Supplementary Materials for

Deciphering the effect of traps on electronic charge transport properties of methylammonium lead tribromide perovskite

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S-1 Time of Flight current spectroscopy

In our ToF setup, Current waveforms (CWFs) are generated by the synchronous triggering of the laser pulse to enhance the signal to noise ratio compared to the untriggered sources like alpha particles. It is known that a high external electric field in OMHP devices results in the dynamic decomposition or degradation of the perovskite material, unstable measurement, and device failure. To prevent this, pulse biasing was applied. The ToF experimental setup is based on a direct high frequency amplification of the current pulse flow that is recorded by an ultrafast digital sampling oscilloscope (4 GHz frequency bandwidth, 11-bit resolution). The laser pulses (450 nm wavelength, FWHM ≈ 1 µs, and spot size ~ 3 mm²) which are synchronously driven with the oscilloscope trigger by two-channel master arbitrary waveform generator (Tektronix AFG 3252).

It is mentioned that the above-bandgap laser pulse can only penetrate into a thin layer below the anode surface and therefore, the whole sample, including the bulk of the material, remains unaffected by illumination. The generator also drives an in–house constructed DC bias switching unit for a precise time-correlated pulse biasing of the cathode. This configuration enables
the exact adjustment of a variable laser pulse timing within switched on bias interval. We used 0.5 ms bias on, see Fig. S1 for the timing diagram. Pulse repetition rate and the bias ON/OFF ratio are used to control the overall current loading of the detector (10 Hz, 1:1000 typically), and they are fully variable. We can attenuate the laser pulse intensity by using a variable neutral density optical filter. Due to a low illumination intensity, the noise affects the amplitude of CWFs. Therefore, computer-controlled averaging was used to enhance the signal to noise ratio.

**Fig. S1.** A schematic of bias and light pulsing in the ToF set up.

**S-2 Monte Carlo (MC) simulation**

MC simulation was performed using a one-dimensional (1-D) technique (transverse uniformity of the material is considered) with a total number of particles, \( N = 10^5 \). Each MC particle, labeled with index \( j \), has a position, \( x_j \) and a state, \( s_j \). Initial position, \( x_j \), of each MC particle is generated according to the Beer-Lambert’s law for light absorption. The time domain of simulation \( 10 T_R \) is divided into small time steps, \( \Delta t \) (10000 used here). Each MC particle represents several thousand carriers (electrons or holes) and thus charges in the MC particle is defined as \( q = Q_0/N \), where \( Q_0 \) is the initial photogenerated charge. At each calculation time step \( t_k \), the state of each carrier is determined by a MC technique based on repeated random sampling. The basic concept of MC simulation is shown in Fig. S2. At time \( t_0 \), each carrier position is generated according to the Beer-Lambert law for light absorption. Three evolution paths, which correspond to steps in Fig. S2A, are shown in the bulk of a semiconductor in Fig. S2B.
Fig. S2. Monte Carlo simulation of charge transport. (A) A schematic of 1D MC simulation, where each line represents the time evolution of one carrier. Red circles indicate carriers in the free state and blue circles indicate short-term trapped carriers in a shallow level defect. Green circles demonstrate long-term trapped carriers in a deep level defect. At each time step ($\Delta t$), carriers drift towards the collecting electrode by $\Delta x$ distance, where $\Delta x = v(x)\Delta t$, or remain trapped. Three possible evolution pathways are shown. The first path is the evolution of free carrier that drifts at each simulation step. The second path is the evolution of carrier that drifted in the first simulation step and then trapped in the shallow defect, where the carrier remained for one simulation step and then continued drifting. The third path is given for the carrier that drifted for a one-time step and then trapped for many steps (depending on detrapping time) in a deep trap. (B) Scheme of the MC simulation in the spatial domain, where gold rectangles represent the electrical contacts.

Initially, a drifting charge carrier is in a free state drifting in the valence band towards the collecting electrode by a distance, $\Delta x_j$ given by Equation S1

$$\Delta x_j = \mu E(x_j) \Delta t + u,$$

where $\mu$ is the carrier mobility ($\mu_h$ for holes), $E(x_j)$ is the internal electric field, and $u$ is a small random offset with Gaussian distribution $P(u)$ simulating carrier diffusion,
\[ P(u) = \frac{1}{\sqrt{4\pi D\Delta t}} \exp\left(-\frac{u^2}{4D\Delta t}\right), \quad (S2) \]

where \( D \) is the diffusion coefficient given by the Einstein equation. Repeatedly applying random offset, \( u \), to every carrier at each time step results in carrier spreading that simulates the diffusion phenomenon. If \( x_j + \Delta x_j \geq L \) or \( x_j + \Delta x_j \leq 0 \), the charge carrier is collected on the electrode and does not contribute to the simulation anymore. The electric field \( E(x) \) is an arbitrary function of the position given by space charge inside the device and follows Equation S3

\[ U = \int_0^L E(x) \, dx, \quad (S3) \]

where \( U \) is the applied bias, and \( L \) is the device thickness.

The second state of MC particle is the trapped state (trapped in the \( i \)-th trap level) where the charge carrier can remain trapped or can be detrapped. The trapping-detrapping process is based on probability, and therefore, it’s a random number. The following relation explains the probability of initial free carrier to be trapped into \( i \)-th trap level in \( \Delta t \) time

\[ p_{Ti}(\Delta t) = \frac{\Delta t}{\tau_{Ti}} \quad (S4) \]

Analogically for a carrier trapped in the \( i \)-th trap level, the detrapping probability, \( p_{Di} \), of the charge carrier being detrapped in \( \Delta t \) time is given by a similar equation

\[ p_{Di}(\Delta t) = \frac{\Delta t}{\tau_{Di}} \quad (S5) \]

Here, the direct transition between trapped states is not assumed. The described process is repeated until the required duration of the simulation is reached. The electric current and respective current waveform is further calculated at each time step from the Shockley-Ramo theorem:

\[ I(t_k) = \sum_{j=1}^{N} \frac{q\Delta x_j}{L\Delta t} \quad (S6) \]

The carrier mobility is given by the following equation

\[ \mu_h = \frac{L^2}{T_R U} \quad (S7) \]

where \( L \) is a distance between the electrodes.
S-3 Characterization of free charge transport in a semiconductor by Time of Flight spectroscopy and Monte Carlo simulation

Below we show the results of MC simulation for a semiconductor with one shallow level and a semiconductor with one deep level.

Monte Carlo fit based on least squares regression analysis

In order to fit CWF ToF spectra, we have considered four models based on the number of traps. Table S1 demonstrates the parameters of four models.

**Table S1** Parameters of the least square regression fit

| Model                | τ₁₁ (μs) | τ₁₂ (μs) | τ₂₁ (μs) | τ₂₂ (μs) | τ₃₁ (μs) | τ₃₂ (μs) | τ₄₁ (μs) | τ₄₂ (μs) |
|----------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| Fit with 1 trap      |          |          | 20       | 21       |          |          |          |          |
| Fit with 2 traps     |          |          | 21       | 17       | 123      | 112      |          |          |
| Fit with 3 traps     | 23       | 3        | 24       | 14       | 90       | 120      |          |          |
| Fit with 4 traps     | 50       | 3        | 27       | 17       | 90       | 100      | 49       | 3        |

Electric field distortion

The drift of photo-induced charge carriers in a semiconductor device with a planar electrode structure results in an electric field distortion which affects charge carriers dynamics. Considering the distribution of photo-induced charge carriers in a thin layer localized at distance $x$ from the anode with density $\sigma$, the electric field distortion in the middle of the layer $\delta E(x)$ can be calculated via Gauss law by the following relation

$$\delta E(x) = \frac{\sigma(2x - L)}{2\varepsilon_0\varepsilon_r L} \quad (S8)$$

where $L = 2$ mm, $\varepsilon_0$, and $\varepsilon_r = 28$ are the sample thickness, vacuum permittivity, and relative permittivity of MAPbBr₃, respectively. The non-constant electric field induced by free charge cloud affects the velocity of the drifting charges. The deformation of the electric field is similar to a static space charge screening with an equivalent density $\rho_d = \sigma/L$ uniformly distributed within the sample.

By integrating the CWF in Fig. 3A and normalizing the corresponding charge by the illuminated spot area of 3 mm², $\sigma$ is found $\approx 100$ fC. The normalized space charge, $\rho_d/e_i$, is $9 \times 10^5$ cm⁻³. Such a small concentration of space charges typically leads to a negligible deformation of the electric field. Using previously assessed value of $\sigma$ in Equation S8, we found the electric field
distortion near the anode to be $\delta E = -0.6$ V/cm, which is much smaller than the minimal electric field used in ToF measurements (100 V/cm). Therefore, electric field distortion induced by carriers drift can be neglected here. Generally, the electric field deformation can be induced by free charge cloud, as well as the space charge associated with charge defects. Therefore, the electric field profile should be verified by ToF measurements and MC simulation at different biases.

**Charge transport affected by multiple trap levels**

According to Shockley-Read-Hall (SRH) model, the trapping and detrapping process induced by the $i$-th trap follows equation below:

$$\frac{dp_{ti}}{dt} = \left( -\frac{p}{\tau_{Ti}} + \frac{p_{ti} + \Delta p_{ti}}{\tau_{Di}} \right)$$

Where $p = p_0 + \Delta p$, $\Delta p$ and $p_0$ are the free holes concentration, concentration of photo-generated holes, and concentration of holes in equilibrium, respectively. $p_{ti}$ is the concentration of holes trapped in the $i$-th level and $\Delta p_{ti}$ is the concentration of photo-generated holes trapped in the $i$-th level. Here, we only consider the hole transport. Free electron transport can be also described by the same set of equations substituting free electron concentration, $n$, instead of holes, $p$. The trapping process involving free hole carriers captured by a defect center depends on the trap concentration, $N_{Ti}$, and the hole capture cross section, $\sigma_{hi}$

$$\tau_{Ti} = \frac{1}{(N_{Ti} - p_{ti})\sigma_{hi}v_h}$$

where thermal carrier velocity, $v_h$, is a constant proportional to the effective hole mass. The captured hole can be released from the defect center and return to the valence band. The detrapping process depends not only on the capture cross-section but also on the activation energy of defect level in the band gap according to the equation below:

$$\tau_{Di} = \frac{1}{(p_0 + p_{ti})\sigma_{hi}v_h}$$

where $p_{ti}$ is holes density if the Fermi level is equal to the trap ionization energy. Considering the photo-generated holes drifting in the steady-state regime, the following effective mobility relation can explain the delay of free holes by traps:

$$\mu_h^{eff} = \mu_h \frac{\Delta p}{\Delta p + \sum_i \Delta p_{ti}} = \mu_h \frac{1}{1 + \sum_i \Delta p_{ti} / \Delta p}$$

(S12)
where $\mu_h$ is the holes drift mobility.

To connect the effective mobility ($\mu_h^{\text{eff}}$) with trapping and detrapping parameters of traps, we consider the SRH model in two steady state regimes ($\frac{dp_t}{dt} = 0$): equilibrium in dark (Equation S13) and under illumination (Equation S14):

$$\sigma_h v_h [(N_{Ti} - p_{ti})p_0 - p_{ti}p_{1i}] = 0 \quad \text{(S13)}$$

$$\sigma_h v_h [(N_{Ti} - p_{ti} - \Delta p_{ti})(p_0 + \Delta p) - (p_{ti} + \Delta p_{ti})p_{1i}] = 0 \quad \text{(S14)}$$

The ratio between trapped and free photo-induced holes can be found by combining Equations S13-S14 and comparing it with trapping and detrapping times in Equations S10-S11:

$$\frac{\Delta p_{ti}}{\Delta p} = \frac{N - p_{ti}}{p_0 + \Delta p + p_{1i}} \approx \frac{\tau_{Di}}{\tau_{Ti}} \quad \text{(S15)}$$

Here, a low concentration of photo-induced holes $p_0 > \Delta p$ is assumed to simplify Equation S15. where $p_0 = 6 \times 10^8 \text{ cm}^{-3}$ (according to 6-probe measurements) and $\Delta p \sim 10^6 \text{ cm}^{-3}$ (found by integrating current waveform). Finally, by substituting Equation S15 in S12, the effective mobility, $\mu_h^{\text{eff}}$, can be described based on trapping and detrapping parameters of traps:

$$\mu_h^{\text{eff}} = \mu_h \frac{1}{1 + \sum_i \frac{\tau_{Di}}{\tau_{Ti}}} \quad \text{(S16)}$$

**Definitions of transit time in ToF experiment**

![Current vs Time graph](image)

**Fig. S3** The inflection, intersection, and MC transit times demonstrated in CWF at 20 V bias.
The evolution of the charge cloud computed by the Monte Carlo simulation and Time of Flight currents

Movie S1 shows the effect of traps on the dynamics of free holes depicted by ToF and MC simulation. The left panel in Movie S1 demonstrate ToF CWF measured at 100 V. The red curve shows the best MC simulation fit with three traps. The top right panel shows the time evolution of the free charge cloud (subdivided according to their trapping-detrapping history) during the drift process. The bottom right panel demonstrates respective normalized concentrations of never trapped holes, trapped, and delayed holes in the material.

Movies S2-S4 show the spatial and temporal distribution of free and trapped charges in MAPbBr₃ at electric biases of 100 V, 20 V, and 1 V respectively. The left panel demonstrates the evolution of free holes and the occupation of trap states in a MAPbBr₃ device. The right panels show the simulated visualization of the spatial distribution of traps (top panel), the distribution of occupied trap density (middle panel), and the profile of the charge cloud.