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1 Ionic Field Screening in MAPbBr₃ Crystals Revealed from Remnant Sensitivity in X-ray Detection

3 Agustin O. Alvarez, Ferdinand Lédée, Marisé García-Batlle, Pilar López-Varo, Eric Gros-Daillon,
4 Javier Mayén Guillén, Jean-Marie Verilhac, Thibault Lemerrier, Julien Zaccaro, Lluís F. Marsal,
5 Germà Garcia-Belmonte,* and Osbel Almora*



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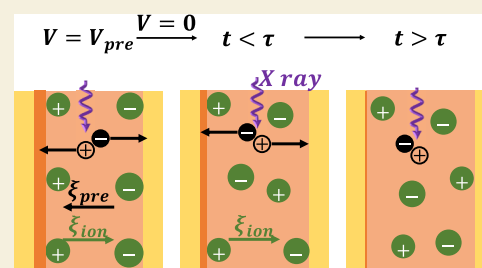


Article Recommendations



Supporting Information

6 **ABSTRACT:** Research on metal halide perovskites as absorbers for X-ray
7 detection is an attractive subject due to the optimal optoelectronic properties of
8 these materials for high-sensitivity applications. However, the contact degradation
9 and the long-term instability of the current limit the performance of the devices, in
10 close causality with the dual electronic-ionic conductivity of these perovskites.
11 Herein, millimeter-thick methylammonium-lead bromide (MAPbBr₃) single and
12 polycrystalline samples are approached by characterizing their long-term dark
13 current and photocurrent under X-ray incidence. It is shown how both the dark
14 current and the sensitivity of the detectors follow similar trends at short-circuit (V
15 = 0 V) after biasing. By performing drift-diffusion numerical simulations, it is
16 revealed how large ionic-related built-in fields not only produce relaxations to equilibrium lasting up to tens of hours but also
17 continue to affect the charge kinetics under homogeneous low photogeneration rates. Furthermore, a method is suggested for
18 estimating the ionic mobility and concentration by analyzing the initial current at short-circuit and the characteristic diffusion times.
19 **KEYWORDS:** ion migration, X-ray detectors, metal halide perovskites, sensitivity, ion diffusion



1. INTRODUCTION

20 The use of methylammonium-lead bromide (MAPbBr₃) as an
21 absorber for X-ray detection has been established since
22 2016^{1–3} thanks to the high mobility-lifetime product and
23 small surface charge recombination velocity, which allow
24 relatively high sensitivity (see Table S1 in the [Supporting](#)
25 [Information](#), SI). Yet, even though the high quality of the
26 single crystals and the thickness of polycrystals are
27 challenging,⁴ the instability of the contacts⁵ and the long-
28 term current response^{6–10} remain arguably the key issues for
29 the development of perovskite X-ray detectors (PXD) in
30 general¹¹ and MAPbBr₃-based devices in particular. Monitor-
31 ing the photocurrent at a given reverse bias voltage with
32 respect to the reference and stable dark saturation current is a
33 primary requirement for typical applications in ionizing
34 radiation imaging. Directly related to both contact degradation
35 and long-term current evolution,¹² the dual ionic-electronic
36 conductivity of these materials continues to be a puzzling
37 subject of intensive research.¹³
38 The ionic properties of millimeter-thick perovskite samples
39 with symmetric or rectifying contacts have been theorized in
40 previous works.^{6,8–10,13–15} Notably, a method for estimating
41 ionic mobility from the short-circuit (SC) diffusion regime
42 after bias polarization has been proposed following the ionic
43 dynamic doping (IDD) model.⁶ Similarly, exotic behaviors
44 upon poling suggesting bias dependency of mobility have also
45 been approached in the ballistic-like voltage-dependent

mobility (BVM) model. Furthermore, numerical drift-diffusion
46 simulations of the dark saturation current of PXD have pointed
47 out the major influence of the ionic charge field screening in
48 biasing conditions (voltage $V \neq 0$ V).¹³ Yet, a description of
49 the charge density profile and the field distributions as these
50 samples relax toward equilibrium at SC ($V = 0$ V) after external
51 pre-biasing is still missing.

52 An interesting behavior has been revealed while character-
53 izing MAPbBr₃ single and polycrystalline samples, as shown in
54 [Figure 1a](#). A detailed description of the fabrication method and
55 material characterization of similar samples can be found in
56 previous works^{9,16} and further specifics on our studied samples
57 are in the experimental section S2 in the [Supporting](#)
58 [Information](#). The general energy diagrams, with processes of
59 charge carrier generation, recombination, and injection, are
60 schemed and commented on in [Figure S1](#) for typical photon
61 detectors based on intrinsic semiconductor absorbers. [Figure](#)
62 [1b](#) shows the dark current density (J_{dark}) and the X-ray-
63 absorbing photocurrent (J_{ph}) during polarization ($V = 10$ V) 64

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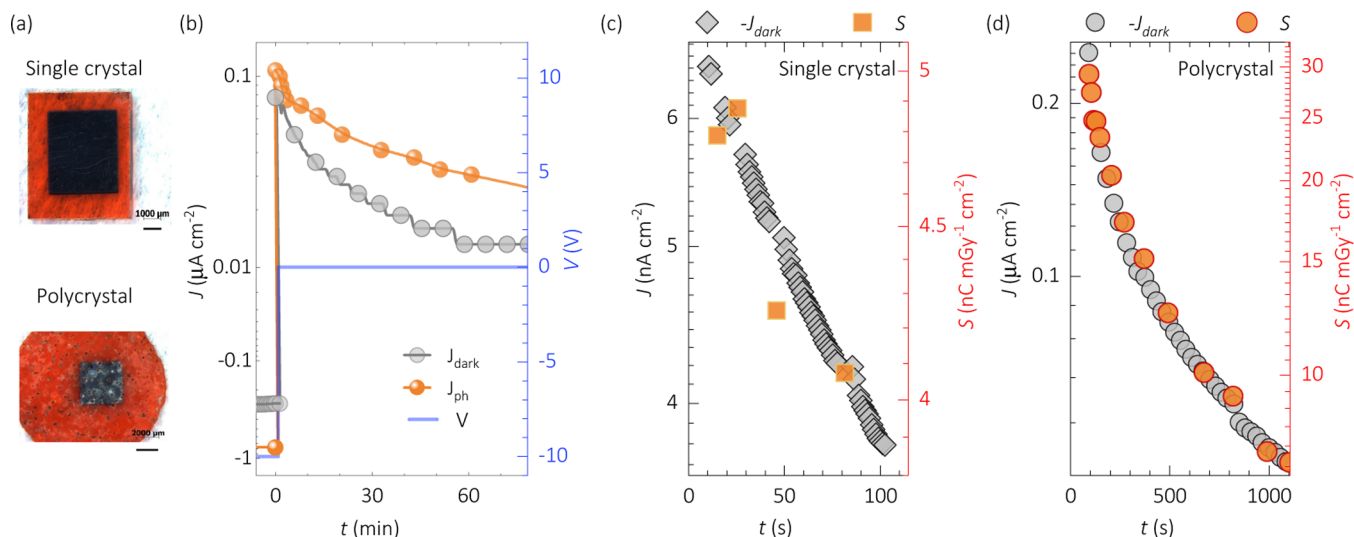


Figure 1. Time evolution of dark current (b–d), photocurrent (b), and sensitivity (c,d) of millimeter-thick MAPbBr₃ single (c) and polycrystal (b,d) samples such as those pictured in (a). The transition from biasing to the SC condition is shown in (b), while the corresponding sensitivities are in (c,d).

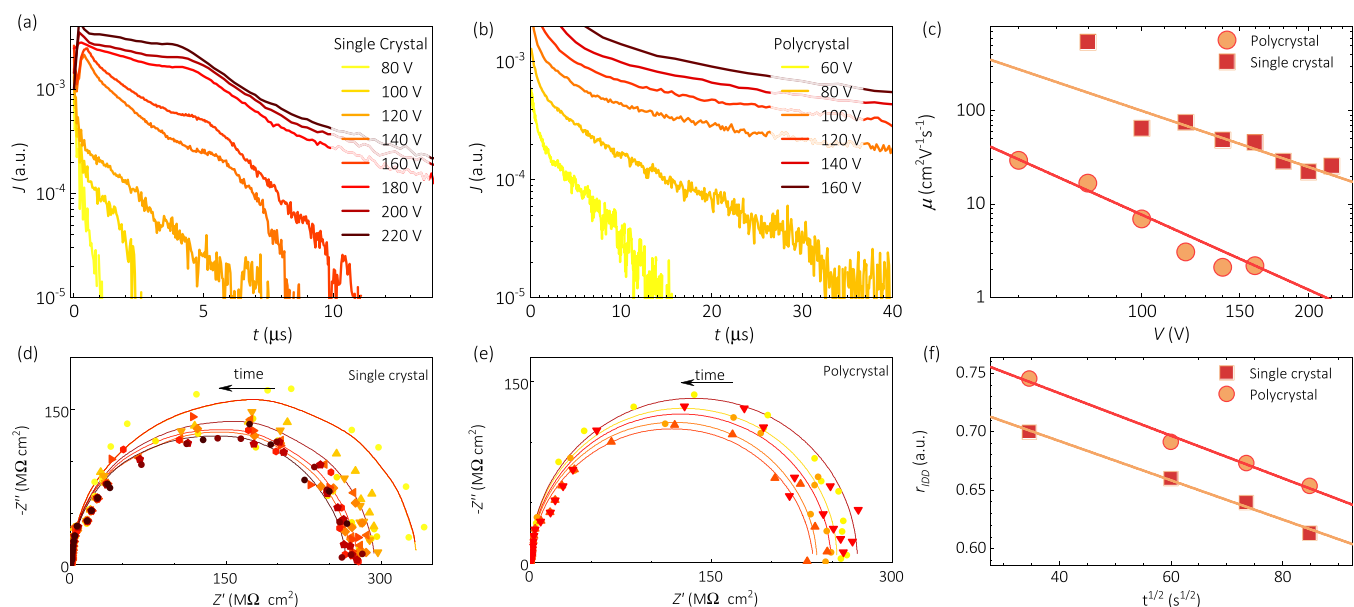


Figure 2. Experimental characterization of charge carrier mobility: electronic (a–c) and ionic (d–f). The time-of-flight measurements versus voltage are shown for single (a) and polycrystalline (b) samples with the corresponding maximum hole mobilities (c). The impedance spectroscopy spectra in Nyquist representation are presented for single (d) and polycrystalline (e) samples with the corresponding IDD model ratio as a function of the square root of time (f) for estimation of the ionic diffusivity. The solid lines in (c–f) indicate fittings: (c) $\mu \propto V^{-n}$, $n \sim 2$ (d,e). The full data for (a,b) is shown in Figure S4 in the SI.

65 and the subsequent SC ($V = 0$ V) regimes for the studied
 66 samples. During the polarization time, J_{ph} reaches values nearly
 67 three times higher than those of J_{dark} . Furthermore, no
 68 reproducible similarities in the current–time curves $J_{\text{ph}}-t$
 69 and $J_{\text{dark}}-t$ during biasing were observed in our samples
 70 (neglected range in Figure 1). This could be explained due to
 71 the combination of electron injection and generation, which
 72 changes the charge mobilities and ionic-electronic concen-
 73 tration ratios, producing different kinetic mechanisms with
 74 respect to the dark condition. However, in the absence of
 75 injection due to external biasing (i.e., at $V = 0$ V after biasing),
 76 the current sign is inverted, and not only is the absolute value
 77 of J_{ph} just slightly higher than that of J_{dark} but also the

78 corresponding $J_{\text{ph}}-t$ and $J_{\text{dark}}-t$ curves seem to mirror each
 79 other while transiting from a current maximum toward
 80 equilibrium. Notably, the reproducibility of the $J_{\text{ph}} \sim J_{\text{dark}}$
 81 trend at SC was found regardless of the fabrication method,
 82 crystallinity, and contact materials (e.g., Cr/MAPbBr₃/Cr and
 83 ITO/MAPbBr₃/Cr) of the samples. This behavior is magnified
 84 in terms of the X-ray detection sensitivity (S) for different
 85 samples of single and polycrystalline natures in Figure 1c,d,
 86 respectively. Apparently, similar sections of the dark current
 87 decay at SC produce different values of S , i.e., a higher
 88 sensitivity is reported for the polycrystalline samples over the
 89 single crystal ones. Yet, the similarity of the time evolution $S-t$
 90 with respect to $J_{\text{dark}}-t$ is remarkable. This suggests that the

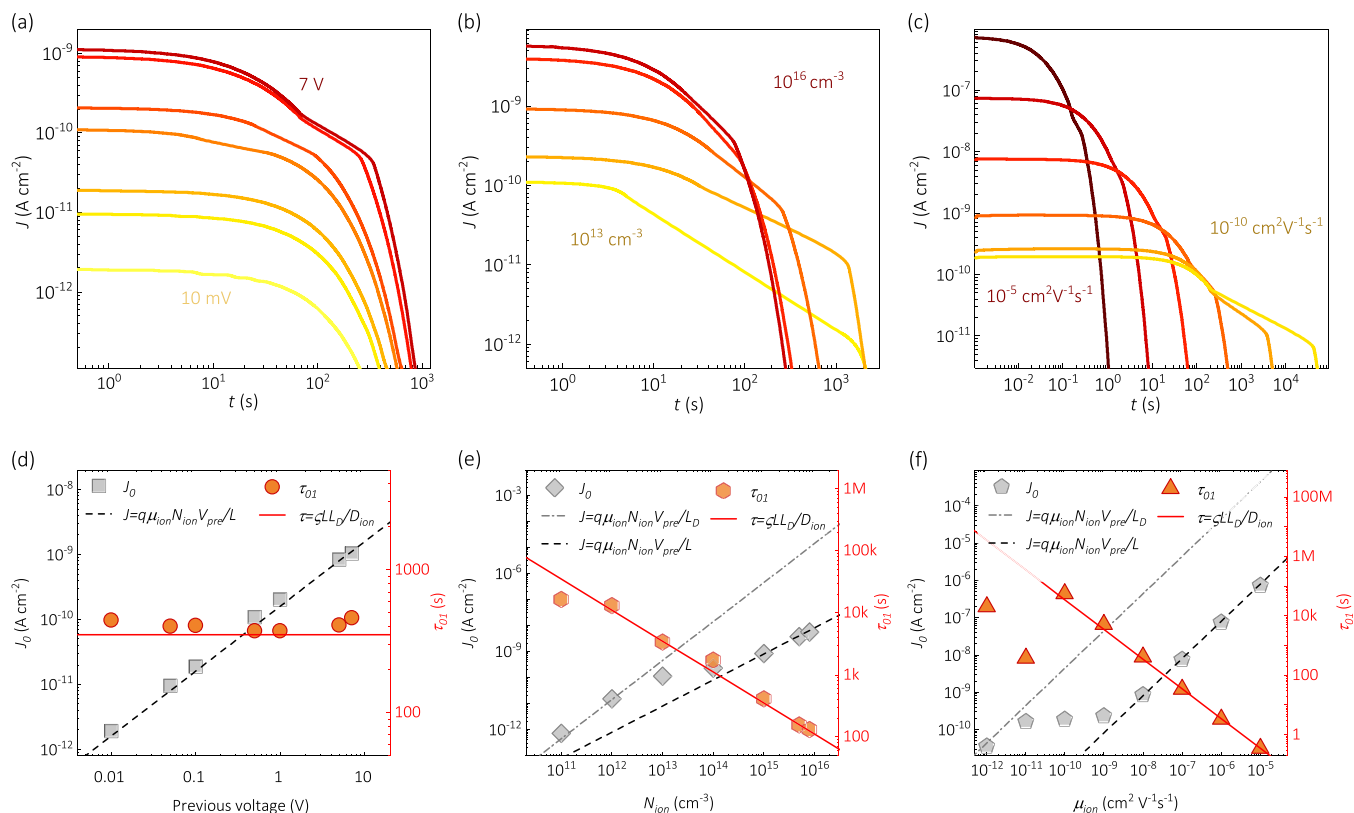


Figure 3. Numerical simulation of current versus time at SC ($V = 0$ V) after biasing. The effect of different polarization biases prior to the SC regime is shown in (a), whereas the change in ion concentration and ion mobilities are shown in (b) and (c), respectively. In (d–f) are the corresponding initial currents J_0 and time τ_{01} to achieve 1% of that J_0 for (a–c), respectively. Herein, $L = 100$ μm , $\mu_e = 1$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, and $\mu_p = 10$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for (a–f); $\mu_{\text{ion}} = 10^{-8}$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for (a,b,d,e); $N_{\text{ion}} = 10^{15}$ cm^{-3} for (a,c,d,f); previous $V_{\text{pre}} = 5$ V for (b,c,e,f), $\zeta = 0.5$ in (d–f).

91 inner field distribution caused by the mobile ion rearrangement
92 after polarization in the early moments of the SC regime is not
93 significantly changed with respect to the dark situation for
94 small generation rates in the order of those reported in the
95 studied samples.

96 In this work, the electrical response of millimeter-thick
97 MAPbBr₃-based PXD at SC after polarization is characterized
98 and modeled. The similar time evolution of dark current and
99 sensitivity is highlighted, and several time-dependent current–
100 voltage experiments are conducted for attesting reproducibility.
101 The behavior and orders of magnitudes of the electronic and
102 ionic mobilities are explored in a set of simulations and
103 analyzed. The simulated devices follow the Schottky-diode-like
104 configuration from previous works,^{13,14,17} where up-to-
105 millimeter-thick perovskite pellets are sandwiched between
106 metals of different work functions (WFs). For the numerical
107 simulations, the open-source MATLAB code Driftfusion¹⁸ was
108 employed. Our results indicate the importance of interface
109 phenomena and field screening behind the slow kinetics of
110 thick PXDs during the diffusion regime of relaxation toward
111 equilibrium at SC after biasing.

2. RESULTS AND DISCUSSION

112 Our first approach is to evaluate the charge carrier mobility of
113 the samples, which will allow us to use the proper parameter
114 ranges in the numerical simulations. Regarding the electronic
115 (hole) mobility, the time-of-flight (ToF) current decay as a
116 function of pulse bias is shown for single and polycrystalline
117 samples in Figure 2a,b, respectively. As is typical in metal
118 halide perovskite (MHP) samples,^{15,19} there is more than one

119 decay regime where exponential and/or power law behaviors
120 can be argued. Nevertheless, assuming the smallest (sharpest-
121 exponential-like region) transit time (τ_{ToF}), a maximum
122 mobility can be estimated from the Mott–Gurney relation²⁰
123 $\mu \cong L^2/(\tau_{\text{ToF}}V)$, where L is the thickness of the sample.
124 Apparently, the τ_{ToF} between electrodes is smaller for the
125 single crystal (1–20 μs) than for the polycrystalline sample
126 (10–40 μs), which results in maximum mobility values ranging
127 from 20–300 and 2–30 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively (see Figure
128 2c). The negative slope of the mobility versus voltage curve has
129 also been previously reported in the literature for other
130 MHPs.^{15,21}

131 The impedance spectroscopy over time at SC (after pre-
132 biasing) was measured within the framework of the IDD
133 model⁹ and shown for the single and the polycrystal samples in
134 Figure 2d,e, respectively. The high resistivity of the samples
135 (slightly higher for the single crystal sample) results in noisy
136 spectra, yet a decreasing trend can be extracted where the
137 resistance transits from an initial value R_{t_0} toward a saturation
138 value R_{t_∞} , which is typically^{8–10,14} around 10% from the
139 initial value, i.e., $R_{t_\infty}/R_{t_0} = \alpha \sim 0.1$. Even though the stability of the
140 contacts prevented us from measuring R_{t_∞} , the IDD model
141 ratio (see derivation in Section S3.1) can be rewritten as

$$r_{\text{IDD}} = \frac{R - R_{t_0}}{R_{t_0}(1 - \alpha)} = -\frac{3\sqrt{2D_{\text{ion}}t}}{L} \quad (1)$$

142 where the ion diffusivity D_{ion} can be used to estimate the ion
143 mobility by means of the Einstein equation as $\mu_{\text{ion}} = qD_{\text{ion}}/k_B T$,
144 where q is the elementary charge and $k_B T$ the thermal energy
145

146 (see detailed derivation is Section S3.1 of the Supporting
147 Information). Figure 2 shows the linear behavior between the
148 τ_{IDD} and $t^{1/2}$, where a ratio-time slope RTS can be used to
149 obtain $D_{\text{ion}} = (RTS \cdot L/3)^2/2$ following the approximation of eq
150 1. The values resulted in $D_{\text{ion}} \sim 2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and $\mu_{\text{ion}} \sim 9$
151 $\times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which agree with previous estimations in
152 the literature.^{6,8–10,14}

153 The drift-diffusion numerical simulation is a common
154 approach among perovskite photovoltaic cells^{18,22–24} and
155 similar formalisms have been explored for X-ray detectors.^{13,25}
156 In our case, the simulation of current versus time follows the
157 same assumptions as our previous work¹³ at SC, as illustrated
158 in Figure 3a–c for different previous applied voltages, mobile
159 ion concentrations, and ion mobility, respectively. Figure 3d–f
160 shows the corresponding initial current density J_0 in each case,
161 as well as the time τ_{01} for which the current is 1% of the initial
162 one, i.e., $J(\tau_{01})/J_0 = 0.01$. The effect of previous bias is shown
163 in Figure 3a,d to have no significant impact on the relaxation
164 time, whereas the initial J_0 increases linearly with the previous
165 voltage. This suggests a typical capacitive discharge behavior,
166 where the response time $\tau = RC$ is affected by both the
167 capacitance (C) and the resistance of the sample and is
168 independent of the charging voltage. Similarly, the higher the
169 voltage, the higher the discharge current, in order to converge
170 to equilibrium within the same timescale.

171 The effect of mobile ions in the simulated current relaxation
172 is shown to have a major impact in Figure 3b,c,e,f. The ion
173 concentration N_{ion} not only significantly increases the initial J_0
174 at the same previous voltage but also decreases the relaxation
175 time. The higher the value of N_{ion} the higher that of J_0 and the
176 lower that of τ_{01} . Interestingly, a clear trend $\tau_{01} \propto N_{\text{ion}}^{-1/2}$ can
177 be identified, whereas $J_0 \propto N_{\text{ion}}^{1/2}$ is suggested only for specific
178 ranges. Regarding the dependency on ion mobility μ_{ion} (Figure
179 3c,f), the trends are similar but intensified in terms of the
180 power law: $\tau_{01} \propto \mu_{\text{ion}}^{-1}$ and $J_0 \propto \mu_{\text{ion}}$ are apparent in the
181 simulated range. From here, one can propose an approach
182 similar to the ToF experiment,¹³ but based on the effective
183 ionic field screening ξ_{ion} created by the ions confined within
184 the Debye length

$$L_D = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{q^2 N_{\text{ion}}}} \quad (2)$$

186 where ϵ_0 is the vacuum permittivity, and ϵ_r is the dielectric
187 constant. Subsequently, the relaxation time can be approached
188 by the diffusion time, $\tau = LL_D/D_{\text{ion}}$,^{6,26,27} and through
189 Einstein's relation,²⁸ one can define

$$\tau_{01} = \frac{\zeta L}{\mu_{\text{ion}}} \sqrt{\frac{\epsilon_0 \epsilon_r}{N_{\text{ion}} k_B T}} \quad (3)$$

191 where ζ is a parameterization dimensionless coefficient
192 introduced with the definition of τ_{01} . Similarly, the parameter-
193 ization of the initial current depends on the ionic mobility and
194 concentration. For instance, for high values of μ_{ion} and N_{ion} , an
195 ohmic-like behavior is obtained as a function of the previous
196 voltage V_{pre} and

$$J_0 = \frac{q \mu_{\text{ion}} N_{\text{ion}} V_{\text{pre}}}{L} \quad (4)$$

198 This trend is represented with dashed lines in Figure 3d–f.
199 However, the smaller the values of μ_{ion} and N_{ion} , the stronger

the influence of the Debye length, and thus a better description
would be obtained by $J_0 = q \mu_{\text{ion}} N_{\text{ion}} V_{\text{pre}}/L_D$, which results as 201

$$J_0 = q^2 \mu_{\text{ion}} V_{\text{pre}} \sqrt{\frac{N_{\text{ion}}^3}{\epsilon_0 \epsilon_r k_B T}} \quad (5) \quad 202$$

This is represented with dot-dashed lines in Figures 3e,f and
S5. Notably, the transition between the transport regimes
(TTR) expressed by eqs 4 and 5 is found for ionic properties
with values smaller than $\mu_{\text{ion}} = 10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $N_{\text{ion}} =$
 10^{14} cm^{-3} . Accordingly, only samples with high or low enough
concentrations would be out of the TTR range and display a
linear dependence with V_{pre} whose slope would correspond-
ingly match those of eqs 4 and 5. Experimentally, the
application of these formalisms for J_0 not only depends on
the values of μ_{ion} and N_{ion} and the TTR. The temperature and
the stability of the contacts can also affect the current
relaxation. For instance, Figure S6 in the Supporting
Information shows several experimental current–time curves
at SC after different V_{pre} values, where the linear behavior is
similarly found only for V_{pre} larger than a threshold value that
depends on the geometric and crystalline properties of each
sample.

A method for estimating the mobility and concentration of
mobile ions for perovskite samples, where further evidence
suggests that $\mu_{\text{ion}} > 10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $N_{\text{ion}} > 10^{14} \text{ cm}^{-3}$, was
already suggested in our previous work (focused on the pre-
biasing period).¹³ There, μ_{ion} and N_{ion} were attainable by
processing the slopes of the linear trends of the ionic time-of-
flight τ_{IToF} versus $LT^{1/2}/V$ and the biased dark saturation
current J_B versus qV/L . Complementarily, here, we suggest that
eqs 3 and 4 can be used to analyze τ_{01} versus $LT^{-1/2}$ and J_0
versus qV_{pre}/L from which the slopes of the linear trends would
deduce μ_{ion} and N_{ion} . This diffusion-focused approach to the
dark current at SC after biasing should deliver similar values to
those of the biasing-focused method suggested in our previous
work.¹³

The illustrative time evolution of the simulated electrostatic
potential (φ), field (ξ), charge density profiles (electrons, n ;
holes, p ; anions, a ; and cations, c), and the corresponding
current density components (electron current density, J_n ; hole
current density, J_p ; anionic current density, J_a ; and cationic
current density, J_c) are presented in Figure 4 as a function of
the position x inside the perovskite. After 1 ms without
external bias, the electrostatic potential distributes in a way that
resembles the one-side abrupt p–n junction, with φ behaving
almost linearly in two main regions: the depletion region
toward one electrode (at $x = 0$) and the remaining bulk of the
perovskite layer in Figure 4a. Accordingly, the initial electric
field due to the ionic reordering is outlined in Figure 4b
showing a nearly flat profile in the bulk, increasing by two
orders of magnitude in the depletion region. The charge
density distribution is presented in Figure 4c, where the initial
depletion region occurs with the nearly sole distribution of
fixed anions toward the left electrode while electrons, holes,
and mobile cations reorder toward the bulk. The situation
produces an ohmic-like main contribution of the cationic
current in the early moments of the relaxation toward
equilibrium at SC after biasing, as can be seen in Figure 4d.
At this stage, it is clear that, even though no external bias is
applied, the drift effect related to the internal ionic-related
remnant field is a major contribution to the current in addition
to the expected diffusion process.

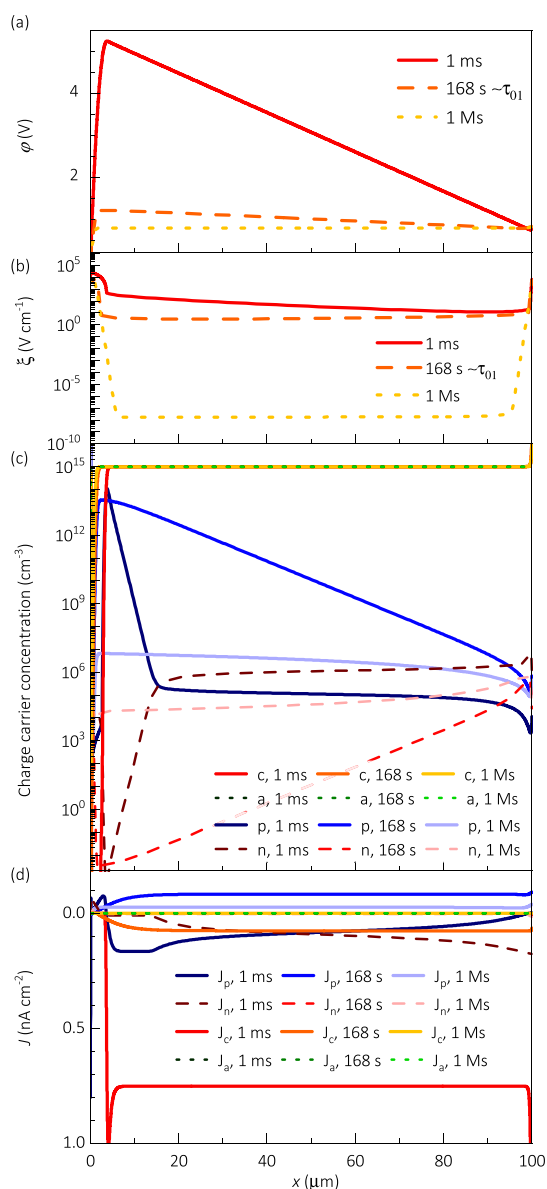


Figure 4. Numerical simulation of (a) electrostatic potential, (b) electric field, (c) charge density profile, and (d) current density components as a function of the position inside the perovskite at SC ($V = 0$ V) after 5 V of previous biasing for $\mu_{\text{ion}} = 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $N_{\text{ion}} = 10^{15} \text{ cm}^{-3}$.

At the characteristic diffusion time (168 s for Figure 4), most of the electrostatic potential and electric field profiles have flattened in Figure 4a,b. The consequent shrinking of the depletion layer produces an exponential gradient of electronic charge carriers in the perovskite bulk (see Figure 4c). Accordingly, not only is the diffusion electronic current in the order of magnitude of the cationic current, but it has an opposite sign that can cancel the total current or invert its sign (see Figure 4d).

In the long-term (e.g., 1 Ms \approx 278 h), the electrical response approaches equilibrium at SC after biasing. Therefore, not only is the electrostatic potential practically flat, but also the electric field decreases by up to 10 orders of magnitude, as displayed in Figure 4a,b, respectively. Accordingly, the charge carrier concentration reaches a more even distribution, where no significant concentration gradients appear in the bulk, resulting

in negligible current contributions from neither the electronic nor the ionic charge carriers, as can be seen in Figure 4c,d, respectively. The longer the time at SC, after the pre-biasing, the lower the field, and thus the diffusion component becomes a principal current mechanism in the electrical response of the samples.

The previously discussed simulations for dark conditions illustrate the nature and effects of the ionic migration in the L_D region toward the interface. Subsequently, we present in Figure 5 the simulated behavior of current over time at SC after

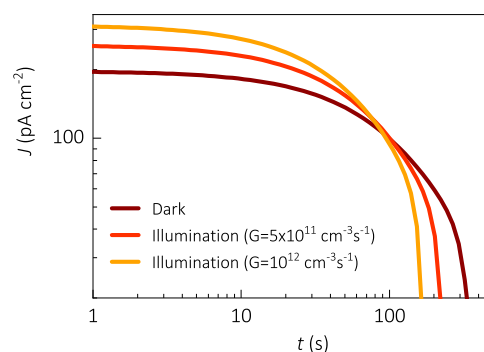


Figure 5. Numerical simulation of the current relaxation in the dark and under low illumination intensities with homogeneous charge carrier generation as indicated at SC ($V = 0$ V) after 5 V of previous biasing for $\mu_{\text{ion}} = 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $N_{\text{ion}} = 10^{15} \text{ cm}^{-3}$.

previous polarization for dark and homogeneous low generation rates of illuminations. Notably, this may be a rough approximation since the charge carrier generation and consequent recombination mechanisms under X-ray photon flux do not fully agree with the typical visible-to-near infrared radiation considered in the simulation code Driftfusion. Nevertheless, our calculations suggest that, for sufficiently low generation rates, the charge density profiles and electric field distributions are not drastically changed in such a way that the photocurrent follows a general behavior very similar to that of dark conditions.

3. CONCLUSIONS

In summary, a set of experiments and simulations have been presented, attesting to the evidence of ionic charge-related field screening in millimeter-thick MAPbBr₃ single and polycrystalline samples for application in X-ray detectors. By analyzing the dark current and photocurrent under ionizing energy radiation at SC after biasing, a similar long-term relaxation trend is reported, which mirrors the sensitivity of the samples as X-ray detectors. Subsequently, the ToF and impedance spectroscopy measurements allowed us to estimate the electronic and ionic mobility in the ranges of 2–300 and $9 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.

A series of simulations have been presented illustrating the effects of ionic concentration and mobility on current relaxation. It is revealed how a high internal electric field can be built upon the migration of the mobile ions when the depletion zone near an electrode during the polarization regime, prior to the relaxation to equilibrium. The tradeoff between the internal built-in and the diffusion of charge carriers is able to enhance the relaxation time by up to tens of hours, depending on the concentration and mobility of the migration ions. Purposely, for perovskite samples with $\mu_{\text{ion}} >$

318 $10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $N_{\text{ion}} > 10^{14} \text{ cm}^{-3}$, a method has been
319 proposed for estimation of the mobility and ionic concentra-
320 tion based on analyzing J_0 and τ_{01} as a function of the
321 previous voltage, distance between electrodes, and temper-
322 ature.

323 Last but not least, we approximate the experimental
324 comparison between dark current and X-ray photocurrent in
325 our numerical simulations with homogeneous generation rates.
326 It is shown how, in the proper range, the excess photo-
327 generated electronic charge carrier densities do not produce
328 drastic modifications to the charge balance in such a way that
329 the currents follow similar long-term relaxation trends over
330 time.

4. EXPERIMENTAL SECTION

4.1. Sample Fabrication

331 In total, 6 samples were made for this study: 2 single crystals and 4
332 polycrystalline films. The fabrication procedure followed the steps
333 described in our previous work,^{9,16} and a summary is in Section S2 of
334 the Supporting Information. All the samples were polished prior to
335 chromium electrode evaporation to make devices. In the symmetri-
336 cally contacted samples, the top electrode (the one which receives the
337 X-ray flux) was thinner (30 nm) than the bottom one (100 nm) in
338 order to perform laser ToF.

4.2. Characterizations

339 The measurement of current–voltage–time characteristics was made
340 with a Keithley 2636 B SourceMeter and a PGSTAT-30 AUTOLAB
341 potentiostat, also used for the impedance spectroscopy measurements.
342 The $J_{\text{dark}}-t$, $J_{\text{ph}}-t$, and $S-t$ measurements were carried out with a
343 Keithley 428 current amplifier and a Keithley 487 power supply. The
344 samples were irradiated using a pulsed X-ray tube with an RQAS
345 spectrum (W anode, 70 kVp, filtration: 23.5 mm Al, and 0.8 mm Be)
346 operated at 4 Hz and 100 ms pulse duration. The incident X-ray dose
347 was calibrated with a PTW Unidos dosimeter. J_{ph} is defined as the
348 maximum photocurrent output for 24 $\mu\text{Gy}_{\text{air}}$ X-ray pulses. The
349 sensitivity is calculated as the integration of J_{ph} over the pulse duration
350 and was averaged for 10 consecutive pulses to reduce experimental
351 error.

352 The measurement of laser hole ToF was made with a pulsed N_2
353 laser with a 337 nm wavelength and an 800 ps pulse duration. The
354 laser beam was attenuated with a neutral density filter before
355 irradiating the samples through the top semi-transparent Cr electrode
356 with a 30 nm thickness. A negative voltage was applied to the back Cr
357 electrode. The ToF current waveforms were acquired with a
358 Tektronix TDS 744A oscilloscope and a Stanford Research Systems
359 PS310 high voltage supply.

4.3. Numerical Simulations

360 The simulations were made within the framework of Driftfusion,¹⁸ as
361 a direct continuation of our previous work on the long-term
362 polarization regimes of thick PXDs,¹³ including both radiative and
363 non-radiative recombination and taking four main assumptions. First,
364 (I) the bulk of the perovskite is initially taken as intrinsic, meaning
365 that the total equilibrium concentrations of fixed and mobile ions
366 should be balanced, i.e., the same total number of cations and anions
367 (our simulation case) or effectively in the order of the intrinsic
368 concentration (possible experimental situation). Second, (II) the
369 interface regions between the perovskite and the contacts are
370 unintentionally doped, forming depletion layers with thicknesses in
371 the order of tens of nanometers. Third, (III) only one type of mobile
372 ions is considered to effectively contribute to the current and the
373 reordering of the charge density profile. Lastly, (IV) the built-in field
374 forming the Schottky-diode-like detector is only defined by the
375 difference in WF between the two metals. An illustrative set of
376 simulation parameters is presented in Table S2, and a comprehensive
377 explanation of the use and setting up of the Driftfusion code can be
378 found in the original publication.¹⁸

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at
<https://pubs.acs.org/doi/10.1021/acsphyschemau.3c00002>.

Introductory data on sensitivity, fabrication procedure
and morphological characterization of samples, X-ray
diffraction data, and simulation parameters (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Germà García-Belmonte – Institute of Advanced Materials,
Universitat Jaume I, 12071 Castelló, Spain; orcid.org/0000-0002-0172-6175; Email: garcia@uji.es

Osbel Almora – Department of Electronic, Electric and
Automatic Engineering, Universitat Rovira i Virgili, 43007
Tarragona, Spain; orcid.org/0000-0002-2523-0203;
Email: osbel.almora@urv.cat

Authors

Agustín O. Alvarez – Institute of Advanced Materials,
Universitat Jaume I, 12071 Castelló, Spain; orcid.org/0000-0002-0920-5390

Ferdinand Lédée – Grenoble Alpes University, CEA, LETI,
DOPT, F38000 Grenoble, France; orcid.org/0000-0001-9949-0529

Marisé García-Batlle – Institute of Advanced Materials,
Universitat Jaume I, 12071 Castelló, Spain; orcid.org/0000-0002-9142-2430

Pilar López-Varo – Institut Photovoltaïque d'Île-de-France
(IPVF), 91120 Palaiseau, France

Eric Gros-Daillon – Grenoble Alpes University, CEA, LETI,
DOPT, F38000 Grenoble, France; orcid.org/0000-0002-4196-7854

Javier Mayén Guillén – Grenoble Alpes University, CEA,
LITEN, DTNM, F38000 Grenoble, France; orcid.org/0000-0002-2732-3809

Jean-Marie Verilhac – Grenoble Alpes University, CEA,
LITEN, DTNM, F38000 Grenoble, France

Thibault Lemercier – Grenoble Alpes University, CNRS,
Grenoble INP, Institut Néel, F38042 Grenoble, France

Julien Zaccaro – Grenoble Alpes University, CNRS, Grenoble
INP, Institut Néel, F38042 Grenoble, France; orcid.org/0000-0002-8150-3827

Lluís F. Marsal – Department of Electronic, Electric and
Automatic Engineering, Universitat Rovira i Virgili, 43007
Tarragona, Spain; orcid.org/0000-0002-5976-1408

Complete contact information is available at:
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Author Contributions

A.O.A.: investigation and writing-original draft; M.G.-B.:
investigation; P. L.-V.: investigation, formal analysis, and
writing—review and editing; L.F.M.: writing—review and
editing and funding acquisition; G.G.-B.: conceptualization,
methodology, formal analysis, funding acquisition, project
administration, and writing—review and editing; O.A.:
conceptualization, methodology, investigation, formal analysis,
writing-original draft, and writing—review and editing; J.M.:
single crystal growth; T.L.: polycrystal growth; J.M.V.:
materials and device fabrication; F.L.: characterization; E.G.:
investigation; and J.Z.: crystal growth. CRediT: Agustín O.

437 Alvarez data curation (equal), investigation (equal), software
438 (equal), validation (equal), visualization (equal), writing-
439 original draft (equal), writing-review & editing (equal);
440 Ferdinand Lédée data curation (equal), funding acquisition
441 (equal), investigation (equal), project administration (equal),
442 validation (equal), visualization (equal), writing-review &
443 editing (supporting); Marisé Garcia-Batlle data curation
444 (supporting), investigation (equal), writing-review & editing
445 (supporting); Pilar López-Varo investigation (equal), software
446 (lead), validation (equal), writing-review & editing (support-
447 ing); Eric Gros-Daillon investigation (equal), writing-review
448 & editing (supporting); Javier Mayén Guillén investigation
449 (equal), writing-review & editing (supporting); Jean-Marie
450 Verilhac investigation (equal), writing-review & editing
451 (supporting); Julien Zaccaro investigation (equal), writing-
452 review & editing (supporting); Lluís F. Marsal funding
453 acquisition (supporting), writing-review & editing (support-
454 ing); Germà Garcia-Belmonte conceptualization (equal),
455 formal analysis (equal), funding acquisition (lead), inves-
456 tigation (supporting), methodology (equal), project admin-
457 istration (lead), resources (lead), supervision (lead), validation
458 (supporting), visualization (supporting), writing-review &
459 editing (supporting); Osbel Almora conceptualization
460 (lead), data curation (lead), formal analysis (lead), inves-
461 tigation (lead), methodology (lead), software (equal), super-
462 vision (equal), validation (lead), visualization (lead), writing-
463 original draft (lead), writing-review & editing (lead).

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477 ■ REFERENCES

478 (1) Birowosuto, M. D.; Cortecchia, D.; Drozdowski, W.; Brylew, K.;
479 Lachmanski, W.; Bruno, A.; Soci, C. X-Ray Scintillation in Lead
480 Halide Perovskite Crystals. *Sci. Rep.* **2016**, *6*, 37254.
481 (2) Wei, H.; Fang, Y.; Mulligan, P.; Chuirazzi, W.; Fang, H.-H.;
482 Wang, C.; Ecker, B. R.; Gao, Y.; Loi, M. A.; Cao, L.; Huang, J.
483 Sensitive X-Ray Detectors Made of Methylammonium Lead
484 Tribromide Perovskite Single Crystals. *Nat. Photonics* **2016**, *10*,
485 333–339.
486 (3) Heiss, W.; Brabec, C. Perovskites Target X-Ray Detection. *Nat.*
487 *Photonics* **2016**, *10*, 288–289.
488 (4) Peng, J.; Xu, Y.; Yao, F.; Lin, Q. Thick-Junction Perovskite X-
489 Ray Detectors: Processing and Optoelectronic Considerations.
490 *Nanoscale* **2022**, *14*, 9636–9647.
491 (5) Armaroli, G.; Ferlauto, L.; Lédée, F.; Lini, M.; Ciavatti, A.;
492 Kovtun, A.; Borgatti, F.; Calabrese, G.; Milita, S.; Fraboni, B.;
493 Cavalcoli, D. X-Ray-Induced Modification of the Photophysical
494 Properties of Mapbbr₃ Single Crystals. *ACS Appl. Mater. Interfaces*
495 **2021**, *13*, 58301–58308.
496 (6) García-Batlle, M.; Baussens, O.; Amari, S.; Zaccaro, J.; Gros-
497 Daillon, E.; Verilhac, J.-M.; Guerrero, A.; Garcia-Belmonte, G.
498 Moving Ions Vary Electronic Conductivity in Lead Bromide

Perovskite Single Crystals through Dynamic Doping. *Adv. Electron.* **1999**
Mater. **2020**, *6*, 2000485.
(7) Chai, Y.; Juan, Z.; Wu, Y.; Liu, Y.; Li, X. Suppressing the Ion
Migration in Halide Perovskite Wafers for Current-Drift Free X-Ray
Detectors. *ACS Appl. Electron. Mater.* **2023**, *5*, 544–551.
(8) García-Batlle, M.; Zia, W.; Aranda, C.; Saliba, M.; Almora, O.;
Guerrero, A.; Garcia-Belmonte, G. Observation of Long-Term Stable
Response in Mapbbr₃ Single Crystals Monitored through Displace-
ment Currents under Varying Illumination. *Solar RRL* **2022**, *6*,
2200173.
(9) García-Batlle, M.; Mayén Guillén, J.; Chapran, M.; Baussens, O.;
Zaccaro, J.; Verilhac, J.-M.; Gros-Daillon, E.; Guerrero, A.; Almora,
O.; Garcia-Belmonte, G. Coupling between Ion Drift and Kinetics of
Electronic Current Transients in Mapbbr₃ Single Crystals. *ACS Energy*
Lett. **2022**, *7*, 946–951.
(10) García-Batlle, M.; Deumel, S.; Huerdler, J. E.; Tedde, S. F.;
Almora, O.; Garcia-Belmonte, G. Effective Ion Mobility and Long-
Term Dark Current of Metal-Halide Perovskites of Different
Crystallinity and Composition. *Adv. Photonics Res.* **2022**, *3*, 2200136.
(11) Li, Z.; Zhou, F.; Yao, H.; Ci, Z.; Yang, Z.; Jin, Z. Halide
Perovskites for High-Performance X-Ray Detector. *Mater. Today*
2021, *48*, 155–175.
(12) O'Kane, S. E. J.; Richardson, G.; Pockett, A.; Niemann, R. G.;
Cave, J. M.; Sakai, N.; Eperon, G. E.; Snaith, H. J.; Foster, J. M.;
Cameron, P. J.; Walker, A. B. Measurement and Modelling of Dark
Current Decay Transients in Perovskite Solar Cells. *J. Mater. Chem. C*
2017, *5*, 452–462.
(13) Almora, O.; Miravet, D.; Gelmetti, I.; Garcia-Belmonte, G.
Long-Term Field Screening by Mobile Ions in Thick Metal Halide
Perovskites: Understanding Saturation Currents. *Phys. Status Solidi*
RRL **2022**, *16*, 202200336.
(14) García-Batlle, M.; Deumel, S.; Huerdler, J. E.; Tedde, S. F.;
Guerrero, A.; Almora, O.; Garcia-Belmonte, G. Mobile Ion-Driven
Modulation of Electronic Conductivity Explains Long-Timescale
Electrical Response in Lead Iodide Perovskite Thick Pellets. *ACS*
Appl. Mater. Interfaces **2021**, *13*, 35617–35624.
(15) Almora, O.; Matt, G. J.; These, A.; Kanak, A.; Levchuk, I.;
Shrestha, S.; Osvet, A.; Brabec, C. J.; Garcia-Belmonte, G. Surface
Versus Bulk Currents and Ionic Space-Charge Effects in Cspbbr₃
Single Crystals. *J. Phys. Chem. Lett.* **2022**, *13*, 3824–3830.
(16) Baussens, O.; Maturana, L.; Amari, S.; Zaccaro, J.; Verilhac, J.-
M.; Hirsch, L.; Gros-Daillon, E. An Insight into the Charge Carriers
Transport Properties and Electric Field Distribution of Ch₃nh₃pbbr₃
Thick Single Crystals. *Appl. Phys. Lett.* **2020**, *117*, 041904.
(17) Deumel, S.; van Breemen, A.; Gelinck, G.; Peeters, B.; Maas, J.;
Verbeek, R.; Shanmugam, S.; Akkerman, H.; Meulenkamp, E.;
Huerdler, J. E.; Acharya, M.; García-Batlle, M.; Almora, O.;
Guerrero, A.; Garcia-Belmonte, G.; Heiss, W.; Schmidt, O.; Tedde,
S. F. High-Sensitivity High-Resolution X-Ray Imaging with Soft-
Sintered Metal Halide Perovskites. *Nat. Electron.* **2021**, *4*, 681–688.
(18) Calado, P.; Gelmetti, I.; Hilton, B.; Azzouzi, M.; Nelson, J.;
Barnes, P. R. F. Drifffusion: An Open Source Code for Simulating
Ordered Semiconductor Devices with Mixed Ionic-Electronic
Conducting Materials in One Dimension. *J. Comput. Electron.* **2022**,
21, 960–991.
(19) Turedi, B.; Lintangpradipto, M. N.; Sandberg, O. J.;
Yazmaciyan, A.; Matt, G. J.; Alsalloum, A. Y.; Almasabi, K.;
Sakhatskiy, K.; Yakunin, S.; Zheng, X.; Naphade, R.; Nematulloev,
S.; Yeddu, V.; Baran, D.; Armin, A.; Saidaminov, M. I.; Kovalenko, M.
V.; Mohammed, O. F.; Bakr, O. M. Single-Crystal Perovskite Solar
Cells Exhibit Close to Half a Millimeter Electron-Diffusion Length.
Adv. Mater. **2022**, *34*, 2202390.
(20) Mott, G. R. NF, "Electronic Processes in Ionic Crystals." *J.*
Chem. Educ. **1965**, *42*, A692.
(21) Shrestha, S.; Fischer, R.; Matt, G. J.; Feldner, P.; Michel, T.;
Osvet, A.; Levchuk, I.; Merle, B.; Golkar, S.; Chen, H.; Tedde, S. F.;
Schmidt, O.; Hock, R.; Rührig, M.; Göken, M.; Heiss, W.; Anton, G.;
Brabec, C. J. High-Performance Direct Conversion X-Ray Detectors

- 567 Based on Sintered Hybrid Lead Triiodide Perovskite Wafers. *Nat. Photonics* **2017**, *11*, 436–440.
- 569 (22) Olyaeefar, B.; Ahmadi-Kandjani, S.; Asgari, A. Bulk and
570 Interface Recombination in Planar Lead Halide Perovskite Solar
571 Cells: A Drift-Diffusion Study. *Phys. E* **2017**, *94*, 118–122.
- 572 (23) Bertoluzzi, L.; Patel, J. B.; Bush, K. A.; Boyd, C. C.; Kerner, R.
573 A.; O'Regan, B. C.; McGehee, M. D. Incorporating Electrochemical
574 Halide Oxidation into Drift-Diffusion Models to Explain Performance
575 Losses in Perovskite Solar Cells under Prolonged Reverse Bias. *Adv.*
576 *Energy Mater.* **2021**, *11*, 2002614.
- 577 (24) Moia, D.; Gelmetti, I.; Calado, P.; Hu, Y.; Li, X.; Docampo, P.;
578 de Mello, J.; Maier, J.; Nelson, J.; Barnes, P. R. F. Dynamics of
579 Internal Electric Field Screening in Hybrid Perovskite Solar Cells
580 Probed Using Electroabsorption. *Phys. Rev. Appl.* **2022**, *18*, 044056.
- 581 (25) Jia, S.; Xiao, Y.; Hu, M.; He, X.; Bu, N.; Li, N.; Liu, Y.; Zhang,
582 Y.; Cui, J.; Ren, X.; Zhao, K.; Liu, M.; Wang, S.; Yuan, N.; Ding, J.;
583 Yang, Z.; Liu, S. Ion-Accumulation-Induced Charge Tunneling for
584 High Gain Factor in P–I–N-Structured Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ X-Ray
585 Detector. *Adv. Mater. Technol.* **2022**, *7*, 2100908.
- 586 (26) Bazant, M. Z.; Thornton, K.; Ajdari, A. Diffuse-Charge
587 Dynamics in Electrochemical Systems. *Phys. Rev. E* **2004**, *70*, 021506.
- 588 (27) Almora, O.; Guerrero, A.; Garcia-Belmonte, G. Ionic Charging
589 by Local Imbalance at Interfaces in Hybrid Lead Halide Perovskites.
590 *Appl. Phys. Lett.* **2016**, *108*, 043903.
- 591 (28) Einstein, A. Über Die Von Der Molekularkinetischen Theorie
592 Der Wärme Geforderte Bewegung Von in Ruhenden Flüssigkeiten
593 Suspendierten Teilchen. *Ann. Phys.* **1905**, *322*, 549–560.
- 594 (29) Calado, P.; Barnes, P.; Gelmetti, I.; Azzouzi, M.; Hilton, B.
595 Driftfusion. 2019, <https://github.com/barnesgroupICL/Driftfusion>
596 (accessed April 17, 2023).