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Temperature-Dependent Crystallization in Two-Step Perovskite Deposition Revealed by In-Situ GIWAXS and Machine Learning-Guided Analysis

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ABSTRACT

The performance and stability of perovskite solar cells are strongly governed by the crystallization behavior of their active layer. In two-step sequential deposition, early-stage film formation plays a decisive role in determining final phase purity and device quality. Guided by a data-driven analysis of nearly 39,000 devices in the FAIR perovskite database, we identified solvent-mediated quenching and thermal processing as key variables affecting power conversion efficiency (PCE), particularly in two-step fabrication. To investigate these effects in real time, we designed and implemented a custom-built, temperature-controlled spin-coating system, enabling precise thermal modulation during precursor deposition. Using this platform, we performed in situ GIWAXS measurements to study the crystallization dynamics of FA_{0.5}MA_{0.5}PbI₃ films over a temperature range of 30–90 °C. Our results reveal a non-monotonic relationship between spin-coating

temperature and α -phase formation, governed by the interplay between precursor interdiffusion, PbI_2 crystallinity, and δ -phase suppression. The custom thermal control enabled us to isolate and quantify these competing effects during the earliest stages of film formation, providing mechanistic insight into how spin-coating temperature governs both phase purity and kinetic pathways in two-step perovskite systems. Temperature-dependent SEM and photovoltaic device measurements further demonstrate that early-stage crystallization pathways directly translate into differences in morphology, charge-transport continuity, and device performance. These findings inform targeted strategies for optimizing deposition protocols to balance rapid nucleation, phase stability, and device performance.

1. Introduction

The accelerating global demand for sustainable power has propelled solar technologies to the forefront of the energy transition, and perovskite solar cells (PSCs) now stand out as the most versatile and cost-effective candidates for next-generation photovoltaics. Organometal-halide perovskites have already migrated beyond solar cells into light-emitting diodes, lasers, and photodetectors because their defect-tolerant lattices combine strong absorption, long carrier diffusion lengths, and band-gap tunability.^[1–4] Laboratory efficiencies have climbed steeply, from the seminal 3.8 % report in 2009^[5] to today's certified records of 27.3 % for single-junction devices, 30.1 % for all-perovskite tandems, and 35 % for two-terminal perovskite-on-silicon tandems.^[6] These leaps stem from coordinated advances in solvent/additive chemistry, defect passivation, interface engineering, and, above all, crystallization control.^[7]

Hybrid organic-inorganic perovskites adopt the ABX_3 framework in which an organic A-site cation (commonly methylammonium, MA^+ , formamidinium, FA^+ , or cesium, Cs^+), a divalent metal B-site (Pb^{2+} or Sn^{2+}), and halide X-site anions (I^- , Br^- , Cl^-) co-assemble into a three-dimensional network. This hybrid lattice is particularly well-suited for solar cell applications due to its unique optoelectronic characteristics, which include the material with high absorption coefficients, tunable band gaps, electrically benign defects, and solution-processability, all critical prerequisites for low-cost photovoltaics.^[8–11]

The perovskite layer's film morphology and defect density, however, dictate device performance and long-term stability. Among the various fabrication routes, the one-step antisolvent method and

the two-step sequential deposition method dominate laboratory practice; the latter affords finer control over nucleation, crystal growth, and film thickness, consistently yielding smoother, pinhole-free layers.^[12–16] The microstructural quality of a perovskite film is governed by its crystallization pathway; thus, every parameter that alters this process decisively shapes the final film integrity and performance. For example, temperature plays a pivotal role during both precursor deposition and post-treatment, as it modulates intermediate-phase chemistry, solvent evaporation, and nucleation kinetics.^[17–19]

Among many perovskite materials, the mixed-cation formamidinium methylammonium lead iodide ($\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$) stands out because it combines a high absorption coefficient and a tunable band gap with straightforward, low-temperature processing, enabling next-generation solar cells that rival silicon efficiencies while promising markedly lower production costs.^[20–22] Most importantly, the $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ composite retains the favorable FA-based band gap. At the same time, the inclusion of MA^+ shrinks the lattice slightly. It suppresses the spontaneous conversion of photoactive black perovskite alpha phase (α -phase) FAPbI_3 into its yellow non-perovskite delta phase (δ -phase).^[23–25] Nevertheless, stabilizing the α -phase under ambient conditions remains a significant challenge. Particularly for solution-processed perovskites, several strategies have been proposed to stabilize the α -phase and inhibit the formation of the δ -phase. Researchers have alloyed A-site cations (e.g., Cs^+ or MA^+) with smaller radii or mixed halides (Cl^- , Br^-) into the FAPbI_3 lattice to reinforce the perovskite framework and retard the $\alpha \rightarrow \delta$ transition.^[26–30]

Early work on perovskite solar cells focused almost exclusively on tuning deposition protocols, such as antisolvent drips, spin speeds, and annealing profiles, and on identifying the “ideal” stoichiometric window, most notably the MAI:FAI ratio that maximizes phase stability.^[31,32] Progress, however, advanced broadly through labor-intensive trial-and-error campaigns. Achieving genuinely defect-lean, scalable films requires mechanistic insight into nucleation and growth, an understanding that ex-situ characterization often obscures because the thermal and chemical microenvironment evolves immediately once the film leaves the spin coater. In-situ probes circumvent this limitation by capturing transient intermediates and kinetic bottlenecks that remain invisible or misleading when analyzed post-growth.^[33–35]

Recent advances in data-driven materials science have introduced machine learning (ML) as a powerful framework for uncovering hidden correlations between processing conditions and

material properties.^[36–38] In perovskite research, ML models trained on large experimental datasets can capture latent trends that are often obscured by the complexity of fabrication–structure–property relationships. Interpretable algorithms such as decision tree regressors enable systematic ranking of fabrication variables by their influence on key performance indicators and, more importantly, provide indirect insight into crystallization pathways and microstructural evolution.^[36,39,40] Even in the absence of direct structural data, such models can identify which processing conditions most consistently lead to favorable material formation—such as uniform phase purity, minimized intermediate retention, or suppressed δ -phase formation. Similar approaches have recently been used to rationalize impurity-phase formation, where decision trees trained on synthesis records guided experimental validation of crystallization outcomes.^[41,42]

Pure FAPbI₃ can crystallize either as the photoactive black perovskite α -phase or as the indirect bandgap δ -phase, and the thermodynamic balance between the two hinges sensitively on temperature.^[43,44] At room temperature, the oversized FA⁺ cation destabilizes the corner-sharing octahedral framework, making α -FAPbI₃ prone to spontaneous conversion into δ -FAPbI₃.^[34,45,46] Introducing smaller methylammonium cations mitigates this lattice strain: MAI-FAI mixtures contract the perovskite framework and strengthen the PbI₆⁴⁻ network, thereby suppressing the $\alpha \rightarrow \delta$ transition and stabilizing the perovskite lattice during and after film formation.^[47,48] In these studies, adding either A-cations (methylamine [MA] or cesium [Cs]) or X-halides (chloride [Cl] or bromide [Br]) into the FAPbI₃ crystal structure is the key solution to tackling this problem^[49–53]

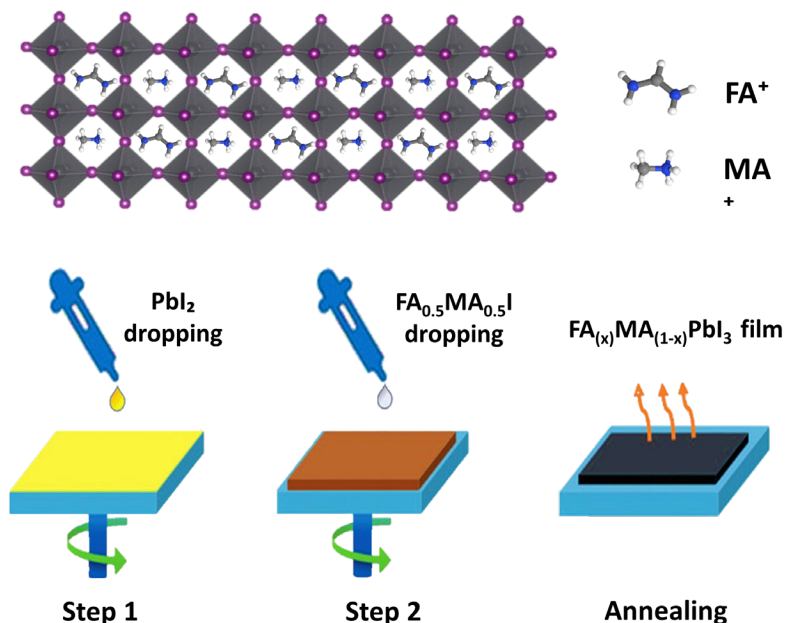
Despite these compositional strategies, process development has historically relied on intuition-driven, incremental optimization.^[37,38] Large, open databases, most notably the FAIR-compliant Perovskite Database, which contains over 43,750 devices, offer a unique opportunity to identify which fabrication choices are most significant, enabling researchers to examine the field’s collective experimental record quantitatively.^[54] In this study, we reverse the traditional, intuition-driven optimization loop. We begin by mining the entire FAIR Perovskite Database^[54] using an interpretable decision tree regressor, ranking the fabrication parameters that most strongly dictate power conversion efficiency (PCE) in both the one-step antisolvent route and the two-step sequential process. Treating high PCE as a proxy for superior crystallographic quality, given the absence of direct structural descriptors in the database, we used a decision-tree analysis to rank

fabrication parameters and identify solvent choice, quenching strategy, and thermal conditions as dominant variables. Although spin-coating temperature is not explicitly recorded in the FAIR database, the data-driven analysis consistently identified solvent choice during the second step and thermal annealing conditions as the primary determinants of efficiency in two-step devices. Importantly, these two variables are physically coupled during the spin-coating window, a critical temporal stage that is not explicitly captured in the database. We therefore hypothesized that the thermal state during this spin-coating window governs solvent evaporation kinetics and the structural state of the PbI_2 precursor scaffold, thereby controlling subsequent interdiffusion and crystallization pathways. To test this hypothesis, we designed targeted in situ GIWAXS experiments to directly probe the early-stage thermal–chemical interactions that the machine-learning analysis identified as critical but could not resolve. Using this approach, GIWAXS isolates the influence of early-stage thermal control on nucleation, intermediate-phase evolution, and final phase purity during two-step $\text{FA}_{0.5}\text{MA}_{0.5}\text{PbI}_3$ deposition.

While previous in situ GIWAXS/XRD studies have established the influence of temperature on intermediate-phase evolution and δ -phase suppression in perovskite films, temperature-dependent effects in these studies are most often examined during post-deposition thermal treatment, with the spin-coating step typically performed under nominal or fixed conditions.^[55–57] In contrast, this work directly probes the role of temperature during the spin-coating stage itself, where solvent evaporation, PbI_2 crystallization, and organic cation interdiffusion occur simultaneously and dictate early nucleation pathways. By combining a custom-built, temperature-controlled spin-coating platform with real-time GIWAXS, we reveal a non-monotonic crystallization behavior in $\text{FA}_{0.5}\text{MA}_{0.5}\text{PbI}_3$, in which premature PbI_2 crystallinity at elevated temperature acts as a kinetic barrier to complete conversion, independent of δ -phase formation. Guided by a machine-learning analysis of device-performance trends across thousands of reported solar cells, this work establishes a mechanistic link between early-stage thermal control during deposition and final film quality in two-step sequential processing.

This study, therefore, combines data-driven insights with time-resolved GIWAXS structural probes. By monitoring phase evolution at 30 °C, 50 °C, 70 °C, and 90 °C, we reveal how precursor diffusion, intermediate phase formation, and final α -phase yield are affected during the thin film fabrication process. This deposition sequence, featuring temperature-controlled spin coating of

both PbI_2 and $\text{FA}_{0.5}\text{MA}_{0.5}\text{I}$ layers followed by annealing, is summarized in **Scheme 1**. The resulting mechanistic picture provides actionable guidelines for scalable, defect-lean perovskite films and, ultimately, higher-efficiency PSCs. The resulting mechanistic picture provides actionable guidelines for scalable, defect-lean perovskite films and, ultimately, higher-efficiency PSCs.



Scheme 1. Schematic illustrations of the $\text{FA}_{0.5}\text{MA}_{0.5}\text{PbI}_3$ thin film fabrication process.

2. Results and discussion

2.1 Data-driven ranking of fabrication variables

To guide our experimental design, we performed a data-driven analysis of approximately 39,000 device entries from the FAIR-compliant Perovskite Database, using a decision-tree regressor to identify which fabrication parameters strongly influence power conversion efficiency (PCE).^[54,58] The decision tree model was selected for its inherent interpretability and its efficient handling of high-dimensional, multi-category feature spaces, enabling transparent ranking of influential fabrication variables without requiring computationally intensive preprocessing. To justify this model choice, we benchmarked the decision tree regressor against Random Forest and Linear Regression models, with the comparative performance summarized in Table S1 of the Supporting Information. While more complex models can offer marginally higher predictive accuracy, the decision tree provides a favorable balance between interpretability and performance for the

purpose of experimental prioritization. Additional details of the machine-learning workflow are provided in the Experimental Section, and the complete analytical pipeline is illustrated in **Figure 1a**. As shown in **Figure 1b**, the majority of devices (71.9%) were fabricated using one-step deposition methods, while 24.6% followed the two-step sequential approach. Only 3.5% used alternative fabrication routes. For further analysis, we partitioned the dataset into two subgroups based on deposition strategy: one-step (~28,000 devices) and two-step (~9,000 devices). These subsets serve as the basis for the comparative evaluation presented in the following sections.

Feature importance rankings for the one-step method (**Figure 1c**) highlight three dominant variables: quenching-induced crystallization protocols (14.0%), perovskite deposition solvent choice (15.1%), and hole-transport-layer (HTL) stack architecture (10.7%). Notably, the two-step process involves the introduction of a second precursor solution - commonly FAI/MAI in IPA - which acts similarly to an antisolvent by inducing rapid crystallization upon contact with the PbI_2 layer. This functional analogy to quenching in one-step methods helps explain why solvent choice consistently ranks as the most influential variable across both fabrication routes as shown in **Figure 1 c-d**.

Solvent-mediated crystallization and thermal annealing conditions dominate the feature importance rankings in both deposition methods as shown in **Figure 1c-d** and **Figure S1**. In two-step devices specifically, thermal annealing temperature and time emerge as high-impact variables (**Figure 1d**, **Figure S1**), reflecting the importance of thermal control in directing phase formation. Although spin-coating temperature is not explicitly recorded in the FAIR dataset, it is tightly coupled to early-stage thermal dynamics, particularly solvent evaporation, precursor interdiffusion, and intermediate-phase evolution. These connections motivated our targeted experimental investigation of spin-coating temperature as a critical, underexplored parameter governing crystallization pathways and final film quality in two-step perovskite deposition.

To systematically evaluate how material composition influences device efficiency, we extracted the ten highest-performing perovskite absorber formulations from the FAIR database for both the one-step and two-step deposition methods. These are presented in **Figure S2** (Supporting Information) as bar plots ranked by average PCE. The corresponding top 10 compositions specific to two-step devices are listed in **Table 1**, based on reverse-scan PCE data. Entries in **Table 1** were selected from the FAIR database and subsequently verified against the original literature; reports based on one-step deposition, non-standard illumination conditions, tandem architectures, or non-

AM1.5G (1 sun) testing protocols were excluded. Notably, specific compositions exhibit significantly higher average PCE values, indicating that material formulation plays a crucial role in optimizing efficiency within the two-step process. These formulations share common structural features: all are iodide-dominant perovskites with only modest bromide content (typically ≤ 0.25), and most incorporate small A-site cations such as cesium (Cs^+) or methylammonium (MA^+) alongside formamidinium (FA^+). This combination has been shown to stabilize the perovskite lattice and reduce the likelihood of forming the undesirable δ -phase. In particular, moderate MA^+ incorporation appears beneficial, as it contracts the lattice just enough to reinforce the PbI_6^{4-} framework without introducing strain or triggering the thermal or phase-segregation observed at higher MA fractions. Notably, several high-performing compositions also feature quasi-2D additives, including OA_2PbI_4 , FEA_2PbI_4 , and $\text{C}_6\text{H}_{13}\text{NH}_{32}\text{PbI}_4$, which are increasingly recognized for their ability to passivate surface defects and suppress ion migration.

Process-level analysis reveals additional efficiency drivers, as detailed in **Figure S3**. In one-step deposition, the choice of antisolvent significantly impacts device performance: chlorobenzene (CB) and isopropanol (IPA) yield higher average PCEs compared to protic solvents such as methanol (**Figure S3a**). While CB shows the best performance in one-step devices, it is incompatible with two-step deposition due to its inability to dissolve formamidinium and methylammonium iodide (FAI/MAI). In contrast, IPA, which ranks as the second-best quenching solvent, is fully compatible with FAI/MAI and is therefore widely used in two-step fabrication to induce rapid crystallization. As shown in **Figure S3b**, incorporating an explicit quenching step in one-step devices improves PCE by approximately 3.5% absolute. In two-step deposition (**Figure S3c**), this quenching effect is inherently introduced through the second-step drop-casting of FAI/MAI in IPA, a practice that is nearly universal among high-performing devices.

Taken together, these findings highlight the central role of solvent-mediated crystallization and thermal processing in controlling perovskite film quality. In one-step devices, quenching-induced crystallization and antisolvent choice are key levers, while in two-step deposition, rapid nucleation is typically achieved through the second-step drop of FAI/MAI in IPA. Although spin-coating temperature is not directly recorded in the dataset, the machine learning analysis emphasizes the importance of thermal annealing conditions in two-step fabrication (**Figure 1d**), suggesting that early-stage thermal control is equally critical. Building on this insight, we identified spin-coating

temperature as an underexplored yet mechanistically relevant parameter. It governs solvent retention, PbI_2 crystallinity, and intermediate-phase evolution, all of which influence the extent and uniformity of α -phase conversion. The following sections present in-situ GIWAXS measurements designed to isolate the effect of spin-coating temperature on phase evolution in $\text{FA}_{0.5}\text{MA}_{0.5}\text{PbI}_3$ films.

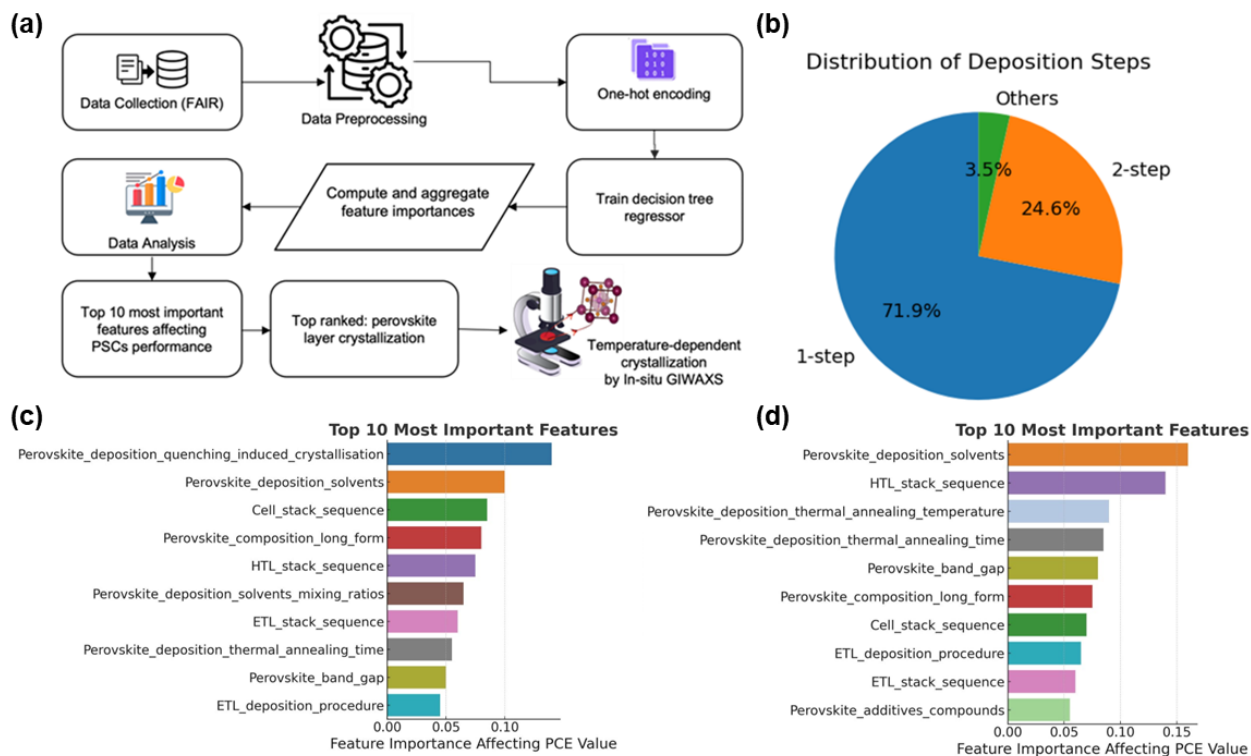


Figure 1 Data-driven selection of critical fabrication variables. (a) The workflow used for feature ranking is based on a decision-tree regressor trained on device-level entries from the FAIR perovskite database. (b) The distribution of fabrication methods in the dataset shows that 71.9% of devices were fabricated using one-step deposition, 24.6% using the two-step sequential route, and 3.5% by other methods. (c) The top 10 aggregated feature importances for one-step devices are shown, with solvent choice, quenching protocols, and HTL design ranking highest. (d) The top 10 aggregated feature importances for two-step devices highlight solvent choice, annealing conditions, and stack architecture as dominant variables. Bars represent mean $\pm$ standard deviation from 20 bootstrap resamples. The full list of the top 25 features is provided in **Figure S1**.

Table 1. Average PCE of selected top-performing compositions fabricated by the two-step route.

Perovskite Composition ^a	Mean PCE (%) ^b	Ref ^c
FAPbI ₃ @MAFa ^d	24.1	[9]
FA _{0.92} MA _{0.08} PbBr _{0.24} I _{2.76}	22.61	[59]
FA _{0.95} MA _{0.05} PbBr _{0.15} I _{2.85}	22.6	[60]
FA _{0.95} MA _{0.03} Cs _{0.02} PbBr _{0.09} I _{2.91}	22.3	[61]
FA _{0.81} MA _{0.09} Cs _{0.1} PbBr _{0.1} I _{2.9}	21.7	[62]
FA _{0.65} MA _{0.3} Cs _{0.05} PbBr _{0.15} I _{2.85}	21.52	[63]
FA _{0.92} Cs _{0.05} MA _{0.03} PbBr _{0.09} I _{2.91}	21.5	[64]
FA _{0.57} MA _{0.43} PbBr _{0.04} I _{2.96}	21.44	[65]
FA _{0.54} MA _{0.41} Cs _{0.05} PbBr _{0.06} I _{2.94}	21.3	[66]
FA _{0.57} MA _{0.43} PbBr _{0.13} I _{2.87} (Cl)	21.21	[67]

^a Compositions are reported as described in the original references; stoichiometric indices are rounded to two decimal places for clarity.

^b Mean PCE represents the average reverse-scan efficiency of devices fabricated using the two-step sequential deposition route and measured under standard AM 1.5G, 1 sun illumination.

^c Candidate compositions were initially identified through screening of the FAIR perovskite database and subsequently verified against the original literature sources. Reports based on one-step deposition routes, monochromatic illumination, indoor lighting conditions, tandem architectures, or non-standard testing protocols were excluded from this table, even when higher peak efficiencies were reported.

^d MAFa (methylamine formate) is an ionic liquid used during PbI₂ deposition.

2.2 The effect of spin coating temperature on the first layer structure

To understand how spin-coating temperature governs the crystallization behavior and reactivity of the PbI₂ layer in two-step FA_{0.5}MA_{0.5}PbI₃ deposition, we performed in-situ GIWAXS measurements across a range of temperatures (30 °C, 50 °C, 70 °C, and 90 °C). To enable this investigation, we developed a custom-built spin-coating system with precise temperature control during precursor deposition, allowing systematic evaluation of thermal effects on film formation. The structural state of the PbI₂ layer immediately after deposition was found to be highly sensitive to temperature, which in turn modulated its interaction with the FA_{0.5}MA_{0.5}I precursor and dictated

the subsequent crystallization pathway, ultimately determining the phase purity and quality of the resulting perovskite film. The evolution of the perovskite phase was captured through time-resolved 2D GIWAXS contour plots (**Figure 2a, c, e, g**), recorded during spin coating and thermal annealing at 108 °C. Corresponding phase evolution was analyzed through integrated intensity profiles (**Figure 2b, d, f, h**), obtained by integrating characteristic reflections associated with the α -phase and PbI_2 . The normalized intensity of these phases is presented in **Figure 3** to enable direct comparison across different spin-coating temperatures.

For all samples, the in situ GIWAXS measurements reveal common crystallization features. Notably, immediately upon dropping of $\text{FA}_{0.5}\text{MA}_{0.5}\text{I}$ precursor, a sharp diffraction feature emerges near $q \approx 1.0 \text{ \AA}^{-1}$, corresponding to the rapid crystallization of the perovskite α -phase.^[55,68] This transformation proceeds almost immediately and intensifies further during annealing, as evidenced by the continued growth in the perovskite scattering peak intensity (**Figure 2b, d, f, h**). Although these general trends are prevalent across all samples, significant variations emerge based on the spin-coating temperature. Additional time-resolved 1D GIWAXS profiles extracted over 300 s for all temperatures are shown in **Figure S4**.

At 30 °C (**Figure 2a-b**), the early stage scattering profile exhibits a broad scattering feature centered around $q \approx 0.7 \text{ \AA}^{-1}$, indicative of an amorphous PbI_2 layer with no detectable crystalline domains.^[55,57] The amorphous nature of the PbI_2 layer is evident in the early GIWAXS profiles at 30 °C (**Figure S4a**), which show a broad scattering halo centered near $q \approx 0.7 \text{ \AA}^{-1}$ and no crystalline PbI_2 features throughout the entire measurement window. Upon introduction of the $\text{FA}_{0.5}\text{MA}_{0.5}\text{I}$ precursor, a sharp α -phase peak emerges near $q \approx 1.0 \text{ \AA}^{-1}$, indicating rapid perovskite crystallization even before thermal annealing begins. Furthermore, at the end of the spin-coating stage, the α -phase perovskite peak reaches approximately 45% of the maximum intensity observed after annealing, indicating that less than half of the total crystallization occurs during spin coating, while the majority develops during the subsequent thermal treatment.

Raising the spin-coating temperature to 50 °C (**Figure 2c-d**) retains the amorphous character of the PbI_2 layer during the initial stage, but the introduction of $\text{FA}_{0.5}\text{MA}_{0.5}\text{I}$ leads to the simultaneous appearance of two peaks: one at $q \approx 1.0 \text{ \AA}^{-1}$ (α -phase) and another at $q \approx 0.87 \text{ \AA}^{-1}$, corresponding to the photoinactive δ -phase. Based on the q -position ($q \approx 0.87 \text{ \AA}^{-1}$), this signal is more consistent with a 6H hexagonal polytype rather than the conventional 2H δ -phase, suggesting that hexagonal

stacking sequences may become increasingly favorable at elevated temperatures and could emerge transiently during intermediate crystallization stages.^[69,70] The early emergence and persistent presence of this δ -phase signal is visible in **Figure S4b**. Although the α -phase remains the dominant signal, the δ -phase persists throughout annealing, indicating incomplete conversion. The perovskite peak at 50 °C reaches ~55% of its final intensity by the end of spin coating, higher than at 30 °C, suggesting accelerated crystallization during the initial stage. However, the overall α -phase growth slows down during annealing (**Figure 2d**), likely due to kinetic competition with the δ -phase. This premature δ -phase nucleation acts as a barrier to full α -phase conversion, limiting grain growth and film quality. These findings suggest that while moderate heating accelerates initial α -phase nucleation, it also increases the likelihood of δ -phase formation, which competes with and impedes the completion of the crystallization process. Compared to 30 °C, the 50 °C film forms more α -phase during spin coating (~55% vs. ~45%) as shown in **Figure 3b**, but its crystallization stalls during annealing, resulting in a lower final conversion rate and persistent phase heterogeneity. This underscores the importance of temperature-controlled nucleation dynamics in achieving phase-pure perovskite films.

Further increases in spin-coating temperature induce a distinct shift in the crystallization pathway of the PbI_2 layer. At 70 °C (**Figure 2e-f**), the PbI_2 film begins to crystallize during spin coating, evidenced by the appearance of a sharp diffraction peak at $q \approx 0.92 \text{ \AA}^{-1}$ (**Figure 2e**), indicating that solvent evaporation is sufficiently fast to trigger early PbI_2 nucleation.^[71] This pre-crystallized PbI_2 rapidly converts to the α -phase upon $\text{FA}_{0.5}\text{MA}_{0.5}\text{I}$ deposition, as confirmed by the emergence of a perovskite peak at $q \approx 1.0 \text{ \AA}^{-1}$ and the concurrent reduction in the PbI_2 signal (**Figure 2e-f**). A weak peak at $q \approx 0.87 \text{ \AA}^{-1}$ also emerges, attributed to the 6H δ -phase, which gradually intensifies during annealing (**Figure S4c**), suggesting that phase competition remains an issue. Despite these competing effects, the perovskite peak reaches ~60% of its post-anneal intensity by the end of spin coating, the highest among all temperatures tested, indicating rapid but incomplete conversion.

A different behavior emerges at 90 °C (**Figure 2g-h**). While PbI_2 again crystallizes immediately during spin coating, as shown by the strong $q \approx 0.92 \text{ \AA}^{-1}$ peak (**Figure 2g** and **Figure 3a**), the α -phase peak develops less efficiently during spin coating, reaching only ~50% of its final intensity (**Figure 2h** and **Figure 3b**). Importantly, no δ -phase signal is observed. In contrast to the $q \approx 0.87 \text{ \AA}^{-1}$ feature assigned to a 6H δ -phase polytype at intermediate temperatures (50–70 °C), its

absence at 90 °C suggests that higher thermal energy may suppress hexagonal stacking instabilities and promote direct α -phase nucleation, consistent with previous reports showing the α -phase becomes more thermodynamically favorable above 70 °C.^[55] However, **Figure 3a** shows that the PbI₂ peak at 90 °C emerges more rapidly but persists for a longer duration than at 70 °C, indicating fast initial crystallization but slower consumption. This behavior points to a kinetic barrier; the highly crystalline PbI₂ layer restricts FA⁺/MA⁺ cation interdiffusion, limiting complete perovskite conversion during annealing.

Beyond the primary PbI₂ and α -phase features, an additional weak diffraction peak appears at $q \approx 0.74 \text{ \AA}^{-1}$, visible only in the 90 °C dataset (**Figure S4d**). This feature is tentatively assigned to the (320) reflection of FA₂PbI₄, a layered Ruddlesden–Popper (RP)–type perovskite. Multiple FA-based low-dimensional iodide phases have been reported, including FA₂PbI₄ and FA₃PbI₅, which typically form under iodide-rich or off-stoichiometric conditions.^[23,72] Although the observed $q \approx 0.74 \text{ \AA}^{-1}$ position aligns best with FA₂PbI₄, its low intensity, delayed onset, and partial overlap with perovskite reflections preclude a definitive structural assignment. A zoomed-in view of the 90 °C profile is presented in **Figure S5** to emphasize this feature. Its emergence is likely to reflect localized reorganization of residual PbI₂ and FAI into layered structures, favored by high-temperature processing where evaporation and incomplete interdiffusion dominate.

Thus, while δ -phase formation is suppressed at 90 °C, complete crystallization is not achieved. The reduced α -phase growth compared to 70 °C supports the interpretation that excessive PbI₂ pre-crystallization impedes full conversion. This is further corroborated by the more persistent PbI₂ intensity in **Figure 2g-h** and **Figure 3a**. Collectively, these results highlight the need for a balanced thermal processing window that enables rapid nucleation while preserving sufficient precursor mobility—avoiding both δ -phase emergence and premature PbI₂ crystallization that limit α -phase yield.

These results highlight a non-monotonic trend in early α -phase formation: the intensity reached at the end of spin coating increases from 45% at 30 °C to 55% at 50 °C and peaks at 60% at 70 °C, before declining to 50% at 90 °C (**Figure 3b**). This trend reflects the dual role of temperature: modest heating promotes rapid precursor interdiffusion and nucleation, while excessive heating accelerates premature PbI₂ crystallization, restricting ion transport and hindering full conversion, even in the absence of δ -phase formation. These insights conclude our analysis of kinetic

evolution, setting the stage for understanding how these pathways affect film texture and orientation.

To quantitatively assess the temperature-dependent crystallization kinetics revealed by in situ GIWAXS, the time evolution of the integrated diffraction intensities associated with the α -phase perovskite and PbI_2 was analyzed using a Johnson–Mehl–Avrami–Kolmogorov (JMAK) framework.^[73,74] The peak intensity of a specific phase was fitted as a function of time to extract effective crystallization rate constants (k) and Avrami exponents (n) for both the spin-coating and annealing stages (**Figure S7** and **Tables S2–S3**, Supporting Information). We emphasize that this analysis is employed to compare relative kinetics under identical experimental conditions, rather than to infer strict rate-limiting steps. During the spin-coating stage, the extracted rate constants (k) for α -phase formation increase monotonically with temperature, indicating accelerated initial appearance of the perovskite phase at elevated temperatures. In contrast, the corresponding Avrami exponents (n) decrease systematically with increasing temperature. At 30 °C, the Avrami exponent is close to unity ($n \approx 1$), which is consistent with a diffusion-controlled conversion process in which FA^+/MA^+ ions can readily infiltrate an amorphous and permeable PbI_2 precursor, enabling continuous and spatially uniform perovskite growth throughout the film.

At higher spin-coating temperatures (50–90 °C), the Avrami exponent falls below unity ($n < 1$), indicating deviation from ideal diffusion-controlled growth. Such reduced effective exponents have been reported in perovskite systems when diffusion pathways become partially blocked or when intermediate or competing phases form and must first decompose before further perovskite growth can proceed.^[75] In the present case, this behavior correlates directly with the premature crystallization and texturing of the PbI_2 precursor observed in situ, as well as the emergence of secondary phases at intermediate temperatures, both of which restrict FA^+/MA^+ transport and confine perovskite formation to localized regions rather than the entire film volume.

A similar mechanistic trend is observed during the annealing stage. While the effective rate constant for α -phase growth exhibits a non-monotonic temperature dependence, reaching a maximum for films processed at intermediate spin-coating temperatures (50–70 °C) and decreasing at 90 °C, the Avrami exponent remains well below unity at elevated temperatures. This behavior indicates that annealing-driven crystallization is governed not simply by thermal activation, but by the need to overcome structural constraints inherited from the precursor state,

including PbI_2 crystallinity and residual intermediate phases. Notably, the reduced growth rate at 90 °C persists despite suppression of δ -phase formation, demonstrating that PbI_2 crystallinity itself constitutes an independent kinetic barrier to complete α -phase conversion.

Analysis of the PbI_2 peak evolution further supports this interpretation. At elevated temperatures, PbI_2 formation occurs rapidly and its subsequent consumption deviates from ideal JMAK behavior, reflecting competing processes associated with perovskite conversion and structural reorganization rather than a single-step transformation. Collectively, the kinetic analysis provides quantitative support for the non-monotonic crystallization pathway identified by in situ GIWAXS and confirms that early-stage thermal control during spin coating governs the balance between diffusion-enabled growth and growth inhibition by precursor crystallinity and intermediate phases.

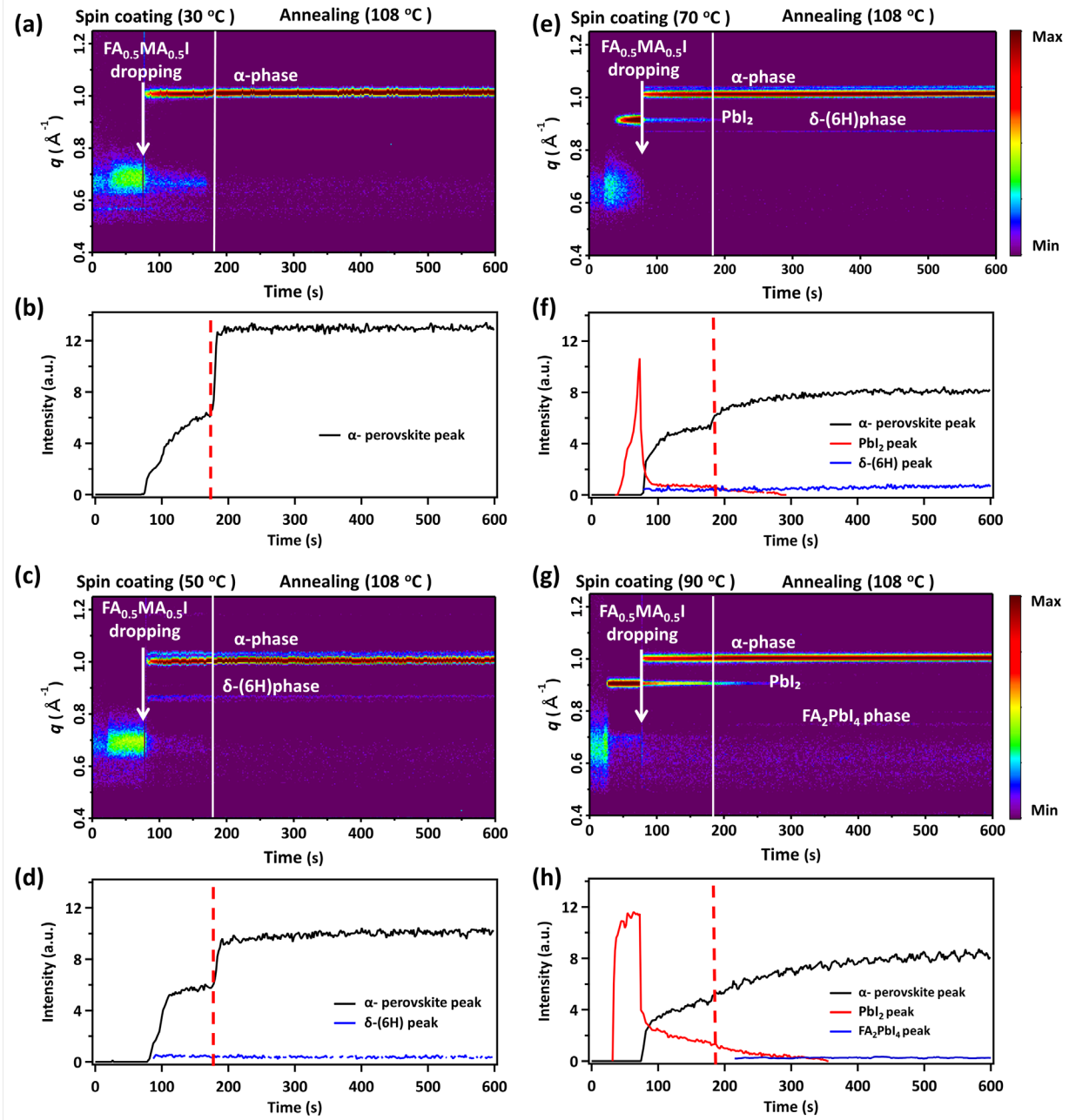


Figure 2. In situ GIWAXS analysis of crystallization dynamics during two-step deposition of $\text{FA}_{0.5}\text{MA}_{0.5}\text{PbI}_3$ at various spin-coating temperatures. GIWAXS contour plots recorded at (a) 30 °C, (c) 50 °C, (e) 70 °C, and (g) 90 °C show scattering intensity (color scale) as a function of time (horizontal axis) and scattering vector q (vertical axis). The vertical arrow indicates the drop of the $\text{FA}_{0.5}\text{MA}_{0.5}\text{I}$ solution. Each panel is divided at ~180 s to separate the spin-coating stage (left) from post-deposition annealing at 108 °C (right). Corresponding kinetic analyses of phase

evolution extracted from GIWAXS are shown in (b) 30 °C, (d) 50 °C, (f) 70 °C, and (h) 90 °C. The vertical red dashed line marks the onset of annealing.

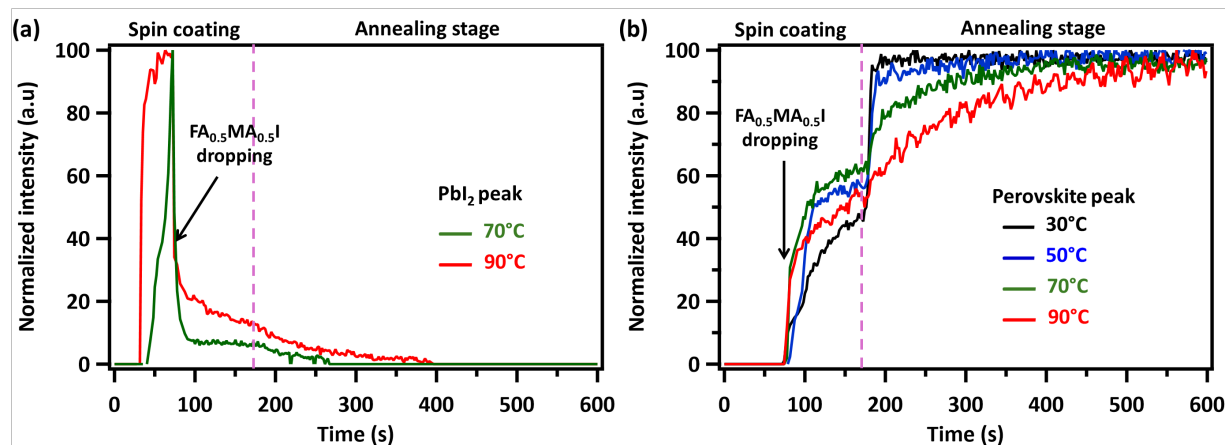


Figure 3. Kinetic analysis of phase evolution during two-step $\text{FA}_{0.5}\text{MA}_{0.5}\text{PbI}_3$ formation. (a) Direct comparison of the PbI_2 peak intensity ($q \approx 0.92 \text{ \AA}^{-1}$) at 70 °C (blue) and 90 °C (red) shows enhanced PbI_2 stability at 90 °C, confirming that pre-crystallized PbI_2 resists FA/MA cation infiltration. (b) Overlay of the α -perovskite peak intensity ($q \approx 1.0 \text{ \AA}^{-1}$) for all four temperatures highlights the non-monotonic temperature dependence: early α -phase formation improves from 30 °C to 70 °C but declines at 90 °C due to the kinetic barrier imposed by a highly ordered PbI_2 precursor.

2.3 Temperature-Dependent Film Texture and Phase Evolution at Discrete Processing Stages

The structural pathway from PbI_2 to perovskite is not only governed by kinetics but also imprints a temperature-dependent crystallographic texture onto the final film. Static 2D GIWAXS patterns in **Figure 4** reveal how the spin-coating temperature affects both the intermediate PbI_2 structure and the orientation of the resulting $\text{FA}_{0.5}\text{MA}_{0.5}\text{PbI}_3$ films. These measurements were collected at three key processing stages: immediately after PbI_2 deposition, directly after $\text{FA}_{0.5}\text{MA}_{0.5}\text{I}$ application, and following annealing at 108 °C.

At 30 °C (**Figure 4a**), the PbI_2 layer shows a diffuse, featureless halo, consistent with a fully amorphous structure. After $\text{FA}_{0.5}\text{MA}_{0.5}\text{I}$ deposition and subsequent annealing, the perovskite reflections emerge as circular, isotropic diffraction rings, indicating an orientation-random, polycrystalline α -phase. The absence of angular intensity variation across q_{xy} and q_z confirms that the grains are randomly oriented, consistent with uniform cation infiltration and homogeneous

conversion. Similarly, the PbI₂ layer deposited at 50 °C (**Figure S6b**, Supporting Information) remains largely amorphous, though with slightly increased diffuse scattering, indicating the onset of local ordering. The resulting perovskite still shows predominantly isotropic diffraction features, suggesting that the film retains a mostly random texture with only minor signs of preferential alignment beginning to emerge.

In contrast, the PbI₂ layer deposited at 70 °C (**Figure 4b, left plot**) already exhibits a sharp diffraction ring at $q \approx 0.92 \text{ \AA}^{-1}$ in the out of plane direction, revealing crystallinity in PbI₂ layer and a degree of out of plane alignment. After conversion, the resulting α -phase diffraction arcs are no longer isotropic but show intensity concentration along the out of plane directions (**Figure 4b, middle and right plots**). This preferred orientation suggests that grain growth is guided along pre-existing crystalline domains in the PbI₂ layer. The persistence of PbI₂ reflections and the emergence of δ -phase features after annealing, also visible in **Figure S6c** (Supporting Information), further support the conclusion of incomplete conversion and phase competition at this intermediate temperature.

This trend becomes more pronounced at 90 °C (**Figure S6d**, Supporting Information), where the PbI₂ layer is even more crystalline and displays sharper, more anisotropic diffraction features before and after perovskite conversion. Although no δ -phase is observed at this temperature, the final film shows strong texturing and residual PbI₂ peaks, indicating that excessive precursor crystallinity inhibits complete transformation. The combination of high crystallinity and reduced cation diffusivity leaves portions of the PbI₂ network unconverted, limiting phase purity despite the suppression of δ -phase formation.

These GIWAXS observations support the conclusion that spin-coating temperature directly dictates the initial microstructure and resulting texture of the perovskite film. Amorphous PbI₂ scaffolds promote uniform nucleation and isotropic grain orientation, while crystalline PbI₂ induces preferential alignment and restricts ion access, resulting in texture-driven anisotropy, incomplete conversion, and in some cases, δ -phase formation.

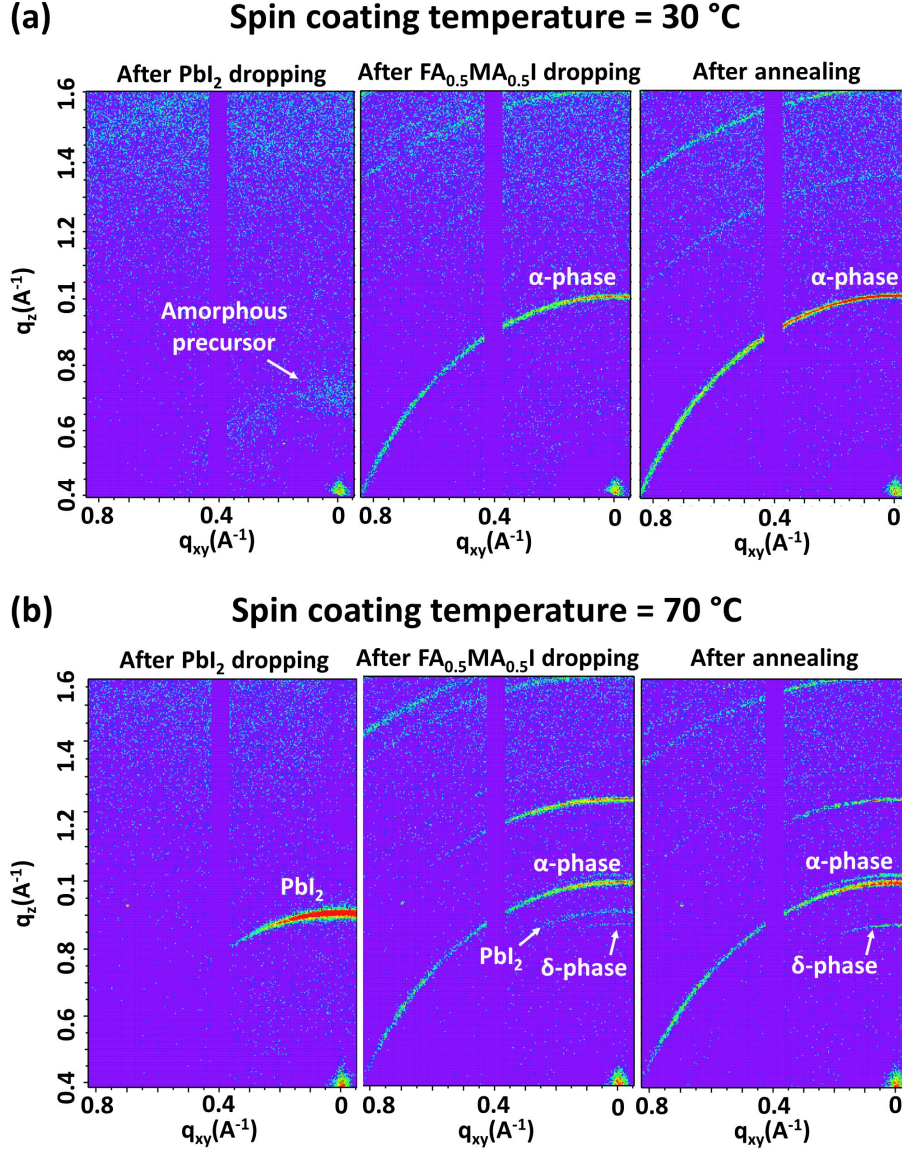


Figure 4. Static 2D GIWAXS snapshots acquired at key stages of two-step FA_{0.5}MA_{0.5}PbI₃ fabrication. (a) 30 °C route: (left) immediately after PbI₂ deposition, displaying only a diffuse halo that signifies an amorphous precursor; (center) after FA_{0.5}MA_{0.5}I spin coating, where a sharp diffraction arc ($q \approx 1.0 \text{ \AA}^{-1}$) marks rapid nucleation of the α -perovskite; (right) after a 108 °C anneal, showing a single intensified perovskite ring and no detectable PbI₂ reflections. (b) 70 °C route: (left) PbI₂ layer already exhibits a pronounced ring at $q \approx 0.92 \text{ \AA}^{-1}$, evidencing partial crystallinity; (center) FA_{0.5}MA_{0.5}I deposition yields coexisting perovskite ($q \approx 1.0 \text{ \AA}^{-1}$) and residual PbI₂ diffraction; (right) post-anneal pattern retains weak PbI₂ features and reveals preferential orientation of the perovskite lattice, illustrating how pre-crystallized PbI₂ influences

subsequent phase evolution. Intensity is plotted on a logarithmic color scale; axes correspond to in-plane (q_{xy}) and out-of-plane (q_z) momentum transfer.

2.4 Temperature-Dependent Morphology and Device Performance

Top-view Scanning Electron Microscopy (SEM) imaging was performed to visualize the morphological consequences of the temperature-dependent crystallization pathways revealed by in situ GIWAXS. As shown in **Figure 5a**, films fabricated at a spin-coating temperature of 30 °C exhibit a compact and homogeneous microstructure composed of closely packed, well-defined grains with minimal voids or cracks. This morphology is consistent with the in situ GIWAXS results, which indicate an initially amorphous PbI_2 layer that enables uniform FA^+/MA^+ interdiffusion and complete α -phase conversion during annealing. At an intermediate temperature of 50 °C (**Figure 5b**), the film morphology becomes less uniform, with reduced grain definition and the emergence of microcracks and surface roughness. This evolution correlates with the onset of competing crystallization pathways observed in the GIWAXS measurements, where accelerated α -phase nucleation is accompanied by partial formation of secondary phases, leading to spatially nonuniform conversion.

At higher spin-coating temperatures of 70 °C and 90 °C (**Figure 5c,d**), the films exhibit increasingly heterogeneous morphologies characterized by pronounced roughness, irregular grain growth, and the formation of voids and poorly connected domains. These features are consistent with premature PbI_2 crystallization identified in situ, which restricts FA^+/MA^+ interdiffusion and limits complete perovskite conversion. Overall, the SEM images in **Figure 5** provide direct real-space confirmation that the non-monotonic crystallization behavior revealed by in situ GIWAXS translates into distinct microstructural outcomes, highlighting the importance of maintaining a disordered and permeable PbI_2 scaffold during early-stage film formation.

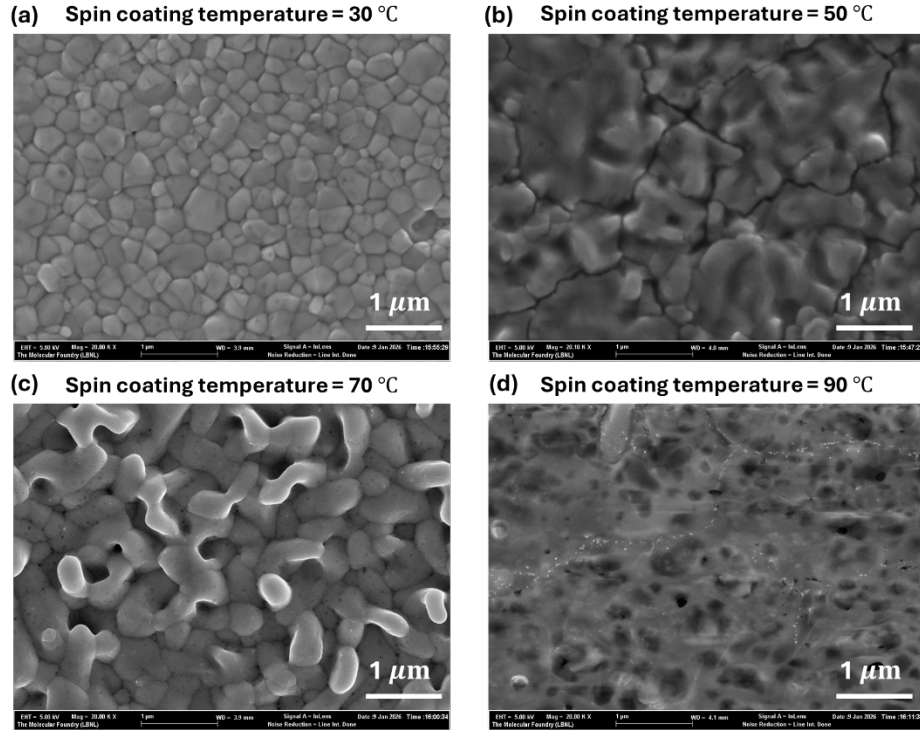


Figure 5 Top-view SEM images of $\text{FA}_{0.5}\text{MA}_{0.5}\text{PbI}_3$ films fabricated at spin-coating temperatures of (a) 30 °C, (b) 50 °C, (c) 70 °C, and (d) 90 °C. The films exhibit a clear temperature-dependent morphological evolution, transitioning from compact and uniformly packed grains at low temperature to increasingly heterogeneous and porous morphologies at elevated temperatures.

To connect the temperature-dependent crystallization pathways identified by in situ GIWAXS with device-relevant film quality, photovoltaic performance was evaluated for solar cells fabricated under laboratory conditions. Device fabrication was performed using substrate preheating prior to $\text{FA}_{0.5}\text{MA}_{0.5}\text{I}$ deposition, which reproduces the same nominal temperature conditions but does not employ continuous temperature control during spin coating. Representative J–V curves are shown in **Figure 6a**, photographs of representative devices are shown in **Figure 6b**, and the corresponding performance metrics are summarized in **Table S4**.

Devices fabricated at the lowest preheating temperature show the best performance. At 30 °C, the average device exhibits $\text{PCE} = 16.22 \pm 0.66\%$, with $J_{sc} = 23.13 \pm 0.07 \text{ mA cm}^{-2}$, $\text{FF} = 65.26 \pm 2.14\%$, and $V_{oc} = 1.074 \pm 0.013 \text{ V}$ (**Table S4**). Increasing the preheating temperature to 50 °C leads to a moderate decrease ($\text{PCE} = 14.22 \pm 0.92\%$, $J_{sc} = 21.88 \pm 0.16 \text{ mA cm}^{-2}$, $\text{FF} = 61.15 \pm 3.34\%$, $V_{oc} = 1.062 \pm 0.014 \text{ V}$). At higher temperatures, performance degradation becomes

pronounced: 70 °C yields $\text{PCE} = 10.87 \pm 0.39\%$ with a strong FF reduction ($\text{FF} = 50.29 \pm 1.27\%$), and 90 °C further decreases to $\text{PCE} = 9.50 \pm 0.98\%$ ($\text{FF} = 46.84 \pm 3.50\%$) alongside reduced J_{sc} (**Table S4**). These trends are consistent with the SEM observations (Figure 5), where compact, well-connected morphologies at low temperature transition to increasingly heterogeneous and porous films at elevated temperatures, which can hinder long-range charge transport and increase series/shunt losses.

The optical appearance of the devices (**Figure 6b**) provides additional qualitative evidence of temperature-dependent film uniformity and conversion. Films prepared at 30 °C appear uniformly dark/black, whereas films fabricated at higher temperatures show progressively faded and non-uniform coloration (e.g., brown/red regions at 70 °C and orange-toned regions at 90 °C). Such color inhomogeneity is consistent with spatially heterogeneous conversion and/or the presence of residual non-perovskite inclusions (e.g., precursor-rich or secondary-phase regions), in agreement with the structural and morphological trends inferred from in situ GIWAXS and SEM.

Steady-state PL spectra (**Figure S8**) show an increase in PL intensity with increasing processing temperature. Importantly, higher PL does not necessarily translate into improved device performance: isolated or weakly connected crystalline domains can exhibit enhanced PL due to carrier confinement and reduced extraction, which favors radiative recombination, even while macroscopic connectivity and charge collection degrade. Therefore, the coexistence of higher PL at elevated temperature with lower FF/PCE is consistent with a film that contains locally well-crystallized domains but suffers from increased morphological discontinuity and spatially heterogeneous conversion. Overall, the combined SEM (**Figure 5**) and device data (**Figure 6**) demonstrate that early-stage thermal processing governs not only local crystallinity but also large-area film continuity and conversion uniformity, which ultimately control device-level charge extraction and photovoltaic performance.

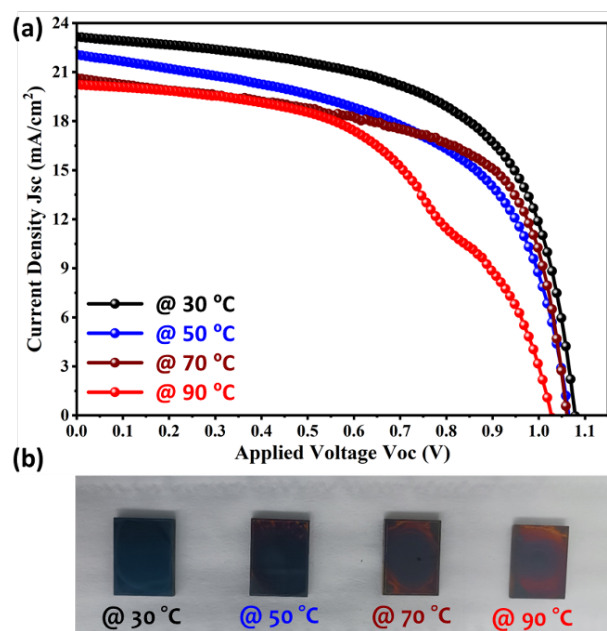


Figure 6 Temperature-dependent photovoltaic performance of FA_{0.5}MA_{0.5}PbI₃ solar cells fabricated using a two-step deposition protocol with substrate preheating prior to FA/MAI deposition. (a) Representative current–voltage (J–V) curves measured under simulated AM 1.5G illumination for devices processed at different preheating temperatures of 30 °C, 50 °C, 70 °C, and 90 °C. (b) Optical photographs of representative films, showing a progressive change from uniformly dark films at low temperature to increasingly non-uniform coloration at elevated temperatures.

2.5 The effect of PbI₂ structure on the α -phase crystallization mechanism

The GIWAXS analysis confirms that the microstructure of the PbI₂ layer, determined by spin-coating temperature, plays a pivotal role in directing cation infiltration, phase evolution, and overall film quality. At lower spin-coating temperatures, the PbI₂ layer remains amorphous, promoting more uniform FA⁺/MA⁺ diffusion and complete α -phase formation. Conversely, high temperatures induce premature PbI₂ crystallization, creating a dense and rigid framework that restricts interdiffusion and limits perovskite conversion. This mechanistic picture is illustrated schematically in **Figure 7**, which captures both the spin-coating and annealing stages across low and high temperature regimes, as well as the resulting microstructural outcomes.

This mechanistic picture is illustrated schematically in **Figure 7**. In the top panel of **Figure 7a**, a low-temperature spin-coating condition produces a loosely packed, amorphous PbI₂ layer

containing abundant voids and grain boundaries. FA^+ and MA^+ cations (green arrows) readily infiltrate this porous network, allowing the lattice to reorganize into a homogeneous, orientation-random α -perovskite. Notably, this amorphous state may also reflect the retention of coordinated solvent molecules, including both DMSO and DMF, which are known for their strong coordination with Pb^{2+} .^[55–57] At low temperatures and short spin times, solvent evaporation is incomplete, leading to solvent-rich films. Several prior studies have reported the persistence of DMSO in PbI_2 layers after spin coating and before annealing, with in-situ XRD and FTIR showing solvent- PbI_x complexation that delays crystallization and stabilizes intermediate phases.^[76,77] The bottom panel of **Figure 7a** shows the result of annealing: a uniform and fully converted α -phase perovskite film, with no evidence of residual PbI_2 or secondary phases, consistent with the in situ GIWAXS data.

In contrast, the top panel of **Figure 7b** depicts a PbI_2 layer formed at higher spin-coating temperatures. Here, rapid solvent evaporation and thermal activation lead to premature PbI_2 crystallization. The resulting close-packed lattice has limited free volume and few accessible pathways for A-site cation infiltration (indicated by red arrows with $\times$ symbols), confining conversion to isolated grain boundaries. The bottom panel of **Figure 7b** illustrates the resulting annealed film, where incomplete α -phase conversion is accompanied by unreacted PbI_2 (highlighted in darker domains) and the formation of secondary impurity phases. These include parasitic δ -phase domains at intermediate temperatures (e.g., 70 °C) and potentially layered FA_2PbI_4 at 90 °C, as identified in GIWAXS (**Figures S4–S5**). This structural heterogeneity arises from restricted ion mobility and premature PbI_2 crystallization during spin coating.

Together, these results establish that the spin-coating temperature exerts a dual influence: it not only dictates the initial structural state of the PbI_2 layer but also governs the balance between desired α -phase growth and undesired impurity formation. Achieving phase-pure, defect-lean perovskite films therefore requires thermal conditions that maintain a disordered, permeable PbI_2 network during spin coating, enabling uniform cation interdiffusion and suppressing kinetic traps. This understanding bridges early-stage crystallization pathways with final film morphology and informs a practical processing window for high-performance perovskite solar cells.

While the specific temperature window identified in this study is tied to the processing conditions examined here, the observations suggest broader implications for two-step perovskite deposition. Effective conversion in two-step fabrication is expected to benefit from a first precursor layer that

remains sufficiently disordered and permeable, enabling interdiffusion during the second deposition step. Based on these observations, we propose that processing conditions which sustain ionic mobility may favor more uniform conversion, whereas excessive early-stage heating may accelerate precursor crystallization and partially restrict interdiffusion, leading to heterogeneous film formation; this mechanistic consideration may be broadly applicable across different two-step coating approaches and material formulations. Although different deposition methods can introduce additional factors that influence crystallization dynamics, these results highlight the potential importance of managing early-stage precursor crystallinity in two-step fabrication. Further studies will be required to assess the generality of these effects under different processing conditions.

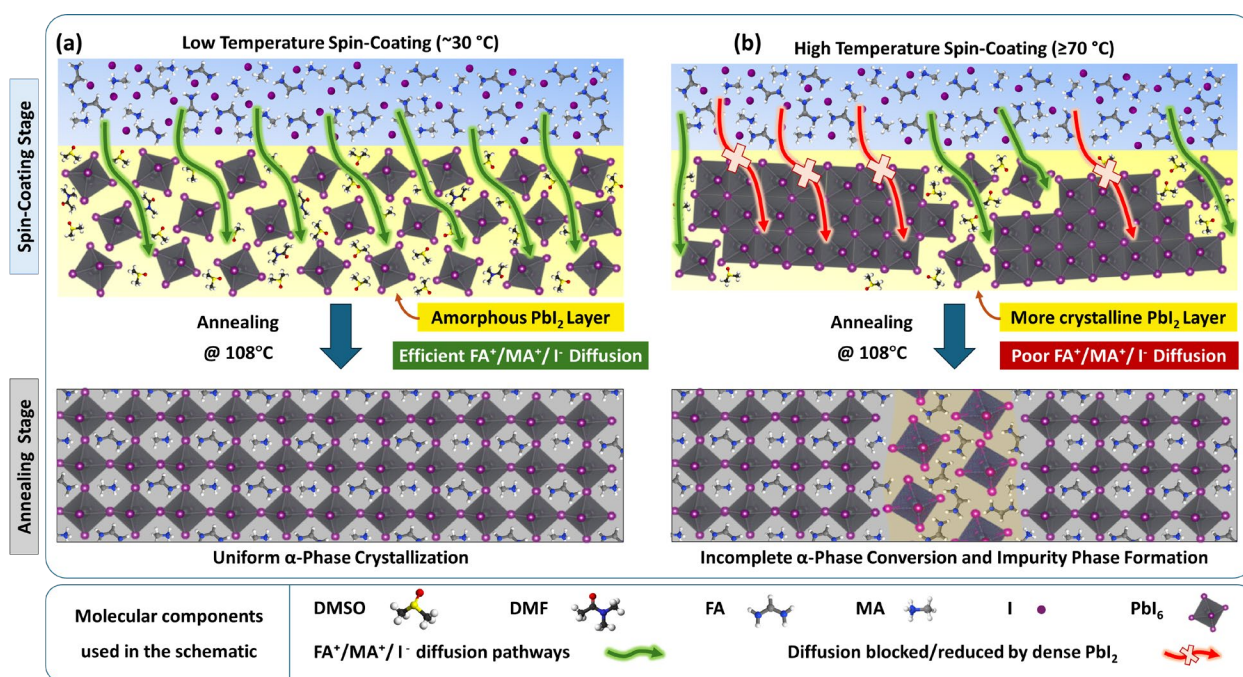


Figure 7. Multiscale schematic illustrating how spin-coating temperature governs precursor diffusion and phase evolution in two-step perovskite film formation. (a) At low spin-coating temperature ($\sim 30^\circ\text{C}$), the PbI_2 layer remains amorphous, permitting efficient $\text{FA}^+/\text{MA}^+/\text{I}^-$ diffusion during the second step, resulting in complete α -phase conversion upon annealing at 108°C . (b) At higher temperatures ($\geq 70^\circ\text{C}$), PbI_2 crystallizes prematurely, restricting interdiffusion and hindering full conversion. At intermediate temperatures, this leads to δ -phase (6H) formation. At 90°C , δ -phase is suppressed, but a weak FA_2PbI_4 impurity phase emerges, suggesting local off-stoichiometric reorganization from unreacted precursors. These outcomes

highlight distinct kinetic traps and impurity pathways that limit phase purity at elevated temperatures.

3. Conclusion:

This study integrates large-scale device data analysis with in-situ structural characterization to first identify the most important features affecting power conversion efficiency, and second, to understand how processing conditions influence crystallization pathways in FA_{0.5}MA_{0.5}PbI₃ films prepared by two-step deposition. A decision tree regressor trained on nearly 39,000 reported devices identified solvent choice and thermal conditions as among the most impactful fabrication parameters linked to power conversion efficiency (PCE). The data also reaffirmed the critical role of antisolvent-induced quenching, which strongly governs film quality in one-step deposition and is functionally mirrored in two-step protocols by the rapid crystallization triggered when FA_{0.5}MA_{0.5}I in IPA is dropped onto PbI₂.

Motivated by these trends, in-situ GIWAXS experiments were performed to reveal how spin-coating temperature influences phase evolution and film formation. The developed temperature-controlled spin-coating setup enabled precise control of thermal conditions during deposition, allowing us to isolate early-stage crystallization events from post-deposition annealing. At low temperatures (30 °C), the PbI₂ layer remains amorphous and solvent-rich, allowing for efficient diffusion of FA⁺/MA⁺ cations and complete α -phase conversion upon annealing. At intermediate (50 °C) and high (70–90 °C) temperatures, however, the PbI₂ layer either crystallizes prematurely or promotes the emergence of non-perovskite phases, restricting precursor interdiffusion and leading to residual unconverted PbI₂. Quantitative time-resolved kinetic analysis further reveals a non-monotonic crystallization behavior, in which increasing temperature accelerates early crystallization onset while constraining sustained growth. These outcomes are rooted in diffusion-limited access to Pb²⁺ centers once the PbI₂ matrix becomes rigid or textured.

Mechanistically, the results establish that maintaining an amorphous, permeable PbI₂ scaffold, through controlled spin-coating temperature and the immediate introduction of the FA_{0.5}MA_{0.5}I precursor before solvent evaporation completes, is essential for achieving phase-pure, defect-lean, and orientation-random perovskite films. This solvent-rich intermediate state mimics the function of antisolvent quenching in one-step routes, offering a comparable strategy to control nucleation

and promote uniform crystal growth in two-step fabrication. Temperature-dependent SEM, device performance, and photoluminescence measurements confirm that early-stage crystallization pathways directly translate into differences in morphology, charge-transport continuity, and photovoltaic performance. Rather than relying on post-deposition optimization, the developed setup enabled us to demonstrate that early-stage microstructural control emerges as a robust and scalable design rule for advancing perovskite solar cell performance. While the specific temperature window explored here is tied to the processing conditions studied, the mechanistic insights provide a general framework for understanding early-stage crystallization control in two-step perovskite fabrication.

4. Experimental section:

Data mining and feature engineering: We downloaded the complete device-level dataset (version 5.4) from *perovskitedatabase.com* (accessed May 10, 2025), which compiles perovskite solar-cell records extracted from the literature. To ensure data quality, we restricted the dataset to single-junction devices by excluding entries with reverse-scan PCE > 27%. This conservative cutoff eliminates likely tandem or concentrator devices and extreme outliers, retaining 38,912 plausible single-junction records. The dataset includes both continuous and categorical variables. For preprocessing, categorical variables (e.g., stack-related fields) were one-hot encoded, resulting in separate binary columns to ensure the model treats them numerically without assuming ordinal relationships. Continuous variables were kept in their original numerical format. All data preprocessing and modeling steps were performed in Python. **Figure 1a** shows the full pipeline used for model building. All preprocessing and modelling were executed in Python. To ensure full reproducibility, the complete Python code used for data preprocessing, feature encoding, model training, and feature-importance analysis is publicly available at GitHub.^[78]

Model training: We used a decision tree regressor as our ML model to predict PCE from the engineered feature matrix (one-hot encoded). Given the large number of features in our dataset, the decision tree was selected for its inherent interpretability and efficient handling of high-dimensional, multi-category features without the need for computationally expensive preprocessing.^[79, 80] To justify this selection, we performed a benchmarking analysis against Random Forest and Linear Regression models, summarized in **Table S1** of the Supporting Information. While the Random Forest model achieved a slightly higher R² of 0.72 compared to

0.60 for the Decision Tree, it required significantly more computational resources for a marginal improvement in performance. Conversely, Linear Regression performed poorly ($R^2 = -0.52$), failing to capture the dataset's non-linear complexities. Both the Decision Tree and Random Forest models identified "Perovskite deposition quenching media" as the primary top feature, confirming the robustness of our feature ranking and the suitability of the decision tree for guiding experimental prioritization. Additionally, decision trees are highly efficient when dealing with datasets that contain both categorical and continuous variables, as they can handle multi-category features (such as those generated by one-hot encoding) without the need for computationally expensive preprocessing or assumptions about feature relationships. Although more advanced models may offer higher predictive accuracy, they often require more complex data transformations. They are less interpretable, which can be a limitation when the goal is to prioritize experimental variables. Given the large number of features in this dataset, a decision tree strikes a balance between model complexity and interpretability, making it the most suitable option for this study.^[79, 81] After training, we extracted the model's built-in feature importance scores, which quantify each feature's contribution to reducing the split criterion (e.g., mean squared error). This method of calculating feature importance is intrinsic to decision trees and provides clear, interpretable insights. By ranking these features by importance, we identified which had the most significant influence on PCE, providing a data-driven basis for prioritizing subsequent experimental investigations. This analysis supports transparent decision-making in experimental design by directly highlighting the most influential parameters.

Materials: Lead iodide (PbI_2 , 99.99% purity) was supplied by TCI. The organic halide salts, formamidinium iodide (FAI) and methylammonium bromide (MAI), were acquired from Greatcell Solar. Solvents including dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.8%), isopropyl alcohol (IPA, 99.9%), ethanol (EtOH, anhydrous, 99.8%), and chlorobenzene (CB, anhydrous, 99.8%) were obtained from Sigma-Aldrich (USA). Fluorine-doped tin oxide (FTO) glass (2.2 mm thick) was purchased from Ossila. MeO-2PACz, phenyl-C61-butyric acid methyl ester (PCBM), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were acquired from Ossila. Silver ingots (Ag, 99.8%) were purchased from Well-Being Enterprise Co. were purchased from Sigma-Aldrich. All the chemicals were used as received without further purification. All materials were used as received, without any additional purification steps.

Perovskite Solution Preparation: For solution preparation, we prepared a 1.5M PbI_2 solution in DMF:DMSO (9:1, v:v), equating to 690 mg/mL, by stirring at 80°C overnight. Additionally, we prepared a 0.5M FAI:MAI solution, with concentrations of 43 mg/mL FAI and 39.7 mg/mL MAI, in 1 mL of IPA. All solution preparation and handling were carried out inside a nitrogen-filled glovebox ($\text{O}_2 < 0.1$ ppm, $\text{H}_2\text{O} < 0.5$ ppm).

In-situ Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS): In-situ GIWAXS measurements were conducted during spin coating and thermal annealing using a custom-built spin coater integrated into beamline 12.3.2 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The spin coater is fully enclosed within a sealed nitrogen-filled chamber, ensuring an inert atmosphere during precursor deposition and in situ characterization. The incident X-ray beam, with an energy of 10 keV, was directed at a shallow angle of 1°. Diffraction data were recorded using a DECTRIS Pilatus 1M X-ray detector positioned at an angle of 35° relative to the sample plane and a sample-to-detector distance of approximately 223.9 mm. Data acquisition was performed at a frame rate of 1.875 per s. The resulting images were processed and analyzed using Igor Pro 8 software, supplemented with the NIKA packages.^[82]

The setup enabled precise temperature control during spin coating, allowing measurements at various spinning temperatures (30°C - 90°C) and subsequent thermal annealing at 108°C. The temperature during spin coating was monitored using a Raytek MI3 infrared pyrometer. The pyrometer was independently calibrated prior to the experiments using thermocouple-based reference measurements on a stationary heating stage, as direct thermocouple contact is not feasible during high-speed rotation. To ensure stable and reproducible emissivity for infrared temperature measurements, the heating stage was coated with black paint. Heating was supplied by a BK Precision 1902B power supply (limited to 24 V) and regulated using a PID feedback control loop implemented in LabVIEW, interfaced with the pyrometer and power supply. The reported temperatures of 30–90 °C therefore correspond to the surface temperature of the heating stage on which the substrate is mounted.

To systematically investigate the temperature-dependent crystallization dynamics of $\text{FA}_{0.5}\text{MA}_{0.5}\text{PbI}_3$ films, we employed a two-step sequential deposition protocol (Scheme 1) implemented on the in situ GIWAXS spin-coating platform. In the first step, the PbI_2 precursor solution was spin-coated at 3500 rpm for 19 s to form the initial PbI_2 layer. Immediately after this deposition, the rotation speed was reduced to 100 rpm, and the substrate was heated to the target

temperature (30, 50, 70, or 90 °C) using the temperature-controlled chuck. The sample was held under slow rotation until the temperature stabilized (typically ~ 30–60 s). In the second step, the FA_{0.5}MA_{0.5}I in IPA solution was dispensed onto the PbI₂ layer using an automated pipetting system while maintaining 100 rpm. After complete dispensing, the substrate was immediately accelerated to 3500 rpm and spin-coated for 19 s to initiate conversion to the perovskite phase. The film was then ramped to the annealing temperature (108 °C) and annealed to complete crystallization.

Solar Cell Device fabrication and Characterization: Patterned FTO glasses were cleaned sequentially as follows: using a commercial detergent solution (4% in RO-H₂O) at 70°C for 30 min, RO-H₂O in an ultrasonic bath for 30 min, DI-H₂O in an ultrasonic bath for 30 min, and finally dried with an air-gun and a hairdryer. Fifteen minutes of UV-O₃ treatment were used to eliminate organic pollutants. The hole transport layer (HTL) layer was deposited on the top of glass/FTO substrate at 3000 rpm for 20 s using MeO-2PACz as SAMs then annealed at 125 °C for 20 min. The perovskite films were fabricated via a two-step sequential deposition technique. The PbI₂ precursor was first deposited onto SAM layer using a spin-coating technique at a speed of 3500 rpm for 19 seconds, with a ramp rate of 1000 rpm/sec. Samples were preheated to substrate temperatures of 30–90 °C for 60 s and transferred immediately to the spin coater chuck to deposit the 2nd layer. An equimolar mixed FA_{0.5}MA_{0.5}I solution was introduced onto the preheated PbI₂ layer and spin-coated at the same speed of 3500 rpm for another 19 seconds. The freshly deposited films were then annealed at 108 °C for 20 min. After cooling to room temperature, PCBM layer was spin-coated as ETL at 2000 rpm for 40 s. Then, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) layer as a hole blocking layer was dynamically spin-coated at 3000 rpm for 25 s, and finally silver (90 nm) was thermally evaporated onto the substrates to finish the device fabrication. The device area was defined and characterized as 0.0256 cm² by metal shadow mask.

The optical properties of the films were investigated by measuring steady-state photoluminescence (PL) spectra were recorded using a Quantaaurus-Tau C16361 photoluminescence spectrometer (Hamamatsu, Japan). The current density-voltage (J-V) characteristics of PSCs were evaluated at room temperature using a computer-controlled digital PVIV-1A, 91150V source meter (Keithley, USA). This was done under simulated sunlight (AM 1.5G) generated by a class ABA LED solar simulator (LSH-7320, Newport, USA) at an intensity of 100 mAc^m⁻². A monocrystalline silicon photodiode (KG3, Oriel, USA) was employed to calibrate the light intensity. No light soaking was

applied before scanning. The J-V curves were recorded in both reverse (from 1.2 V forward bias to -0.1 V short circuit) and forward (from 0.1 V to 1.2 V) scan directions, with a step voltage of 100 mV. The illuminated active area during measurements was fixed using a metal photomask of 0.0256 cm².

Scanning Electron Microscopy (SEM): SEM images were collected using a Zeiss Ultra60 at accelerating voltages of 2kV and 5kV. Prior to imaging, 2 nm of Au+Pd was deposited via DC magnetron sputtering using a Denton Desk V sputtering system.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Two-step deposition, spin-coating temperature, in situ GIWAXS, crystallization control, machine learning-guided optimization, metal halide perovskites.

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