Understanding and controlling structural phase transitions in metal halide perovskites is important for designing stable and efficient optoelectronic devices. Using in situ nanoscale cathodoluminescence microscopy, we visualize the thermally driven transition to the perovskite phase in CsPbIBr$_2$ nanowires. Combined with molecular simulation, we reveal that the transformation proceeds despite a substantial energy barrier via ion diffusion through a liquid-like interface between the two structures. While cations disorder in this liquid-like region, the halide ions retain substantial spatial correlations to template the perovskite phase.

HIGHLIGHTS

- Halide ion diffusion mediates CsPbIBr$_2$ double-chain to perovskite phase transition
- EM and in situ CL microscopy of CsPbIBr$_2$ nanowires characterize structural transition
- MD simulation shows disorder yet correlations at interface boundary between phases
- Disorder and diffusion aid to overcome the sizable energy barrier for the transition
Liquid-like Interfaces Mediate Structural Phase Transitions in Lead Halide Perovskites

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SUMMARY

Microscopic pathways of structural phase transitions in metal halide perovskites are difficult to probe because they occur over disparate time and length scales and because electron-based microscopies typically used to directly probe nanoscale dynamics of phase transitions often damage metal halide perovskite materials. Using in situ nanoscale cathodoluminescence microscopy with low electron beam exposure, we visualize nucleation and growth in the thermally driven transition to the perovskite phase in hundreds of non-perovskite phase nanowires. In combination with molecular dynamics simulations, we reveal that the transformation does not follow a simple martensitic mechanism, but proceeds despite a substantial energy barrier via ion diffusion through a liquid-like interface between the two structures. While cations are disordered in this liquid-like region, the halide ions retain substantial spatial correlations. This detailed picture not only reveals how phase transitions between disparate structures can proceed, but also opens the possibility to control such processes.

INTRODUCTION

Metal halide perovskites are promising semiconductor materials for optoelectronics, and are an ideal platform for investigating solid-solid phase transitions. Metal halide perovskites undergo numerous structural phase transitions that affect their optoelectronic properties. One significant structural phase transition is between the perovskite phase and so-called “yellow” non-perovskite phase of CsPbI$_3$. Numerous efforts have aimed to stabilize the perovskite phase of CsPbI$_3$, which is thermodynamically unstable at room temperature and ambient pressure. Much like CsPbI$_3$, the metal halide perovskite material, CsPbBr$_2$, undergoes a thermally driven phase transition from a low-temperature non-perovskite phase (LT-CsPbBr$_2$) to a high-temperature perovskite phase (HT-CsPbBr$_2$) upon heating (Figure 1A). CsPbBr$_2$ is kinetically trapped in the HT-CsPbBr$_2$ phase upon cooling, and the phase transition is therefore typically not reversible, although its transition back to the LT-CsPbBr$_2$ phase can be catalyzed by humidity. This phase transition contributes to the instability of perovskite photovoltaics and has been utilized for generating nanoscale p-n heterojunctions and thermochromic smart window technologies. Despite much interest, the mechanism of this phase transition has not been explained. In contrast to structurally similar perovskite phases known to interconvert, LT-CsPbBr$_2$ and HT-CsPbBr$_2$ are not related by simple elastic deformations. Transitions between these dissimilar lattices thus require a more complex rearrangement of atoms, suggesting the possibility to observe a diffusive transformation and to evaluate the effect of the anharmonic, soft, and ionic nature of the structural transition.
of the material affects its dynamics. \(^{20}\) Additionally, the volume of the material increases by approximately 7\% during the transition from LT-CsPbI\(_3\) to HT-CsPbI\(_3\),\(^{21}\) suggesting that disparate interfacial energies and lattice strain could play an important role in nucleation and growth.

Direct, non-invasive imaging of structural changes is challenging in relatively delicate materials such as metal halide perovskites. For instance, structural phase transitions are often probed using bulk characterization techniques, such as in situ X-ray diffraction (XRD),\(^{22–24}\) yet these techniques average over microscopic dynamics. On the other hand, transmission electron microscopy (TEM) has been used to directly image structural phase transitions with atomic resolution,\(^{25,26}\) yet the high electron beam dose is only compatible with select hard materials and beam-induced damage precludes prolonged imaging of metal halide perovskites. Cathodoluminescence (CL) microscopy uses a focused, scanning electron beam to excite the sample of interest, and the emitted light is collected by a parabolic mirror and directed to a detector to form an image (Figure 1B). Previously, CL microscopy has been used to image steady-state properties\(^{18,27–31}\) and dynamic processes\(^{32,33}\) of metal halide perovskites. Because of the low current and accelerating voltage of the electron beam, sample damage is limited even at relatively high temperatures in comparison with typical TEM studies.\(^{34}\) Compared with optical microscopies, such as photoluminescence (PL) microscopy, the key benefits of CL imaging are its higher spatial resolution, multiscale nature (tens-of-nanometers resolution to hundreds-of-micrometers field of view), and, most importantly, its ability to easily spatially correlate the high-resolution structural information, found in the secondary electron images obtained in tandem, to the optical CL emission maps.

Here we reveal the mechanism of an important yet heretofore elusive non-martensitic, diffusive structural transformation in an ionic alkali metal halide semiconductor on the nanoscale by exploiting differences in CL emission of different crystal structures and combining those observations with molecular dynamics (MD) simulations and coarse-grained models. With low-dose in situ scanning electron CL imaging, we follow the structural transformation in CsPbI\(_3\)\(\_Br_2\) nanowires with high temporal and spatial resolution over a large field of view, allowing the simultaneous characterization of the nucleation and growth kinetics in a statistically significant number of single particles. The multiple scales covered by our experimental observations and modeling enable us to determine the microscopic mechanisms of the structural transformation. We find that both nucleation and growth are characterized by strongly anisotropic kinetics and that the boundary between crystal structures is propagated by activated ion diffusion through a thin, yet finite, liquid-like interface. Despite the overall disorder of the interface, long-range anionic charge density correlations are observed, suggesting that they promote the crystallographic registration of the two crystal phases. Our observations provide a detailed view of the complex dynamic pathways by which two distinct crystal structures interconvert.

**RESULTS AND DISCUSSION**

We use CL imaging with in situ heating to monitor the phase-transition kinetics of CsPbI\(_3\)\(\_Br_2\). Similarly to CsPbI\(_3\) nanowires, single-crystal LT-CsPbI\(_3\)\(\_Br_2\) nanowires were synthesized with the edge-sharing octahedral chains oriented along the long axis of the nanowires, as confirmed by continuous rotation electron diffraction (cRED) (Figure S1). Helpful to this study, the LT-CsPbI\(_3\)\(\_Br_2\) phase has an indirect band gap, resulting in low PL emission, whereas the direct bandgap HT-CsPbI\(_3\)\(\_Br_2\) phase exhibits bright PL emission (Figure 1C). This large difference in emission intensity produces strong contrast

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The combination of the nanowire geometry and the high spatial resolution of CL imaging allows for a quantitative analysis of the phase-propagation rates along the
length of the nanowire. The quasi-one-dimensional sample geometry of the nanowires enables straightforward tracking of a single interphase boundary along a single axis, uncomplicated by grain boundaries or variations in defect concentration found in polycrystalline lead halide perovskite thin films. The transverse wire dimensions are also large enough to study intrinsic properties without introducing quantum confinement effects, and we do not expect the thermodynamics of the phase transition to differ from those of a bulk sample.

Using CL microscopy, we measure a large field of view containing tens to hundreds of these CsPbBr₂ nanowires to build up statistics on nucleation and growth kinetics. A secondary electron (SE) image of a typical field of view is shown in Figure 1D, containing ~150 nanowires that are monitored simultaneously; CL images showing the nanowires before and after the phase transition are shown in Figures 1E and 1F, respectively. The evolution of the nanowires from the LT-CsPbBr₂ to the HT-CsPbBr₂ phase from this larger field of view is depicted in Figure S2A and Video S1. Without heating, we do not observe the phase transition upon repeated CL imaging (Figure S2B). We select individual nanowires from this larger field of view (Figure 1G) and measure phase-propagation rates. Figure 1H shows a time series of simultaneously acquired SE and CL images that illustrate the evolution from LT-CsPbBr₂ to HT-CsPbBr₂ in a single nanowire upon heating. Although no changes are obvious in the SE images, the CL images initially show a nanowire entirely composed of LT-CsPbBr₂ followed by nucleation of the bright HT-CsPbBr₂ phase at the nanowire ends and phase propagation along the length of the wire until the wire is completely converted to HT-CsPbBr₂. The CL intensity as a function of time and distance along the wire axis is shown for this process in Figure S2C. Temperature-dependent in situ XRD before and after the phase transition confirms the presence of the two phases (Figure S3).

Taking advantage of the ability to probe the phase-transition dynamics in many CsPbBr₂ nanowires simultaneously, we provide a statistical analysis of the HT-CsPbBr₂ phase growth rate as a function of temperature. We record the phase-propagation dynamics of a population of nanowires at temperatures ranging from 163°C to 182°C. To do so, we first rapidly increase the stage temperature to a given set point. Stage temperature equilibration occurs fast enough (a few tens of seconds, Figure S4) that we are able to subsequently capture the initial stages of the phase transition. By following the phase boundary propagation over a few minutes, we determine the ~constant phase-propagation rate in each nanowire, considering frames only once the stage is maintaining a constant temperature (see Supplemental Information and Figure S5 for more details). Figure 2A shows the distribution of phase-propagation rates at three different temperatures with typical time series of individual nanowires shown in the inset. At 163°C, 177°C, and 182°C, we observe average propagation rates of 3.1 ± 0.2 nm/s, 11 ± 1 nm/s, and 33 ± 3 nm/s, respectively. We do not observe any dependence of the propagation rate on either nanowire length or diameter. The strong temperature dependence of the propagation rate, combined with the increase of the rate distribution widths with temperature, suggests that phase propagation is controlled by thermally activated microscopic processes. Indeed, we find that the propagation rate as a function of temperature exhibits Arrhenius-like behavior with an activation energy of 210 ± 60 kJ/mol (Figure 2B), about 50-times the scale of a typical thermal fluctuation (k_B T). (Uncertainty provided represents 95% confidence interval.) Given this substantial energetic barrier, there must be a significant compensating increase in entropy for interphase boundary propagation to proceed at the observed rates.
To reveal the microscopic mechanism of phase propagation, we use electronic structure calculations to parameterize a classical force field for CsPbBr$_3$ crystals (see Tables S1 and S2, Figure S6, and Supplemental Information) and employ this force field in MD simulations. We use CsPbBr$_3$ as a proxy for the mixed halide system because

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**Figure 2. Energetics of Perovskite Phase Propagation**

(A) Histograms of the propagation rate of three different populations of nanowires heated at three different constant temperatures, 163°C (purple), 177°C (orange), and 182°C (green). The insets show a characteristic nanowire at each temperature with a countdown time axis for full conversion to the perovskite phase shown at the top. Scale bars, 2 µm.

(B) Arrhenius plot of experimental and MD simulation data. Red points correspond to the experimental propagation rate of different nanowire populations measured at different temperatures, where the units of k are m/s, also shown in the inset; from the simulation data, light-blue points indicate growth rates of <100> HT-CsPbBr$_3$ along the wire axis, as observed in cRED and SAED (Figure S1), and dark blue points indicate growth rates of <110> HT-CsPbBr$_3$ along the wire axis. Data are presented as mean ± SEM. The solid red line is the linear fit to the experimental data (210 ± 60 kJ/mol), and the solid blue line is the linear fit to the simulation data (140 ± 80 kJ/mol). The red and blue shaded regions show the 95% confidence interval of the experimental and simulation fits, respectively, with the overlapping (mauve) region showing the overlap between these two regions. While the <110> HT-CsPbBr$_3$ plane is not observed to be transverse to the wire axis in SAED, the growth rates thus obtained are statistically indistinguishable and further constrain the fit to simulation data. See Figure S16 for further details and for additional simulations on CsPbI$_3$ that are consistent with those shown here.

(C) Snapshots from the MD simulation of phase propagation as a function of time at 267°C, showing the disordered interface between the LT-CsPbBr$_3$ and HT-CsPbBr$_3$ phases. Here, t = 0 ns refers to the earliest simulation time after the initial simulation condition, a pristine interface between the two phases, has equilibrated. Scale bar, 2 nm.

(D) Charge density profiles from the MD simulation at 267°C, obtained by projecting ion positions onto the direction of the wire axis. Data are averaged over a 50-ns time window.

See also Figures S1 and S2.
its simpler composition greatly facilitates the development of a reliable force field. Since both the Br/I and pure Br materials display halide diffusion-limited dynamics, we estimate that the energy scales for defect diffusion and rearrangement in CsPbBr$_3$ and CsPbI$_2$ differ by no more than 5%–10%. To further justify our use of the pure Br material in lieu of CsPbI$_2$ we have performed additional simulations of CsPbI$_3$ using a different force field. We observe the same transformation mechanisms in both materials, as described below, and activation energies for phase propagation are identical to within the uncertainty of our calculations (see Supplemental Information).

We start our simulations from configurations that include planar interfaces between the LT-CsPbBr$_3$ and HT-CsPbBr$_3$ phases, employing the relative crystallographic orientations suggested by single-area electron diffraction (SAED) ((100) LT-CsPbBr$_3$ abutting (100) HT-CsPbBr$_3$), as seen in Figure 2C. We considered additional interfacial possibilities, such as (110) LT-CsPbBr$_3$ planes abutting (100) HT-CsPbBr$_3$, described further in Supplemental Information. In several long MD simulations at temperatures of 227°C, 247°C, and 267°C we consistently observe growth of the HT-CsPbBr$_3$ phase, in agreement with experiments (Figures S7 and S8; see also Supplemental Information). Propagation rates estimated from at least three independent simulations for each aforementioned interface at each temperature are plotted in Figure 2B. An Arrhenius-type analysis of these data yields an activation energy of 140 ± 80 kJ/mol, and a similar analysis of simulation data at higher temperatures on CsPbI$_3$ (Figures S6, S7, and S9; Tables S1 and S3) is also in reasonable agreement with experiments. A direct comparison of phase-propagation rates obtained at the same temperature in both experiments and simulations remains challenging. Phase propagation at temperatures below 227°C is intractably slow in MD simulations, which cannot exceed the microsecond timescale. On the other hand, the high temperatures used in the simulations are challenging to achieve in the in situ CL measurements on account of accentuated damage induced through electron beam irradiation at high temperatures and heat-associated drift.

The simulations reveal the formation of a structurally disordered, liquid-like interfacial layer, characterized by diffusive ion behavior in the interfacial plane (Figure S10). This disorder is the likely origin of the large activation entropy hypothesized from our experiments to partly compensate the substantial measured energetic barrier to advancing the interphase boundary. Large energetic barriers to phase propagation, as measured in our experiments and simulations, can be interpreted as describing activated ion-diffusion events between stoichiometrically different coordination environments. Growth of the HT-CsPbBr$_3$ structure proceeds via diffusion of ions across this disordered interface (Figure 2C and Video S2). Due to the marked structural differences of the two phases, growth cannot proceed layer by layer. In particular, (100) layers of HT-CsPbBr$_3$ have an ionic composition different from that of (100) layers of LT-CsPbBr$_3$. Completion of a new layer of HT-CsPbBr$_3$ thus requires the recruitment of ions from at least two (100) layers of LT-CsPbBr$_3$.

Despite the disordered, liquid-like region between the two phases, using SAED we find the same crystallographic orientation of the HT phase in all nanowires probed rather than a random distribution of crystallographic orientations as might be expected. To rationalize the observation of a preferred crystallographic orientation, we separately compute the distribution of each ion species within the interfacial region in the molecular simulations (Figure 2D). While the positions of the cations are essentially disordered, the positions of the halides remain correlated across the entire liquid-like interface. These correlations manifest as oscillations in the halide
density distribution, shown in Figure 2D, and likely act to template the formation of the growing HT phase, dictating its crystallographic orientation despite the incoherent interface. These persistent anionic density correlations are reminiscent of those templating the association of metal nanoparticles in dense ionic solutions.

In our experiments, we observe nucleation of the HT-CsPbI\textsubscript{2} primarily at nanowire ends; a minority of wires also displays nucleation along the lateral surface. Preferential nucleation on nanowire ends is evident from Figure 3A, which shows a histogram of all nucleation events in \(~100\) nanowires as a function of time, observed at 163°C (see Supplemental Information and Figure S11 for more details). Here, time zero is defined by the image frame in which we first observe a single HT-CsPbI\textsubscript{2} phase pixel above the LT-CsPbI\textsubscript{2} background CL intensity threshold. The distributions of end and side nucleation events are clearly different; the earlier peak of the end nucleation distribution indicates faster nucleation at nanowire ends than sides. To extract a nucleation rate at each of the nanowire ends and sides, we examine distributions of waiting times, which are exponentially distributed, as expected for an
independent, reaction-limited process. We find that nucleation at nanowire ends occurs with a rate of 0.045 s$^{-1}$, whereas nucleation at wire sides occurs with a rate of 0.013 s$^{-1}$ (Figure S12). This threefold difference likely reflects a higher density of high-energy sites at the wire ends than wire sides owing to the higher density of unterminated bonds at the ends (100) relative to the side surfaces or other exposed facets at wire ends that are not perfectly flat. The nucleation rates at early times are consistent with those inferred at later times using an Avrami analysis, accounting for a constant rate of growth measured independently (see Supplemental Information for details). The inset of Figure 3A shows CL and SE images of part of a single nanowire after nucleation has occurred at the end and side of the nanowire. Time series of the CL and SE images of the nuclei growth at the nanowire end and nanowire side are depicted in Figures 3B and 3C, respectively (Videos S3 and S4). Additional nucleation events are shown in Figure S13. Nucleation at the nanowire end leads to the new phase, expanding until it occupies the full width of the nanowire and then propagating along the long axis of the wire (Figure 3B). Because axial growth can occur in two opposite directions, new regions of HT-CsPbBr$_2$ formed on the nanowire side are seen to clearly grow asymmetrically with a faster growth rate along the long axis of the nanowire (Figure 3C). By analyzing the extent to which the perovskite phase is circular in the image frames at early times, we find that nucleation at the nanowire sides results in a more anisotropically shaped perovskite phase volume with faster growth along the length of the wire (Figure S14).

We develop a phenomenological model to describe both the preferential location of nucleation sites at the wire end and the anisotropic growth rate at the nanowire side (see Figure S15 and Supplemental Information for additional details). Specifically, we use a simple lattice model of crystal growth with anisotropic bond and surface energies that are greater along the long axes of the wire compared with the short axes. This model phenomenologically accounts for the anisotropy in lattice orientations of the HT-CsPbBr$_2$ and LT-CsPbBr$_2$ phases. The lattice is initialized in the pure LT-CsPbBr$_2$ phase and is instantly quenched to favor the HT-CsPbBr$_2$ phase. Figure 3D shows two distributions of nucleation events at nanowire ends and nanowire sides from the model, which qualitatively match our experimental results, suggesting that preferential nucleation at nanowire ends is caused by the tendency to minimize interfacial energies between the two phases. Two time series of simulation snapshots of end and side nucleation are shown in Figures 3E and 3F. Growth from the nanowire end proceeds almost isotropically, whereas growth on the nanowire side occurs anisotropically due to the alternation between octahedral double chains and gaps in between them. Specifically, growth occurs at a faster rate in the direction of the lead halide octahedral chains (i.e., along the wire axis); growth in perpendicular directions is noticeably slower. Our MD simulations confirm these anisotropic growth rates: interfaces involving (010) and (001) layers of LT-CsPbBr$_3$, which are parallel to the nanowire axis, display slower average phase propagation compared with orthogonal (100) layers (Figure S16).

The kinetic pathways of the structural phase transition are also apparent in the morphology and photophysical properties of the resulting HT-CsPbBr$_2$ nanowires. In some cases, when the nanowire is not uniformly contacting the substrate, changes in the nanowire morphology are evident upon the formation of the perovskite phase. As the phase transition proceeds, lattice stress associated with the 7% increase of nanowire volume results in nanowire expansion and bending (Figure S17). Additionally, HT-CsPbBr$_2$ nanowires with multiple nucleation sites sometimes display dark regions where two phase boundaries meet (Figure S18), suggesting the formation of dislocations with suppressed CL emission.
Conclusion
Through in situ dynamic CL imaging and multiscale modeling of the LT-CsPbIBr$_2$ to HT-CsPbIBr$_2$ structural phase transition, we have uncovered the mechanism of the complex, non-martensitic double-chain to perovskite structural transformation in cesium lead halide. The measured activation energy for phase propagation is consistent with a disordered interface between the two phases through which ions must diffuse, as observed in MD simulations. This liquid-like interface is observed far from the melting point of the involved solids and presents strong anion density correlations, which we suspect are responsible for the fixed crystallographic orientation of the nascent perovskite phase within the nanowire, as observed in SAED. The spontaneous formation of an incoherent interface suggests that an ordered solid-solid interface between these two structurally dissimilar phases is thermodynamically less favorable than the sum of LT-CsPbIBr$_2$-liquid and HT-CsPbIBr$_2$-liquid interfaces, plus the concomitant enthalpy required to disorder the interfacial layer, even when such liquid-like configurations are not stable by themselves. Our findings are yet another manifestation of the liquid-like dynamics that have been observed in these highly anharmonic metal halide perovskite lattices that result from the low cohesive energy of their ionic bonds, in contrast to traditional covalent semiconductors.

Our results suggest that similar mechanisms might occur in a large range of materials with disparate structural phases, including other perovskite materials, which crystallize in structures that do not share simple epitaxial interfaces. The experimental method for observing dynamic structural changes introduced in this work could also be extended to other systems, such as 2D transition metal dichalcogenides$^{40, 41}$ and metal-organic frameworks,$^{42, 43}$ in which a change in the luminescence intensity or wavelength accompanies a structural change. We expect that similar in situ monitoring of phase transitions will significantly aid our ability to characterize phase behavior, enabling quantitative comparison with theoretical results and creating opportunities to manipulate solids and their properties on the nanoscale.

EXPERIMENTAL PROCEDURES
Resource Availability
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Materials Availability
This study did not generate new unique materials.

Data and Code Availability
All experimental data, computational data, and code are available upon reasonable request to the Lead Contact author.

Low-Temperature Phase CsPb$_{1-x}$Br$_3$ Nanowire Synthesis
All of the chemicals were purchased from Sigma-Aldrich unless otherwise stated. PbI$_2$ (460 mg; 99.999%) was dissolved in 1 mL of anhydrous dimethylformamide and stirred at 70°C overnight before further use. The PbI$_2$ solution was spun on O$_2$ plasma-treated glass substrates at 3,000 rpm for 60 s and annealed at 100°C for 15 min. The PbI$_2$ film was carefully dipped into a glass vial with a mixed solution of 0.4 mL of 8 mg/mL CsI (99.999%)/methanol (anhydrous 99.8%), 1 mL of 8 mg/ CsBr (99.999%)/methanol (anhydrous 99.8%), and 0.8 mL of methanol (anhydrous 99.8%). The PbI$_2$ side was facing up during the reaction. The reaction was carried out at room temperature for 12 h with the glass vial capped tightly, after which
the substrate was taken out and washed in anhydrous isopropanol for 30 s. The sample was then dried at 50°C for 5 min. The whole growth process took place in a N₂-filled glovebox. The PL emission peak of the corresponding heating transformed high-T phase is the same as that of the CsPbBr₃J composition in our previous report.⁹

Cathodoluminescence Microscopy
CL and SE images were collected with a Zeiss Gemini SUPRA 55 S2 scanning electron microscope modified with a home-built CL detection setup and a home-built heater stage with custom ScopeFoundry software. An aluminum parabolic reflector was positioned above the sample in order to couple a 1.3π sr solid angle of emission into a photomultiplier tube (Hamamatsu, H7421-40) outside of the vacuum chamber. All CL images were acquired with 512 × 512 pixels, a scan rate of ~10 ms/line, a beam current of ~300 pA, and an accelerating voltage of 3.0 kV. The heater is composed of a 0.32-inch diameter O₂ button heater (101275-29, HeatWave Labs) with a thermocouple temperature readout placed adjacent to the sample on an identical Si substrate. For monitoring the phase transition upon heating, the temperature was ramped to an initial set point and then held constant (Figure S4). CL image acquisition was initiated at the initial set point and recorded until the phase transition was complete.

Selected Area Electron Diffraction Measurements
LT-CsPbBr₂ nanowires were transferred by lightly pressing a TEM grid on a nanowire film. Due to the electron dose required in TEM, these measurements cannot be performed in situ to, for example, show the different crystal structures of a half-converted nanowire. For HT-CsPbBr₂ nanowires, LT-CsPbBr₂ nanowires were first transferred onto a TEM grid and then heated to induce the phase-transition process in a glovebox. Inside the glovebox, the TEM grid was heated on a hotplate at ~200°C for about 10 min. A temperature higher than the phase-transition temperature was used to ensure the completion of the phase transition, given the possible inefficient thermal transport to nanowires suspended on the TEM grid. The TEM images and SAED patterns in Figure S1 were acquired by using the FEI Titan microscope at the National Center for Electron Microscopy. All measurements were performed at 300 kV.

Continuous Rotation Electron Diffraction Measurements
The dried film was scraped from the glass substrate and then coated on a copper grid with the carbon film (STEM150 Cu grids, Okenshoji) directly. The three-dimensional reciprocal lattices of both low-temperature and high-temperature phases were reconstructed from cRED data (Figure S1). cRED data were collected using a transmission electron microscope (JEOL JEM-2100-LaB₆) operated at an accelerating voltage of 200 kV. The sample was cooled down to ~178°C using a cryo-holder filled with liquid N₂. A Gatan Orius camera was used for imaging and locating appropriate crystals for electron diffraction data collection. The cRED data were collected via continuous tilting of the goniometer in the angle range between ±30°. A high-speed hybrid TimePix camera (Amsterdam Scientific Instrument) operated by SoPhy software was used for recording the cRED data. The data were processed using XDS and REDp. TEM bright-field images and energy-dispersive spectra were also collected on the same transmission electron microscope.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.matt.2020.07.015.
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AUTHOR CONTRIBUTIONS

C.G.B., M.L., Z.F., D.T.L., M.G., P.Y., and N.S.G. wrote the manuscript. C.G.B., M.L., D.L., D.T.L., P.Y., and N.S.G. conceptualized the experiments. M.L. synthesized the LT-CsPbI₂Br nanowires and performed the PL and XRD measurements. C.G.B. performed the CL experiments and analyzed the CL nucleation and growth data. D.T.L. conceptualized and performed the Ising model simulations. Z.F., P.D., D.T.L., and M.G. conceived the MD simulations and analyzed simulation results. Z.F., P.D., D.D., and M.G. developed the force field and performed MD simulations. A.S.E., J.S., and H.C. collected and analyzed the cRED. T.L. performed the SAED.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

Liquid-like Interfaces Mediate Structural Phase Transitions in Lead Halide Perovskites

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Supplemental Experimental Procedures

Additional Methods:

Photoluminescence (PL) spectra
Photoluminescence measurements were performed using an OBIS 375nm LX 50mW Laser (The intensity of the beam is 1 mW) with emission collected on a Nikon A1 microscope coupled to a multimode fiber coupled to a liquid-nitrogen-cooled Si CCD.

X-ray diffraction (XRD)
The XRD pattern was acquired by using a Bruker AXS D8 Advance diffractometer equipped with a lynxeye detector, which used Cu Kα radiation. GIWAXS data of the low-temperature to high-temperature transition were collected at SSRL beamline I11-3. The glass substrate with as-grown nanowires was heated in situ on a hot plate in a helium chamber.

Analysis of nanowire perovskite phase propagation
Analysis of perovskite phase propagation was performed in Matlab R2017B and is summarized in Figure S5. CL image time series were first registered to account for lateral drift by first registering the SE image series and then applying the image registration to the corresponding CL dataset. Nanowires were then selected from the larger field of view, cropped, and reoriented. Overlapping nanowires and nanowires that moved during CL image series acquisition were not included in the analysis of phase propagation rates. Phase propagation rates were determined for individual nucleation events by measuring the movement of the 50% CL intensity point at the phase boundary along the length of the nanowire. The analysis was repeated for different temperature set points to generate the histogram data shown in Figure 2A. At temperatures higher than ~185 °C, propagation rates could not be determined because the rates exceeded the temporal resolution of our CL imaging.

Analysis of perovskite nucleation events
Analysis of nucleation events was performed in ImageJ 1.51w and Matlab R2017B. The nucleation analysis is summarized in Figure S11. CL image time series were registered as described above. Initial nucleation event times were determined by identifying pixels with an intensity value 1.5x
the nanowire background CL. Later nucleation times were identified as the time that nuclei reached ~250 nm across (similar to the width of the nanowires). Plots of the number of nucleation events versus time were fit with the Johnson-Mehl-Avrami-Kolmogorov equation (Figure S12):

\[ x(t) = 1 - \exp(-kt^n) \]

where \( x(t) \) is the number of nucleation events in time, \( k \) is the convolved rate of nucleation and growth to reach the size threshold, and \( n \) is related to the geometry of the transformation.

Measurement and analysis of individual nucleation events
To visualize the growth of individual nuclei, CL time series were acquired at a smaller field-of-view of 5 x 5 µm. Individual nuclei were cropped and plotted as a time series. Circularity analysis was performed in ImageJ 1.51w by thresholding the intensity of the nuclei and measuring the circularity with the following equation:

\[ c = 4\pi \left( \frac{A}{P^2} \right) \]

where \( A \) is the area of the nucleus and \( P \) is the perimeter.

Molecular Dynamics Methods

Material composition: CsPbBr\textsubscript{3} vs. CsPbIBr\textsubscript{2}
In our simulations, we primarily used a force field for CsPbBr\textsubscript{3} to study phase transitions of experimental CsPbIBr\textsubscript{2} nanowires. This choice was made because a reliable force field for the four-component mixed halide system is considerably more difficult to obtain than for CsPbBr\textsubscript{3}. The two materials have somewhat different phase diagrams. In particular, the non-perovskite LT-CsPbBr\textsubscript{3} phase is not thermodynamically stable for CsPbBr\textsubscript{3}, but it is metastable and not significantly less stable than for CsPbIBr\textsubscript{2} at comparable temperatures \(^1\). Furthermore, vacancy formation energies and activation barriers for vacancy hopping are very similar for different halides and independent of composition \(^2\). Based on data given in Ref. 6, we estimate that the energy scales for defect diffusion and rearrangement in CsPbBr\textsubscript{3} and CsPbIBr\textsubscript{2} differ by no more than 5-10%. Since the growth mechanism observed in our simulations involves similar
microscopic rearrangements, we expect that differences in the activation energy for growth are of the same magnitude, well within the uncertainty of our calculations. To further verify these estimates we also performed simulations of a model of CsPbI\(_3\) and obtained similar results, as described below.

Parameterization of CsPbX\(_3\) force field

We use pairwise additive, radially symmetric interactions to model CsPbX\(_3\) crystals. The pair potentials consist of short-range repulsive and attractive dispersion forces, as well as Coulomb interactions. Specifically, ions of type \(i\) and \(j\) interact via

\[
\begin{align*}
  u_{ij}(r) &= \frac{q_i q_j}{4 \pi \varepsilon_0 r} + 4 \varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right].
\end{align*}
\]

Similar models have been successfully used in the past to model other ionic semiconductor solids. Lennard-Jones parameters for interactions between ions of the same type (H\(\text{Cs}\), H\(\text{Pb}\), H\(\text{X}\), V\(\text{Cs}\), V\(\text{Pb}\), and V\(\text{X}\)) were determined by fitting to lattice constants, elastic properties, and energy differences between different crystal structures, as described below; standard combining rules, \(\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}\) and \(\sigma_{ij} = (\sigma_i + \sigma_j)/2\), were used to determine cross-interactions. For the ionic charges \(q\), we use partial charges determined by Bader charge analysis in the cubic perovskite structure (HT-CsPbX\(_3\) phase), as described below. Final force field parameters are listed in Table S\(_1\); the pair potentials are plotted in Figure S\(_6\).

The data set used for fitting included lattice constants, elastic properties, and energy differences of five crystal structures of CsPbX\(_3\), including four perovskite structures and the non-perovskite LT-CsPbX\(_3\) phase. The four perovskite structures include the well-known cubic (space group #221) and orthorhombic (space group #62) phases, as well as two tetragonal (space group #127 and #140) structures; the non-perovskite structure is an orthorhombic phase (space group #62) that is found in CsPbI\(_3\) at low temperature. These data were obtained from density functional theory (DFT) calculations carried out with the Vienna Ab-initio Simulation Package (VASP) with the projector augmented wave (PAW) method. We initially compared data obtained with three different density functionals, including GGA-PBE, PBEsol, and SCAN. All DFT results are listed in Tables S\(_2\) and S\(_3\). While PBEsol and SCAN produced comparable values, lattice parameters obtained with PBEsol overall provided the best match with known experimental values. We
therefore chose to use PBEsol data as a reference for lattice constants and elastic properties. (Note that experimental values were obtained at finite temperature, while DFT values are ground state (0 K) energies.) However, among the three DFT methods only PBE yielded the correct energetic order of CsPbBr$_3$ crystal structures (i.e., $E_{\text{HT-ort}} < E_{\text{HT-tet}} < E_{\text{HT-cub}}$; $E_{\text{HT-ort}} < E_{\text{LT}}$) $^{10}$. We therefore chose energy differences obtained with PBE as the reference for our force field parameterization.

We used a Monte Carlo simulated annealing (MCSA) method $^{11,12}$ to fit the six remaining force field parameters ($\varepsilon_{\text{Cs}}$, $\varepsilon_{\text{Pb}}$, $\varepsilon_{\text{X}}$, $\sigma_{\text{Cs}}$, $\sigma_{\text{Pb}}$, and $\sigma_{\text{X}}$) to the DFT data. Compared to more straightforward methods (e.g., gradient descent), the MCSA method more efficiently samples high-dimensional parameter spaces and provides a means of escaping local minima in the fitness landscape, defined via

$$f = \sum_{i=1}^{N} \sqrt{w_i (A_i^o - A_i^c)^2}.$$ 

Here, $N$ is the total number of fitted quantities, $A_i^c$ and $A_i^o$ are the force field and reference values of the $i$th quantity, respectively, and $w_i$ is the fitting weight assigned to that quantity. All properties of the force field model (lattice and elastic constants, bulk modulus, and energy differences) were calculated with GULP $^{13}$. The final parameter set is provided in Table S1 and the quantities used for fitting are compared to their reference values in Tables S2 and S3. More details about force field derivation and validation will be provided elsewhere.

**MD simulations**

MD simulations were carried out using the LAMMPS simulation package $^{14}$. All simulations were performed in the NPT ensemble at zero pressure and a time step of 2 fs. Temperature and pressure were controlled by a Nose-Hoover thermostat and barostat, respectively, as implemented in LAMMPS. We simulated different interfaces between the LT-CsPbBr$_3$ and HT-CsPbBr$_3$ phases, including (100)$_{\text{HT}}$/ (100)$_{\text{LT}}$, (110)$_{\text{HT}}$/ (100)$_{\text{LT}}$, (110)$_{\text{HT}}$/ (010)$_{\text{LT}}$, and (110)$_{\text{HT}}$/ (001)$_{\text{LT}}$. For CsPbI$_3$, only the (100)$_{\text{HT}}$/ (100)$_{\text{LT}}$ interface was considered. Systems were first equilibrated at a temperature of 300 K for 2 ns, then the temperature was increased from 300 K to the target temperature (500, 520, or 540 K for CsPbBr$_3$ and 700, 720, or 740 K for CsPbI$_3$) in another 2 ns simulation. After equilibration, long simulation runs (1-2 $\mu$s) were performed at each temperature to observe the
propagation of the boundary between the LT-CsPbBr₃ and HT-CsPbBr₃ phases and to measure transition rates. We performed 3-5 independent simulations of each system and temperature.

Distinguishing HT-CsPbX₃ and LT-CsPbX₃ phases

We distinguish HT-CsPbIX₂ and LT-CsPbX₃ phases based on different coordination environments of Pb ions in the two structures. Specifically, we used the number n of anions (Br or I) within a cutoff distance around a given Pb as an order parameter. The cutoff distances for CsPbBr₃ and CsPbI₃ are 5.4 and 5.8 Å, respectively. As shown in Figure S7, while n = 6 in the HT-CsPbX₃ phase (corresponding to the coordination octahedron around a given Pb), n ≈ 9 in the LT-CsPbX₃ phase, due to the fact that anion octahedra share edges in this structure. We thus characterize all Pb ions with n ≤ 6 as belonging to the HT-CsPbX₃ phase and use the fraction of HT-CsPbX₃ phase Pb ions as a proxy for the fraction of HT-CsPbX₃ phase present in the simulation. The two panels of Figure S8 show the time evolution of the fraction of HT-CsPbBr₃ phase at different temperatures for two different interface configurations. Figure S9 shows the time evolution of the fraction of HT-CsPbI₃ phase at different temperatures. We calculate the rate of interface propagation v from the slopes k of linear fits to these data via \( v = \frac{Lk}{2} \), where L is the length of the simulation box side perpendicular to the HT-LT interface and the factor of 2 is included to account for the presence of two interfaces in the simulation box. In some simulations, we observed an initial stage of abnormally fast growth of the HT-CsPbX₃ phase (see, for instance, the trajectory at 540 K in Figure S8 top), which we attribute to the relaxation of the initial configuration. To ensure that propagation rates calculated from our simulations are representative of a steady-state growth regime, we excluded the initial 200 ns from the analysis of all trajectories.

Ising Model Simulations of Nucleation and Early Growth

In order to understand the relative importance of geometric, thermodynamic and kinetic factors in the nucleation and growth of the perovskite phase in the nanowires, we have simulated a simple Ising model with anisotropic energetics. Specifically, we have studied a Hamiltonian of the form

\[
H = - \sum_{\langle ij \rangle} J_{ij} \sigma_i \sigma_j - \sum_i h_i \sigma_i
\]
where $s_i = \pm 1$ are spin variables that represent the perovskite and non-perovskite phases, $J_{ij}$ are pair interactions equal to $J_x$ and $J_y$ along the long and short axes of the lattice respectively, and $h_i$ are local fields that are equal to $h_b$ in the bulk of the lattice, and $h_x$ and $h_y$ on the exposed long and short surfaces. The calculations are done on a 2d square lattice, and we consider interactions between only nearest neighbor spins.

We study the model at $T k_B / J_x = 1.2$, where $k_B$ is Boltzmann’s constant, which is well below the critical point and set $h_b = -0.15$ so that spin up is metastable with respect to spin down. To study nucleation, which is a rare event, we compute the free energy to grow a cluster of size $N_c$ down spins in a bulk lattice or in the presence of an extended interface, where the cluster is defined as that set of spins sharing a nearest neighbor of common spin state. We do this using umbrella sampling and Metropolis Monte Carlo with single spin flip moves. Previous studies have shown that for the Ising model, while classical nucleation theory is not able to quantitatively describe the nucleation kinetics of phase transformations, the size of the largest cluster is a good reaction coordinate for these kinetics. To sample these fluctuations, we add a potential of the form

$$U = \frac{k}{2} (N_c - N'_c)^2$$

where $k$ is the spring constant restricting fluctuations which we take to be 0.02 $J_x$ and $N'_c$ is the minimum of the potential, which we take to span 0-200 in steps of 10. We use MBAR to combine data from each window into the free energies in Figure S15 for a variety of ratios $J_y / J_x$. In order to match the relative nucleation rate found experimentally for the end to side nucleation we find that we must use $h_x = -0.2$ and $h_y = -0.15$ and that the relative nucleation rates are insensitive to $J_y / J_x$. though the absolute barrier changes.

In addition to computing nucleation rates from the nucleation barrier heights, we have computed the interface motilities as a function of $J_y / J_x$. Specifically, beginning in a nanowire of equal proportions of spin up and spin down, under the same conditions are those used in the calculation of the nucleation barrier height, we compute the mean time to convert the lattice into 90% spin down. The results of these calculations are shown in Figure S15. We find that choosing $J_y / J_x =$
1.5 is sufficient to explain the factor of 3 growth rate difference measured experimentally. The distribution of first passage times and example trajectories shown in Figure 3 of the main text are computed using these optimized conditions with a stopping point equal to 1.1 $N_c^*$, where $N_c^*$ is the critical cluster size determined by the maximum of the free energy function. In order to compare to experiments we associate a single Ising lattice site to a length scale of 2 nm and assign a single MC sweep to a timescale of 0.1 s. These scales are set in order to match the growth velocity and mean nucleation time at the end of the nanowire.
Supplemental Figures

**Fig. S1. 3D reciprocal lattice of both phases reconstructed from the c-RED data and transmission electron microscopy single area electron diffraction (SAED).** (A) 3D reciprocal lattice of LT-CsPbIBr$_2$ showing that the octahedral chains are oriented along the length of the wire. (B) 3D reciprocal lattice of HT-CsPbIBr$_2$ after the phase transition is completed. (C,D) 2D projections of LT-CsPbIBr$_2$ and HT-CsPbIBr$_2$ nanowire diffraction, respectively, used in conjunction with c-RED data to determine the lead-halide octahedral packing direction along the nanowires. Altogether these data enable determination of the crystallographic configurations on either side of the interphase boundary. (E,F) High-resolution SE images of the LT-CsPbIBr$_2$ nanowires, showing that the wires are smooth prior to the above TEM exposure.
Fig. S2. Time series of a larger field-of-view of CsPbIBr₂ nanowires undergoing the structural phase transition and ambient temperature control experiment. (A) SE and CL time series of the same field-of-view as shown in Figure 1D-F and Video S1 showing nucleation and growth in > 100 nanowires simultaneously. (B) We observe no significant changes in the nanowire CL intensity with repeated imaging at ambient temperature. (C) CL intensity cross section of a single nanowire as a function of time, demonstrating nucleation at the ends and phase propagation to the middle of the nanowire.
Fig. S3. *In situ* X-ray diffraction (XRD) of the LT-CsPbIBr$_2$ to HT-CsPbIBr$_2$ phase transition. The temperatures in the legend refer to the heater setpoint and not the temperature of the nanowire film being measured. We assume that the transition appears to occur in the setpoint temperature range of ~200-225 °C (higher than the phase transition temperature) because the nanowire film is less well thermally contacted to the heater than the more dispersed sample employed in the *in situ* CL measurement.
Fig. S4. Example of temperature traces while acquiring SE and CL data to monitor the phase transition kinetics. CL and SE images are recorded starting at 0 s. The dotted line represents when the temperature plateaus and phase front propagation rates are first recorded. The temperature was measured from a thermocouple on an Si substrate adjacent to the sample substrate (< 5 mm from the sample).
Fig. S5. Workflow for analyzing nanowire phase propagation rates. Large field-of-view SE and CL movies are aligned. Isolated wires are selected, cropped, and rotated. Propagation rates are measured based on the position of the 50% intensity contour. The process is repeated for many wires at different temperature to generate the histograms and Arrhenius plot shown in Figure 2.
Figure S6. Plots of interaction potentials for all pairs of ion types.
Figure S7. Average number $n$ of anions within a distance $r$ of a central Pb ion. Simulations were performed for the high-T and low-T phases of CsPbBr$_3$ and CsPbI$_3$ at 500 and 700 K, respectively. The vertical dashed line indicates the distance (5.4 Å for CsPbBr$_3$ and 5.8 Å for CsPbI$_3$) used to define the order parameter that distinguishes the LT-CsPbX$_3$ and HT-CsPbX$_3$ phases.
Figure S8. Time evolution of the fraction of HT-CsPbBr$_3$ phase in the (top) HT(100)-LT(100) and (bottom) HT(110)-LT(100) nanowire at three different temperatures.
Figure S9. Time evolution of the fraction of HT-CsPbI₃ phase in the HT(100)-LT(100) nanowire at three different temperatures.
**Figure S10.** Transverse mean squared displacement of ions in a 0.9 nm thick (containing ~ 3 atomic layers) region at the interface between LT-CsPbBr$_3$ and HT-CsPbBr$_3$ from a simulation performed at 540 K. The approximately linear curves indicate that ion motion in the interfacial plane is largely diffusive, suggesting liquid-like behavior.
Fig. S11. Workflow for analyzing nanowire nucleation events. After registering the SE and CL images, nanowire end and side nucleation events are selected. Times of nucleation are recorded by taking the time that a single pixel intensity reaches a threshold higher than the background intensity. A multiple pixel threshold is also imposed to record later nucleation plus growth times (5 x 5 pixels above the background). After these data are recorded for a large field-of-view, histograms of the nucleation times are constructed.
Initial nucleation

\[
\begin{align*}
a &= 0.00878 \pm 0.0052 \\
n &= 1.515 \pm 0.18
\end{align*}
\]

Growth to wire width

\[
\begin{align*}
a &= 0.01009 \pm 0.0022 \\
n &= 1.061 \pm 0.05
\end{align*}
\]

\[
\begin{align*}
a &= 0.0005641 \pm 0.00022 \\
n &= 1.974 \pm 0.1
\end{align*}
\]

\[
\begin{align*}
a &= 0.0002458 \pm 0.00006 \\
n &= 1.698 \pm 0.05
\end{align*}
\]

Fig. S12. Nucleation events versus time and Avrami fits.
Fig. S13. Additional single nucleation events at nanowire ends and sides. CL and SE time series of nucleation events at (A-B) nanowire ends and (C-D) nanowire sides.
Fig. S14. Circularity analysis of nuclei. Example of circularity measurements for (A) end and (B) side nuclei. An intensity threshold above the background CL of the LT-CsPbIBr$_2$ nanowire is applied and the area and perimeter of each nucleus is used to determine the circularity parameter. (C) Histograms of the circularity of nuclei for end and side nucleation events. The average circularity for end nuclei is 0.86 (standard deviation is 0.046, N = 48) and the average circularity for side nuclei is 0.67 (standard deviation is 0.12, N = 48).
Fig. S15. Nucleation and growth for the Ising model. (A) Free energy as a function of cluster size for side and end growth in blue and red respectively. The circles are for $J_y/J_x = 1.5$ and the squares are for $J_y/J_x = 1$. (B) Phase growth velocity along the direction of the long axis as a function of $J_x/J_y$ in units of lattice length and Monte Carlo sweeps.
Fig. S16. Arrhenius plots of experimental data and simulation data. (A) A reproduction of Figure 2D of the main text with additional information. In addition to the experimental (red) and simulation (light and dark blue) data and respective fits and 95% fit confidence intervals, the purple and orange data points represent growth of the (110) HT-CsPbBr$_3$ plane parallel to the wire axis in contact with the (010) and (001) planes of the LT-CsPbBr$_3$ phase, respectively. These data are not included in the fit, as they represent slower growth in a direction orthogonal to the wire axis of primary relevance to the discussion of Figure 3 in the main text. (B) A similar Arrhenius plot that includes simulation data of the interphase boundary propagation of CsPbI$_3$ (green) in addition to the simulation data of CsPbBr$_3$ (blue) and the experimental data (red). The resulting activation energy for the CsPbI$_3$ data is 230 ± 160 kJ/mol 95% confidence interval. (Note, the standard error associated with these data is ± 20 kJ/mol, and the corresponding standard errors for the CsPbBr$_3$ simulation and the experimental data are both ± 30 kJ/mol.) Together these data support that a similar and substantial activation energy and a correspondingly substantial activation entropy are found for all halide compositions, which suggests a similar mechanism for the phase transition, whereby the interface translates by first disordering.
Fig. S17. Nanowire bending and expansion upon phase transition. (A) CL and SE time series showing a nanowire bending during the phase transition. (B) The length of the wire (top) is correlated to the percent of the nanowire converted to the HT-CsPbIBr\textsubscript{2} phase (bottom).
Fig. S18. SE and CL images of nanowire phase boundaries where two fronts meet. (A) SE and CL images of a time series showing phase propagation. (B) Cross-section of the CL image at 270 s (across the blue dotted line in A). The green dotted line signifies where the two phase fronts meet in the middle of the nanowire.
### Supplemental Tables

**Table S1.** Force field parameters.

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Table S2. Physical properties of four structures of CsPbBr$_3$ calculated with our force field, DFT-PBEsol, DFT-PBE, and DFT-SCAN, together with available experimental results. Lattice parameters $a$, $b$, and $c$ are given in units of Å; elastic constants $c_{ij}$ in units of GPa; bulk modulus $B$ in GPa; energy differences $\Delta E$ with respect to the cubic perovskite structure in meV/f.u.; and the transition temperatures $T$ of the orthorhombic-tetragonal (O-T) and tetragonal-cubic (T-C) transitions in K. Values in bold face were used for fitting.

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Table S3. Physical properties of four structures of CsPbI$_3$ calculated with our force field, DFT-PBEsol, DFT-PBE, and DFT-SCAN, together with available experimental results. Lattice parameters $a$, $b$, and $c$ are given in units of Å; elastic constants $c_{ij}$ in units of GPa; bulk modulus $B$ in GPa; energy differences $\Delta E$ with respect to the cubic perovskite structure in meV/f.u.; and the transition temperatures $T$ of the orthorhombic-tetragonal (O-T), tetragonal-cubic (T-C), and yellow-black (Y-B) transitions in K. Values in bold face were used for fitting.

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Supplemental References


