Reversible Decomposition of Single-Crystal Methylammonium Lead Iodide Perovskite Nanorods

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ABSTRACT: Perovskite solar cells offer remarkable performance, but further advances will require deeper understanding and control of the materials and processing. Here, we fabricate the first single crystal nanorods of intermediate phase (MAI-PbI2-DMSO), allowing us to directly observe the phase evolution while annealing in situ in a high-vacuum transmission electron microscope, which lets up separate thermal effects from other environmental conditions such as oxygen and moisture. We attain the full determination of the crystal structures and orientations of the intermediate phase, evolving perovskite, precipitating PbI2, and e-beam induced PbI2 during phase conversion and decomposition. Surprisingly, the perovskite decomposition to PbI2 is reversible upon cooling, critical for long-term device endurance due to the formation of MAI-rich MAPbI3 and PbI2 upon heating. Quantitative measurements with a thermodynamic model suggest the decomposition is entropically driven. The single crystal MAPbI3, nanorods obtained via thermal cycling exhibit excellent mobility and trap density, with full reversibility up to 100 °C (above the maximum temperature for solar cell operation) under high vacuum, offering unique potential for high-performance flexible solar cells.

INTRODUCTION

Organo-lead trihalide hybrid perovskites (MAPbX3, where MA is CH3NH3 and X is a halogen atom such as I, Br, or Cl) have enabled remarkable progress in the field of solar cells, including power conversion efficiency (PCE) of over 20%, due to their high optical absorption coefficients, long charge-carrier diffusion lengths, high defect tolerance, and tunable band-gaps with low-cost production processes. The key to high efficiency is the quality of crystallization and morphology, which is achieved using antisolvent engineering to precipitate an intermediate phase. This process requires thermal annealing to convert the intermediate phase to the crystalline perovskite, but heat is also one of the main drivers (together with moisture, oxygen, light, etc.) for perovskite decomposition. Annealing beyond the minimum temperature needed for perovskite formation leads to decomposition with formation of PbI2, degrading the performance.

MAPbI3 bulk single crystals were first studied in 2015. Subsequently, perovskite bulk single crystals with different compositions were synthesized and the properties of these materials were also characterized in detail. All of the reported perovskite bulk single crystals exhibited superior properties, including red-shifted absorption, favorable charge transport properties, and good stability, leading to great success in the application of these materials in X-ray detectors, γ-ray detectors, and visible light photodetectors. Early perovskite single crystals had millimeter-scale thicknesses, far greater than the carrier diffusion length, which was problematic for photovoltaics. Therefore, methods were developed to grow micrometer-thick perovskite single crystal thin films (SCTFs), such as cavitation-triggered asymmetrical crystallization, vapor phase epitaxial growth, surface-tension assisted growth, and a top-down method. Still, several challenges remain to grow high-quality and large area SCTFs, to form good interface contacts between the SCTFs and substrates, and to preserve their properties over a range of operating conditions. These factors ultimately control the efficiency of solar cells.

Hence, to further improve the efficiency and stability of perovskite solar cells requires a fundamental understanding of the various phases and their transition, in particular perovskite decomposition with PbI2 precipitation. In situ transmission electron microscopy (TEM) has already enabled direct observation of perovskite degradation at high resolution, and here we extend this powerful technique by growing single crystalline intermediate-phase nanorods and observing their transformations in situ during thermal processing in a high-...
vacuum TEM, which effectively guards the nanorods against oxygen and moisture.

It has been generally believed that decomposition of MAPbI₃ occurs by irreversible loss of MAI via evaporation or reaction with oxygen or moisture.²²,⁴⁴,⁴⁵ Here we find a very different and remarkable behavior. When MAPbI₃ is protected from extrinsic reactants, perovskite decomposition to PbI₂ still occurs even at temperatures too low for MAI evaporation. Remarkably, this decomposition is reversible upon cooling. The reversibility appears critical for the long-term device endurance at the elevated temperatures that occur during normal solar cell operation. Our quantitative measurements let us develop a model explaining the reversible decomposition as entropically driven, with the excess MAI accommodated in stacked perovskite sheets.⁴⁶ Thus, the decomposition is not a cumulative destructive process but rather a fundamental part of the equilibrium phase diagram.

Annealing the intermediate-phase nanorods at 100 °C transforms them to single-crystal perovskite with excellent electrical properties; the hole mobility is nearly the same as that of bulk single crystals,²⁴ and the trap density is much lower than epitaxial films.⁴⁷ The electrical properties of these single crystal perovskite nanorods are temperature-dependent, reflecting the decomposition of the perovskite: with increasing temperature, the electrical properties degrade as the amount of PbI₂ precipitation from the perovskite increases. Most importantly, the properties are fully reversible under thermal cycling up to 100 °C, which exceeds the maximum temperature for solar cell operation. Using electron diffraction and high-resolution, in situ TEM during thermal cycling, we obtain a full determination of the sequence of transformations and the crystal structures of the resulting phases. These include the original intermediate phase, the evolving perovskite, and PbI₂ formed by decomposition. By varying the e-beam dose, we clearly distinguish between the actual phase evolution and e-beam effects.

■ RESULTS AND DISCUSSION

To determine the initial structure of the nanorod, we carry out TEM measurements. Figure 1a shows a typical TEM bright field (BF) image of a broad view of the nanorods on a SiO₂ membrane grid obtained at room temperature (RT). The nanorods are formed on a SiO₂ membrane grid by spin-coating the precursor solution to which controlled amounts of γ-butyrolactone (GBL) and dimethyl sulfoxide (DMSO) solvent are added (see the Methods section for more details.) As expected, the nanorod is comprised of an intermediate phase,¹⁰ as identified by X-ray diffraction (XRD) and selected area electron diffraction (SAED). Figure 1c in the Supporting Information compares our XRD spectrum with that of the intermediate phase from ref¹⁰.

Figure 1. Images of intermediate phase nanorods characterized by TEM. (a) BF image of a large view of the nanorods on a SiO₂ membrane TEM grid. The scale bar is 1 µm. (b) BF image of a nanorod marked in a square in part a with the corresponding SAED pattern. The scale bar is 100 nm. (c) HRTEM image of the white square region in part b with the corresponding FFT. The lattices with red and white indicate the main and twin crystal structures, respectively. The width of twin varies. The scale bar is 2 nm. The lattice spacings of (150) and (180) are marked as 0.365 ± 0.005 and 0.337 ± 0.005 nm, respectively. (d) Schematic of indexing the diffraction patterns of intermediate (purple), PbI₂ particle (orange), and PbI₂ matrix (sky-blue). (e) Schematic of indexing the diffraction patterns of intermediate (purple), PbI₂ particle (orange), cubic perovskite (blue), and tetragonal perovskite (violet).
Diffraction spots are elongated in the direction normal to the nanorod axis, which we interpret as reflecting the presence of polysynthetic twins with a distribution of lamella widths (Figure 1c). We note that the structure is stable under e-beam exposure at a dose rate of $28 \times 10^2$ e$^-$/nm$^2$ s up to about 10 min at room temperature during TEM measurements.

To directly monitor the conversion of the intermediate phase into perovskite, we used in situ TEM during the annealing cycle for the sample in Figure 1. It is well-known that heating transforms the intermediate phase into perovskite,$^{10}$ and the perovskite decomposes to PbI$_2$ under e-beam exposure. Here we deliberately used an e-beam with a dose rate of $28 \times 10^2$ e$^-$/nm$^2$ s which is sufficient to instantly evaporate MAI from a perovskite, without damaging the intermediate phase. This leaves a PbI$_2$ crystal (called PbI$_2$ matrix) with crystal orientation inherited from the perovskite,$^{48}$ as shown below.

Figure 2. In situ TEM observation during annealing cycle. (a–h) Sequence of BF images acquired from a video obtained during heating and cooling cycles for perovskite conversion, decomposition, and recovery. The images (a–d and e–h) were obtained at 80, 100, 130, 155, 100, 80 °C, and room temperature, respectively. The dark particles with strong contrast are PbI$_2$. The scale bar is 50 nm. (i–k) BF images of the nanorods taken at room temperature after annealing cycles, with maximum annealing temperatures of 80, 100, and 130 °C during the respective cycles. The scale bar is 50 nm. The white arrows indicate PbI$_2$ ($R\bar{3}m$:$H$) matrix, and orange and purple arrows indicate PbI$_2$ ($P\bar{3}m1$) particles and intermediate phase, respectively. (l) An indexed SAED pattern obtained at 100 °C with a weak e-beam without evaporating MAI from perovskite. (m–o) HRTEM images of the PbI$_2$ ($R\bar{3}m$:$H$) matrix from parts d and h and of a PbI$_2$ ($P\bar{3}m1$) particle from part d. The scale bar is 2 nm.

Figure 2a–d shows a series of BF images of representative nanorods extracted from a video where the sample was heated in stages to 80, 100, 130, and 155 °C, respectively. At 80 °C, we see a nanorod plus a few tiny PbI$_2$ particles (see arrows in the BF image of Figure 2a), and we determine the detailed crystal structure using SAED (Figure 2a inset). The nanorods still consist primarily of an intermediate phase oriented to [001]. In addition they include some PbI$_2$ particles with strong contrast (Figure 2a inset) and of a PbI$_2$ ($P\bar{3}m1$) particle from part d. The scale bar is 2 nm.
The index in Figure 1d reveals that [011̅0] and [101̅0] of the PbI₂ matrix are tilted clockwise and counterclockwise ∼15.7° about [0001] of PbI₂ particles with respect to [101̅0] and [011̅0] of PbI₂ particles, respectively, and both planes of the PbI₂ matrix have much shorter lattice spacings (0.317 nm) than those of PbI₂ particles (0.394 nm). Additionally, (1120) of the PbI₂ matrix are parallel to (101̅0) of PbI₂ particles, but the former has a much shorter lattice spacing (0.223 nm) than the latter (0.394 nm). Furthermore, all of (200) of the intermediate, (1120) of the PbI₂ particle, and (1108) of the PbI₂ matrix are parallel and have identical lattice spacings (0.226 nm). As mentioned above, we note that thermally and electron beam induced PbI₂ structures are different. Because a cubic perovskite aligned in [001] is nearly identical to PbI₂ matrix aligned in [4401] except for {100} and {110} which are only involved in the perovskite, the relationship of structural orientation among intermediate, perovskite, and PbI₂ particle can be inferred from Figure 1d as exhibited in Figure 1e. It is noteworthy that the spot elongation present before annealing disappears, presumably due to the removal of a considerable amount of DMSO.

Complete transformation to single crystal perovskite was achieved at 100 °C, reflected by the PbI₂ matrix crystal oriented in [4401] and no intermediate phase left in the nanorod, with a small amount of PbI₂ particles precipitated as exhibited in Figure 2b. To confirm that the PbI₂ matrix is converted from perovskite and their diffraction patterns are correspondent except for {100} and {110} in perovskite, SAED was carried out using a weak e-beam (dose rate of 1 × 10² e⁻/nm² s) for less than a minute, which avoids beam-induced decomposition but is insufficient for BF imaging to quantify the precipitated PbI₂ particles. The SAED pattern acquired before taking the BF image at a higher dose rate in Figure 2b is shown in Figure 2f, confirming that the nanorod is composed of a perovskite aligned in [001] and PbI₂ particles aligned in [0001], in the crystal orientation described in Figure 1e. With increasing temperature, the sizes of PbI₂ particles become larger while maintaining their crystal orientation with the perovskite (Figure 2c,d), and this decomposition by heating leads to increasing roughness of the underlying nanorod. The crystallinity of the PbI₂ matrix and particles are confirmed by using high-resolution transmission electron microscopy (HRTEM) images as shown in Figure 2m–o, respectively.

Real-time observation also allows us to quantify the growth kinetics of the PbI₂ particle at different temperatures. To avoid beam-induced effects, we frequently moved the sample to observe fresh nanorods at nonirradiated sites at each time and temperature. We measured the volume fractions of the PbI₂ particles as time progressed, Figure 3a. At each temperature, the PbI₂ particles appear stable with time. Evidently, when temperature is increased, they grow too quickly for us to observe, reaching a new stable size within a few seconds. The temperature dependence of the stable volume fractions of the PbI₂ during annealing is plotted in Figure 3b and is found to be consistent with Arrhenius behavior (inset of Figure 3b). Details of measurement method and the particle size distribution are given in the Supporting Information and Figures S4 and S5. To ensure against e-beam effects on PbI₂ precipitation, we also monitored one nanorod for an extended time. No observable change in the sizes and number of the PbI₂ particles was identified at 155 °C for ∼5 min (Figure S3).

Following the sequence discussed above, we cooled the sample through the same sequence of temperatures (Figure 3a) and examined its morphology and phase content at each temperature. The BF images of typical nanorods in Figure 2e–h were acquired at 130, 100, 80, and 25 °C, respectively. Surprisingly, the size and density of the PbI₂ particles decrease with decreasing temperature and at 25 °C only a single-crystal PbI₂ matrix remains (inset of Figure 2h,n). This implies that the nanorods had converted back to tetragonal perovskite thermally before being decomposed by the e-beam. To confirm this, as before, we performed SAED of a nanorod at each temperature using a weak beam (i.e., dose rate of 1 × 10¹⁵ e⁻/nm² s) to avoid beam damage (Figure S6). The SAED patterns taken at 25 °C of the nanorods that experienced thermal cycles up to 100, 130, and 155 °C are shown in Figure S6d,h,l, respectively. All three exhibit the diffraction pattern of single crystal perovskite, confirming that the decomposition is completely reversible during thermal cycling. To confirm the reversibility of PbI₂, we repeated the annealing cycle 10 times at various temperatures (gray data in Figure 3b). The data for all heating and cooling cycles collapse onto a single curve of PbI₂ fraction vs temperature. We note that the in situ results shown in Figures 2 and 3 are consistent with the nanorods in the whole area of the sample.

The thermal decomposition of MAPbI₃ is generally attributed to irreversible processes—evaporation of MAI or reaction with oxygen or moisture.
such lossless decomposition requires protecting the material from moisture and oxygen, which we achieve by maintaining high vacuum in our TEM (1 × 10⁻⁷ Torr). In these cases, the PbI₂ fraction increased more rapidly with temperature than in the high-vacuum TEM, and as the thermal cycle to 100 °C (regime I), 80 to 100 °C (regime II), 100 to 155 °C (regime III), and 155 °C to RT (regime IV). The dotted arrows indicate the cooling cycles after heating to 100 °C (green), 130 °C (orange), and 155 °C (blue). Note that the purple data is the repeated heating cycle to 100 °C after complete conversion to perovskite via thermal cycle to 100 °C.

To explain how heating could drive reversible decomposition, we consider a highly simplified model, which contains only the minimal elements required to illustrate the effect. The elementary building blocks in this model are the molecules MAI and PbI₂, with stochiometric MAPbI₃ being an ordered compound consisting of two molecules per formula unit and with the possibility to insert excess MAI molecules into the MAPbI₃, (We approximate the PbI₂ as pure, for simplicity.) Precipitation of PbI₂ leaves excess MAI in the MAPbI₃, increasing the enthalpy but also the entropy. From these assumptions, the equilibrium fraction f of PbI₂ vs temperature is

$$f_{\text{PbI}_2} \approx \frac{\alpha \nu}{2} \exp\left(-\frac{H}{kT}\right)$$

(1)

to the lowest order in f, where α is the number of possible sites for insertion of MAI per formula unit of MAPbI₃, ν is the number of internal configurations (e.g., rotations) for each site, H is the enthalpy change per MAPbI₃ unit for decomposition, and k is the Boltzmann constant. Equation 1 gives an excellent description of the data in Figure 3b with $H = 0.6 \text{ eV}$ and $\nu = 3 \times 10^3$, and it allows us to calculate the phase boundary of the MAPbI₃ as shown in Figure 3c, consistent with the values measured by EDX (Figure S8). We emphasize that the actual perovskite/intercalation system is far more complex than this, so the fitted parameters H and ν may not directly correspond to physical properties of this system, but the model clearly illustrates how the observed phenomena can arise thermodynamically, because decomposition into nonstoichiometric material increases the entropy.
For photovoltaic applications, the electrical properties are critical. To characterize the temperature dependence of hole transport in the nanorod, we fabricated two-terminal single-nanorod devices. Pt electrodes were deposited at both ends using FIB. An SEM image of the device is shown in the inset of Figure 4a (see the schematic illustration of the device in Figure S14a); the channel length is 1.9 μm and the rod’s width is 248 nm. We confirmed that the intermediate phase of the nanorod remained intact after FIB, using SAED measurements. The device dark current was measured in real time while annealing the device in vacuum (same pressure as in the TEM) to estimate the trap density and carrier mobility using the space-charge-limited current (SCLC) model23,47,52 (Figure S11). As seen in Figure 4a–d (the thermal cycle to 155 °C), the J−V traces of the nanorod at varied temperatures feature a general trend. There is a linear (ohmic) J−V relation at low bias. With increasing bias, there is a remarkable increase of the current injection, which we attribute to filling of traps. At still higher bias, we observe the child regime, with a quadratic dependence of the current density on the applied voltage. The trap density (n_t) of the nanorod was calculated by trap-filled limit voltage (V_TFL), and the carrier mobility (μ) was evaluated in the child regime using the Mott–Gurney law; see the Supporting Information for relevant equations.

To calculate carrier mobility and trap density in the nanorod, we first determined the temperature dependent dielectric constants (ε) by measuring capacitances of the same material in the thin film form during the annealing cycle53 (see the Supporting Information for details and Figure S12). The variation of film properties with temperature is nearly identical to those of nanorods, implying that these behaviors are general and not limited to a particular morphology (see the in situ TEM BF and the relevant plots in Figure S13). The ε vs T plot (Figure 4e) exhibits nearly ideal reversibility, presumably reflecting the reversibility of decomposition and the almost identical ε of perovskite and intermediate phases. Dielectric constants measured at different temperature cycles show similar reversibility (Figure S12c–h). Based on the rule of mixtures, the ε of perovskite and PbI₂ with their volume fractions should determine the ε of the total system,54 allowing us to estimate55 temperature dependence of ε of the MAI-rich single crystal perovskite (see the Supporting Information for details and Figure S12c), which is infeasible to obtain at such a wide range of temperatures due to perovskite decomposition.

Temperature dependence of the carrier mobility and trap density are plotted in Figure 4f.g. We first address annealing to 100 °C, since this is the minimum temperature for complete perovskite conversion and is above the maximum temperature for typical solar cell operation. During heating, the mobility slowly decreases at first (regime I), followed by a large decrease by a factor of 20, down to 5 × 10⁻²⁷ cm² V⁻¹ s⁻¹ at 100 °C (regime II). During cooling, the mobility fully recovers (regime IV, green data). The trap density initially decreases with heating, slowly until 80 °C (regime I) and then more rapidly, dropping by 33% from 80 to 100 °C, to 6.74 × 10⁻¹⁴ cm⁻² s⁻¹ (regime II). During cooling the trap density decreases again by 32% (regime IV, green data). We repeated the cycle to 100 °C and confirmed that after the initial conversion from the intermediate phase to perovskite, both properties are fully reversible (see the purple data in Figure 4f.g). This suggests that the traps and mobility reduction reflect the excess MAI and/or PbI₂ precipitates during reversible decomposition.

It is important to note that annealing at 100 °C produces single crystal perovskite nanorods with mobility (1.41 cm² V⁻¹ s⁻¹) nearly equal to single crystal perovskites24 and trap density (4.58 × 10⁻¹⁴ cm⁻³) an order of magnitude smaller than epitaxial perovskite thin films.57 While there is already significant decomposition (~3%) and an order of magnitude decrease in mobility at 100 °C, the excellent electrical properties are preserved after thermal cycling, reflecting the reversible decomposition. Solar cells can get quite hot during operation, but still their maximum temperature is typically well below 100 °C.23,50 This suggests that in a device with an appropriate protective coating,56–61 thermal decomposition still occurs unavoidably, but it is not a cumulative path to degradation and failure. Rather, the decomposition appears fully reversible, so it does not limit the operational lifetime.

Next, we measured the transport properties on different samples during the thermal cycle to higher temperatures, 130 and 155 °C. As the maximum temperature increases from 100 °C (green data) to 155 °C (blue data), mobility and trap density degrade over the entire cooling cycle with the additional regime III (Figure 4f.g). There is still a partial recovery (a factor of ~40 improvement) upon cooling, again reflecting the reversible decomposition (Figure S11a–h). We repeated the annealing-cycle measurements at these three maximum temperatures with five devices for each, providing consistent trends (the deviation of the data is ~12%). These trends directly correlate with the degree of roughness visible in Figure 2h,j,k. Other properties (f_PVI which reflects the amount of excess MAI in perovskite and ε) are reversible over this range of temperature. We therefore believe that the degradation results from the roughening of the nanorod occurring during the process of reversible decomposition of perovskite at higher temperatures.

It seems surprising that the mobility gets worse even while the trap density is improving during conversion from intermediate phase to perovskite (~100 °C). It is reasonable that initially mobility decreases due to formation of interphase boundaries between the intermediate phase and perovskite, followed by a faster decrease caused by scattering by the roughness, excess MAI in the perovskite, and perhaps other defects introduced during decomposition. We also suggest that the decrease in trap density reflects the elimination of planar defects as illustrated above (Figure 2i), which are aligned along the current path. Thus, this trend does not significantly contribute to the mobility.

■ CONCLUSION

We believe that the results shown here are of fundamental importance for understanding and optimizing perovskite processing for applications including photovoltaics. Our results provide new insight into the conversion from an intermediate phase and the decomposition induced by subsequent heating as well as the effect on dielectric and charge transport properties. All of these are essential in optimizing the power conversion efficiency and stability of photovoltaics. Synthesizing single crystal nanorods in an intermediate state is shown to be an ideal approach to quantify the intrinsic aspects of the aforementioned phenomena in an in situ TEM whose high-vacuum state lets up separate thermal effects. The fabrication of single crystal perovskite nanorods by spin-coating and subsequent annealing is simple and cost-effective, compared to other methods such
as vapor phase deposition,\textsuperscript{62–64} and it may enable flexible devices based on single crystal perovskite nanorods.\textsuperscript{65,66}

\section*{METHODS}

\textbf{Material Preparation.} CH\textsubscript{3}NH\textsubscript{3}I (MAI) was synthesized by reacting 27.86 mL of CH\textsubscript{3}NH\textsubscript{2} (40\% in methanol, Sigma-Aldrich) and 30 mL of HI (57 wt \% in water, Sigma-Aldrich) in a 250 mL round-bottom flask at 0 °C for 4 h with stirring. The white-colored MAI powder was obtained using a rotary evaporator and redissolved in 80 mL of ethanol, recrystallized from 300 mL of ethyl acetate, and dried at 60 °C in a vacuum oven for 24 h. The prepared MAI and PbI\textsubscript{2} (Sigma-Aldrich) were mixed in a 1:1 molar ratio, and then 0.04 M precursor solution dissolved in a mixture of γ-butyrolactone (GBL) and dimethyl sulfoxide (DMSO) (7:3 v/v) was stirred vigorously at 60 °C for 12 h. The concentration range of the precursor in solution to form nanorods is relatively narrow (0.03–0.07 M); at lower concentrations, the rods are too thin and becomes dissociated, while at higher concentrations, the density of rods is so high that they become entangled and form films. The mixed precursor solution (10 μL) was spin-coated onto the SiO\textsubscript{2} membrane grid (3 mm size, TEM windows) by 3,000 rpm for 30 s with toluene (30 °C). The nanostructured perovskite films were UV/ozone-treated for 10 min to control the surface energy of the glass, Marienfeld Superior from Germany) and subsequently baked at 150 °C for 2 h in a vacuum sealed chamber whose base pressure is 2 × 10\textsuperscript{−5} Torr.

\textbf{In Situ Analysis of Dielectric and Charge Transport Properties.} To investigate the dielectric and charge transport properties of thin films and individual nanorods, respectively, the thin film and nanorod with intermediate phase were spin-coated onto the SiO\textsubscript{2}/Si substrate using the aforementioned methods (see the first paragraph in the Methods), and then two-terminal devices were fabricated as follows. The Pt electrodes were deposited by FIB for the thin film and nanorod (see the real devices and their schematic illustrations in Figure S14): for the thin film, the channel length is 200 nm, film thickness is 50 nm, and the rod width is 200 μm, while for the nanorod, the typical channel length is 2 μm and the rod’s width is 250 nm. The dielectric and charge transport properties of the thin film and nanorod devices were measured in a vacuum sealed chamber whose base pressure is 2 × 10\textsuperscript{−7} Torr, similar to the vacuum level in TEM, using a semiconductor characterization system (Keithley 4200-SCS).

\section*{ASSOCIATED CONTENT}

\textbf{Supporting Information}

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.0c00385.

More details on the equations to calculate the trap density and the carrier mobility, the measurement of capacitances of intermediate-phase thin films, the definition of dielectric constant and loss, the model to evaluate the dielectric constant of perovskite from the system with multiple phases, and the results of XRD, TEM SAED and BF, AFM, TGA, EDX, particle statistics, and device structures (PDF)

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Notes

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