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Thermochromic halide perovskite solar cells

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Smart photovoltaic windows represent a promising green technology featuring tunable transparency and electrical power generation under external stimuli to control the light transmission and manage the solar energy. Here, we demonstrate a thermochromic solar cell for smart photovoltaic window applications utilizing the structural phase transitions in inorganic halide perovskite cesium lead iodide/bromide. The solar cells undergo thermally-driven, moisture-mediated reversible transitions between a transparent non-perovskite phase (81.7% visible transparency) with low power output and a deeply coloured perovskite phase (35.4% visible transparency) with high power output. The inorganic perovskites exhibit tunable colours and transparencies, a peak device efficiency above 7%, and a phase transition temperature as low as 105 °C. We demonstrate excellent device stability over repeated phase transition cycles without colour fade or performance degradation. The photovoltaic windows showing both photoactivity and thermochromic features represent key stepping-stones for integration with buildings, automobiles, information displays, and potentially many other technologies.

Smart windows with reversible and persistent colour changes to modulate visible light transmittance have been reported using electrochromic, thermochromic, and liquid crystal materials. The transparency of such windows is controlled simply by absorbing or reflecting sunlight without actually converting the solar energy into a useful form. To date, semi-transparent photovoltaics have been demonstrated for power-generating windows that provide shading, lighting, and power output, but without any colour-changing characteristics. Photovoltaic windows with switchable transparencies—smart photovoltaic windows—which can harvest and manage the incoming solar energy have been developed only by combining semi-transparent solar cells with additional chromic components to form multi-junction tandem devices. It is highly desirable to develop a stable and photoactive material possessing two intrinsic states that have large colour contrast, one with high transparency to ensure the greatest brightness, and the other with strong light absorption to produce sufficient electrical energy, where the two states can be reversibly switched back and forth in response to the external environment. Materials with structural phase transitions have been found inherently linked to substantially different optical, electronic, and/or thermal properties due to distinct atomic arrangements of each specific crystal structure. In particular, non-volatile and fully-reversible phase transitions suggest the possibility of applications in smart photovoltaic windows. The concept has not been realized because most of the semiconductors cannot be switched between a transparent phase and a non-transparent phase reversibly, without deteriorating their electronic properties. 

Recently, halide perovskites of an ABX₃ structure [A = CH₃NH₃⁺ (MA), HC(NH₂)₂⁺ (FA), Cs⁺; B = Pb²⁺, Sn²⁺; X = I⁻, Br⁻, Cl⁻] have emerged as intriguing photovoltaic materials and become a rapidly evolving field. The prototypical organic—inorganic hybrid perovskite methylammonium lead iodide (MAPbI₃) was reported to undergo multiple temperature-dependent phase transitions, with a change from the tetragonal to the cubic phase at ~60 °C, within the solar cell operating temperature range. However, the structural properties vary only little between the two phases, with slight tilting of the three-dimensional metal-halide octahedral network. Consequently, both the optoelectronic properties and solar cell performances do not alter significantly upon phase transition. Another promising halide perovskite material is the purely inorganic version, cesium lead iodide/bromide (CsPbI₃, Brₓ; 0 ≤ x ≤ 3). These inorganic perovskites have achieved significantly enhanced thermal and environmental stability, and are considered to be potentially on a par with the organic–inorganic hybrid species in terms of intrinsic solar cell performance ability. Substantial structural changes occur in these inorganic perovskites upon phase transitions, often between a room-temperature non-perovskite phase (low-T phase) and a high-temperature perovskite phase (high-T phase). These two phases feature distinct optoelectronic properties such as the bandgap, photoluminescence (PL) quantum efficiency, and charge carrier mobility and lifetime. Here we examine the structural phase transition behaviours in such inorganic mixed halide perovskite CsPb₁₋ₓBrₓ thin films. The large structural changes induced by phase transitions lead to films with two switchable characteristic states with distinct visible transparencies and photovoltaic device efficiencies, making them promising candidates for smart photovoltaic windows.

Figure 1a schematically illustrates the crystal structure change between the low-T and high-T phases of CsPbI₃, Brₓ. The low-T to high-T phase transition occurs upon reaching the transition temperature by thermal heating (in inert or ambient condition) with the high-T phase being kinetically trapped and metastable in an inert environment when cooled to room temperature. Critical to

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achieving full phase reversibility is the back-conversion of the high-T to low-T phase. It is known that the metastable high-T phase of CsPbI\textsubscript{3} can be transitioned to the low-T phase by reheating to about 200 °C in an inert atmosphere\textsuperscript{19}. When Br is added, the high-T phase is more stable, and difficult to revert to the low-T phase by mild heating. Instead, we find that, in general, moisture exposure effectively triggers this phase transition at room temperature. Methanol and ethanol vapours can also trigger the phase transition, but not as efficiently as moisture (Supplementary Fig. 1a).

Fig. 1 shows the visually distinct images of the non-coloured low-T and orange-red-coloured high-T phase CsPbIBr\textsubscript{2} films, suitable for window applications. These transition processes could be potentially leveraged during normal device operation where sunlight is used to heat the film and drive off moisture (or assisted by extra heating), inducing a phase transition to the photovoltaically active high-T phase, while moisture ingress results in a subsequent phase transition back to the transparent low-T phase.

We use CsPbIBr\textsubscript{2} as a model system to characterize in detail the low-T and high-T phases. The powder X-ray diffraction (XRD) pattern of CsPbIBr\textsubscript{2} in the low-T phase matches well with the simulated pure iodide (CsPbI\textsubscript{3}) and bromide (CsPbBr\textsubscript{3}) low-T orthorhombic and high-T cubic phases. Absorption (dashed lines) and PL (solid lines) spectra of the low-T (black) and high-T (red) CsPbIBr\textsubscript{2} films. Variation of the high-T to low-T phase transition time of CsPbIBr\textsubscript{x} films measured at different humidity conditions with RH = 20—80%. Error bars indicate the standard deviation. The inset shows the corresponding photographs of the high-T and low-T phase thin films (from left to right: x = 1, 1.5, and 2). The high-T phase films display different colours from dark brown to orange-red, while the low-T phase ones are fully transparent.

The stable and reversible switching of the absorption (550 nm) of the three CsPbIBr\textsubscript{x} thin films over 100 phase transition cycles. XRD patterns of the low-T (black) and high-T (red) phase films before and after 100 cycles of phase transitions, showing full reversibility of the crystal structures.
Mechanism of the moisture-triggered phase transition in inorganic perovskites.

**Fig. 2** | Mechanism of the moisture-triggered phase transition in inorganic perovskites. **a.** Reversible work, \( \Delta F(z) \), to transfer an I\(^-\) atom from the solid perovskite to the thin adsorbed water layer, where \( z \) is the direction perpendicular to the interface. **b.** Snapshot from a molecular dynamics simulation near the top of the barrier in a showing the lead halide sub-lattice in grey and orange, the Cs\(^+\) ions in green, the oxygens of the water in red and their hydrogens in white. **c.** Vacancy concentration, \( \rho_v \), per unit cell as a function of relative humidity, \( \rho/\rho_v \). **d.** Free energy to transform the high-T phase into the low-T phase, \( \Delta G(Q) \), with or without an I\(^-\) vacancy, where \( Q \) is an order parameter that interpolates between the two crystal phases. **e.** Snapshot from a molecular dynamics simulation of the interface between the low-T and high-T phases with the same colouring as in **b.** **f.** Average nucleation time, \( r \), as a function of vacancy concentration for CsPbBr\(_3\) and CsPbI\(_2\)Br.

( Supplementary Fig. 2). A similar peak shift has been observed for the CsPbBr\(_3\) high-T phase as compared to the CsPbI\(_2\) and CsPbI\(_3\)Br cubic phases (Fig. 1d). The unit cell of the high-T phase is determined to be \( a = 5.926 \, \text{Å} \) with the space group \( Pm-3m \) (Supplementary Fig. 3 and Table 1). The large changes in the crystallographic structures indicate the first-order nature of the phase transition. The phenomenon of phase transition is different from the other observed transition behaviours between different colour states in halide perovskites accompanied by chemical reactions and new compound formation\(^2\). During the high-T to low-T transition process, the characteristic high-T XRD peak gradually diminishes while the low-T peak appears upon continuous exposure to moisture, and finally the high-T peak completely vanishes, indicating full conversion to the low-T phase (Supplementary Fig. 1b). Accordingly, the film shows a macroscopically homogeneous and gradual colour change across the entire region (Supplementary Fig. 1c and Supplementary Videos 1, 2) that tracks well with the XRD data. Fig. 1e quantitatively shows the optical absorption and PL spectra of the high-T and low-T phase thin films with light absorption above the band edge at about 2.1 and 2.9 eV, respectively. In the PL emission spectra, the high-T phase shows a narrow band edge emission, whereas the emission becomes much broader and weaker for the low-T phase.

The high-T to low-T phase transition rate is found to be strongly dependent on the composition \( (x = 1, 1.5 \) and 2) and relative humidity (RH = 20–80%, Fig. 1f). The inset in Fig. 1f shows the photographs of both the high-T and low-T phase films. The reversibility of the structural transitions between the low-T and high-T phases of the inorganic perovskite CsPbI\(_3\)Br is monitored by the absorption spectra, which show no apparent changes after more than 100 repeated cycles (see Fig. 1g). Furthermore, no shift of the characteristic peaks or emergence of any impurity peaks (such as CsI, CsBr, PbI\(_2\) or PbBr\(_2\)) is observed in the XRD patterns of either phase after repeated phase transition cycles (Fig. 1b). It is worth noting that, as compared to the freshly prepared high-T phase film, the (110)/(100) peak intensity ratio initially increases and subsequently remains stable during cycling, corresponding to a phase-transition-induced variation of the CsPbI\(_3\)Br thin-film morphology, but without a significant change of the top surface roughness and grain dimensions (Supplementary Fig. 4). This observation can be explained by the rearrangement of crystal orientations in the thin film to reach the lowest surface energy.

The moisture adsorbed on the inorganic halide perovskite film surface can effectively catalyse the high-T to low-T phase transition at room temperature by introducing vacancies into the crystal lattice and lowering the free-energy barrier to nucleation\(^2\). Shown in Fig. 2a, free-energy calculations of a molecular model of CsPbI\(_3\) show that there is a significant enhancement of halide vacancies when a thin water film is in contact with the perovskite interface\(^2\), as pictured in Fig. 2b. This is a consequence of the large solvation enthalpy of halide ions and their accompanying low vacancy formation energy\(^2\). The characteristic time for a vacancy to be created at the interface is computed to be 1 ms, with an equilibrium concentration that depends on the relative humidity as in Fig. 2c and is up to five orders of magnitude larger than the expected defect concentration in the bulk of the material. Additional free-energy calculations shown in Fig. 2d report that there is a significant reduction of the surface tension between the low-T and high-T structures in the presence of halide vacancies. This reduction results from mitigating the ionic bonding constraints within the interfacial region of the lead-halide octahedra, which share corners in the high-T phase but share edges...
in the low-T phase (see Fig. 2e). This reduction of the free-energy barrier to nucleation at the sites of halide vacancies results in a transition rate that changes exponentially in the presence of a vacancy, as quantified in Fig. 2f for CsPbIBr$_2$ and CsPbI$_2$Br. The moisture triggered phase transition was further characterized by ambient pressure X-ray photoemission spectroscopy (AP-XPS). When exposing to water vapour, the adsorbed oxygen amount on surface increases but does not change with the probing depth (Supplementary Fig. 5), indicating that water is adsorbed only on the surface without penetrating interior of the lattice. The results reveal that the phase transition is fundamentally different from the hydration/dehydration process observed in hybrid perovskite MAPbI$_3$ 24–26, which suffers from decomposition after water molecule intercalation.
Fig. 4 | The evolution and reversibility of photovoltaic properties during phase transition cycles. a. In situ observation of the time-dependent performance of a CsPbBr$_3$ solar cell from high-T to low-T phase at RH = 60%, and temperature-dependent device performance from low-T to high-T phase by heating. b–e. Short-circuit current density ($J_S$) (b), open-circuit voltage ($V_{OC}$) (c), fill factor (FF) (d), power conversion efficiency (PCE) (e) of devices over 10 transition cycles between the high-T (red squares) and low-T (black circles) phases. Error bars indicate the standard deviation; 10 separate CsPbI$_3$ cells were used. The slight fluctuation is associated with different perovskite film crystallinity during each heating cycle.

To achieve solar cell devices with switchable power output utilizing the phase transitions, a sufficiently robust architecture that can withstand the moisture or heating treatment needs to be designed. Initially, we have explored the use of typical organic interlayer materials in devices (see Methods), but they undergo a severe irreversible thermal degradation upon heating above 150 °C. By applying solution-processed high-quality metal oxide-based hole and electron extraction layers$^{27-29}$, an all-inorganic solar cell using an inorganic p-i-n heterojunction geometry consisting of glass/fluorine-doped tin oxide (FTO)/NiO (−80 nm)/CsPbI$_{1-x}$Br$_x$ (−200 nm)/ZnO (−70 nm)/Al (Fig. 3a,b) is realized that maximizes the thermal and environmental stability. The overall surface roughness after coating with dense ZnO nanoparticles is as low as ~7 nm. Fig. 3c shows the $J−V$ curves, with the solar cell based on CsPbI$_3$, in the high-T phase showing an open-circuit voltage ($V_{OC}$) of 1.01 V, a short-circuit current density ($J_S$) of 8.65 mA cm$^{-2}$, and a fill factor (FF) of 63.6%, corresponding to a power conversion efficiency (PCE) of 5.57%. The same cell after switching to the low-T phase exhibits a $V_{OC}$ of 0.84 V, a $J_S$ of 0.31 mA cm$^{-2}$, an FF of 43.9%, and a PCE of 0.11%. A ~50-fold difference in PCE between the two phases is observed. The device in the high-T phase shows a low $J−V$ hysteresis with respect to the scan direction and gives a stabilized power output of 5.10% under continuous one-sun illumination (Supplementary Fig. 6 and Table 2). According to the external quantum efficiency (EQE) measurements shown in Fig. 3d, the photocurrent onsets are at approximately 590 and 430 nm for the high-T and low-T phases, respectively.

For mixed halide perovskite CsPbI$_{1-x}$Br$_x$ (0 ≤ x ≤ 3), the bandgap of the high-T phase can be tuned continuously in the range 1.7−2.3 eV by controlling the bromide to iodide ratio in the alloy (Supplementary Fig. 7a). The corresponding solar cell devices show the peak PCEs above 7% (for x = 1, 1.5, Fig. 3c, Supplementary Fig. 7b and Table 3). Although CsPbI$_3$ has a more desirable bandgap for photovoltaics, the device shows a low PCE, probably due to the high phase instability at room temperature. As x increases (0 ≤ x ≤ 2.5), the phase transition temperature decreases nearly linearly from 320 to 105 °C (Fig. 3e). The structural phase transition was further confirmed by variable-temperature grazing-incidence wide-angle X-ray (GIWAX) diffraction (see Supplementary Fig. 8). On the other hand, the high-T phase becomes more stable against moisture with increasing x (Fig. 1f). For CsPbBr$_3$, moisture treatment at room temperature does not result in the low-T phase, probably because the high-T phase is thermodynamically more stable at ambient conditions$^{25}$.

Approaches towards semi-transparent devices were further explored with the replacement of Al with transparent top electrodes to study the compatibility with the transparent conductive layers$^{21-31}$. A 50 nm layer of solution-processed Al-doped ZnO was applied to the air layer on top of the ZnO, followed by sputtering a 120-nm-thick indium tin oxide (ITO) to form the top transparent electrode (see Methods). After post annealing of the complete device at approximately 200°C, the ITO layer shows a high transparency. Fig. 3f shows the images of the devices based on a transparent ITO top layer at the low-T and high-T phases, respectively. The high-T phase device yields a $V_{OC}$ of 1.00 V, a $J_S$ of 7.92 mA cm$^{-2}$, an
more ideal bandgaps for higher power output, lower phase transition temperatures for self-adaptive transparency, and more robust device architectures for long-term stability. Our results indicate that halide perovskites are not only ideal for low-cost and high-efficiency solar cells, but also possess rich phase change behaviours for switchable optoelectronics.

Methods

Methods, including statements of data availability and any associated accession codes and references, are available at https://doi.org/10.1038/s41563-017-0006-0.

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Author contributions
J.L., M.L., L.D. and P.Y. conceived the idea and designed the study. J.L., M.L. and L.D. contributed to all the experimental work. C.S.K. performed the AFM measurements. H.C., F.P. and J.S. carried out the RED experiments and data analysis. D.L., S.A.H., C.X. and F.C. helped with the device characterizations. D.T.L. performed the molecular modeling. J.L. and P.Y. wrote the manuscript. All authors discussed the results and revised the manuscript.

Competing interests
The authors declare no competing financial interests.

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Methods

Oxide and perovskite film deposition. Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich Chemical and used as received. Nickel oxide (NiO) film was prepared as follows. 0.1 M nickel (II) acetate tetrahydrate with 0.1 M ethanolamine was mixed in ethanol, and stirred at 60 °C for 3 h. The resulting solution was spin-coated on pre-patterned FTO glass at 2,000 r.p.m. for 60 s. Then the substrate was annealed at 270 °C for 30 min. Afterwards, the substrate was transferred to a N₂-filled glovebox for further processing. Mixed halide CsPbI₃·Br thin film (0 ≤ x ≤ 2) was prepared by a single-step method, in which 0.5 M caesium lead halide precursor solution was prepared by mixing appropriate amounts of CsI, CsBr, CsPbBr₂ and PbBr, powders (99.999%) into N,N-dimethylformamide (DMF) or dimethylsulfoxide (DMSO). The solution was stirred for 2 h and filtered by 0.2 μm polytetrafluoroethylene (PTFE) filter syringes before use. Then the solution was spin-coated onto a NiO layer, 1,500 r.p.m. for 90 s. The thin film was annealed at different temperatures for 10 min. For a more bromide-rich CsPbI₃·Br thin film (x = 0.2), a two-step method was adopted, in which a 10% PBr₆, in toluene was spin-coated at 4,000 r.p.m. onto the NiO layer, and then heated at 75 °C for 30 min. The perovskite film was grown by dipping the PbBr₂ film in 8–16 mg ml⁻¹ methanol solution with different CsBr-CsI mole ratios at a solution temperature of 75 °C for 10 min, and then washing immediately with 2-propanol (IPA) for 30 s. The substrate was then dried by heating to 135 °C for 10 min. The two-step method generated a nanocuboid film morphology. Zinc oxide (ZnO) nanoparticles were prepared in methanol via hydrolysis of zinc acetate by potassium hydroxide. The as-prepared ZnO nanoparticles (~4 nm size) were dispersed in chloroform with 2 wt.% concentration, spin-coated on the perovskite surface at 4,000 r.p.m. for 10 s, and then annealed at 75 °C for 10 min.

Devices. The inverted p-i-n (deposition order) device with the glass/FTO/NiO/CsPbI₃·Br/ZnO/Al structure was fabricated. A 100-nm-thick Al electrode was thermally evaporated through a shadow mask under a high vacuum of ~5 × 10⁻¹⁰ torr at a rate of 0.1 nm s⁻¹. The moisture treatment was conducted in a humidity control box with flowing N₂ gas containing moisture at room temperature (N₂-H₂O). The temperature was calibrated by a digital thermometer. The perovskite film and device were treated by heating or moisture exposure without encapsulation. The heating process was conducted in the glovebox, on a hotplate with ramping rate of 20 °C min⁻¹. The moisture treatment was conducted in a humidity control box with flowing N₂ gas containing moisture at room temperature (N₂-H₂O). The humidity (RH) was controlled in the range 20 ± 10%.

Film characterization. The morphologies of films and devices were analyzed by a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6490). The size of nanoparticles was analysed by transmission electron microscopy (TEM, Hitachi H-7650). The transmittance and absorption spectra were obtained by means of an ultraviolet-visible spectrophotometer (UV-3101, Shimadzu). The luminous transmittance of the film is characterized by the visible luminescence transmittance (CIE 1931 human perception of transmittance) averaged over the spectral range 400–780 nm (ref. 12). The device area was restricted to be 4 mm² by means of a metal mask. The stabilized power output was measured under continuous illumination over 400 s at the maximum power point. The temperature-dependent J–V curves were measured by placing the device on a hotplate and the temperature was allowed to equilibrate for 5 min. The external quantum efficiency (EQE) was measured by standard lock-in techniques. In brief, the device was excited by chopped (77 Hz) long-pass-filtered monochromatic light (Acton monochromator, Ortels 300 Xenon lamp) while connected to a 50 Ω resistor in parallel with an SR830 lock-in amplifier. The resulting signal was converted into a quantum efficiency by comparison with a calibrated silicon photodiode (Newport 818) measured under identical conditions.

Molecular dynamics models. The molecular dynamics simulations were accomplished with force fields of the form of a Buckingham potential, as parameterized for MgNO₃ by Nakanishi et al. and rescaled for CsPbI₃. Such models of CsPbI₃ are able to reproduce the experimental lattice constants and relative stabilities of different crystal structures. Interactions between water molecules were modelled with the SPC/E water and ion water interactions were modelled with Lennard-Jones potentials. These parameters were chosen to recover known hydration energies for the ions, and provide an interfacial structure of water on CsPbI₃, that is consistent with ab initio studies. Molecular simulations were run in LAMMPS with initial conditions taken from known crystal structures. Integration of the equations of motion were done first in an NPT ensemble using a Parinello–Rahman barostat, for 100 ps, followed by 10 ns runs with NVT dynamics using a Langevin thermostat. Periodic boundary conditions were used in all cases. Calculations employing free interfaces accounted for the altered electrostatic environment using a slab-corrected Ewald summation with a slab-width Ewald summation. Unless otherwise noted, the calculations used a super cell of size 10 × 10 × 10 perovskite unit cells. For the hydrated interfaces, we begin by simulating a bare surface with semi-Grand Canonical hybrid Monte Carlo, where the chemical potential is set by differing values of the relative humidity based on equilibrium vapour pressure calculations.
from REF-DL7. We find that complete monolayer formation occurs only at 40% relative humidity. After 40% p/p , layering increases exponentially fast with increasing relative humidity, allowing us to assume that the ion concentration increases with the increasing volume of liquid.

**Umbrella sampling calculations.** Calculations to determine the free energy for transferring an I from a pristine PbI-terminated interface of the high-T phase of CaPbI, to an adsorbed thin water film were accomplished using umbrella sampling. These free-energy calculations were computed with 1.000 waters, in a region 5×5×12 nm. This particular interface was studied, as it is known been shown the most stable to water, and as such is expected to set up an upper bound for the transfer free energy relative to higher index interfaces, Ca+ -terminated surfaces, or defective surface. Similarly, I is more weakly hydrated than Br, so we would expect a large driving force for dissolution for Br over I. The umbrella sampling calculations were accomplished with harmonic biasing potentials, 15 simulations, spaced 0.5 Å apart and with a 10 kcal Å potential. The weighted histogram analysis method (WHAM) was used to unbias these simulations and produce Fig. 2b. The Bennet-Chandler method was used to compute the associated rate for dissolution, with transition state associated with the peak free energy along the direction perpendicular to the interfaces and a recrossing coefficient computed to be 0.1.

**Finite temperature string calculations.** In order to study the free energy required to transition between the low-T and high-T phases, shown in Fig. 2d, we used the finite-temperature string method. A much smaller system size of 24 CaPbI, unit cells was used to compute the free-energy profiles between the two phases. An initial interpolation between the two phases was produced using Wang-Landau sampling with an order parameter, Q, defined as an interpolation between two overlap functions

\[ Q[r] = \theta(r_\sigma)/(\theta(r_\sigma) + \theta(r_o)) \]

where \( r \) are the instantaneous coordinates of the system, \( r_\sigma \) are the equilibrium lattice coordinates for phase \( \sigma \) and the overlap function is defined as

\[ \theta[r_\sigma] = \frac{1}{N} \sum_{i=1}^{N} e^{-|r_i - r_\sigma|^2} \]

where \( r = 1.5 \) Å is small enough to ensure \( \theta \) is bounded by 1. Initial simulations included only hard-core interactions between the molecules. Initial pathways produced in this way were used as initial conditions for the free-energy calculations that were evaluated by the finite-temperature string method using 20 windows. Calculations required 1 ns for each window to converge. Calculations were done with initial strings parameterized with or without various defects and from both directions (low-T phase to high-T phase and vice versa) to ensure sampling hysteresis was mitigated. Only I- defects were found to decrease the free energy. Pb+ and Cs+ defects increase the barrier heights to transformation. For these charged defects, electroneutrality was accomplished using a uniform neutralizing background charge. These calculations were compared with direct simulations to compute the excess interface energy of a variety of pristine solid–solid boundaries, which clarifies that the free-energy change has significant entropic character.

Given the large difference in the barrier to nucleation with and without a vacancy, we assume the characteristic transition time follows a simple model of heterogeneous nucleation. Specifically, we assume that the observed rate of interconversion is equal to the sum of the rate in the presence of the vacancy, times the vacancy concentration, plus the rate away from a vacancy, times one minus the vacancy concentration. We fit the data at different relative humidities for each composition, and use the free-energy calculations to predict the timescale for interconversion as a function of vacancy concentration, shown in Fig. 2f.

**Data availability.** The experimental and simulation data that support the findings of this study are available from the corresponding author upon request.

**References**


