothermal deflection spectroscopy shows that strain also increases electronic disorder near the free exciton absorbance. Broad emission in films can be recovered by slowing growth kinetics, which removes the strain acquired from spin-casting and increases domain size. These results help extend the utility of 2D perovskites by providing design rules for how to grow films with the targeted phase and emission.

INTRODUCTION.

Two-dimensional hybrid perovskites are attractive for optoelectronic applications such as solar cells and light-emitting devices because their optical emission can be controllably changed by their structure.¹⁻⁵ Many 2D perovskites belong to the Ruddlesden-Popper (RP) family, which has a layered $(A')_2(A)_{n-1}B_nX_{3n+1}$ structure, where A' and A are cations, B is a divalent metal and X is a halide.⁴⁻¹⁰ By changing the number n of B-X octahedral sheets that sit between large, organic A' cations (called spacer cations), the energies of the band gap and the free exciton shift, leading to tunable emission across the entire visible spectrum. Increasing distortions in B-X octahedral bond lengths and angles has been found to broaden the emission, with some compounds emitting white light.¹¹⁻¹⁷ This broad emission has been proposed to originate from radiative recombination of self-trapped excitons (STEs).^{11-15,17-21} The detailed mechanism(s) of broad emission are under debate, however, and include different types of STEs,^{17,18,22} coupling of STEs to specific point defects,¹⁶ coupling of phonons to spacer cation stacking,²³ phonon replicas,²⁴ polaron self-localization,²⁵ extrinsic effects,^{26,27} and shallow traps.²⁸ Because of the potential applications of 2D perovskites, understanding the impact of structure on optical properties continues to be an important goal.

Because perovskite optoelectronic devices typically comprise polycrystalline thin films,^{3,29-34} much work has been devoted to determining how the growth of RP phases in polycrystalline form affects optical properties. RP phases with narrow emission (i.e., free exciton emission) exhibit similar spectral features in single crystals and in phase-pure polycrystalline thin films.^{9,35,36} Strain, which is typically present in films,³⁷⁻⁴² results in a small energy shift in the free exciton emission.⁴³ The growth conditions used to cast films of RP-phases can produce impurities, which are typically higher- n RP phases and 3D phases, that cause the emission to red-shift relative to that of the intended phase.⁴⁴⁻⁵⁰ However, being able to tune the emission color of RP-based LEDs or

lasers requires elimination of the undesired, higher- n RP phases and 3D phases.^{34,45,46,51–53} Many attempts have been made to control the phase composition of RP films, and include changing the annealing procedures, the growth kinetics, the stoichiometry of the precursors, the solvent, and introducing additives to the precursor solution.^{35,44,48,49,54–61} While recent work has achieved growth of phase-pure RP films with narrow emission,³⁶ less is known about growing polycrystalline films of broad/white emitting perovskites. In particular, the impacts of growth conditions on the optical properties of broad-emitting, 2D perovskites are not yet understood.

Here, we find that film growth can greatly affect the proportions of broad vs. narrow luminescence emitted by a solution-cast 2D phase. We found that using a single A/A'-site cation, ethylammonium (EA), enables spin-casting of phase-pure RP films of (EA)₂(EA)₂Pb₃Br₁₀. The optimal size of this cation also prohibits off-target phase formation due to unfavorable tolerance factor and octahedral distortions. Strain that occurs in thin films favors high-energy, narrow emission. In contrast, slowing the growth kinetics and removing strains encourages broad, lower-energy emission. Lower-energy emission appears to be phonon-coupled, and can be attributed to self-trapped exciton emission or to phonon replicas.

EXPERIMENTAL SECTION.

Materials Lead bromide (PbBr₂, 99.999 %), ethylammonium bromide (EABr, ≥ 98 %), lead oxide (PbO, ≥ 99.0 %), N-N-dimethylformamide (DMF, 99.8%, anhydrous), poly (methyl methacrylate) (PMMA, molecular weight 350000), and hydrobromic acid (HBr, ACS reagent, 48%) were purchased from Sigma Aldrich and used as received. Polished z-cut quartz substrates (15 × 15 × 0.5 mm) were purchased from University Wafer.

Film casting Quartz substrates were cleaned via ultrasonication in isopropyl alcohol for 10 min and exposed to oxygen plasma at ≈ 300 mTorr for 10 min. All subsequent solution preparation and film fabrications were performed in a nitrogen-filled glove box. Precursor solutions for $(\text{EA})_2(\text{EA})_2\text{Pb}_3\text{Br}_{10}$ were fabricated by dissolving 0.375 mmol (47 mg) EABr and 0.25 mmol (92 mg) PbBr_2 (molar ratio of EA/Pb = 1.5) in 0.5 mL DMF, to make an 0.5 mM solution (based on Pb). To make other compositions ($(\text{EA})_2\text{PbBr}_4$ and mixed-phase films), the ratio of EABr/ PbBr_2 was adjusted following **Figure S18**. The solutions were left stirring overnight at 60°C to ensure good dissolution. Films were spin-cast at 4000 rpm for 60 seconds without antisolvent rinse, and promptly annealed at 100°C (verified by thermocouple) on a hot plate with a heat diffuser. After the films cooled, 60 μL of a PMMA solution (75 mg PMMA in 3 mL toluene) was spin-cast on top of the films at 2000 rpm for 30 seconds. The films were stored in a nitrogen glove box until characterization. For SEM, PDS, and certain stability experiments, the same spin-casting procedures were employed, but PMMA was not cast on the films. Films for PDS were cast on separate amorphous quartz substrates.

Growth of $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ bulk crystals $(\text{EA})_2(\text{EA})_2\text{Pb}_3\text{Br}_{10}$ bulk crystals were grown similarly to the previously-published procedure.¹² Briefly, PbO and EABr (in 3:4 molar ratio) were dissolved in HBr, and the solution was heated. Large crystals of $(\text{EA})_2(\text{EA})_2\text{Pb}_3\text{Br}_{10}$ formed upon cooling.

GIWAXS characterization. Grazing Incidence Wide-Angle X-Ray Scattering (GIWAXS) experiments were performed on beamline 11-3 (12.7 keV, wiggler side-station) at the Stanford Synchrotron Radiation Lightsource (SSRL). The source-to-detector (two-dimensional Rayonix MX225 CCD) distances were calibrated using lanthanum hexaboride (LaB6). All raw images were geometrically corrected using Nika. Au nanoparticles (100 nm) drop-cast on quartz substrates were used to verify chi-q alignment during post-processing. Sections (cakeslices) of the 2D GIWAXS

patterns at specific angles were selected and integrated to obtain 1D patterns (see **Figure S4**). The two cakeslices used were near-out-of-plane (“nOP”, 3°-21°) and near-in-plane (“nIP”, 70°-88°), both with a chi-q angle width of 18°. An incidence angle of 0.5° was chosen for the following reasons: (1) it is shallow enough to properly detect the nIP (0*k*0) peaks (these were cut off when large incidence angles, such as 2°, were used) and (2) it is well above the critical angle. The critical angle was calculated to be near 0.17° using GIXA;⁶² this value is slightly below the measured critical angles (0.2°-0.26°) of similar 2D hybrid perovskites.⁶³ It is important to be far enough above the critical angle to avoid double diffraction, which may manifest in the nOP (but not nIP) peaks.⁶⁴ All peaks were fit to Pseudo-Voigt patterns using Igor, with Gaussian and Lorentzian contributions kept constant (Igor Multipeak “shape” factor of 1) across all peaks.

PDS characterization Photothermal Deflection Spectroscopy (PDS) measurements were performed using a homebuilt instrument as previously described.⁶⁵ Briefly, monochromated light from either a 150 W Xenon or a 100 W halogen lamp was modulated at 0.5 Hz with a mechanical chopper and then split to be separately focused onto the sample and a pyroelectric detector. Degassed and filtered perfluorohexane (C₆F₁₄, 3M Fluorinert FC-72) was employed as the deflection medium. The deflection of a HeNe laser aligned perpendicularly to the pump beam to also be parallel and proximal to the sample surface was measured by a position-sensitive Si detector using a lock-in amplifier. Analysis and fitting were performed using MATLAB. Absorbance peak positions are best determined from UV-Vis (**Figure 3a**), since the PDS signal is less accurate above 3 eV.

Powder X-Ray Diffraction patterns were obtained using a Panalytical Empyrean powder diffractometer in reflection mode with a Cu-K α source, operating with an accelerating voltage of 45 kV and beam current of 40 mA. Au nanoparticles (100 nm) drop-cast on quartz substrates were

used to calibrate peak positions for strain characterization. All peak locations were obtained by Pseudo-Voigt fits using Igor Pro 8.

Plotting X-Ray crystal structures VESTA software was used to plot the CIF files of $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ and $(\text{EA})_2\text{PbBr}_4$, which were determined in prior work.^{12,13} Color schemes for the octahedra and ions were modified, to highlight patterns in octahedral distortions. Bond lengths and angles were also measured using VESTA.

Scanning Electron Microscopy was performed using an FEI Nova Nano 650 FEG SEM operating at 7-10 keV accelerating voltage with beam currents of 0.40-0.80 nA. For SEM measurements, the samples were sputter-coated with gold to prevent charging.

Absorbance spectra were extracted from transmission measurements made on a Shimadzu UV-2600 ultraviolet-visible spectrophotometer at room temperature and in ambient conditions.

Photoluminescence spectra were acquired using a Horiba FluoroMax 4 spectrometer (i.e., fluorimeter) calibrated with Milli-Q water. The fluorimeter's excitation source was a 150 W xenon, continuous output, ozone-free lamp; the excitation energy was obtained using a monochromator. The detector was a PMT, also equipped with a monochromator. Photoluminescence spectra reported in in the main text were all collected using an angle of 75° between the excitation and emission port to reduce scattering. Some PL spectra in the SI (**Figures S1, S8**) were acquired using an angle of 25° for comparison, since the proportions of different features can be angle dependent.^{18,22} All measurements were performed with an excitation wavelength of 370 nm (3.35 eV). A 400 nm long-pass filter was placed in front of the mission port to reduce scattering. Spectra were fit to Gaussians using Igor Pro 8.

Temperature-Dependent Photoluminescence measurements were performed using a home-build photoluminescence spectrometer. For the temperature control, the samples were placed into a LN₂-cooled cold finger cryostat (Janice VPF-100) with Lakeshore 335 temperature controller. An 80 MHz laser pulse train with wavelength of 370 nm (3.35 eV) was used as the excitation source; the pulse energy was in sub 100 pJ range and the diameter of the laser spot was about 100 μ m. The UV laser light was produced by frequency doubling the output of Spectraphysics Tsunami Ti: Sapphire femtosecond laser oscillator with the fundamental wavelength of 740 nm in Coherent/Inrad optical harmonics generator. We verified that at the given laser energy density level there was no photoinduced damage to the sample, as the PL spectra did not change over time under continuous laser illumination. The PL emission was collected in near 90 degrees geometry by a system of lenses and focused on the input slit of a spectrometer (Acton Research SP500). The stray laser light was blocked by an interference long pass filter (Omega Filters) with cut on wavelength 380 nm. The spectra dispersed by the spectrometer were recorded by a charge-coupled device detector (Princeton Instruments PIXIS:400). The spectra collected were corrected for the instrument response by measuring the response of the setup to the light of a black body-like source (Ocean Optics LS-1) and calculating appropriate correction factors. All spectra were fit to Gaussians using Igor Pro 8.

RESULTS AND DISCUSSION.

Figure 1. (a) Crystal structure of $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ with (b) Pb-Br bond lengths and octahedral distortions. (c) Top-view and (d) cross-sectional SEM images of an $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ film spin-cast on quartz. Films were capped with PMMA for most measurements, but not for top-view SEM. The black color in the background of (c) is the substrate.

We aimed to understand relationships between growth and optical properties in polycrystalline thin films of RP phases that exhibit broad emission. One challenge encountered during the growth of films of RPs phases with $n > 1$, is that the A-site and A'-site (spacer) cations can segregate into different phases, resulting in highly-emissive 3D impurities.⁴⁸ To circumvent this challenge, we sought to study the growth of RP phases in which A and A' are identical. We therefore selected the $(\text{EA})_2(\text{EA})_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ family, where EA is ethylammonium. The structures of the $n = 1$ and $n = 3$ phases of this family have been determined from bulk crystals.^{12,13} The $n = 1$ phase contains single sheets of Pb-Br octahedra separated by EA cations (**Figure S1**). The structure of the $n = 3$ phase, $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$,¹² is shown in **Figure 1**. To accommodate the large size of EA in the A-site (274 pm),^{66,67} the 3-layer inorganic sheet forms two substructures, comprising highly-distorted

outer octahedra and relatively undistorted inner octahedra (**Figure 1b**). The bond lengths of the outer, distorted octahedra show large variations ($\approx 20\%$), with the shortest at 2.75 Å and the longest at 3.31 Å, while those of the inner octahedra have less variation. The outer layers also exhibit significant out-of-plane tilting, contrary to the inner octahedra. The angle and bond length^{11–17} distortions in the outer layers are thought to encourage formation of self-trapped excitons (STEs), which create broad, lower-energy photoluminescence.^{12,16} Both the $n = 1$ and $n = 3$ phases of the $(\text{EA})_2(\text{EA})_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ family exhibit pronounced narrow emission from free excitons, as well as broad emission at room temperature.^{12,13} Thus, studying the properties of $(\text{EA})_2(\text{EA})_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ films can reveal if strain and growth kinetics impact emission.

We first verified the phase composition of $n = 3$ and $n = 1$ $(\text{EA})_2(\text{EA})_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ films before assessing how growth conditions impact optical emission. To prepare films of $n = 3$, we spun-cast precursor salts in nearly-stoichiometric proportions (see **Experimental Section**). A very small excess of EA was found to be necessary to grow the films, likely counteracting strong Pb-Br-DMF complexation.⁶⁸ Films were then capped with PMMA to prevent possible degradation. The as-cast $n = 3$ films exhibit ≤ 200 nm domain size and thickness and many pinholes (**Figure 1c-d**). Bulk crystals of $n = 3$ were grown using literature methods¹² and the crystal structure was verified (see **Experimental Section** and **Figure S2**). We also prepared $n = 1$ films and confirmed their composition for comparison with the $n = 3$ films (**Figure S1**).

Figure 2. (a) XRD pattern of a spin-cast $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ film, with % strain labeled for $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ peaks, and a simulated (Sim.) powder pattern assuming no preferred crystallite orientation. (b) Grazing Incidence Wide-Angle X-Ray Scattering (GIWAXS) pattern of a spin-cast $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ film expressed as a function of the scattering vector, $q = 4\pi\sin(2\theta/2)/\lambda$, where λ is the X-Ray wavelength. The near-out-of-plane (nOP) and near-in-plane (nIP) regions are indicated and peaks are indexed by the bulk crystal structure. S indicates spillover from the incident beam. (c) Integrated and normalized nOP and nIP patterns, with *relative* % strain of select peaks. (d) Inset of (c), showing a closer view of the (111) nOP and nIP peak positions. (e) Schematic of the two primary crystallite orientations identified from the GIWAXS pattern: one oriented with $(0k0)$ in-plane (q_{xy} axis) and the other oriented with $(0k0)$ out-of-plane (q_z axis). Out-of-plane-oriented peaks have mild compressive strain: (111) nOP is more compressed than for the in-plane-oriented crystallites.

X-ray scattering from the as-prepared $n = 3$ films is consistent with the desired $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ phase (**Figure 2**). The X-Ray diffraction (XRD) pattern of the $n = 3$ film is in good agreement with the simulated powder pattern of this material (**Figure 2a**). Peaks corresponding to the $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ phase were present, and the only peaks missing (near 20° , corresponding to (171) and (002)) were off-specular peaks that were later observed via GIWAXS (**Figure 2b**). In the XRD pattern, (**Figure 2a**), the $(0k0)$ and (111) features have approximately the relative intensities that would be expected from the simulated XRD pattern of the single crystal structure.¹² The presence

of (0*k*0) features suggests phase purity, since they appear strongly in phase-pure RP films³⁶ and in powders of the targeted RP *n* phase.⁹ In contrast, the (0*k*0) are weakened relative to other peaks, or absent entirely, in mixed-phase films⁴⁵ due to stacking fault defects that result in intergrowth of different *n* within a single grain.^{45,46} Grazing Incidence Wide-Angle X-Ray Scattering (GIWAXS) patterns of the films were collected to probe off-specular diffraction (**Figure 2b**). All observed peaks are indexed to features of (EA)₄Pb₃Br₁₀ (**Figure S3**) with the only missing peaks predicted to have very small intensity. GIWAXS confirms that there is a distribution of orientations of crystallites in the films (**Figure 2b**). In particular, the presence of (0*k*0) and (111) *only* near *q*_{XY} and *q*_Z, but not in between, reveals that the Pb-Br octahedral sheets prefer to grow either parallel or perpendicular to the substrate (**Figure 2c-d**). Further analysis reveals a slight preference for the crystallites growing with Pb-Br octahedra growing perpendicular to the substrate (**Figure S3**). Thus, the (EA)₄Pb₃Br₁₀ films appear phase-pure and textured based on X-ray scattering.

X-ray scattering also reveals that the crystallites in the *n* = 3 films exhibit strain. Based on the peak shifts seen in XRD (see **Experimental Section**), the film is compressively strained (by under 0.3 %) in the out-of-plane direction (**Figure 2a**). This mild strain is consistent with prior reports of the spin-coating³⁸ and/or annealing³⁷ procedures imparting mild biaxial stress in hybrid organic metal halides. To examine strain in greater detail, sections of the GIWAXS pattern were integrated near-out-of-plane (nOP) and near-in-plane (nIP) (see **Figure S4** for definition of these areas), and normalized for clarity. The position of the (111) nOP is shifted into compression, in agreement with the mild compression observed in XRD, and is additionally more compressed than the (111) nIP (**Figure 2a/c/d**). The difference in strain between the (111) nOP and (111) nIP shows that the mild biaxial strain affects out-of-plane vs. in-plane oriented crystallites differently (**Figure 2d**). In addition, small peaks are identified near the main (0*k*0) and (111) peaks for the nOP and nIP

patterns (**Figure 2d** and **Figure S4**), and are assigned to strained (0*k*0) and (111) features. From peak fits, these weaker peaks have 2-3 % strain relative to their respective main (0*k*0) and (111) peaks. Overall, the films exhibit mild biaxial strain that differently affects in-plane vs. out-of-plane oriented crystallites, with small populations of highly-strained crystallites.

Figure 3. (a) Absorbance and (b) Photoluminescence (excitation 3.35 eV) of bulk crystals and spin-cast films of (EA)₄Pb₃Br₁₀. The inset in (a) shows the energy difference between the $n = 3$ free exciton peak of the bulk crystals and film. The dashed line connecting (a) and (b) is a guide to the eye. Emission peaks are labelled A, B and C. (c) Gaussian area of features A, B, and C (see **Figure S5** for fits and “Fitting the Photoluminescence Data” and “Temperature-Dependent PL” sections in the **Supporting Information** for fit methodology).

The optical properties of polycrystalline films and bulk crystals of (EA)₄Pb₃Br₁₀ show features of only $n = 3$. The UV-Vis absorbance spectra of polycrystalline thin films and bulk crystals (**Figure 3a**) are both in agreement with the previously reported spectrum of bulk crystals.¹² The absorbance spectra of the bulk crystals and film exhibit a sharp increase near the main $n = 3$ excitonic feature at ≈ 3.0 eV (**Figure 3a**). In contrast, thin films of $n = 3$ RP phases that also contain off-target n or 3D impurities frequently show absorbance spectra that have large sub-gap slopes

and poorly-visible $n = 3$ excitonic features.^{45,48,53,63,69} For both films and crystals, the 2.9 eV onset of emission is close in energy to the absorbance onset (dashed line in **Figure 3**), which is a sign of phase purity. If lower band-gap phases were present, even in small concentrations, we would expect emission from excitations funneled to these phases, as observed in mixed-phase $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ RP films.^{45,48} Three primary features are observed in the emission of bulk crystals and films: a high-energy excitonic feature near 2.9 eV (peak A), one near 2.7 eV (peak B), and broad emission below 2.7 eV (peak C - for spectra in nm, see **Figure S6**⁷⁰). No other emissive features are detected. Thus, the optical properties of the films are those of the $n = 3$ phase.

The proportions of the different $n = 3$ emission peaks change considerably from bulk crystals to films (**Figure 3b**). To better assess these changes, we fit the normalized emission spectra (**Figure S5**) and examined the areas of peaks A, B and C (**Figure 3c**). The integrated area of the free exciton at 2.9 eV (peak A) does not change much from bulk crystals to films. However, the area of B (2.7 eV) increased slightly in films, which is the opposite of what is seen from self-absorption, as peaks from self-absorption become weaker in thinner perovskites.⁷¹ Notably, the broad, low-energy tail, C, decreases sharply in area from bulk crystals to polycrystalline films. Broad, low-energy peaks that are far in energy from the free exciton, such as C, are commonly attributed to self-trapped excitons¹¹⁻¹⁷ and not to self-absorption.⁷¹ To further understand the origin of feature C, we excited bulk crystals below-gap (2.75 eV), and observed no emission (**Figure S7**). Thus, C does not come from impurities or extrinsic effects²⁶ and $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ must be excited above-gap for the low-energy emission (peak C) to appear, which is again consistent with attributions of peak C to self-trapped excitons.¹¹⁻¹⁸ We then confirmed that the changes in relative areas of A, B and C were not due to measurement conditions (see **Figure S8-S9**), since the proportions of emissive features in 2D materials can sometimes vary with collection angle.¹⁸ In all cases, the bulk $n = 3$ crystals

exhibit more low-energy tail emission (peak C) than the polycrystalline films. We also notice that the EA $n = 1$ films contain the same emission features as bulk $n = 1$ crystals, but proportionally less low-energy, broad emission than that reported for the bulk $n = 1$ crystals (**Figure S1**).¹³ Thus, the targeted- n emission seems to be preserved in films for both $n = 3$ and $n = 1$, but with large changes to the proportions of emissive species.

Figure 4. Effects of cooling on photoluminescence. (a) Temperature-dependent photoluminescence of bulk crystals (top panel) and film (bottom panel) of (EA)₄Pb₃Br₁₀, with pulsed excitation at 3.35 eV (see **Experimental Section**). Peak D is likely an STE (**Figure S15**). (b) Evolution of integrated area of peaks A, B and C with temperature for bulk crystals (top panel) and a film (bottom panel). For discussion of fits, see **Figures S10-S15**. The black arrow indicates strong overlap between peaks A and B at low temperatures in the bulk crystals, making decoupling A and B difficult at low temperatures. (c) Evolution of peak position with temperature for peaks A, B, and C in the bulk crystals and films. FE stands for free exciton and Phon. for phonon-coupled.

Temperature-dependent emission reveals several types of emission features, which allows us to understand the changes in emission proportions in films (**Figure 4**). The normalized emission spectra with cooling of bulk crystals and films are shown in **Figure 4a**, with peak area (**Figure 4b**) and peak position (**Figure 4c**), and fits in **Figure S10** and **S15**. Similarly to other compounds,^{14,17,20,21,25} a broad peak appears at 110 K near 1.9 eV in both bulk crystals and films (peak D). In agreement with the behavior of certain STEs observed in perovskites,^{14,17,20,21,25} peak D is located at much lower energies than the free exciton and its intensity steadily increases with cooling

(**Figure S11**). This increase is attributed to less de-trapping back to the free exciton state at lower temperatures,^{17,25} which here happens near 110 K (**Figure S15**). Like B and C, D has different proportions in bulk crystals and in films (**Figure 4, S15**); D is stronger in films, suggesting that it has different nature from B and C. Indeed, a red-shift of peak D is observed with cooling for the bulk crystals, consistent with polaron localization of the carriers (**Figure S15**).²⁵ In contrast, B and C blue-shift strongly with cooling, and C seems to disappear at low temperatures. The blue-shift of B with cooling is readily visible in **Figure 4** and we examined different fitting methods to quantify the blue-shift and the disappearance of C (**Figures S10 to S14**). It is possible that B and C blue-shift so strongly with cooling that they overlap with themselves or with peak A, as highlighted by the black arrow in **Figure 4b**. The large blue-shift/disappearance of B and C with cooling is consistent with coupling to phonons, as similar blue-shifts have been previously observed in the phonon-coupled features of (A')₂PbI₄^{18,24} and lithium niobate.⁷² In particular, the energy shifts with cooling of C (277 meV in the crystals) and B (184 meV in the crystals; 72 meV in the film) are on the order of the blue-shifts observed in (A')₂PbI₄ (50-120 meV) over a similar temperature differential.^{18,24} The strongly blue-shifting feature of (A')₂PbI₄ has been assigned to an STE with specific phonon-coupling behavior¹⁸ and separately to a phonon replica;²⁴ both are possibilities for B and C. This large blue-shift/disappearance with cooling of B and C contrasts with the reported behavior of extrinsic features,²⁶ polaron self-localization,²⁵ convolutions of a bright exciton with a localized state,²⁸ or shallow traps,²⁸ as these have different behavior with cooling (e.g. red-shifts or increases in intensity). Self-absorption is also ruled out, as the blue-shifts of B and C are larger (>10x) than shifts expected from self-absorption.⁷¹ In addition, the free exciton (peak A) exhibits a smaller shift with cooling (34 meV and 33 meV in crystals/films respectively) than B and C, consistent with previously-reported free exciton behavior.^{18,24} Overall,

the behavior of B and C is most consistent with phonon-mediated processes, such as STEs or phonon replicas, and D is a more commonly-observed STE.

Strain likely causes the differences in the proportions of emission from A, B, C, and D in bulk crystals and polycrystalline films (**Figures 2, 3, 4**). Film strain observed in the (EA)₄Pb₃Br₁₀ films by X-ray scattering (**Figure 2**) is likely the origin of the small blue-shift (by 0.012 eV) of the main free exciton in the film compared to that in bulk crystals (**Figure 3**). Similar shifts (≈ 0.013 eV) in free exciton energy were observed in other 2D perovskites upon application of ≈ 1 % strain.⁴³ Strain can also affect the lower-energy emission: prior work on bulk crystals of (BA)₂PbBr₄ found that microstrain, caused by different stackings of spacer cations in the bulk region, may enhance emission that is lower-energy and phonon-coupled.²³ Given that B and C exhibit phonon-coupled behavior and that the crystallites are strained (**Figure 2**), it is likely that changes to the emission intensities of B and C are linked to these strains. We would not expect such changes to result from differences in domain size, as major changes to electron-phonon coupling occur on much smaller size scales (≤ 20 nm)^{73,74} than those of our experiment (≤ 200 nm). Experimentally decoupling the effects of thickness or domain size is not so easy, as preparing thinner samples involves either spin-casting or mechanical exfoliation, and both of these may lead to imposition of strain.³⁸ We exfoliated bulk crystals of (EA)₄Pb₃Br₁₀; the results are consistent with different strain changing the relative proportions of B and C (see discussion of **Figure S5**). Furthermore, in 1-D or 0-D hybrid halide perovskite-like free-standing crystals, strain has also been found to turn the emission from STEs off or on, depending on whether strain decreases or increases Pb-Br octahedral distortions.^{11,75} In particular, when strain decreased the octahedral distortions,¹¹ the free exciton emission (narrow and higher energy) proportionally increased at the expense of the STE emission. Here, we find that the films contain strain that varied between 0.1 % and 3 % (**Figure 2**), which is

on the order of the deformation that were found to decrease STE emission in free-standing, micron-sized crystals under pressure ¹¹ (see “Further Explanations regarding Strain” in the **Supporting Information** ^{76,77}). The changes in emission intensity of B, C and D from bulk crystals to polycrystalline films thus likely stem from film strain, which can affect both spacer cation stacking and octahedral distortions.

Figure 5. PDS spectra of a bulk crystal and film of $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$, showing fits of different absorption onsets (see **Supporting Information** - “Fitting the PDS Data”) and the extracted Urbach energies E_U . More detail in the 2.6 eV-3.0 eV region, as well as goodness of fits, are shown in **Figure S16**.

Photothermal Deflection Spectroscopy (PDS) was then used to examine more subtle optical changes caused by switching from bulk crystals to polycrystalline films (**Figure 5**). PDS enabled highly sensitive measurement of the absorption onsets throughout the film thickness (see **Experimental Section**). The slight blue-shift of the film’s PDS absorbance with respect to that of bulk crystal is consistent with the UV-Vis measurement of **Figure 3a** (see also **Experimental Section**). The lack of any PDS absorbance feature in the film below the main onset is further indication of $n = 3$ phase purity in the films. In contrast, nominally $n = 3$ films with mixed-phase

composition exhibited low-energy absorbance features, that were indexed to higher- n Ruddlesden-Popper phases.⁴⁸ The bulk crystal of $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ exhibits a tail at low energy, but this tail is non-emissive when excited directly (**Figure S7**), so we rule out emissive impurities or extrinsic effects²⁶ as the source of the tail. We fit portions of the PDS spectra (see **Experimental Section** and “Fitting the PDS Data” in the **Supporting Information**) to extract the Urbach energies E_U , representing the degree of disorder in electronic states near the absorption edge (see also **Figure S16**).

The differences in onset between the film and bulk crystal can be attributed to strain (**Figure 5**). While the bulk crystal only exhibits one absorbance onset with an Urbach energy E_U of 39 meV, the film exhibits two onsets that can be fit with different E_U of 45 meV and 54 meV. GIWAXS reveals populations of crystallites with two different strain states (**Figure 2**). The two absorbance onsets, with their two distinct Urbach energies, likely correspond to these two states because of the sensitivity of free excitons to strain.⁴³ The increase in Urbach energies from the crystal (39 meV) to the film (45 and 54 meV) also likely originates from strain. In addition, the weak, sub-gap absorbance in the bulk crystal below 2.6 eV is likely connected to the larger amount of broad, lower-energy emission from C in the bulk crystals. Direct excitation near the absorbance tail does not lead to emission (**Figure S7**), ruling out emissive impurities as the source of the tail. However, it is clear that making $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ as a film prevents formation of this tail. Thus, strain has two effects: it can increase the electronic disorder of the free excitons present, and may hinder formation of sub-gap states in bulk samples. These results suggest the importance of controlling strain during growth of thin films for modifying the photoluminescence.

Figure 6. (a) XRD patterns of films made by drop-casting the $n = 3$ precursor solution, with/without annealing. (b) Photoluminescence of these films (3.94 eV excitation). The emission spectra of (EA)₄Pb₃Br₁₀ bulk crystals and spin-cast films are also shown.

Having examined the various ways in which film strain can impact the optical properties of (EA)₄Pb₃Br₁₀, we next sought ways to control the optical properties of films by controlling film growth. Film strains suggest that rapid spin-casting may not be the optimal growth method for controlling low-energy emission. Because film strains can originate from stresses acquired during spin-casting³⁸ and from thermal expansion mismatch between the material and substrate during annealing,³⁷ we tried to modify the deposition kinetics to avoid these two factors. We slowed the deposition kinetics by drop-casting the precursor solution and allowed the solvent to slowly evaporate (in N₂ atmosphere glove box for 1h). The samples were then, in some cases, annealed, and then capped with PMMA for protection (see **Experimental Section**). SEM images of the non-annealed and annealed films show large domains, ~20 μm-wide and ~3 μm-thick, without complete coverage of the substrate (**Figure S17**). Thus, in the drop-cast films, the domains grow

on the substrate with few spatial constraints from neighboring domains, in contrast to spin-cast films. The domains exhibit one crystal habit and are isotropic and homogeneous, suggesting that non-RP phases, such as solvates or other intermediates, do not form, in contrast to the behavior of other drop-cast 2D or 3D perovskites.^{48,49,78} XRD patterns of drop-cast films, with and without annealing, are shown in **Figure 6a**. The drop-cast films contain in majority $n = 3$ and the positions of the peaks do not indicate strain. Additionally, small amounts of $n = 1$ and additional features are present. Because only $n = 1$ and $n = 3$ single crystal structures have been reported, we attribute the additional peaks to $n = 2$, by estimation of where the $n = 2$ peaks should be based on analogy with the $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{X}_{3n+1}$ RP peak locations.⁹ These higher- n phases likely appear due to the slight excess of EABr used in the precursor solution, which was found necessary for spin-casting phase-pure $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ films. To make all experiments self-consistent, we employed the same precursor solutions for spin-casting and drop-casting (see **Experimental Section**). Drop-cast films containing only $n = 3$ might be obtained in future studies by slightly modifying the EA: Pb precursor ratio.

Slowing growth by drop-casting enables recovery of the broad emission. **Figure 6b** shows the photoluminescence of the drop-cast films overlaid with those of the spin-cast $n = 3$ film and of the $n = 3$ bulk crystals. The drop-cast films exhibit comparable low-energy emission (peaks B and C) to the bulk crystals. An extra feature is observed near 2.75 eV, possibly originating from the small amount of proposed $n = 2$ in the drop-cast films (see **Figure 6a**). However, the spectra of the drop-cast films closely resemble that of the $n = 3$ bulk crystals, indicating that most of the emission comes from $n = 3$. Since domains in the drop-cast $n = 3$ films grow slowly and with few spatial constraints from neighboring domains, such slow and unconstrained growth of domains seems necessary for retaining the lower-energy emission. The $n = 3$ phase forms without thermal

annealing, and subsequent annealing does not lead to significant changes in emission. We note that mismatches between the thermal expansion coefficients of the substrate and film can lead to stresses in some cases.³⁷ Thus, overall, we find that deposition methods that reduce strain are likely to favor low-energy emission in films.

Figure 7. Origins of phase purity in the $n = 3$ films. (a) Summary of findings of **Figures 2, 3, 6, S18 and S19**, where t stands for the tolerance factor. (b) Illustration of how stacking fault defects lead to intergrowth of n in the (BA)₂(MA) _{$n-1$} Pb _{n} X _{$3n+1$} RP series, and how in contrast, the EA RPs lack different n phases available for intergrowth, resulting in $n = 3$ phase-purity.

Finally, we consider why only $n = 3$ is observed in spin-cast films, rather than other phases in the (EA)₂(EA) _{$n-1$} Pb _{n} Br _{$3n+1$} family, and why it is favorably formed (**Figure 7**). The spin-casting procedures we used typically yield 2D-3D mixed-phase films unless particular care is taken,^{36,45,46,48,49} so the formation of a phase-pure $n = 3$ film via spin-casting is notable. First, no experimental single crystal structure for a 3D EAPbBr₃ phase has been reported to our knowledge. Previous work that attempted to make films of 3D EAPbBr₃ found that a 2D phase formed instead,

⁷⁹ and we believe that prior assignments to the EAPbBr₃ phase in nanocrystals may actually correspond to (EA)₄Pb₃Br₁₀ (see “Further Discussion on 2D and 3D Phases” in the **Supporting Information**). ⁸⁰ We also attempted to make EAPbBr₃ films (**Figure S18** and **Figure 7a**) and obtain non-emissive films with broad features in XRD. The absence of formation of a 3D perovskite phase of EAPbBr₃ is consistent with the tolerance factor for EA with Pb and Br prohibiting 3D phase formation ($t = 1.13$; see **Supporting Information - Methods** for calculation). By itself, EA (274 pm) ^{66,67} is just small enough to fit in the A-site of 2D phases, since the 2D perovskites have less strict requirements for tolerance factor. ^{81,82} The $n = 3$ and $n = 1$ RP phases in the (EA)₂(EA) _{$n-1$} Pb _{n} Br _{$3n+1$} family have been reported as single crystal structures, ^{12,13} but there are no reports of phases with other n values. The phase purity observed in $n = 3$ and $n = 1$ films thus likely originates from lack of available other phases, due to the large size of EA, and consequently unfavorable tolerance factor for impurity 3D or larger- n RP phases. The presence of a single EA cation in the A/A' sites also limits the number of competing precipitations. This phase selectivity is in direct contrast to the behavior of the widely studied (A')₂(A) _{$n-1$} Pb _{n} (I or Br) _{$3n+1$} RPs families, where spin-casting leads to polycrystalline films with mixed RP and 3D phases, unless particular care is taken to suppress their formation. ^{34–36,44–46,48,49,51,52,54–61} For many RP compositions, the tolerance factor of the corresponding 3D structures, MAPbI₃ and MAPbBr₃, are 0.96 and 0.99 respectively, so a large variety of corner-sharing structures can form (**Figure 7b**) leading to more ready formation of off-target RP and 3D phases. ^{34,45,46,48,49,53} The ability to grow phase pure polycrystalline films with EA shows that selecting A-site cations that are too large to form 3D phases, but are within sizes tolerable for layered structures, is a route to eliminating alternative phase formation.

The $n = 3$ phase forms preferentially over the $n = 1$ phase, likely due to specific patterns of Pb-Br octahedral distortions (**Figure 7**). While the stoichiometry of the $n = 3$ precursor solution roughly matched $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$, a large excess of EA (nearly $2\times$) is needed to make thin films of $n = 1$ $(\text{EA})_2\text{PbBr}_4$ (**Figure S18**). Synthesis of $n = 1$ bulk crystals is also reported to require EA excess,¹³ unlike synthesis of $n = 3$ bulk crystals, which follows $n = 3$ stoichiometry.¹² In addition, not only are the $n = 3$ films much more stable to heat and the ambient than the $n = 1$ films, but the $n = 1$ films degrade to $n = 3$ (see discussion of **Figure S19**). Thus, $n = 3$ is much more easily formed and more stable than $n = 1$. This preference likely originates from the large size of EA (274 pm):^{66,67} the $n = 3$ phase forms distorted/undistorted octahedral substructures within the Pb-Br sheets to accommodate this large size, and the less-distorted inner layer of the $n = 3$ likely stabilizes the 3-layer Pb-Br sheet. In contrast, the $n = 1$ contains phase only one highly-distorted octahedral layer (**Figure S1**). The $n = 1$ phase can thus can form in a phase-pure manner but requires significant stoichiometric excess to form (**Figure S18**) and readily transforms into the more stable $n = 3$ structure (**Figure S19**). We hypothesize that the $n = 2$ structure, similarly to the $n = 1$, would only contain highly distorted octahedral sheets, and not have the inner stabilizing layer of the $n = 3$ phase. Thus, the optimal size of the EA cation, creating the inner stabilizing layer and preventing 3D formation, is instrumental to casting phase-pure $n = 3$ RP films. Tailoring the ratio of less: more-distorted layers with cations other than EA may be crucial for spin-casting phase-pure RP films with $n \neq 3$.

CONCLUSIONS.

Overall, we find that that strain can greatly affect the relative proportions of different luminescence features emitted by a solution-cast 2D phase. Film strain can suppress lower-energy, broad emission that is coupled to phonons, in favor of free exciton emission. Film strain also

increases electronic disorder, and removes sub-gap absorbance features that are likely correlated with broad emission. Broad emission can be recovered by slowing the film growth and removing strain that arises from the fast growth during spin casting. This result suggests that growth methods that avoid rapid solvent removal, such as co-evaporation or blade coating, could prove more fruitful for retaining broad emission than spin-casting. For a given composition, strain should be characterized for the growth method chosen, to inform which method might be best. In addition, the use of a single cation (ethylammonium) for both the A-site and spacer of 2D perovskite phases enables casting of phase-pure films. The large size of this cation prevents 3D impurities from forming due to unfavorable tolerance factor, and prevents layered structures with other values of n from forming due to unfavorable octahedral distortions. These results further our understanding of how to control phase composition and emission in films, which extends the utility of 2D perovskites for light-emitting devices and may enable novel fabrication of perovskite-perovskite heterostructures, which are useful in a variety of devices.

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ASSOCIATED CONTENT.

Supporting Information. Calculation of tolerance factors, further explanations regarding strain; additional data/fitting/comparison with simulations for photoluminescence/XRD/GIWAXS/PDS; additional SEM, precursor solution stoichiometry studies, film stability studies, further discussion on 2D and 3D phases with the EA cation (PDF), and further discussions of methods more generally.

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Notes

The authors declare no competing financial interest.

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TOC GRAPHICS

Growth-Controlled Broad Emission in Phase-Pure Two-Dimensional Hybrid Perovskite Films

Supporting Information

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Additional Methods

Calculation of Tolerance Factors

Tolerance factors t were calculated using ion sizes in ^{1,2} and using the equation: ³

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

Where r_A , r_B and r_X are the ion radii of the ABX_3 structure. **Table 1** below shows the ion radii used in pm, and the resulting t s:

A (EA, MA)	Pb	Br or I	t
274 (EA)	98	196 (Br)	1.13
217 (MA)	98	196 (Br)	0.99
217 (MA)	103	220 (I)	0.96

Fitting the PDS Data (Figure 5, S13)

Following previous work, ^{4,5} the Urbach tails were fit according to:

$$PDS = A \exp\left(\frac{E - E_G}{E_U}\right)$$

Where PDS is the PDS signal, A is a prefactor, E_G is the bandgap and E_U is the Urbach energy.

Fitting the Photoluminescence Data

All peak fits were done to Gaussians using Igor Pro 8. Peaks A and B are sharp and peak D is very distinct, so A, B and D can be fit conclusively using one Gaussian per peak. However, peak C is a broad tail. It is likely that peak C is likely a collection of self-trapped excitons, emitting at different energies. Thus, the choice of number of Gaussians with which to fit C is arbitrary. To avoid over-fitting the data and drawing false conclusions, we selected the lowest-possible number of Gaussians for C, which was often 1, but occasionally 2. We tried a number of ways to characterize peak C, these are shown in **Figures S10-S14** (see: “Fitting for Temperature-Dependent PL” page 15). We also attempted various ways to fit the data, including fixing the energy values, but leaving the energies as free variables consistently produced the best fits. Further work is needed to fully understand the nature of C, which we find to be either an STE or a phonon replica.

Further Explanations regarding Strain

Prior work on 1-dimensional Pb-Br compounds found that the broad emission intensity sharply decreased with respect to the free exciton emission when 0.5 GPa of pressure (or stress) was applied.

⁶ The proposed mechanism for this was that under stress, the bond lengths and angles become closer to those of the ideal cubic MAPbB₃. ⁶ While the directional Young's modulus of (EA)₂(EA)₂Pb₃Br₁₀ is not known, we can estimate that it is between the values for (BA)₂(MA)₂Pb₃Br₁₀ and MAPbBr₃, or 4 GPa < E < 30 GPa. ^{7,8} In terms of strain, these stress values correspond to 12.5 % > ϵ > 1.7 %, using the simple stress-strain relationship $\sigma = E\epsilon$. Although these values represent a broad, range, it is reasonable that the strain values measured in **Figure 2** could be big enough to cause emission changes.

Figure S1. Characterization of $(\text{EA})_2\text{PbBr}_4$ ($n = 1$) films. (a) Photoluminescence emission (3.94 eV excitation) at 25- and 75-degree collection angles. (b) Scanning Electron Microscopy of an $n = 1$ film. XRD patterns plotted on (c) linear and (d) log scales. A simulated pattern of $(\text{EA})_2\text{PbBr}_4$ assuming no preferred crystallite orientation, and based on the published structure, is shown as well. The copper X-Ray source has tungsten contamination ($1.4764 \text{ \AA}$), resulting in occasional extra peaks. The simulation in (d) shows the extra peaks from Tungsten-X-Rays as well.

The films appear to be $(\text{EA})_2\text{PbBr}_4$ from X-Ray and photoluminescence characterizations. The crystallites seem to orient with the long b axis normal to the substrate, as evidenced by the strong diffraction from $\{0k0\}$ peaks. The photoluminescence emission energies match well those of published crystals.⁹ However, as with $(\text{EA})_2(\text{EA})_2\text{Pb}_3\text{Br}_{10}$, the broad emission is considerably weakened in favor of the free exciton emission. The large size of $(\text{EA})_2\text{PbBr}_4$ suggests that grain size is not the predominant contributor to this emission change. Other potential factors (e.g., growth kinetics, strain) are discussed in the main text.

Figure S2. Structural characterization of bulk crystals of $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$. (a) Experimental XRD pattern of bulk crystals of $(\text{EA})_2(\text{EA})_2\text{Pb}_3\text{Br}_{10}$. A simulated (Sim.) powder pattern is also shown below (calculated assuming no preferred crystallite orientation - see **Experimental Section**). The crystals were dropped onto quartz substrates, and seem to preferentially orient with $(0k0)$ parallel to the substrate, given the predominance of $(0k0)$ observed in the pattern. Quartz peaks are indicated with an asterisk. (b) Cross-sectional SEM of the bulk crystals, revealing thickness > 10 microns.

Figure S3. Simulated GIWAXS pattern of (EA)₂(EA)₂Pb₃Br₁₀ assuming (a) full out-of-plane crystallite orientation and (b) full in-plane crystallite orientation. Out-of-plane- and in-plane-oriented crystallites are shown above the simulated pattern, with the (020) plane for reference. Main peaks are indexed. (c)-(d) Overlay of these simulated patterns with the experimental (EA)₂(EA)₂Pb₃Br₁₀ GIWAXS film pattern from **Figure 2**, with main peaks indexed. S indicates spillover from the undiffracted beam. (e)-(g) Diffraction or lack thereof for planes (e) aligned along q_y (lack of diffraction), (f) aligned along q_x (diffraction) and (g) aligned along q_z (diffraction). Diffraction peaks in q_{xy} are less intense than those in q_z because a smaller fraction of planes in q_{xy} are probed; whereas all planes in q_z are probed.

The main peaks of the experimental pattern matched with those of the simulated patterns. Simulated patterns were made using the CIF file from prior work and Python code written in house.^{10,11} The (0 k 0), (111) and (202) peaks in the experimental pattern matched well with their expected locations in-plane and out-of-plane (**Figure S3c-d**). This agreement confirmed the presence of the two preferred crystallite orientations. In order to assign off-axis peaks (i.e., not along q_z , or q_{xy}), we overlaid the simulated patterns for crystallites with out-of-plane and in-plane orientation with the experimental GIWAXS pattern of **Figure 2**. Particularly good agreement for off-axis peaks was found

when the crystallites have in-plane orientation (**Figure S3d**), suggesting a greater proportion of in-plane-oriented crystallites. Geometric factors, explained in the caption and in **Figure S3e-g**, cause greater probing of peaks in q_z than in q_{xy} , which likely explains why the $(0k0)$ peaks along q_z appear more intense than those along q_{xy} . In addition, due to the similar location of different peaks (especially near q_z , $q_{xy} = 1$ or 2), some peaks may have several possible assignments. Some of the higher-order peaks (i.e., peaks near q_z and $q_{xy} = 2.5$) were weaker in the experimental pattern than in the simulations. This is due to two reasons: 1) the film is both thin and disordered (strain, two crystallite orientations), so higher-order peaks are weakened and 2) the simulation took only structure factors into account, and no other factors such as Debye-Waller, which make higher-order peaks weaker. Overall, the experimental GIWAXS pattern matched well the simulated GIWAXS patterns, particularly for in-plane crystallite orientation.

Figure S4. (a) Near-out-of-plane (nOP) and (b) near-in-plane (nIP) regions used to obtain the patterns in **Figure 2d**. The nOP region covers angles between 3° and 21° and the nIP region covers angles between 70° and 88° . Both sections were chosen to have equal angular spread of 18° . (c) Integrated and normalized nOP and nIP patterns, with relative % strain of select peaks. Peak fits are also shown in the thinner lines.

Figure S5 (a-c) Fitting of the photoluminescence emission of (a) bulk crystals, (b) exfoliated flakes, (c) film of $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ (see **Figure 3** for PL from the main text from fluorimeter). All spectra were fit to multiple Gaussians using Igor Pro 8. All measurements were performed with an excitation wavelength of 370 nm (3.35 eV - see **Experimental Section**) and an angle of 75° . (d) Overlay of the PL of crystals, flakes and film. (e) Gaussian area of peaks A, B, and C, where the area for C is the sum of the areas of C_1 and C_2 . (f) Cross-sectional SEM of the exfoliated flakes on quartz, with a PMMA capping layer. The flake thickness was highly variable. The origins of differences in emission are discussed in the main text.

To examine how exfoliation may change emission from B and C, we exfoliated bulk crystals of $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$, and obtained a variety of thicknesses, with some as low as 95 nm. Exfoliated flakes of $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ were prepared from bulk crystals via the standard scotch-tape method.^{12,13} Fits for peaks A and B are fairly certain, as A and B are narrow peaks. However, C is a broad tail, and necessitated being decoupled into several peaks, C_1 and C_2 . Different fits were tried; in all cases **the total area of C goes as bulk crystals > exfoliated flakes > film**. It is clear that the proportions of B and C both change with sample preparation. Exfoliation is not completely decoupled from strain, as mechanical exfoliation involves applying pressure to separate the sheets, and this may change the cation stacking.

Figure S6. (a) Photoluminescence emission and (b) absorbance of spin-cast films and powders of $(\text{EA})_2(\text{EA})_2\text{Pb}_3\text{Br}_{10}$ from **Figure 3**, shown here in nm (excitation 3.35 eV; 370 nm).

The optical data were collected in nm and converted to eV. For emission spectra, a Jacobian transformation¹⁴ was applied to the intensities:

$$Intensity_{Converted} = \frac{1240 \times Intensity_{Collected}}{Energy^2}$$

Where $Intensity_{Converted}$ is the PL intensity of the plot in eV, $Intensity_{Collected}$ is the PL intensity of the plot in nm, and $Energy$ is 1240/wavelength.

Figure S7. Photoluminescence emission (75-degree collection angle) of $(\text{EA})_2(\text{EA})_2\text{Pb}_3\text{Br}_{10}$ bulk crystals and film. The excitation was selected to be 2.75 eV to verify that broad emission only occurs when exciting the material above the absorption edge. Despite use of a long-pass filter, some scattering was observed in all samples characterized in this study at energies closest to the excitation energy, most noticeably when no (or little) photoluminescence was present in the sample. Here, the only signal observed was this scattering, confirming that sub-onset excitation does not produce broad emission.

Figure S8. Changes (or lack thereof) in emission in films and bulk crystals of $(\text{EA})_2(\text{EA})_2\text{Pb}_3\text{Br}_{10}$ with excitation energy and/or collection angle. Although some variations in the free exciton: broad emission proportions were observed when changing angle and/or excitation, the films consistently had a greater proportion of free exciton emission, and the bulk crystals consistently had a greater proportion of broad emission. “L” stands for scattered light from the excitation lamp (see **Figure S9**).

Figure S9. Excitation spectrum of the lamp, and photoluminescence emission of $(\text{EA})_4\text{Pb}_4\text{Br}_{10}$ bulk crystals from **Figure 3**. Some small peaks appear in the bulk crystal samples, due to incomplete filtering of the lamp by the fluorimeter's monochromator. When spectra are collected using a laser and CCD detector (**Figure 4**) instead of a monochromator-based fluorimeter (**Figure 3**), the sharp peaks disappear, but the proportions of A, B and C remain similar. This confirms that the proportions of A, B and C are inherent to the materials studied in both bulk crystals and films, and that the small, sharp peaks are from the fluorimeter's lamp.

Fitting for Temperature-Dependent PL

Figure S10. Temperature-dependent photoluminescence emission of the (a) bulk crystals and (b) film of $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ (see **Figure 4**). All spectra were fit to multiple Gaussians using Igor Pro 8. Measurements were performed with an excitation wavelength of 370 nm (3.35 eV), using a pulsed laser, and at an angle of 90° (see **Experimental Section**). Differences between these fits and those from **Figure S5** may be due to different experimental conditions (notably angle), as lower-energy features can sometimes vary in intensity with angle (**Figure S8**).^{12,13} However, all trends remain the same.

Methodology for fitting and determining trends

The main challenge with fitting these spectra is that C is a broad tail. Therefore, while peaks A (free exciton), B (phonon-coupled) and D (STE) are fairly obvious, it is not clear how many peaks should be used to fit C. Depending on the instrument setup, it was found that 2 Gaussians were needed to fit C at 300 K (**Figure 3, S5**) or only one (**Figure S10**). In the main text (**Figure 4**), we reported results

using the lowest possible number of Gaussians, so as to not overfit the data. Below, we show additional fits, to confirm that C disappears and blue-shifts with cooling.

We tried to keep the position of C constant in **Figure S10**; this resulted in unsuccessful fits (the fit curve was not touching the experimental spectrum), providing indication that C likely blue-shifts.

We then tried to always use two Gaussians used for C, in order to match **Figure S5**. A clear blue-shift is seen for C_1 ; trends for C_2 are less clear (**Figure S11**):

Figure S11. Gaussian fitting of the bulk crystals with cooling, assuming that C is two Gaussians, C_1 and C_2 , at all temperatures.

We can plot the energy shift and Gaussian area of C_2 . No discernable trends are seen until 110 K, at which point the behavior of the STE peak D is obvious (**Figure S12**):

Figure S12. Evolution of the fourth Gaussian from **Figure S11**. This Gaussian becomes peak D at low temperatures (blue shading). See also **Figure S15** for comparison with film behavior.

Since it is not clear how many Gaussians should be used to fit C, we can also look at the residuals, once peaks A, B and D are accounted for:

Figure S13. Gaussian fitting (bulk crystals) of A, B, and D, showing the residuals (assumed to be peak C), if the Gaussians C₁ and C₂ are deleted from **Figure S11**.

From **Figure S13**, it is clear that a broad peak is present at room temperature. This peak is roughly symmetric at 300 K, but becomes gradually weaker and less symmetric cooler temperatures, suggesting that C is both decreasing in intensity and blue-shifting. The asymmetry also suggests overlap between C and A/B, as also suggested by **Figures S10** and **S11**.

Finally, if we assume no overlap between C and A/B (**Figure S14**), we see from the residuals that C seems to strongly blue-shift.

Conclusion: C blue-shifts and decreases in intensity with cooling.

Figure S14. Gaussian fitting (bulk crystals) of A, B, and D, showing the residuals (assumed to be peak C), if there is no overlap between A, B and C (unlikely).

Figure S15. Temperature-dependent photoluminescence emission of the bulk crystals and film of $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$ (see **Figure 4**), focusing on the peak at 1.9 eV (peak D). (a) Spectra for 210 K and below, (b) Changes to peak position and (c) Changes to peak intensity, obtained from Gaussian fits (intensity was used rather than area, as the peaks are cut off).

Peak D gradually increases in intensity below 140 K for both bulk crystals and films. This behavior is consistent with that of self-trapped excitons studied elsewhere.^{15,16} The red-shift with cooling (bulk crystals) is further consistent with STEs that are associated with localized polarons.¹⁶ However, D behaves different in bulk crystals vs. films: the films exhibit more intense peak D, and the bulk crystals exhibit a more intense red-shift. While peak D is different in nature than B and C, here again, **Peak D (STE) behaves differently in bulk crystals and in films.**

Figure S16. PDS in the 2.6-3.0 eV region for the bulk crystal and film, with goodness of fit parameters from MATLAB: the sum of squares due to error (SSE), R-square (R), Adjusted R-square, and the Root mean squared error (RMSE).

Figure S17. SEM of the drop-cast films from **Figure 6**, with the inset of (c) showing a cross-section.

Figure S18. XRD patterns of spin-cast and annealed films, for which the EA/Pb molar ratio of the precursor solutions was steadily increased. Only for EA/Pb = 1.5 and for EA/Pb = 3.8 were phase pure films obtained, and these were $n = 3$ and $n = 1$ films respectively. However, the large excess of EA (nearly twice the stoichiometric amount) needed for the $n = 1$ film formation shows that $n = 1$ is not easily formed. No 3D film or phase was formed.

To further understand the limits of phase formation in the $(\text{EA})_2(\text{EA})_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ family, we tried to make ethylammonium-based RP films of different n via spin-casting (**Figure S18**). The molar ratio of EABr: PbBr_2 (EA/Pb for short) in the precursor solutions was steadily increased from 1.0 (EAPbBr_3 3D stoichiometry) to 3.8 (nearly twice the $n = 1$ ($\text{EA})_2\text{PbBr}_4$ stoichiometry). For EA/Pb = 1.0, which corresponds stoichiometrically to EAPbBr_3 , we obtained broad peaks, likely indicating an amorphous phase (the film was also non-emissive). A slight excess of EA is thought to be needed for $n = 3$ film formation because Pb and Br form strong complexes with DMF.¹⁷ In addition, no 3D-like phase was conclusively observed in any of the EA compositions tested. Despite the large range of EA/Pb molar ratios tested, only the $n = 1$ and $n = 3$ compositions could be cast as phase-pure films.

Figure S19. XRD patterns under different stability testing conditions for (a) $n = 3$ and (b) $n = 1$ spin-cast films.

We examined the stability of $n = 1$ and $n = 3$ spin-cast films, in order to better understand which phases are thermodynamically favorable (**Figure S19**), and summarized the results in **Figure 7**. Films were spin-cast with or without the PMMA capping layer. Four testing conditions were employed, to test stability to heat and air: (1) *control*: as-cast (with PMMA capping), (2) *heat test*: heating at 70°C in the glove box (nitrogen environment) for 80 min (with PMMA capping), (3) *air test*: storage in air at 20°C for 240 min (no PMMA capping) and (4) *heat and air test*: heating at 70°C in air for 80 min (no PMMA capping).

The $n = 3$ phase proved more thermodynamically stable than the $n = 1$ (**Figure S19**). Heating encapsulated $n = 3$ films in a nitrogen environment produced no change in structure, indicating that $n = 3$ is thermodynamically stable under mild conditions. In contrast, this mild heating resulted in clear phase-change in the encapsulated $n = 1$. The novel peaks were tentatively assigned to $n = 3$ and $n = 2$, although the low number of non- $n = 1$ peaks made full assignment challenging. The greater thermodynamic stability of the $n = 3$ may help explain why it formed more favorably in films.

The $n = 3$ also appeared to be much more air-stable than the $n = 1$ (**Figure S19**). Short, unencapsulated storage in air resulted in retention of the $n = 3$ phase, albeit with large peak intensity increase and out-of-plane (0 k 0) stacking preference. Humidity-induced increase in grain size has been previously reported for MAPbI₃; ¹⁸ it is possible that humidity caused recrystallization here as well. This rearrangement is encouraging, as it suggests that post-casting treatments could control film orientation for $n = 3$. In contrast, short, unencapsulated storage in air resulted in degradation of the $n = 1$ film. Finally, heating unencapsulated $n = 3$ and $n = 1$ films in air resulted in obvious degradation of both films, indicating that encapsulation will likely be necessary for ethylammonium RP device use. The originally- $n = 3$ film contained peaks near 14 and 29 degrees, perhaps indicating a 1D degradation product. Interestingly, the originally- $n = 1$ film now very clearly contained $n = 3$ as well as some $n = 2$, indicating that $n = 3$ is a degradation product $n = 1$. The $n = 1$ to $n = 3$ phase change in heated unencapsulated films also suggests that ethylammonium desorbed. Overall, the $n = 3$ EA RP was considerably more stable than the $n = 1$.

Further Discussion on 2D and 3D phases with the EA cation

Previous work that attempted to make films of 3D EAPbBr_3 found that a 2D phase formed instead.¹⁹ Given the location of the XRD peaks of this film, it is likely that the $n = 3$ phase formed in the film in the prior study.¹⁹ Perhaps the use of an antisolvent in prior work helped $n = 3$ phase formation, which might be otherwise hindered by excess of lead in the EAPbBr_3 solution stoichiometry. Another report claimed formation of EAPbBr_3 in nanocrystals.²⁰ However, the optical properties of the resulting nanocrystals matched $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$, and XRD data was not collected in the range characteristic for 2D phases (below $2\theta = 10^\circ$),²⁰ suggesting that the nanocrystals might instead be $(\text{EA})_4\text{Pb}_3\text{Br}_{10}$. EA can be incorporated into 3D phases, provided there is a small A-site cation (e.g. MA) that it can alloy with, to form $(\text{EA,MA})\text{PbBr}_3$.¹⁹

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