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Mapping the polymorphic phase transformations of CsPbI₃ perovskite thin filmsRudolph Holley III, Quinn C. Burlingame[✉] and Yueh-Lin Loo[✉]

Inorganic perovskite CsPbI₃ has a bandgap of 1.7 eV, making it an ideal complementary absorber to Si for integration into tandem solar cells. However, the black, photoactive CsPbI₃ phases are metastable and readily transform into a yellow non-perovskite δ -CsPbI₃ phase at room temperature, posing a significant challenge to long-term device stability. In this study, we investigate the temperature-dependent dynamics of these phase transitions in CsPbI₃ thin films using a combination of *in situ* X-ray diffraction and time-resolved optical microscopy. We find the transformation rate to be highly temperature-dependent, with the fastest conversion occurring at 225 °C, where 50% of the film transformed to δ -CsPbI₃ within 17 minutes. To identify processing temperatures with longer phase-stability windows, we used the time- and temperature-dependent phase dynamics data to generate a time-temperature-transformation diagram for thin film CsPbI₃. Processing near the peak conversion temperature must be completed within two minutes to retain black-phase purity, while processing above 280 °C or below 150 °C provides a much wider processing window with <1% conversion to δ -CsPbI₃ occurring after 10 minutes. Conversely, it may be useful to hold CsPbI₃ solar cells or thin films with phase-stabilizing modifications near 225 °C to accelerate potential phase transitions and maximally stress their stability.

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Introduction

Lead-halide perovskite solar cells (PSCs) have emerged as a promising energy harvesting technology in recent years due to their rapidly increasing solar-to-electric power conversion efficiencies,^{1–5} and the tunable optoelectronic properties and low-cost energy-efficient processability of perovskites.^{1–3} Of particular interest are tandem photovoltaics comprising perovskite top cells with lower bandgap bottom cells, such as Si. Tandems reduce thermalization losses of high-energy photons by absorbing them in a wide bandgap top cell, while transmitting low-energy photons to the bottom cell, resulting in combined efficiencies higher than either sub-cell can achieve alone. An ideal top cell to pair with Si in a tandem cell requires an absorber with a bandgap of approximately 1.7 eV, which can be achieved with hybrid organic–inorganic perovskite alloys and inorganic CsPbI₃.^{6–9} Among these options, CsPbI₃ is a particularly promising candidate for such applications because it lacks volatile organic cations that can lead to thermochemical instability in hybrid PSCs.^{7–11} However, CsPbI₃ is polymorphic as shown in Fig. S1, and its most thermodynamically stable phase at room temperature is its yellow non-perovskite orthorhombic phase (δ -CsPbI₃) with poor optoelectronic properties.

The cubic polymorph (α -CsPbI₃) is only stable at high temperatures (> 320 °C),^{12,13} while the other black photoactive phases of CsPbI₃ (tetragonal β -CsPbI₃ and orthorhombic γ -CsPbI₃) are only metastable at room temperature.¹¹ Thus, even with active layers kinetically trapped in these phases, they will spontaneously convert to δ -CsPbI₃ given time, leading to catastrophic PSC performance degradation.

To address this challenge, considerable research effort has been devoted to understanding the phase behavior of CsPbI₃ and to stabilizing β - and γ -CsPbI₃ at room temperature.^{14–18} Calculations from Zhao *et al.* suggest that γ -CsPbI₃ can be stabilized by reducing the size of CsPbI₃ grains to ~100 nm, which sufficiently increases their surface area-to-bulk ratio.¹⁹ Our group has since integrated this nanocrystalline morphology into highly stable PSCs with projected lifetimes >50 000 hours of continuous operation, though this lifetime came at the expense of reduced power-conversion efficiency compared to PSCs comprising large-grain CsPbI₃ active layers.^{20–22} It has also been observed that the interfacial strain between CsPbI₃ and underlying transport layers has a significant role in governing phase transition rates.^{16,17,23–25} For example, Liu *et al.* reported that β -CsPbI₃ films could be phase stabilized by depositing a thin organic layer between the perovskite and the underlying electron transport layer.²⁵ Previous studies have also mapped the equilibrium phase transitions of CsPbI₃ powders (including solid-state synthesis routes and decomposition pathways at elevated temperatures in the presence

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of oxygen)—for instance, prior work on CsPbI_3 powders revealed rapid synthesis at 400 °C but eventual decomposition into Cs_4PbI_6 over longer timescales,¹² while thermal degradation studies in air highlighted instability above 350–400 °C due to oxidation and phase segregation.²⁶

In this study, we detail the time- and temperature-dependent kinetics of CsPbI_3 phase transitions in a device-relevant thin-film form factor without any phase-stabilizing interventions. We measured the temperature-dependent dynamics of the black CsPbI_3 phases as they transform into δ - CsPbI_3 with *in situ* X-ray diffraction (XRD), and we used time-resolved optical microscopy to measure the propagation velocity of δ - CsPbI_3 grain boundaries as the films transform. Unlike prior *in situ* XRD studies of hybrid perovskites,^{8,27} we isolate the intrinsic behavior of inorganic CsPbI_3 by excluding humidity, oxygen, and permanent organic additives, enabling direct correlation of transformation rates with processing temperatures. Leveraging the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model,^{28–30} we fit the high-temperature CsPbI_3 phase transformation kinetics and extracted the temperature-dependent transformation rate constants and the time until various δ - CsPbI_3 conversion fractions. Overall, these findings quantify the phase transition kinetics of CsPbI_3 thin films, which can inform processing protocols to access desired phases within experimental time/temperature constraints. CsPbI_3 is particularly prone to rapid phase conversion between 175 °C and 250 °C, as the time to initiate transformation to δ - CsPbI_3 is less than three minutes in this range. Since ensuring long-term phase stability is critical for practical photovoltaic applications, temperatures within this range may be particularly useful for accelerated stress testing.

Results

To quantify the phase transformation dynamics of CsPbI_3 thin films, ~ 500 nm β - CsPbI_3 films were prepared on Si substrates, as described in Methods, and as shown in Fig. 1. We then heated the films to 350 °C to convert them into cubic α - CsPbI_3 and rapidly quenched them to temperatures between 150 °C and 300 °C to produce β/γ - CsPbI_3 , before holding the films isothermally to monitor their phase transition to δ - CsPbI_3 under an optical microscope. Since β - CsPbI_3 and γ - CsPbI_3 have nearly identical optoelectronic properties, we cannot distinguish between these phases here. Thus, we refer to the temperature regimes measured by Marronnier *et al.* (β - CsPbI_3 between 281 °C and 184 °C, with γ - CsPbI_3 at lower temperatures) for their assignments.³¹ As shown in the representative time series of micrographs in Fig. 2a, at 230 °C, spherulites of δ - CsPbI_3 (bright red) grow radially at the expense of the black CsPbI_3 phase. After several minutes, the largest δ - CsPbI_3 spherulites have diameters on the order of millimeters. Tracking the radial growth of these spherulites, we plot their average interface velocity as a function of temperature in Fig. 2b. We find that interface velocity increases with temperature up to 250 °C, where it peaks at 170 mm min^{-1} . Above this temperature, the spherulite interface velocities begin to slow as the thermodynamic driving force for phase transition decreases with increasing temperature.

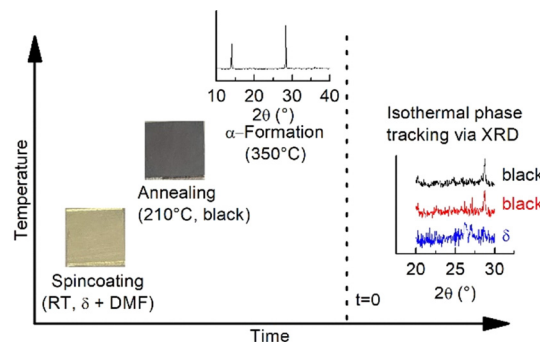


Fig. 1 Diagram showing the temperature and sequence of the processes used to prepare CsPbI_3 thin films for time-dependent isothermal polymorph identification measurements conducted between 150 °C and 300 °C. The image in the lower-left corner of the plot is a photograph of a CsPbI_3 film immediately after spin-coating. To the right of that is an image of a β - CsPbI_3 film immediately after annealing at 210 °C for 5 min. At the top of the figure is an *in situ* XRD plot of α - CsPbI_3 at 350 °C. The rightmost plot shows CsPbI_3 XRD spectra evolving from β - CsPbI_3 to δ - CsPbI_3 after the film was quenched from 350 °C and held isothermally (at 225 °C in this case) for XRD characterization.

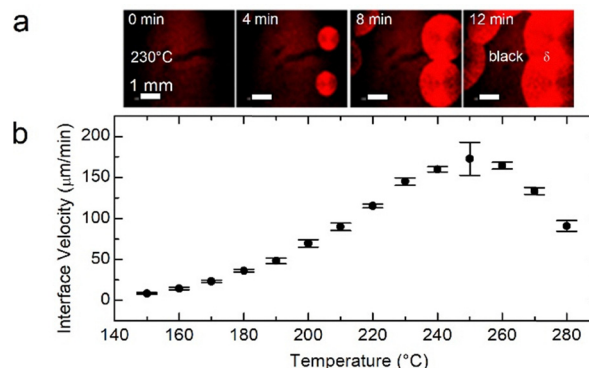


Fig. 2 (a) Optical microscope images showing the phase conversion of a black CsPbI_3 film to δ - CsPbI_3 while held isothermally at 230 °C. A 1 mm scale bar is included on each panel. (b) The temperature dependence of the perovskite (β , or γ)- CsPbI_3 to δ - CsPbI_3 interface velocity derived from time-dependent optical micrographs. Horizontal bars represent the minimum and maximum velocities recorded. At least 3 samples were characterized at each temperature.

To further characterize the extent and kinetics of structural transformations in CsPbI_3 thin films, we employed an *in situ* XRD setup with two heating stages, as described in Methods. As shown in Fig. 1, the absence of peak splitting and low symmetry reflections in the first XRD inset indicates that CsPbI_3 films convert to α - CsPbI_3 upon heating to 350 °C. They were then rapidly transferred onto a heating stage inside the XRD sample chamber, pre-set to a temperature between 25 °C and 300 °C to convert them into metastable β - or γ - CsPbI_3 . The samples were then held isothermally as XRD traces were collected to monitor the diminishing intensity of the (110) reflection of both β - and γ - CsPbI_3 , located at $2\theta = 14.2^\circ$. A representative set of time-dependent XRD spectra is shown in Fig. 3a for a black CsPbI_3 film as it was quenched from 350 °C and held isothermally at 200 °C. Integrating the area under the (110) reflection of



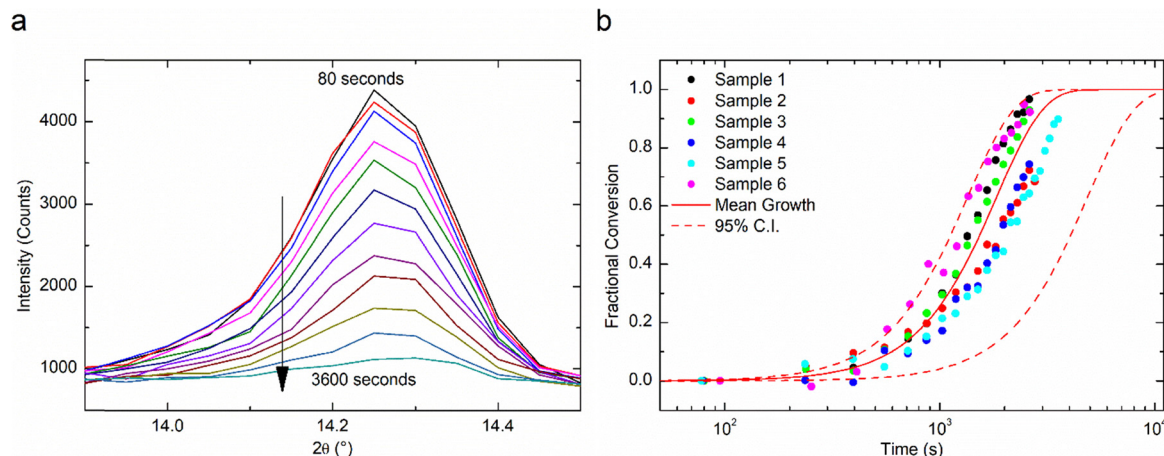


Fig. 3 (a) XRD traces showing the time evolution of the (110) reflection of a β/γ -CsPbI₃ film quenched from 350 °C and held isothermally at 200 °C during measurement. (b) The fraction converted to δ -CsPbI₃ tracked for 6 different perovskite films having undergone quenching from 350 °C and isothermal transformation at 200 °C. The fractional conversion was calculated by integrating the area under the (110) reflection and assuming 0% conversion at the first measurement point. The fractional conversion vs. time curves for each sample were fitted with the JMAK equation by varying the JMAK rate constant and holding the dimensionality constant at two. The solid and dashed lines represent JMAK projections using the mean rate constant and its 95% confidence intervals, respectively.

β/γ -CsPbI₃ in each spectrum and normalizing by the integral of the first spectrum (which we assume represents 0% δ -CsPbI₃) yields the time-dependent fraction of the black CsPbI₃ phase in the film. Subtracting these quantities from unity yields the fraction of the film that has converted to δ -CsPbI₃, as plotted in Fig. 3b. To ensure the robustness and reproducibility of these measurements and to account for sample-to-sample variation, we repeated this same isothermal experiment several times with fresh samples at each temperature, as shown in Fig. 3b, where 6 films were characterized. Similar data collected at other temperatures are plotted in Fig. S2. Samples held at temperatures below 150 °C converted too slowly for *in situ* XRD to be practical. Thus, the 100 °C and 25 °C samples were rested in a N₂ glovebox (on a hot plate in the case of 100 °C) between *ex situ* XRD measurements and photographed with the time stamps shown in Fig. S3. Structural transformation was measurable within 14 hours at 100 °C, and after 41 days at 25 °C. To probe the influence of the substrate in determining phase transformation kinetics, we also quenched CsPbI₃ films from 350 °C to 200 °C on glass substrates coated with indium tin oxide (ITO) and TiO₂ and quantified their phase transformation *via* XRD to compare with the transformation dynamics of CsPbI₃ on Si as shown in Fig. S4. The results show that transformation kinetics are virtually identical on both substrates.

To quantify the phase transition to δ -CsPbI₃, we fit the time-dependent fractional conversion data in Fig. 3b and Fig. S2 using the JMAK equation:

$$f(t) = 1 - e^{-kt^n} \quad (1)$$

where f represents the fraction of the film that has transformed to δ -CsPbI₃, k is the conversion rate constant, t is time, and n denotes the dimensionality and growth constant. The values of k and n are interdependent, and thus small changes to the dimensionality constant can compensate for large changes in the rate constant. To eliminate this interdependency, we note that the spherulite diameters are much larger than the film thickness and nucleation appears to be heterogeneous and instantaneous, as evidenced by similar spherulite radii in Fig. 2a. We therefore fixed the value of the Avrami exponent to $n = 2$, corresponding to 2-dimensional growth.³² A representative fit to the 200 °C transformation kinetics using the JMAK equation with $n = 2$ is shown in Fig. 3b with 95% confidence interval bounds. The JMAK equation fits the CsPbI₃ phase transformation data collected between 150 °C and 300 °C well. The parameters extracted from these fits are reported in Table 1, where transformation rate constants vary from $3.4 \times 10^{-10} \text{ s}^{-2}$ at 300 °C to $6.6 \times 10^{-7} \text{ s}^{-2}$ at 225 °C.

Table 1 Avrami rate constants, 1%, 50%, and 99% conversion times for CsPbI₃ transformations from perovskite phases to the δ -phase. The upper and lower bounds of the 95% confidence interval for each parameter are given in brackets

T (°C)	k	$\times 10^{-7} \text{ (s}^{-2}\text{)}$	t_1	$\times 10^2 \text{ (s)}$	t_{50}	$\times 10^2 \text{ (s)}$	t_{99}	$\times 10^2 \text{ (s)}$
150	0.20	[0.18, 0.23]	7.0	[6.6, 7.5]	59	[55, 62]	150	[140, 160]
175	2.1	[0.32, 3.9]	2.2	[1.6, 5.6]	18	[13, 47]	47	[34, 12]
200	3.0	[0.42, 5.5]	1.8	[1.4, 4.9]	15	[11, 41]	39	[29, 10]
225	6.6	[3.3, 9.9]	1.2	[1.0, 1.7]	10	[8.4, 14]	26	[22, 37]
250	1.8	[0.70, 3.0]	2.3	[1.8, 3.8]	20	[15, 31]	50	[39, 81]
275	0.81	[0.34, 1.3]	3.5	[2.8, 5.4]	29	[23, 45]	75	[60, 120]
300	0.0034	[0.0016, 0.0052]	55	[44, 80.]	450	[370, 660]	1200	[940, 1700]



The time- and temperature-dependent XRD data allow us to generate the time-temperature-transformation (TTT) diagram for CsPbI₃ films shown in Fig. 4. We denote the δ -to- α -CsPbI₃ transformation temperature with a horizontal line at 326 °C based on differential scanning calorimetry data shown in Fig. S5. This is similar to the 320 °C transition temperature reported by Ke *et al.*³³ We also added horizontal lines at 281 °C and 184 °C corresponding to the α - to β -CsPbI₃ and the β - to γ -CsPbI₃ transitions reported by Marronnier *et al.*³¹ The fastest transformation to δ -CsPbI₃ occurred at 225 °C where 1% of the film converted after just under 120 seconds, and 50% of the film converted in 17 minutes. The transformation rate decreased with temperature from 225 °C, with the transformation at 25 °C requiring over a month in N₂ to accumulate an appreciable amount of δ -CsPbI₃, as shown in the photographs in Fig. S3.

Discussion

Previously, Marronnier *et al.* measured the phase transition temperatures between the four CsPbI₃ polymorphs by gradually cooling a powder sample under vacuum at 2.5 °C min⁻¹.³¹ Here, we attempted to more closely replicate the thin-film form factor of practical CsPbI₃ photoactive layers and their fabrication conditions by rapidly quenching thin films from the α -phase.²³ The isothermal nature of our experiments also keeps the energetics (*i.e.*, thermodynamic driving force and probability of hopping over the kinetic barrier) constant over the course of the measurement. We performed our experiments in N₂ to emulate an encapsulated solar cell, as humidity is known to have a significant catalytic effect on CsPbI₃ phase transitions.³⁴ For example, in a study of the atmospheric phase stability of

CsPbI₃, Straus *et al.* demonstrated that γ -CsPbI₃ is kinetically stable in vacuum (>39 days) and dry oxygen (>25 min) but rapidly transforms to δ -CsPbI₃ under humid argon flow (<1 min).³⁴ The absence of δ -CsPbI₃ conversion in vacuum after 39 days is comparable to our finding that a γ -CsPbI₃ film began to convert to δ -CsPbI₃ after 41 days in an inert atmosphere.

The overall phase transformation rate is influenced by several factors, including the transformation driving force and kinetic limitations, which both depend strongly on temperature. The chemical potential difference between the initial and final phases increases with undercooling and causes the transformation rate to increase as the CsPbI₃ film cools below the δ - to α -CsPbI₃ transition temperature. Conversely, as temperature decreases, reduced thermal energy decreases atomic mobility, which causes the transformation to slow. Competition between the driving force and kinetic limits thus governs the phase transformation rate as a function of temperature. As a result of this competition, a peak spherulite boundary velocity is observed in Fig. 2b at 250 °C. The tradeoff between kinetic limitations and transformation driving force is often observed in polymorphic materials that undergo solid–solid phase transformations, such as carbon-containing steels.³⁵ For example, in eutectic steel, austenite transforms slowly into pearlite at temperatures close to the transition temperature (700 °C), slowly into bainite at temperatures (~300 °C) far from the transition temperature, and quickly transforms into bainite at 550 °C. Additionally, we note that previous studies suggest that the internal energy of high-symmetry CsPbI₃ phases is not minimized in a monomorphous state.^{36,37} Rather, these phases contain networks of local symmetry-breaking distortions such as Jahn–Teller distortions,³⁸ octahedral tilting,³⁶ and small shifts in atomic equilibrium positions from the expected Wyckoff positions.^{14,37–39} Because they are local, these patterns are generally not measurable with structural characterization techniques such as XRD.

Another potential source of variance in kinetics is the substrate beneath the CsPbI₃ layer. Here, we primarily employed bare Si due to its atomically smooth surface, chemical inertness, lack of ions and Lewis base/acid sites, and thin amorphous oxide layer, which we thus expect to interact minimally with CsPbI₃. However, we also measured the time-dependent fractional conversion of CsPbI₃ films on glass coated with ITO and TiO₂ for comparison to Si after quenching from 350 °C to 200 °C, as shown in Fig. S4. The CsPbI₃ films deposited on this device-relevant electrode/electron-transport layer exhibited time-dependent fractional conversions that aligned closely with those measured on Si substrates over 6×10^3 s. This suggests that, under these conditions, transformation kinetics are relatively insensitive to substrate roughness, interfacial strain, and chemical interactions. One effect we do observe is that the thermal mass, thickness, and thermal conductivity of the substrate do play a role in how quickly the film heats and converts (*e.g.*, 2.2 mm-thick glass substrates coated with fluorinated tin oxide convert to α -CsPbI₃ more slowly upon heating). In this work, we tried to maximize thermal responsiveness and minimize time before reaching the isothermal setpoints by using thin (<0.7 mm) substrates for all measurements.

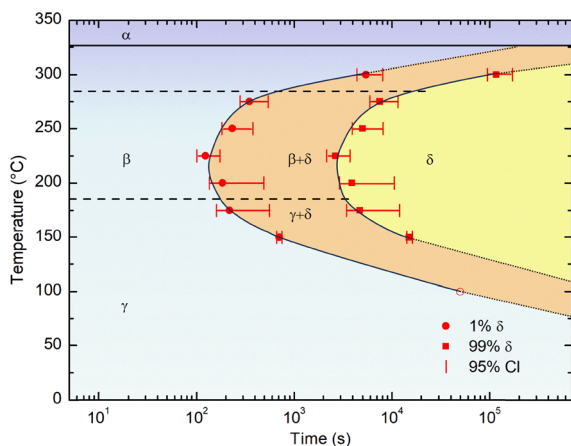


Fig. 4 A time-temperature-transformation diagram for CsPbI₃ thin films. Dashed lines at 281 °C and 184 °C denote temperature limits of β and γ stability, respectively, as reported by Marronnier *et al.*³¹ The solid line at 326 °C marks the δ - α transformation temperature determined by DSC (Fig. S5). Error bars signify the 95% confidence interval, and the extrapolated dotted lines represent linear projections of polymorphic stability limits. The hollow circle at 100 °C signifies a photographed film's approximate onset of δ -CsPbI₃ on a hot plate (Fig. S3).



The overall transformation rate is the product of the δ -CsPbI₃ boundary velocity and nucleation rate (which also results from competition between the driving force and atomic mobility).³⁵ The temperature-dependence of nucleation causes the overall transformation rate to peak at a slightly lower temperature (225 °C in Fig. 4) than the peak boundary velocity (250 °C in Fig. 2b). This peak transformation rate is also reflected in the JMAK fits in Table 1, where a rate of $6.6 \times 10^{-7} \text{ s}^{-2}$ is found at 225 °C. The data represented visually in the TTT can be used to develop processing routes for CsPbI₃ as well as thermally accelerated phase stability testing protocols. Films will begin to transition to δ -CsPbI₃ within ~ 2 minutes at 225 °C, while much longer processing windows are available at both higher and lower temperatures. Similarly, 225 °C is a good temperature to test the efficacy of phase-stabilization schemes under maximum stress. Understanding the kinetic limit-driving force tradeoff is essential for optimizing processing parameters and designing CsPbI₃-based devices with enhanced stability and performance.

Conclusions

In this study, we employed a combination of *in situ* XRD and optical microscopy to study the transformation kinetics of photoactive CsPbI₃ phases into δ -CsPbI₃ in N₂ at temperatures ranging from 150 °C to 300 °C after quenching thin films from 350 °C. We also studied the transformation kinetics of CsPbI₃ films at 100 °C and room temperature using *ex situ* XRD and optical photography. The results of these experiments were used as a basis to create a CsPbI₃ TTT diagram. The peak transition rate occurs at 225 °C, where δ -CsPbI₃ is detected within 120 seconds of quenching from 350 °C, while films aged at room temperature require nearly six weeks to begin transforming. The onset of δ -CsPbI₃ formation in thin films initiates *via* heterogeneous nucleation and grows into spherulitic domains with boundaries that expand at a constant temperature-dependent velocity. The transformation kinetics fit well with the JMAK model, assuming 2-dimensional growth. The results of this study can be used to inform processing routes for photoactive CsPbI₃ films and to identify the highest stress conditions for accelerated phase stability testing of devices comprising CsPbI₃ active layers with various phase-stabilization schemes.

Conflicts of interest

YLL and QCB hold patents and have filed patent disclosures related to perovskite solar cells. QCB has a financial interest in Rayleigh Solar Tech Inc.

Data availability

The data supporting this work are included in the manuscript and SI. See DOI: <https://doi.org/10.1039/d5tc01126d>

Additional raw files are available from the corresponding authors upon reasonable request.

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