

Demystifying phase transformations in metal halide perovskites

Chengchangfeng Lu,^{1,4} Yifan Wang,^{1,4} Ruiqi Zhang,^{2,4}
and Sheng Xu^{1,2,3,*}

Metal halide perovskites have become one of the most studied optoelectronic materials, but their stability remains a grand challenge due to the lack of understanding of the phase transformation process. Recently, scientists at the University of California, Berkeley have devised direct monitoring methods to track the phase transformation process of metal halide perovskites. Their results shed light on the mechanisms of this phase transformation, providing a basis for stabilizing this class of exciting materials under various conditions.

Metal halide perovskites have emerged as extraordinary next-generation optoelectronic materials. The outstanding carrier dynamics¹ and low manufacturing cost² can yield devices that potentially meet the world's increasing demand for clean energy and high-performance solid-state lighting. However, their long-term stability remains challenging due to the phase transformation from the perovskite phase to the non-perovskite phase^{3,4}. Thus, understanding the fundamental mechanisms and developing potentially preventative strategies for phase transformation is essential for enhancing the long-term stability of perovskite devices for any practical applications.

Research teams from the University of California, Berkeley, led by David T. Limmer, Peidong Yang, and Naomi S. Ginsberg, reported a method to investigate the perovskite's nucleation and growth during heat-induced phase transformations⁵. CsPbI₂Br₂ nanowire is used as a model structure. When heated, a low-temperature (LT) non-perovskite phase tends to transform to a high-temperature (HT) perovskite phase (Figure 1A, left)⁵ and is kinetically trapped in the HT phase when cooling down. In the traditional martensitic transformation, atoms do not diffuse

because they are bounded to each other by strong covalent bonds. Their positions change no more than one lattice spacing during the phase transformation. Here in metal halide perovskites, the atoms are bonded by relatively weaker ionic bonds. Therefore, a more complex rearrangement of atoms is activated, where atoms diffuse through a thin layer of liquid-like interface between the LT and HT phases. The phase transformation is accompanied by a ~7% volume increase. Without the liquid-like interface, the associated large interfacial energy and lattice strain between the two phases would result in a significant energy barrier that prevents the phase transformation from happening.

Cathodoluminescence imaging is used to track the interphase boundaries across the nanowire axis under *in situ* heating. The changes in peak position and intensity of the cathodoluminescence from the indirect bandgap LT phase to the direct bandgap HT phase provide a clear view of the phase propagation. Simultaneous measurements of over 150 nanowires give a statistical analysis of the phase growth rate as a function of the temperature. The rate increases from 3.1 nm/s to 33 nm/s when the temperature rises from

163°C to 182°C, indicating the thermally activated nature of the phase transformation. By fitting the Arrhenius curve, the associated energy barrier is found to be as high as 210 ± 60 kJ/mol, indicating a significant increase in entropy is required for the observed high growth rate.

Molecular dynamics simulations illustrate the possible phase transformation process. A classical force field containing interaction potentials between different ion pairs is built based on the electronic structures of CsPbBr₃ and CsPbI₃. The results reveal a disordered liquid-like interface with diffusive ion behaviors (Figure 1A, right), which corresponds to the significant entropy gain from the LT phase to the liquid-like phase. However, the entropy loss from the liquid-like phase to the HT phase should have also been taken into consideration for the entire phase transformation. Selected-area electron diffraction shows that the crystallographic orientations of the transformed HT phase are the same in all nanowires, indicating that the liquid-like interface differs from the precursor solution where homogeneous nucleation with random crystal orientations could have taken place. Here the identical crystal orientations are explained by the correlated positions of the halide anions, which might have templated the growth of the HT phase; the cations, however, are essentially disordered.

Additionally, the nucleation can be initiated at either the ends or the sides of the CsPbI₂Br₂ nanowires (Figure 1B), with the occurring rate of the former

¹Department of Electrical and Computer Engineering, University of California San Diego, La Jolla, CA 92093, USA

²Department of Nanoengineering, University of California San Diego, La Jolla, CA 92093, USA

³Department of Materials Science and Engineering, University of California San Diego, La Jolla, CA 92093, USA

⁴These authors contributed equally

*Correspondence: shengxu@ucsd.edu
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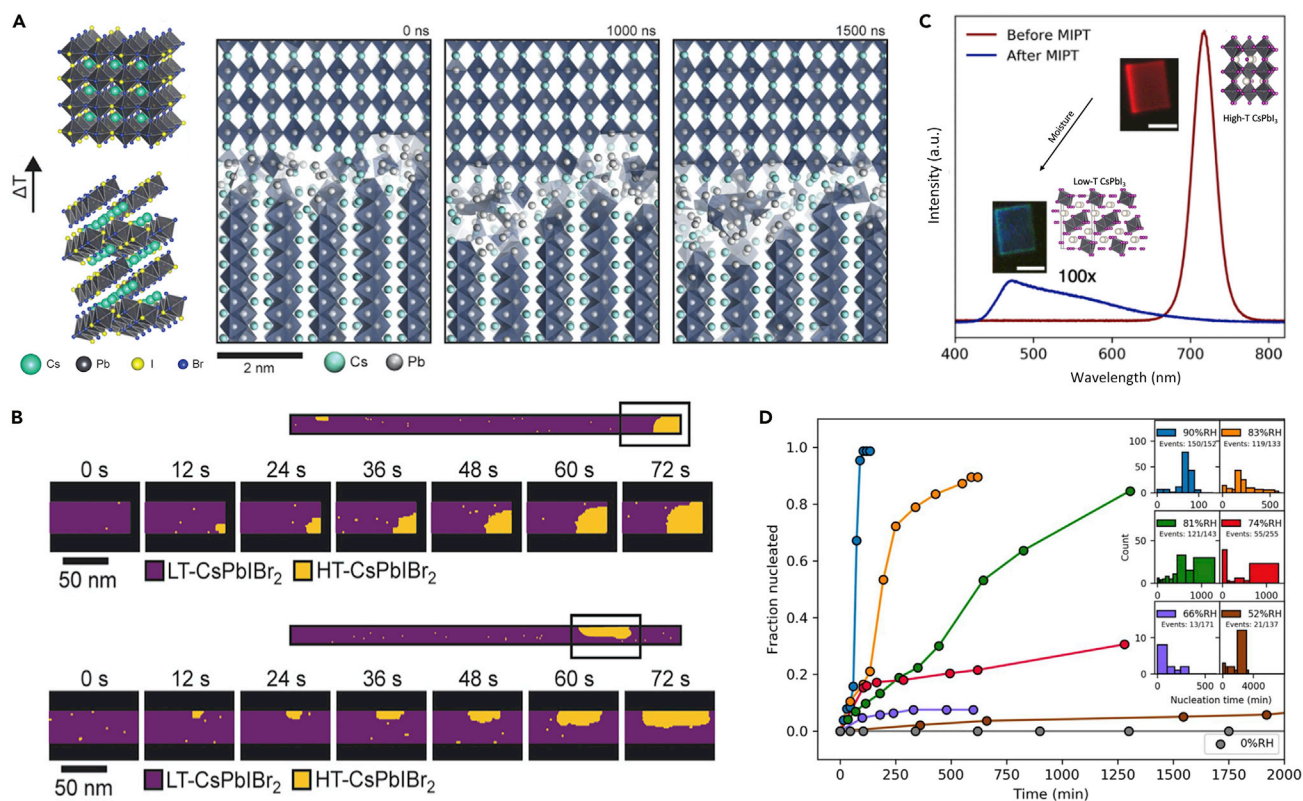


Figure 1. Simulated and experimental results of phase transformations in Cesium-based perovskite

(A) Phase transformation of LT-CspbBr₂ to HT-CspbBr₂ under heating (left) and a liquid-like interface with disordered cations and correlated anions between LT-CspbBr₂ and HT-CspbBr₂ (right).

(B) Simulated time series showing a single nucleation event at the nanowire end (top) and side (bottom).

(C) Photoluminescence spectra of CsPbI₃ before and after moisture-induced phase transformation (MIPT). Insets are their corresponding optical images. Scale bars: 10 μm.

(D) The distribution of crystal nucleation times (inset) and the corresponding nucleation probability distribution at 0%, 52% (ambient), 66%, 74%, 81%, 83%, 90% relative humidity (RH).

(A)–(B) are reproduced and adapted from the paper by Bischak et al.; (C)–(D) are reproduced and adapted from the paper by Lin et al.

(0.045 counts/s) approximately three times of the latter (0.013 counts/s), possibly due to the lower density of dangling bonds at the sides. A phenomenological model (free energy versus cluster size) is built to describe the preference in nucleation sites and the growth rate from the sides. As predicted by the model, the growth from the sides is anisotropic because the growth rate is higher along the correlated lead halide octahedral chains in the axial direction and lower between these chains in the radial direction of the nanowire. The anisotropic growth rates result in a larger interface, and thus larger interfacial energy, between the two phases. Therefore, a lower

probability for phase transformation is found at the sides.

The kinetically trapped HT phase can still transform back to the LT phase, particularly when catalyzed by humidity. Yang's group studied the phase transformation of CsPbI₃ from the HT phase to the LT phase in moist environments (Figure 1C)⁶. They choose single crystal microcrystals rather than polycrystalline thin films or nanocrystals, because nucleation lacks independence between adjacent domains in the former or is too fast in the latter. Molecular dynamics simulations show that a thin water layer on the surface would form halide vacancies at the water-perovskite

interface, significantly lowering the phase transformation barrier. Because of the distinct photoluminescence emissions of the HT and LT phases (Figure 1C), the researchers could track the nucleation behavior and quantify the nucleation rate. They find that the nucleation rate of LT-CspbBr₂ increased exponentially with increased relative humidity. The nucleation fraction follows the statistical Poisson distribution⁷ for the relative humidity below 83%, and an apparent deviation from this distribution over time for the relative humidity above 83% (Figure 1D). This nonlinear deviation is attributed to the formation of water microdroplets, which dissolves and degrades the perovskite faster than

moisture on the surface. Based on the classical nucleation theory⁸, the activation energy barrier for nucleation is extracted: 55.40 ± 3.75 kJ/mol under 73% relative humidity, which is less than half of the 129.08 ± 33.86 kJ/mol under 53% relative humidity.

While it takes a few hours to initiate the nucleation, the LT phase consumes a $\sim 20 \mu\text{m} \times 20 \mu\text{m}$ microplates within a minute. Thus, nucleation is determined to be the rate-limiting step in the moisture-induced phase transformation. At a given relative humidity, the growth rate is almost constant over time. When the relative humidity is above 65%, the growth rate has a weak dependency on the relative humidity. Additionally, detailed nucleation rates are studied under different temperatures and relative humidity levels. In an inert environment, the HT-CsPbI₃ has no phase transformation when the temperature is $< 100^\circ\text{C}$, confirming that pure inorganic metal halide perovskite is stable within the temperature range in this study, and moisture is required for initiating the phase transformation. When the relative humidity is $< 73\%$ and the temperature is $< 33^\circ\text{C}$, increasing the temperature would accelerate the nucleation rate, according to the Arrhenius behavior. When the temperature is $> 33^\circ\text{C}$, however, the nucleation rate drops. The researchers ascribe this unusual behavior to the desorption of moisture from the LT-CsPbI₃ surface under heating, as confirmed by the X-ray photoelectron spectroscopy. When the relative humidity is $> 73\%$, the nucleation rate is overall very high and showed a minimum at around 60°C probably due to the same reason of moisture desorption.

By *in situ* imaging, those studies have uncovered the nucleation dynamics and growth kinetics for the heat- and moisture-induced phase transformations, laying the groundwork for improving the stability of metal halide perovskites. By controlling relevant parameters, it might be possible to increase the transformation energy barrier so that the transformation to the ineffective phase could be curbed. For example, epitaxial lattice strain has been shown to extend the lifetime of particular metal halide perovskites from one day to almost one year⁹. Suppressing the liquid-like interface during the phase transformation would significantly increase the activation energy barrier due to the large volume difference between the two phases and thus prevent the phase transformation. It might also be possible to develop a method of re-transforming the ineffective phase back to the effective phase under certain conditions.

Some challenges still remain unsolved. Although high temperatures in dry environments lead to a higher nucleation barrier, the required high temperature is also harsh for other functional components (e.g., hole- and electron-transport layers) in typical perovskite photovoltaics. Strategies are imperatively needed to improve the stability of the overall assembled devices instead of the perovskite absorbers only. Furthermore, since defects will lower down the phase transformation barrier, it would be more meaningful to study the phase transformation at the interfaces between the perovskites and the other functional layers of fully integrated devices. Nonetheless, these

studies previewed here are expected to have a catalytic impact on stabilizing the metal halide perovskites.

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