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 strong light absorption to produce sufficient electrical energy, and a 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(NH3)3+, (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 (CsPbI2-xBrx, 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-xBr2x 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](https://example.com/figure1a.png) Schematically illustrates the crystal structure change between the low-T and high-T phases of CsPb1-xBr2x. 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...
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 \(_3\) can be transitioned to the low-T phase by reheating to about 200 °C in an inert atmosphere\(^\text{19}\). 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. 1e). Fig. 1b shows the visually distinct images of the non-coloured low-T and orange-red-coloured high-T phase CsPbIBr\(_x\) 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\(_x\) as a model system to characterize in detail the low-T and high-T phases. The powder X-ray diffraction (XRD) pattern of CsPbIBr\(_x\) in the low-T phase matches well with the simulated pure iodide (CsPbI\(_3\)) and bromide (CsPbBr\(_3\)) low-T orthorhombic phases, with the corresponding peak positions sitting between them (Fig. 1c). The crystal structural details of CsPbIBr\(_x\) are derived from rotation electron diffraction (RED) combined with fitting of the XRD pattern, identifying the low-T phase as efficiently as moisture (Supplementary Fig. 1e). 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\(_x\) thin films over 100 phase transition cycles. XRD patterns of the low-T (black) and high-T (red) CsPbIBr\(_x\) films before and after 100 cycles of phase transitions, showing full reversibility of the crystal structures.

Fig. 1 | Phase transitions of inorganic halide perovskites. a, Schematics of the low-T to high-T phase transition by heating and the high-T to low-T transition by exposure to moisture. Caesium and halide atoms are shown in green and red, respectively. The low-T phase is represented by one-dimensional chains of edge-sharing lead-halide octahedra, whereas in the high-T phase the octahedra share corners. b, Photograph of the low-T phase (non-coloured) and high-T phase (orange-red-coloured) thin films. c, Powder X-ray diffraction (XRD) patterns of the CsPbIBr\(_x\) (red) low-T (c) and high-T films (d) deposited on a glass substrate compared with the simulated CsPbI\(_3\) (blue) and CsPbBr\(_3\) (black) low-T orthorhombic and high-T cubic phases.

c, Absorption (dashed lines) and PL (solid lines) spectra of the low-T (black) and high-T (red) CsPbIBr\(_x\) films. f, Variation of the high-T to low-T phase transition time of CsPbI\(_{x-y}\)Br\(_y\) 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. g, The stable and reversible switching of the absorption (550 nm) of the three CsPbIBr\(_x\) thin films over 100 phase transition cycles. h, 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.
A similar peak shift has been observed for the CsPbBr$_3$ high-T phase as compared to the CsPbI$_3$ and CsPbI$_3$Br$_2$ cubic phases (Fig. 1d). The unit cell of the high-T phase is determined to be $a = 5.926$ 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$^{23}$. 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 CsPbBr$_3$ 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, 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 CsPbBr$_3$ 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$^{21}$. 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$^{22}$, as pictured in Fig. 2b. This is a consequence of the large solvation enthalpy of halide ions and their accompanying low vacancy formation energy$^{23}$. 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$_3$, which suffers from decomposition after water molecule intercalation.
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 layers27–30, an all-inorganic solar cell using an inverted planar p-i-n heterojunction geometry consisting of glass/fluorine-doped tin oxide (FTO)/NiO (～80 nm)/CsPbI\textsubscript{0.84}Br\textsubscript{0.16} (～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\textsubscript{Br} in the high-T phase showing an open-circuit voltage (V\textsubscript{OC}) of 1.01 V, a short-circuit current density (J\textsubscript{SC}) of 8.65 mA cm\textsuperscript{-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\textsubscript{OC} of 0.84 V, a J\textsubscript{SC} of 0.31 mA cm\textsuperscript{-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\textsubscript{1−x}Br\textsubscript{x} (0 ≤ x ≤ 3), the band-gap 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. 3e, Supplementary Fig. 7b and Table 3). Although CsPbI\textsubscript{x}, has a more desirable band-gap 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\textsubscript{x} 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 conditions35.

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 layers36–39. A 50 nm layer of solution-processed Al-doped ZnO was applied as the buffer 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\textsubscript{OC} of 1.00 V, a J\textsubscript{SC} of 7.92 mA cm\textsuperscript{-2}, an

![Fig. 4](image-url) The evolution and reversibility of photovoltaic properties during phase transition cycles. a. In situ observation of the time-dependent performance of a CsPbIBr\textsubscript{x} 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\textsubscript{sc}) (b), open-circuit voltage (V\textsubscript{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 CsPbIBr\textsubscript{x} cells were used. The slight fluctuation is associated with different perovskite film crystallinity during each heating cycle.
FF of 59.2%, a PCE of 4.69%, and a stabilized power output of 4.29%, while the low-T phase shows a Voc of 0.97 V, a Jsc of 0.37 mA cm⁻², an FF of 41.6%, and a PCE of 0.15% (Fig. 3g and Supplementary Fig. 9a, b). Unlike the ‘yellow phase’ CsPbI₂, the low-T phase of CsPbBr₃ is fully transparent (Supplementary Fig. 7c). The device at these two phases shows distinct average degrees of visible transparency of 81.7% and 35.4%, respectively (Fig. 3h). The successful deposition of ITO also indicates that the thermal stability of the inorganic perovskite-based devices is an intriguing feature for potential applications as high-temperature stable solar cells that can withstand harsh device-processing conditions.

For cycling tests, the composition CsPbBr₃ was used due to its relatively low phase transition temperature (150°C), high device stability, and good visual characteristics for window applications. The photovoltaic parameters in one phase transition cycle were monitored in situ (Fig. 4a and Supplementary Fig. 10). In the initial stage of the high-T to low-T phase transition by moisture treatment, the device PCE was stable and even slightly enhanced, possibly due to the vacancy accumulation process. Afterwards, the PCE gradually decreased, corresponding to the phase-transition nucleation and propagation, before reaching a stabilized low value indicating full conversion to the low-T phase. For the low-T to high-T transition, the device was gradually heated up to 190°C and then cooled to room temperature in the ambient atmosphere. The PCE increases sharply (more than 8-fold) when approaching 150°C, which suggests the beginning of the phase transition. A further increase in the transition temperature results in the improved PCE, likely as a result of the slow phase transition propagation within the film, before the PCE starts to decay at above 175°C. Upon cooling, the PCE actually gradually increases back to the original value. For a complete cycle, according to our estimation by considering the heating, enthalpy change, and heat loss for the phase transition process, the smart photovoltaic window could achieve a positive net energy balance, provided lower transition temperatures (around 100°C) and faster cycling times (<10 min) are achieved.

Fig. 4b–e shows the statistical analysis of the change in solar cell performance parameters over repeated phase transition cycles. Performance variations of individual solar cells are shown in Supplementary Fig. 11. The characteristic parameters Jsc, Voc, FF, and PCE all show a reversible behaviour. In each cycle, the Jsc and PCE drop sharply when the device turns to the low-T phase by moisture treatment before full recovery by heating. The Jsc of the high-T phase (solar cell operating phase) keeps relatively stable over 10 cycles, which is attributed to the reversible optoelectronic properties of the absorber layer. The initial PCE in the high-T phase is relatively low, and increases gradually in the first two or three cycles. This is directly related to an increase in the Voc at the initial stage, and likely due to the preferred crystal orientation and passivation of the grain boundaries. After reaching steady state, the device performance of the high-T phase shows no obvious degradation during cycling. The evolution of the solar cell parameters between the low-T and high-T phases is in good agreement with the above in situ results. Finally, as an example, we find that, for the semi-transparent device (Supplementary Fig. 9c), more than 85% of the peak PCE is retained after up to 40 repeated cycles of transitions, with no clear downward trend, indicating the high thermal and environmental stability of the all-inorganic solar cells.

We have demonstrated the thermochromic solar cell as a smart photovoltaic window that is realized by controlled transitions between the inorganic perovskite low-T and high-T phases. The solar cell features high thermal stability and fully reversible colour and performance, which are key requirements for successful integration into diverse applications. This phase transition photovoltaic technique has the potential to be extended to other types of halide perovskite composites and nanometre-sized structures featuring 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 ethanethiolate was mixed in ethanol, and stirred at 100°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 CsPbI₂Br 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, CsI, and PbBr₂ powders (99.999%) into N,N-dimethylaniline (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 CsPbI₂Br thin film (x ≤ 1), a two-step method was adopted, in which 1 μM PbBr₂ in 400 s, followed by annealing at 500°C for 20 s, and then annealed at 75°C for 10 min.

Devices. The inverted p-i-n (deposition order) device with the glass/FTO/NiO/ CsPbI₂Br/ZnO/Al structure was fabricated. A 100-nm thick Al electrode was thermally evaporated through a shadow mask under a high vacuum of 5 × 10⁻⁷ Torr at a rate of 0.1 nm s⁻¹. The semi-transparent device was fabricated by replacing the Al electrode with a sputtered indium tin oxide (ITO) layer. First, 25.0 wt% Al-doped ZnO with an average particle size of 15 nm was grown by dipping the PbBr₂ film in 1,200 r.p.m. for 60 s, followed by annealing at 75°C for 10 min as a buffer layer. Afterwards, a 120 nm ITO layer was prepared by radiofrequency sputtering, with a sputtering rate of 9.6 Å s⁻¹. The device active area was restricted to be 4 mm x 4 mm. The relative humidity (RH) was controlled in the range 20–80% (±5%).

Phase transition temperature/rate. The low-T to high-T phase transition temperature and high-T to low-T transition rate were determined by the colour change of the thin films, which is indicative of phase transition, and the crystal phase was confirmed by powder X-ray diffraction (XRD, Bruker D8, Cu Kα, radiation, 1.54056 Å) analysis. XRD spectra were also taken at intervals in the high-T to low-T phase transition process to monitor the changes in the crystal phase. GIWAXS data of the low-T to high-T transition were collected at SRSL beamline I11-3. The sample was heated in situ on a hot plate in a helium chamber.

Crystal structures. Three-dimensional electron diffraction data were collected by using a rotation electron diffraction (RED) data collection program on a JEOL JEM-2100 transmission electron microscope. Transmission electron microscopy (TEM) bright-field images and energy dispersive spectra were also collected on the same TEM. The dried film was scratched from the glass substrate and then coated on a copper grid with the carbon film (STEM/150 Cu grids, Okkenhsjo) directly. The collection angle ranges from ~35° to +35°. The goniometer tilt step is 2°, and the beam tilt step is 0.2°, with a beam tilt range of ±1.0°. The data collection was performed at room temperature. The three-dimensional reciprocal lattice was reconstructed from the RED data for the low-T and high-T phases. On the basis of the three-dimensional data, combined with Le Bail fitting of XRD, the unit cell information was derived directly.

AP-XPS studies. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) was performed at the Lawrence Berkeley National Laboratory Advanced Light Source (ALS) Beamline 9.3.2. A VG-Scienta R-4000 HPP analyzer was used. Samples were prepared on silicon substrates, and XPS spectra were collected using a monochromatized Al Kα X-ray with a pass energy of 300, 730, or 800 eV. The high-T phase sample was measured in ultrahigh vacuum and then in an atmosphere of H₂O (200 mtorr/Ar (50 mtorr) to study the in situ high-T to low-T phase transition. The binding energy for XPS spectra was calibrated with reference to the adventitious C 1s at 284.6 eV. The XPS spectra were analyzed by subtracting a Shirley background.

Film characterization. The morphologies of films and devices were analyzed by a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6400). The size of nanoparticles was analyzed by transmission electron microscopy (TEM, Hitachi H-7650). The transmittance and absorption spectra were obtained by means of an ultraviolet-visible spectrophotometer (UV-3100, Shimadzu). The luminescent transparency of the film is characterized by the visible luminescent transmittance (CIE 1931 human perception of transmittance) averaged over the spectral range 400–780 nm (ref. 2).

Device testing. The performance parameters of the devices were measured under full sunlight (AM 1.5 G, 100 mW cm⁻²). A class A solar simulator (300 W, Oriel) was used for irradiation and the light intensity was calibrated with a Si reference cell (Mono-Si with KG5 filter, NIST). Photocurrent–voltage (J–V) curves were obtained by applying forward and reverse voltage scans using a source meter (Keithley 4200) without any device preconditioning. The scan rate was set at 20, 400, and 780 nm (ref. 41).

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Film characterization. The morphologies of films and devices were analyzed by a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6400). The size of nanoparticles was analyzed by transmission electron microscopy (TEM, Hitachi H-7650). The transmittance and absorption spectra were obtained by means of an ultraviolet-visible spectrophotometer (UV-3100, Shimadzu). The luminescent transparency of the film is characterized by the visible luminescent transmittance (CIE 1931 human perception of transmittance) averaged over the spectral range 400–780 nm (ref. 2).

Device testing. The performance parameters of the devices were measured under full sunlight (AM 1.5 G, 100 mW cm⁻²). A class A solar simulator (300 W, Oriel) was used for irradiation and the light intensity was calibrated with a Si reference cell (Mono-Si with KG5 filter, NIST). Photocurrent–voltage (J–V) curves were obtained by applying forward and reverse voltage scans using a source meter (Keithley 4200) without any device preconditioning. The scan rate was set at 20, 400, and 780 nm (ref. 41).

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from REF-DL^2. We find that complete monolayer formation occurs only at 40% relative humidity. After 40% p/p_0, 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_2-terminated interface of the high-T phase of CaPbI_3 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^3. This particular interface was studied, as it is known been shown the most stable to water^16, and as such is expected to set an upper bound for the transfer free energy relative to higher index interfaces, CsI-terminated surfaces, or defective surfaces. Similarly, I^- is more weakly hydrated than 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^−2 spring constant and 5 additional windows with 0.2 spring constant near the top of the barrier, with a spring constant of 20 kcal Å^−2. The weighted histogram analysis method (WHAM) was used to unbiased these simulations^41 and produce Fig. 2b. The Bennet-Chandler method^42 was used to compute the associated rate for dissociation, 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_3 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^43 with an order parameter, Q, defined as an interpolation between two overlap functions

\[
Q(r) = \theta(\mathbf{r}, \sigma)/\left[\theta(\mathbf{r}, \sigma) + \theta(\mathbf{r}, -\sigma)\right]
\]

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

\[
\theta(\mathbf{r}, \sigma) = \frac{1}{N} \sum_{i=1}^{N} e^{-(r_{i} - r_{e})^2} / \sigma^2
\]

where \(\sigma = 1.5\) 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^44 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^2+ 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**


Thermochromic halide perovskite solar cells

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1Department of Chemistry, University of California, Berkeley, California, USA. 2Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, USA. 3Department of Physics, Shanghai University of Electric Power, Shanghai, China. 4Davidson School of Chemical Engineering, Purdue University, West Lafayette, Indiana, USA. 5Berzelii Center EXSELENT on Porous Materials, Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden. 6Lawrence Livermore National Laboratory, Livermore, California, USA. 7Kavli Energy NanoScience Institute, Berkeley, California, USA. 8Department of Materials Science and Engineering, University of California, Berkeley, California, USA. Jia Lin, Minliang Lai and Letian Dou contributed equally to this work. *e-mail: p_yang@berkeley.edu
Supplementary Figure 1. The phase transitions and optical properties. a, XRD patterns of the low-T phase obtained by exposure to water, methanol, and ethanol vapors, and standard low-T phase of CsPbI$_3$. b, The evolution of the characteristic XRD peaks of CsPbIBr$_2$ film over time during the high-T to low-T phase transition at RH = 70% (high-T peak: 14.9° (100); low-T peaks: 10.3° (002) and 13.6° (012)). c, Absorbance spectra of CsPbIBr$_2$ as a function of exposure time at RH = 80% during the phase transition. The inset shows the color change of the film.
Supplementary Figure 2. Reconstructed 3D reciprocal lattice of the low-T phase from the RED data. a, The overview of 3D reciprocal lattice. b, The 3D reciprocal lattice along the a-axis. c, d, and e show the hk0, h0l, and 0kl planes. An orthorhombic unit cell could be used to index the RED data.
Supplementary Figure 3. Reconstructed 3D reciprocal lattice of the high-T phase from the RED data. a, The overview of 3D reciprocal lattice. b, The 3D reciprocal lattice along the a-axis. c, d, e and f show the hk0, h0l, 0kl, and hhl planes. A cubic unit cell has been found for the high-T phase. g, The EDS shows that the composition of the material is CsPbIBr$_2$ (Cu is from copper grid for TEM).
**Supplementary Table 1.** The refined unit cell determined by RED combined with XRD data.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition</th>
<th>Space Group</th>
<th>Lattice Parameters (Å)</th>
<th>ICSD Number</th>
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<td>CsPbBr$_3$</td>
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<tr>
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Supplementary Figure 4. AFM surface topography of the CsPbIBr$_2$ film on a NiO$_x$ layer (without top coating). a and b, As-synthesized high-T phase. c and d, Moisture-induced low-T phase. e and f, Re-converted high-T phase. The freshly formed high-T phase thin film features sharp-edged grains at the surface with distinct crystallographic orientations. After moisture or heating treatment, the grain surfaces become more smooth with the appearance of some striations within the grains. Root-mean-square (RMS) factors: a, 15.56 nm, c, 16.93 nm, and e, 16.41 nm, respectively. Scale bars are (a, c, e) 500 nm and (b, d, f) 200 nm, respectively.
Supplementary Figure 5. In situ ambient pressure X-ray photoemission spectroscopy (AP-XPS) study. a, AP-XPS O 1s spectra of the high-T phase CsPbI$_3$ before (under UHV condition) and after exposure to H$_2$O (200 mTorr) and Ar (50 mTorr). At UHV condition, the O 1s peak is very weak, indicating the minimal oxygen contamination during the transfer of the sample to XPS chamber. Incident X-ray energies of 630, 730, and 800 eV were used to probe the O amount on the surface with different depth. The peak at 535.2 eV indicates the gaseous H$_2$O in the chamber, and its intensity would not change with time due to the consistent H$_2$O partial pressure in the chamber. The ratios of the surface adsorbed oxygen to gaseous H$_2$O at different probing depth after exposure to H$_2$O/Ar atmosphere are 1.825 (630 eV), 1.836 (730 eV), and 1.834 (800 eV), respectively. With increased incident X-ray energy, the surface oxygen amount has no obvious increase, indicating that H$_2$O is only adsorbed at the surface without diffusing into the lattice during the phase transition. b, Fitted AP-XPS spectrum of O 1s at 630 eV. The fitted peaks of the surface adsorbed oxygen are assigned mainly to liquid H$_2$O and O-H, and the lower peak to Pb-O bonding.
Supplementary Figure 6. Photovoltaic properties of the CsPbIBr$_2$ solar cell. a, The hysteresis behaviors under forward scan (dashed lines) and reverse scan (solid lines) directions with 20, 100, and 400 mV s$^{-1}$ scan rates. The solar cell shows $\Delta$PCE < 10% at a slow scan rate (20 mV s$^{-1}$) with respect to the scan direction. b, Stabilized power output under the constant voltage of 0.72 V.
Supplementary Table 2. Detailed device performance parameters corresponding to Supplementary Fig. 6a.

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<th>Scan direction</th>
<th>Scan rate (mV s(^{-1}))</th>
<th>(J_{\text{sc}}) (mA cm(^{-2}))</th>
<th>(V_{\text{oc}}) (V)</th>
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<th>PCE (%)</th>
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Supplementary Figure 7. The tunability of optical and photovoltaic properties of CsPbI$_{3-x}$Br$_x$ films. a, PL spectra with different compositions ($x = 0$, 1, 1.5, 2, 2.5, and 3), showing spectral tunability across 530–705 nm. It is noted that high intensity laser beams may induce phase segregation during PL measurement. b, J-V curves of solar cell devices with different halide compositions (reverse scan at 20 mV s$^{-1}$). c, The photographs of the low-T phase CsPbI$_3$ (left) and CsPbIBr$_2$ (right) thin films. The CsPbI$_3$ low-T phase exhibits the yellow color, which is why it's colloquially called the "yellow phase", while the CsPbIBr$_2$ film we demonstrated here appears colorless in the low-T state.
Supplementary Table 3. Detailed device performance parameters corresponding to Supplementary Fig. 7b.

<table>
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<th>Composition</th>
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<th>V&lt;sub&gt;OC&lt;/sub&gt; (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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Supplementary Figure 8. Variable-temperature GIWAX measurement. The CsPbIBr$_2$ thin film shows a low-T to high-T phase transition starting at ~150°C.
Supplementary Figure 9. Photovoltaic properties of the semi-transparent solar cell. a, The hysteresis behavior under forward scan (dashed line) and reverse scan (solid line) directions (20 mV s\(^{-1}\)). b, Stabilized power output under the constant voltage of 0.70 V. c, The power conversion efficiency (PCE) of the high-T phase over 40 transition cycles. In the initial several cycles, we observed an improvement in performance of the semi-transparent device, which is probably due to the improved crystallinity of the interlayer materials and the top ITO electrode.
Supplementary Figure 10. In situ observation of the evolution of the device performance. Variations of short-circuit current density ($J_{SC}$), open-circuit voltage ($V_{OC}$), and fill factor (FF) of the CsPbIBr$_2$ solar cell during the high-T to low-T and low-T to high-T phase transitions.
Supplementary Figure 11. The performance reversibility of the CsPbIBr$_2$ solar cells. The photovoltaic properties of five representative devices show similar variation trends during cycling.