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Chap. 24 : Hybrid perovskites: Charge carrier recombination effects in photovoltaic devices

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Abstract: Hybrid lead halide perovskites emerged at the beginning of 2010s decade as one of the most promising materials for photovoltaic applications. Easy and low-cost solution-based fabrication processes can be used, obtaining perovskite solar cells (PSCs) with efficiencies above 20%. However, there still are some major issues to overcome, like stability, and the general understanding of the recombination mechanisms results particularly puzzling. In this chapter, an analysis is provided on most recent research results about the different mechanisms, location and relationships of charge carrier recombination in PSCs. After introducing the theoretical framework, including the main transport equations and relations with luminescence techniques, the radiative and non-radiative natures of recombination are commented and compared in terms of main contributions. Also, the effects of changing the perovskite composition and morphology are surveyed. The location of the recombination processes, whether in the bulk material or towards the interface, are tackled, as well as related features with the current-voltage hysteresis. On the latter, and along the complete chapter, the dual ionic-electronic conductivity of hybrid lead halide perovskites is particularly attended.

Keywords: HYBRID PEROVSKITES, PEROVSKITE SOLAR CELLS, CHARGE CARRIER RECOMBINATION, IONIC-ELECTRONIC CONDUCTIVITY

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I. Introduction

The perovskite solar cells (PSCs) have been one of the most attractive research subjects in the field of photovoltaics since 2013, when the methylammonium lead iodide $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) was established as a successful light harvesting material.^[1-2]

Figure 1: Perovskite crystal structure, schemed device design of PSCs and recombination pathways.

(a) Cubic or tetragonal phase crystal structure of generic ABX_3 perovskite. (b) Most typical layered structure of perovskite solar cells. A TiO_2 mesoporous scaffold on top of a compact layer is schemed as electron transport layer and spiro-OMeTAD is the example as hole transport layer. The absorber perovskite is schemed as MAPbI₃. (c) Schemed energy diagram of the recombination modes. Electrons (“-” circles) in the bottom of the conduction band (E_C) recombine with holes (“+” circles) in the top of the valence band (E_V) in (1) radiative or (2-4) non radiative ways. Radiative recombination (1a) implies the emission of a photon (1b), while non-radiative recombination transfers the energy to the lattice via (2) Shockley-Read-Hall (SRH) near-mid-gap trap states, (3) surface recombination at the interfaces or grain boundaries, or the less likely (4) Auger recombination where the energy is first transferred to a third particle: an electron (4n) or a hole (4p). Adapted with permission from Almora et al.^[28] (CC BY-NC 4.0).

The MAPbI_3 is a hybrid material which belongs to the wide family known as perovskites, with the general formula ABX_3 and the crystal structure of the mineral perovskite: the calcium titanate (CaTiO_3).

The perovskite crystal structure is illustrated in Figure 1a, where the A-cation is coordinated with twelve X-anions and the B-cation with six. The A-cation for MAPbI_3 is the methylammonium CH_3NH_3^+ (MA), the B cation the lead and iodide is the X anion. Other total or partial substitutions typically include formamidinium $\text{CH}(\text{NH}_2)_2^+$ (FA) and/or Cs^+ and Rb^+ as A cations^[3-6] and other halides like Br or Cl.^[7-11] Also the metallic B-cation have been substituted by Sn^{2+} in lower bandgap absorbers.^[12-14]

The architecture of PSCs basically consists in a light harvesting perovskite sandwiched between the electron and hole transport layers, ETL and HTL respectively, as illustrated in Figure 1b.^[15-16] The manufacturing of these devices involves low cost materials and fabrication methods.^[2, 17] PSCs are also very versatile, with already well performing reports for semi-transparent,^[18] flexible^[19] and tandem^[20] applications. The unprecedented rate of improvement of these cells made it possible to report reproducible power conversion efficiencies (PCE) above 20% in less than 5 years,^[21-22] being the compositions like $\text{Cs}_x(\text{FA}_{0.83}\text{MA}_{0.17})_{(1-x)}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ among the most successful.^[23-24] However, there is still some lack of understanding in terms of working mechanisms and several challenges should be overcome in order to reach the market, e.g. the device stability.^[25-27]

The understanding of the working principles of every photovoltaic device relies on the comprehension one has about their recombination mechanisms. After photon absorption and charge carrier generation, a solar cell is as good as it can extract the highest amount of charge carriers before the electrons and holes recombine. Recombination can occur through several mechanisms: (1) radiative or (2-4) non-radiative, as schemed in the energy diagram of Figure 1c. The dissipation of energy by the electrons in both cases makes power losses via photons or to the lattice, e.g. as acoustic phonons.

In the band-to-band radiative recombination (1a) the electrons in the conduction band (CB) along the bulk return to empty states in the valence band (VB) and (1b) photons are re-emitted, being hardly re-absorbed in photon-recycling events.^[29-30] This is a second order recombination process characterized by the recombination coefficient β in the absorber layer.

Non-radiative recombination can occur via (2) nearly mid-band-gap trap states also along the bulk. This is described by the so-called Shockley-Read-Hall (SRH) recombination model^[31-32] where the electron with energy E_C at the

bottom of the CB steps in the trap level before reaching the energy E_V in the top of the VB, dissipating the energy to the lattice. On the other hand, at the grain boundaries and, more importantly, at the interfaces, (3) surface recombination dominates where several trap states can mediate the path of the electron from the CV to the VB. These are first order recombination processes, typically understood in terms of the SRH recombination lifetime τ .

Last and least likely, after carrier generation, a recombination event can occur where the energy is transferred to another electron (4n) in the CB, which may increase its kinetic energy before dissipating it and returning to the bottom of the CB. This is a three particle event: 1 hole + 2 electrons, or 1 electron + 2 holes (4p in Figure 1c), known as Auger recombination (4), which allows the third particle to still contribute to charge extraction or to another recombination dissipating energy. This is a third order recombination mechanism, described by the coefficient A_r in the absorber material.

Other recombinations between the absorber and the selective contacts are neglected in Figure 1c and the below analyses. Significant radiative recombination between one or both selective contacts and the perovskite would imply red-shifted peaks in the electro- or photo-luminescence spectra of PSCs, of which there is no evidence yet (e.g. see Figure 4). Moreover, a non-radiative recombination between two sides of the heterojunctions without stepping in an interface bandgap defect state would possibly be as or even more unlikely than an Auger recombination process.

The best condition for testing the recombination mechanisms in photovoltaic devices is that of open-circuit voltage V_{oc} under illumination. In this situation the generated charge carriers can only recombine and dissipate energy to the lattice, but no charge carrier is extracted. The general theory can be consulted in the literature.^[33] For simplicity, here we assume the perovskite bulk as intrinsic and neglect the thermal recombination contributions under standard 1 sun illumination. Then the recombination rate can be expressed as

$$U \cong \frac{n}{\tau} + \beta n^2 + A_r n^3 \quad (1)$$

where n is the electron (hole) concentration. This is a general term to consider in the continuity equation. The latter can be considered under low field, field gradients and carrier concentration gradients at open-circuit (OC), when the currents are null or negligible, resulting

$$\frac{dn}{dt} \cong G - U \quad (2)$$

where G is the charge carrier generation rate and the derivative is taken over time t . The continuity equation characterizes bulk sections of the system. At the boundaries, e.g. towards the interface with the electrodes, one can assume perfect selective ohmic contacts (only one type of charge carrier can be extracted at each side) which implies a recombination velocity

$$S_r \cong \frac{D}{n} \frac{dn}{dx} \quad (3)$$

where D is the diffusion coefficient. Note that, in practice, equations (1)-(3) may be redefined separately for electrons and holes, and space dependent, where the assumptions were invalid, meaning that different parameters τ , β , A_r , S_r and D should be considered in every case.

The solution of the equations (1)-(3) for the steady-state condition can be approached to the empirical form of the Shockley equation for the current density J as a function of the voltage V :

$$J = J_0 \left(\exp \left[\frac{qV}{m k_B T} \right] - 1 \right) - J_{ph} \quad (4)$$

where q is the elementary charge, k_B the Boltzmann constant, T the temperature, and m the diode ideality factor. The latter is an empirical parameter associated with recombination typically ranging between 1 and 2, accounting for band-to-band or SRH recombination, respectively.^[34-37] The dark saturation current in (4) can be expressed in terms of Rau's reciprocity relation^[38-39] as

$$J_0 = q EQE_{EL}^{-1} \int_0^{\infty} EQE_{PV} \Gamma_{BB} dE = J_{0,rad} / EQE_{EL} \quad (5)$$

where EQE_{EL} is the absolute electroluminescence (EL) external quantum efficiency (flowing electrons to emitted photons ratio),^[40] EQE_{PV} the photovoltaic quantum efficiency spectrum (aka IPCE: incident photon to converted electron ratio),^[41] Γ_{BB} the Planck's black body radiation spectrum at the temperature of the device in detailed-balanced equilibrium with its

surroundings, the integration over the photon energy E , and $J_{0,rad}$ is the radiative thermal equilibrium recombination current density in the dark ($EQE_{EL}=1$). Similarly, the photocurrent density under standard 1 sun illumination intensity of AM1.5G spectrum ($\Gamma_{AM1.5G}$) results

$$J_{ph} = q \int_0^{\infty} EQE_{PV} \Gamma_{AM1.5G} dE \quad (6)$$

which matches the corresponding short-circuit current density (J_{sc}) if the EQE_{PV} spectrum is measured at $V=0$. Importantly, making $J=0$ in (4) one can approximate the open-circuit voltage as

$$V_{oc} = \frac{mk_B T}{q} \ln \left[EQE_{EL} \frac{J_{ph}}{J_{0,rad}} + 1 \right] \quad (7)$$

which in the radiative recombination limit ($m = EQE_{EL} = 1$) would be

$$V_{oc,rad} = \frac{k_B T}{q} \ln \left[\frac{J_{ph}}{J_{0,rad}} + 1 \right] = V_{oc} + \Delta V_{oc,nr} \quad (8)$$

with the non-radiative recombination photovoltage losses approached to

$$\Delta V_{oc,nr} \cong - \frac{k_B T}{q} \ln \left[EQE_{EL} \left(\frac{J_{ph}}{J_{0,rad}} \right)^{m-1} \right] \quad (9)$$

Similarly, one can focus the analysis on radiative recombination current density J_{rad} via the absolute external photoluminescence quantum yield (incident photons to emitted photons ratio)^[42], which under a given fluence Γ_{PL} characterizes the OC condition as

$$QY_{PL} = \frac{J_{rad}}{J_{ph}} = \frac{J_{rad}}{J_{rad} + J_{nr}} \quad (10)$$

where, assuming the arguable bias independency of J_{ph} ,^[43] the non-radiative recombination current density can be expressed as a function of the short-circuit current density J_{sc} and QY_{PL} as

$$J_{nr} = J_{sc} (1 - QY_{PL}) \quad (11)$$

Furthermore, a simple inspection of equations (1)-(7) suggests that the larger the recombination rate is, the lower the carrier concentration results, and so the photocurrent and photovoltage. On the latter, it is useful to assume the Boltzmann statistics, in order to introduce the quasi-Fermi levels for electrons and holes

$$E_{Fn} = E_C - k_B T \ln \left[\frac{N_C}{n} \right] \quad \text{and} \quad (12a)$$

$$E_{Fp} = E_V + k_B T \ln \left[\frac{N_V}{p} \right] \quad (12b)$$

where p the concentration of holes, and N_C and N_V are the effective density of states in the CB and VB, respectively. Likewise, assuming the perfect selectivity approximation, the voltage between electrodes matches the splitting of the quasi-Fermi levels (ΔE_F , aka QFLS) as

$$\Delta E_F = E_{Fn} - E_{Fp} \cong qV \quad (13)$$

which, for the OC condition, can be expressed as^[37]

$$qV_{oc} \cong E_g - 2k_B T \ln \left[\frac{N_{CV}}{n} \right] \quad (14)$$

where E_g is the band-gap of the absorber material and $N_{CV} = \sqrt{N_C N_V}$. Differently to Equation (7), where the photocurrent is apparently infinitely increasable as $\Gamma_{AM1.5G}$ is in Equation (6), the practical photovoltage limits are explicit in Equation (14). Electrons can only occupy an effective number of states N_{CV} , thus $n < N_{CV}$ makes $qV_{oc} < E_g$.

In this chapter, the recombination mechanisms in PSCs are discussed. Special attention will be paid to the unique features introduced by the perovskite absorbers in photovoltaic device physics. In the following section, the manifestation of each recombination type will be tackled, and the predominant processes will be highlighted. Subsequently, a brief survey on the effects of composition and morphology on the recombination rates will be provided. In a fourth section, the question of where the recombination takes place will be

analyzed. Lastly, the recombination and in relation with the current-voltage hysteresis phenomena will be considered.

Along the complete chapter, general descriptions are provided on the main theoretical and experimental approaches to recombination. In the theoretical formalisms, first-principle calculations and drift diffusion simulations are the most common methods. Experimentally, most often used techniques are the photo-induced transient photovoltage (TPV),^[44-45] the transient and steady-state photoluminescence (PL),^[46] and the impedance spectroscopy (IS).^[45, 47]

II. Radiative versus non-radiative recombination

The discussion on whether the recombination is radiative or non-radiative is of constant attention in photovoltaic applications. In general, maximizing the former is preferred because the possibility of re-absorption while the latter implies larger energy dissipation to the lattice. Along this section, radiative recombination will be first commented. Nevertheless, note that the solution-based fabrication methods most often used for fabrication of PSCs are also a large source of defects that trigger the SRH non-radiative recombination. More importantly, the long recombination lifetimes measured for PSCs, and explaining their good performance results, will be commented along the entire chapter.

Typical measurements of β in MAPbI₃ are claimed to be strongly affected by photon reabsorption, in the study by Crothers et al.^[48] This masks a much larger intrinsic bimolecular recombination rate constant. By investigating a set of films whose thickness varies between 50 and 533 nm, they found that β appears to lower by an order of magnitude as the film thickness increases. However, they determined that a single intrinsic $\beta \approx 6.8 \times 10^{-10} \text{ cm}^3 \cdot \text{s}^{-1}$ is common to all samples irrespective of film thickness. Hence, they postulated that the wide range of literature values reported for such coefficients is partly to blame on differences in photon out-coupling between samples with crystal grains or mesoporous scaffolds of different sizes influencing light scattering, whereas thinner films or index-matched surrounding layers can reduce the possibility for photon reabsorption.

Figure 2: Radiative recombination and bi-molecular recombination coefficient

(a) Schematic diagram of the energy dispersion relation and charge-carrier distributions, which have a determining role in the bimolecular charge-carrier recombination process. The purple and green filled areas show the Fermi–Dirac distributions of the excited electrons and holes in the conduction and valence bands, respectively. (b) Bimolecular recombination rate constant (β) and monomolecular recombination coefficient (τ^{-1}) as a function of temperature, displayed on a semi logarithmic scale. Triangles show β as determined through the van Roosbroeck and Shockley relation^[52] from fits to the experimentally obtained absorption spectra, based on either the electron-hole continuum absorption coefficient including Coulomb interactions (α_C , white triangles), or the free (screened) electron-hole coefficient (α_{Free} , red triangles), with the former applicable at low charge-carrier densities ($n < n_M$) and the latter for charge-carrier densities exceeding the Mott density n_M . Points were fitted with phenomenological expressions (solid line). Circles show values of β and τ^{-1} (fill and empty, respectively) obtained in ref. ^[53] from transient terahertz photoconductivity spectroscopy, and corrected for internal self-absorption effects^[48] to yield intrinsic values of β . Adapted with permission from Davies et al.^[51] Copyright 2020, Springer Nature Limited.

Nevertheless, despite photon-recycling seems to be significant in PSCs,^[30, 49-50] other chemical and morphology effects, and even the competition with non-radiative recombination, are possibly of major influence on β .

Also, β can be fully explained as the inverse process of absorption in MAPbI₃, from the work by Davies et al.^[51] They utilized the van Roosbroeck-Shockley relation^[52] for determining β from absorption spectra and showed that the sharpening of photon, electron and hole distribution functions significantly enhances bimolecular charge recombination as the temperature is lowered, mirroring trends in transient spectroscopy. The Fermi-Dirac distributions of electrons and holes with absorption and emission processes as mediated by the Bose-Einstein functions of the photon radiation field are schemed in Figure 2a. Subsequently, the temperature evolution of β is displayed in Figure 2b, illustrating a good agreement with this theory of radiative bimolecular recombination as the inverse of the absorption process. Intuitively, one could expect a reciprocity between absorption and band-to-band recombination, as expressed in the parallel temperature trend. Note that even the Auger coefficient showed a similar behavior in the work by Milot et al.^[53] Distinctly, also in the latter work and presented in right axis of Figure 2b, the non-radiative down energy transitions increase with temperature. Hence, note that the heating of the cell by effects of the incident radiation and/or current during operation would reduce both τ and β , favoring SRH recombination.

The direct band-gap nature of MAPbI₃, as represented in Figure 2a, has been actually found to have a direct-indirect character. This was proposed by Hutter et al.,^[54] who observed that generation of free mobile charges is maximized for excitation energies just above the indirect bandgap, in time-resolved photo-conductance measurements. They found that second-order electron-hole recombination of photo-excited charges is retarded at lower temperature, which is consistent with a slow phonon-assisted recombination pathway via the indirect bandgap. Purposely, the theoretical analysis by Kirchartz and Rau^[55] similarly highlighted that the indirect bandgap could be of major contribution to the radiative recombination. Subsequently, this slightly indirect bandgap feature has been correlated with the slow radiative recombination in PSCs.^[56-57] Particularly, first-principles analyses by Zhang et al.^[58] indicate that the indirect nature of the bandgap suppresses β by less than

a factor of two, being still as high as those in traditional direct-gap semiconductors. Accordingly, one could say that indirect band-gap effects are further second or third order contributions possibly hindering the radiative recombination in PSCs. Nevertheless, these studies^[54-58] are only focused on MAPbI₃, meaning that state-of-the-art mixed perovskites used in devices with higher V_{oc} could no longer present a significant impact of indirect band-gap processes.

Polaronic states were suggested to suppress the radiative recombination by Ambrosio et al.^[59] from their study of advanced ab initio molecular dynamics in the presence of extra electrons and holes in MAPbI₃. The thermal vibrations of the inorganic sublattice were found to lead to spatial separation between polaronic holes and electrons, which is only moderately affected by the disorder in the orientation of the organic cations. Importantly, the probability of radiative bimolecular recombination is lowered by two orders of magnitude compared with that of optical generation in the case of overlapping between the electron and hole wave functions. In other words, it is proposed that the up-energy transition when an electron absorbs a photon can be up to 100 times more likely than the down radiative recombination transition for polaronic states. Accordingly, one could correlate losses in radiative recombination with to the increase of polaronic states.

The mapping of the splitting of the quasi-Fermi levels ΔE_F via absolute photoluminescence imaging can be used for quantifying non-radiative recombination. Given the heterostructure of PSCs, one can compare the average ΔE_F from a perovskite film with that from a sequence of layers including the perovskite and the electron transport layer (ETL), the hole transport layer (HTL) or both. This method was employed by Stolterfoht et al.,^[60] who studied samples with CsPbI_{0.05}[(FAPbI₃)_{0.89}(MAPbBr₃)_{0.11}]_{0.95}. Figure 3 illustrates the histograms for ΔE_F values from samples with and without contacts and the E_g and $V_{oc,rad}$ values under the given measurement conditions. For the bulk perovskite film, the photovoltage non-radiative recombination losses $\Delta V_{oc,nr,b}$ are around half of those when the contact interface recombination is included with the HTL and ETL films $\Delta V_{oc,nr,b+c}$. Clearly, the actual V_{oc} for complete devices can be up to $2k_B T/q$ lower than $\Delta E_F/q = V_{oc,rad} - \Delta V_{oc,nr,b+c}$, given the extra recombination from the metallic

contacts and/or due to the modifications included during the further fabrication steps for obtaining complete cells.

Figure 3: Visualization of non-radiative interfacial recombination through absolute photoluminescence imaging of films

Quasi-Fermi level splitting (QFLS) representative energy histograms from perovskite-only and a sequence of ETM/Perovskite/HTM films on glass, resembling values as reported by Stollerfoht et al.^[60] The neat perovskite absorber reports average ΔE_F of approximately 1.21 eV (at 300 K), which is below the radiative limit ($qV_{oc,rad} = 1.345 \text{ eV}$ for a $E_g = 1.6 \text{ eV}$ absorber at $T = 300 \text{ K}$ under $100 \text{ mW}\cdot\text{cm}^{-2}$ AM1.5G illumination). The values for $qV_{oc,rad}$ and E_g are indicated with dashed lines. Addition of transport layers induces extra non-radiative recombination pathways, which lower average ΔE_F to approximately 1.12 V. Thus, the photovoltage losses due to bulk and contact interface non-radiative recombination $\Delta V_{oc,nr,b+c}$ are significantly higher than those only in the bulk $\Delta V_{oc,nr,b}$.

The latter aspect is of major influence in these analyses, that is why all the results for assessment should be taken from significantly large and comparable statistical ensembles and displayed in histogram representation. Traps-mediated recombination has been approached by Wright et al.^[61], who investigated the low-temperature PL of FAPbI₃. For temperatures below 30 K, they observed spectrally integrated PL intensity transients following power-law decays like $I_{PL}(t) \propto t^{-1}$ from nanoseconds to milliseconds. Also below 30 K, they found some extra red-shifting E_s 40 meV and broadening σ_s for the PL spectra peaks $I_{PL}(E) \propto \exp\left[-\left((E - E_g + E_s)/(\sigma + \sigma_s)\right)^2\right]$. Subsequently, by using multiple trapping (rate-equation) and hopping (Monte Carlo) models, they suggested that both phenomena arise from an exponential trap-density tail with characteristic energy scale of ≈ 3 meV. Such trap density tails may in part be responsible for V_{oc} losses commonly observed in these materials. Accordingly, in high-quality hybrid perovskites, trap states could predominantly comprise a continuum of energetic levels (associated with disorder) rather than discrete trap energy levels (associated, e.g., with elemental vacancies). Therefore, it would be feasible to consider hybrid perovskites as classic semiconductors whose band-structure picture is moderated by a modest degree of energetic disorder. Note that these results are of major interest for device modeling, despite their limitations for the type of perovskite and their temperature range.

The use of the diode ideality factor m as a figure of merit allows to identify dominating recombination processes that limit the V_{oc} , as shown by Tress et al.^[37] in their study on Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})₃-based devices with SnO₂ or TiO₂ as ETL and with or without spiro-OMeTAD as HTL. They analyzed $J-V$ curves and EL at different temperatures reporting $m \approx 1.6$ for the best performing devices which was suggested to indicate SRH recombination via bulk defects. As degradation took place, $m \approx 2.0$ pointing to an increase in the SRH recombination in the space charge region, possibly due to broad intragap defect distribution.

Subsequently, Almora et al.^[34] also used m as a parametrization of the recombination mechanisms, only that they employed IS measurements of recombination resistance at open-circuit in MAPbI₃ and Cs_{0.1}FA_{0.74}MA_{0.13}PbI_{2.48}Br_{0.39} with several variations in the selective contacts, including 2D capping layers.^[62]

Their results reported $m \approx 1.5$ for the mixed perovskite similarly suggesting bulk recombination predominance. However, for the MAPbI₃ devices $m \approx 2.0$ was the general rule, meaning that probably the MA cations are decisive in the formation of recombination centers at the interfaces. Moreover, Calado et al.^[36] measured transient ideality factors corroborating $m \approx 2.0$ and thus SRH as main recombination pathway in MAPbI₃-based devices.

The Auger non-radiative recombination generally manifests under large photon fluence or in highly doped semiconductors.^[63] First, note that hybrid perovskites are typically intrinsic in PSCs.^[64-65] Moreover, Pazos-Outón et al.^[66] suggested that MAPbI₃ has a larger than expected Auger coefficient A_r , but still not significant at the operating point, where the carrier density is lower than at OC, leading to an optimal PCE of 30.5%, close to ideal for the MAPbI₃ bandgap (31%).^[67] Purposely, Shen et al.^[68] performed first-principles calculations and found that the distortions of PbI₆ octahedra of the MAPbI₃ increase significantly A_r . Nevertheless, Staub et al.^[63] concluded that Auger recombination via traps is most likely not the explanation for some observed nonradiative bimolecular recombination in PSCs. On the other hand, some studies^[69-70] have found significant biexciton Auger recombination in mono-dispersed quantum-confined CsPbBr₃ nanocrystals, which is a challenging effect for light emitting devices.

To sum up, PSCs present low radiative recombination coefficient, which produce long radiative recombination lifetimes. This is a very favorable element for general device performance, and it has been attributed to several factors, e.g. a direct-indirect bandgap character. On the other hand, the SRH non-radiative recombination mechanisms have the larger contribution in PSCs, mainly for MAPbI₃-based devices.

III. Perovskite composition and morphology effects on recombination

The composition of the perovskite absorber defines both, the absorption/radiative recombination mechanisms and the defect distributions, and hence the SRH non-radiative recombination. Purposely, several studies explore the composition changes which keep the well behaving core of the

MAPbI₃ but optimize recombination and/or stability. At the same time, for each composition the morphology features, e.g. grain sizes, are tuned aiming better device performance. In this section, these two aspects are attended.

The slow photoinduced charge carrier recombination rates in MAPbI₃ have been credited to the unique dipolar nature of the molecular methyl ammonium cation.^[71-72] However, this was contradicted by Dastidar et al.,^[73] who applied transient terahertz spectroscopy to perovskite-phase cesium lead iodide (CsPbI₃) thin films, which lack such a dipole. As result, they revealed bimolecular recombination rates of $10^{-10} \text{ cm}^3 \cdot \text{s}^{-1}$ and charge carrier mobility larger than $30 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. These are values similar to those reported for the hybrid perovskites, strongly suggesting that the organic cation does not confer a fundamental advantage. Note that, while these studies focus on structural properties as crystalline materials, it looks like more predominant mechanisms rule the electrical response of PSCs, e.g. morphology/composition and/or ionic conductivity features (see Section V).

The changes in the perovskite composition were studied by Montcada et al.^[74] who analyzed photo-induced charge extraction (PICE)^[75] and TPV measurements.^[44] They showed that varying the organic cation and halide composition with respect to the MAPbI₃ perovskite crystal the charge extraction process varies in close relation with interfacial carrier recombination kinetics under operando conditions. From the TPV decays, where a small perturbation is considered, mixed perovskites showed larger recombination lifetimes than MAPbI₃. On the other hand, PICE photovoltage decays were slower for MAPbI₃, indicating a competition between the recombination processes and the ionic mobility. The latter occurs even in time scales of microseconds, due to the larger V_{oc} perturbation in the PICE experiment.

The influence of the cations on recombination, specifically throughout the variations in the V_{oc} , was explored by Albadri et al.^[3] via bias- and light-intensity modulating spectroscopies.^[76] They characterized triple A-cations Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})₃ and quadruple A-cations Rb_{0.05}(Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95})_{0.95}Pb(I_{0.83}Br_{0.17})₃ absorber materials. Their conclusions suggested that the Rb addition increased the V_{oc} from 1.11 V to 1.19 V, due to a better surface passivation that reduces carrier recombination at the TiO₂/perovskite interface. Similarly, Hu et al.^[4] suggested that Cs-

incorporation reduces the trap density and charge recombination rates in the perovskite layer, accounting for higher V_{oc} in Cs-containing devices. On the other hand, Rb-addition showed an increased charge carrier mobility and reduced $J-V$ hysteresis, being this latter effect an issue along the complete study. Other studies on tuning of recombination by modification of the A-cation composition can be found in the literature, and particularly the inclusion of Cs is believed to improve performance and stability.^[5-6] Moreover, further material engineering on both the A-cation and the X-anion has also been reported to affect recombination.^[77]

The B-cations seem to also have a strong influence in the recombination, as reported in several studies approaching the partial or total substitution of Pb by Sn in PSCs.^[78] For instance, Handa et al.^[12] did a PL study on MASnI_3 thin films and solar cell devices, for which they reported V_{oc} values below 0.3 V, as in Figure 4. Only by adding the right proportion of SnF_2 the amount of unintentional doping is reduced enough to eradicate the PL blue-shift and enhance the injection efficiency to the transport layer. Moreover, Jokar et al.^[14] reproduced V_{oc} values between 0.3 V and 0.6 V in FASnI_3 cells by including ethylenediammonium diiodide (EDAI_2) and butylammonium iodide (BAI) as additives to passivate surface defects. They observed morphological changes which reduced pinholes densities in the surface of the pristine FASnI_3 , a well-known source of leakage recombination current. Similarly, Chen et al.^[13] introduced a phenylethylammonium bromide (PEABr) low-dimensional interlayer between the FASnI_3 and the HTL reporting similar improvements. Subsequently, Jiang et al.^[79] used NH_4SCN additives and tuned the concentration of PEA ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3^+$) in $\text{PEA}_x\text{FA}_{1-x}\text{SnI}_3$ absorber layers and introduced the indene- C_{60} bisadduct as ETL for achieving V_{oc} values as high as 0.94 V. This also suggests a strong role of the Sn composition in the interface recombination.

The charge state of the halogen vacancy was found to modify the non-radiative recombination from the ab initio nonadiabatic molecular dynamics analyses by Li et al.^[80] A missing iodine anion in MAPbI_3 has almost no effect on charge losses.

Figure 4: High recombination lowers V_{oc} in PSCs with Sn as B-cation

Including SnF_2 reduces recombination. Filled and open circles correspond to samples with and without SnF_2 , respectively. Adapted with permission from Handa et al.^[12] Copyright 2017, American Chemical Society.

However, when the vacancy is reduced, the recombination is enhanced by up to 2 orders of magnitude. Their study suggests that iodine anion vacancy can even be beneficial to the performance, while the neutral iodine and iodine cation vacancies should be strongly avoided. Moreover, independently on the control of the halogen defect type, by including the appropriate Br composition the stability and the V_{oc} can be increased,^[7] but the increase in V_{oc} is typically not proportional to the change in E_g .^[8-9] The latter is a critical point regarding the interface engineering and the band alignment in terms of contact surface SRH recombination. For instance, the V_{oc} losses in $(\text{FA}_{0.85}\text{MA}_{0.1}\text{Cs}_{0.05})\text{PbBr}_3$ cells were associated with the perovskite/ETL interface in the study by Zohar et al.^[10] Additionally, Yang et al.^[11] compared the recombination between MAPbI_3 and MAPbBr_3 and correlated larger Auger recombination rate and exciton binding energy in MAPbBr_3 with the three times lower same parameters in MAPbI_3 .

Only the neutral empty traps at open grain boundaries (GB) and/or with high densities in noncompact morphologies can contribute to recombination significantly due to their sign sensitivity upon filling, as suggested by Sherkar et al.^[81] and schematized in Figure 5a. In that study, they modelled $J-V$ curves on vacuum-

deposited p-i-n and n-i-p MAPbI₃ devices and analyzed the different recombination scenarios for PSCs. Because hybrid perovskites are ionic conductors, the associated traps are expected to be electrically charged, which implies neutral filled trap states that mean no significant increase of recombination, as depicted in Figure 5b. It is still arguable, whether the neutral filled trap states are predominant or not in PSCs. Nevertheless, they found a direct correlation between the density of traps, the density of mobile ionic defects, and the degree of hysteresis observed in the $J-V$ characteristics. Importantly, note that despite the direct recombination through GB-trap states is unlikely significant in PSCs, one could still find correlations between large GB trap densities and increase in recombination through the effect of the accumulation of mobile ions and $J-V$ hysteresis (see Section V).

Figure 5: Energy diagram for different charge and filling of grain boundaries

In conventional inorganic photovoltaics, (a) the empty neutral traps at GBs and interfaces (thin short lines) when filled with electrons ("-" circles) result in a weakened transport due to the potential barrier ($q\phi$) and the nonradiative recombination between holes ("+" circles) and trapped electrons is strong. In PSCs, it is likely that (b) the empty traps are positively charged due to accumulated iodide vacancies at GBs and interfaces. Therefore, when filled with electrons, the traps are neutral, electron transport is relatively unaffected, and nonradiative recombination is weak. Adapted with permission from Sherkar et al.^[81] (CC BY-NC-ND).

Large densities of GBs were also correlated with $J-V$ hysteresis in an essay by Castro-Méndez et al.^[82] They further suggested a non-dramatic influence of GBs on recombination, and thus V_{oc} . Similarly, the density of absorber GBs has been also discarded by Correa-Baena et al.^[83] as a major factor for the recombination dynamics in $\text{SnO}_2/\text{FA}_{0.86}\text{MA}_{0.14}\text{PbI}_{0.89}\text{Br}_{0.11}/\text{HTL}$ devices under 1 sun illumination. Contrastingly, Fakharuddin et al.^[84] showed quite the opposite, i.e. a performance enhancement as the amount of grain boundaries increased. In that work, blends of MAPbI_3 perovskites with an insulating polymer (polyvinylpyrrolidone) were employed for tuning the grain sizes. Although the polymer blend systems systematically alter the morphology by creating small grains (more grain boundaries), they were found to reduce nonradiative recombination within the film, enhancing its spatial homogeneity of radiative recombination. This behavior was correlated with a reduction in the density of bulk trap states, as evidenced by an order of magnitude higher PL intensity and a significantly higher V_{oc} when the polymer is incorporated into the MAPbI_3 films.

In sum, the changes in the composition of the absorber perovskite modify drastically the recombination rates in PSCs. Of particularly negative impact is the case of substituting the lead B-cation for tin. The latter is a big challenge for the development of record cells, since the Sn composition lowers the bandgap, approaching the optimal value in the Shockley-Queisser limit.^[85-86] On the other hand, morphology does affect recombination, but most of the studies neglect it as a major factor and/or correlate it with ionic conductivity effects.

IV. Bulk versus Interface recombination

As introduced in Section II, non-radiative recombination is most likely the main recombination pathway in PSCs under standard operation conditions. However, the matter on where it takes place, whether in the bulk or at interfaces, is of major importance in order to optimize device architectures. The predominant role of interfaces is probably the most accepted result, as discussed by Wolff et al.^[87] Nevertheless, care must be taken in each case/device and proper analyses may be validated.

The recombination at the bulk perovskite was suggested to be a major factor by Contreras-Bernal et al.^[88] who studied MAPbI_3 and mixed ion-based

(FAPbI₃)_{0.85}(MABr₃)_{0.15} devices with two different HTLs: Spiro-OMeTAD and P3HT. They did IS and studied the V_{oc} for two excitation wavelengths (blue and red light), in two illumination directions (back and front), and at different temperatures. These are interesting experiments because the light penetration depth and direction allow to separate interface/bulk phenomena in thick enough devices, and the temperature informs on ionic/electronic contributions. Their results indicated that, for the studied devices, the recombination process that determines the V_{oc} is governed by the absorber bulk via a trap-limited mechanism, but surface-mediated recombination cannot be ruled out for P3HT contact or degraded devices.

The inclusion of 2D PEA₂PbI₄ capping layers at the interfaces between Cs_{0.1}FA_{0.74}MA_{0.13}PbI_{2.48}Br_{0.39} and the selective contacts reports stability improvements but did not significantly changed the most likely bulk predominant recombination in these devices, as suggested in IS study by Almora et al.^[34] Similarly, the use of Ga₂O₃ tunneling layers towards the ETM neither modified the recombination dynamics in SnO₂/FA_{0.86}MA_{0.14}PbI_{0.89}Br_{0.11}/HTL devices under 1 sun illumination, as found by Correa-Baena et al.^[83] Instead, the recombination is strongly dominated by the dopants in the HTLs: spiro-OMeTAD and PTAA. They observed evident V_{oc} increase with time of N₂ exposure inhibiting the O₂ doping/dedoping processes in both HTLs and also a clear V_{oc} decreasing trend when varying the Li-TFSI dopand concentration in spiro-OMeTAD.

In the work by Li et al.^[89] they analyzed MAPbI₃-based planar cells with different perovskite thicknesses by the TPV and IS methods and differentiated fast and slow characteristic response time, around micro seconds and milliseconds, respectively. For the former process, they concluded that photo-charges are found to be mainly stored within the selective layers, which can rapidly be recombined through interface defects. Additionally, they associated the bulk charge carrier recombination with the slow photovoltage decays of the cells. Note that the latter is also an arguable correlation, since the ionic conductivity is most likely the mechanism by which the recombination is modified in the slowest time scale.

As a rule, bulk recombination at the perovskite is the predominant mechanism in PSCs with “good” selective contacts, while “bad” selective contacts may change the situation to interface dominant recombination. For instance, this general conception has been seconded by Idigoras et al.^[90] in PSCs. They studied different

recombination effects of 1D and 3D morphologies and the nanocrystalline phase (anatase and amorphous) of TiO_2 as ETL. Interestingly, their study also showed an strong dependence between the morphology of the ETL and the $J-V$ curve hysteresis, showing what seems to be another general rule: “good” devices show less $J-V$ hysteresis than “bad” devices. The latter has been tackled by Neukom et al.^[91] who simulated how the optimal ranges of surface recombination and diffusion length of charge carriers in “good” devices reduce the hysteretic effects, despite the still presence of ionic conductivity.

Bulk and interface recombinations seem to behave in different time scales, as suggested by Almora et al.^[34] They used IS analyses at OC under different illumination intensities for several device structures, including 2D capping layers between the selective contacts and the MAPbI_3 resulting in the spectra as in Figure 6a,b. At lower illumination intensities the shunt resistance is most likely due to surface recombination associated with interface and/or grain boundary leakage currents, as in Figure 6c. These low frequency features are closely linked with the ionic conductivity and the possible accumulation of charge carriers at the interfaces.^[62, 92]

As the illumination intensity increases, the flat-band regime is approached and exceeded, the bulk recombination becomes slightly larger and a large photo induced low-frequency capacitance arises as in Figure 6a. Then where the main recombination takes place gets complicated with the ionic mechanisms and resolving one from the other becomes challenging. Furthermore, the characteristic response times can be obtained from the recombination resistances, multiplied by the corresponding coupled capacitances, resulting as Figure 6d. The high frequency component τ_{Hf} behave exponentially decreasing as light increases, mainly carrying the bulk contribution. These can be interpreted as recombination lifetimes. On the other hand, at lower frequencies τ_{Lf} behaves nearly constant and very sensitive to the composition of the interface. The latter expresses a closely related recombination-capacitive mechanism with slow kinetics which originate hysteretic features in the $J-V$ curve.^[92-96]

The impact of charge transport layers on recombination in the interface with perovskite absorbers has been assessed by Stolterfoht et al.^[42] in their PL study.

Figure 6: Recombination resistance and characteristic response times from impedance spectroscopy at open-circuit in MAPbI₃ devices

The illustrative IS spectra as (a) capacitance C Bode plots and (b) impedance Z Nyquist plots reproduce two main features for lower and higher frequencies f , resulting in the (c) resistance R and (d) characteristic response times τ calculated with equivalent circuit simulations. The recombination resistances at lower and higher frequencies, R_{Lf} and R_{Hf} , are likely due to bulk and surface recombination, respectively. Similarly, two main contributions arise from phenomena at lower and higher frequencies, τ_{Lf} and τ_{Hf} respectively. Adapted with permission from Almora et al.^[34] Copyright 2018, Elsevier Ltd.

Following Equation (11), They quantified the non-radiative recombination current J_{nr} by measuring the QY_{PL} in p-i-n- and n-i-p-type cells with a wide range of commonly used selective layers, including various hole-transporting polymers, spiro-OMeTAD, metal oxides and fullerenes. They illustrated how the interfaces limit the V_{oc} due to the energy barriers at the interfaces. The latter is illustrated in terms of different band alignments in the energy diagram of Figure 7a, as deduced from ultraviolet photoelectron spectroscopy and differential charging capacitance experiments. The barriers induce an additional J_{nr} that is in most cases substantially larger than the loss in the neat perovskite. Then, the least-selective interface sets the upper limit for the V_{oc} of the device. Importantly, the V_{oc} equals the internal ΔE_F in the absorber layer only in high efficiency cells, while in poor performing devices, the V_{oc} is substantially lower than ΔE_F (see Figure 7b).

A quantitative representation of how the photo-generated current is canceled by recombination currents at different regions within the device was also provided by Stolterfoht et al.^[42] at open-circuit condition, as in Figure 7c. More graphically, an scheme is pictured in Figure 7d making an analogy with a bucket with holes where the water level is proportional to the V_{oc} of the cells. The water stream from the tap parallels to the photocurrent from the incident illumination. The flaws in the bucket symbolize the recombination losses at V_{oc} in the bulk and/or interfaces. Depending on the size of the holes, the water level will change so as the V_{oc} of the device.

The effects of energy alignments were also discussed by Gelmetti et al.^[98] and, more specifically, the impact of the conduction band offset at the ETL/perovskite interface in planar-heterojunction PSCs are discussed by Ding et al.^[99] Moreover, an interesting analysis by Kirchartz^[100] illustrated by drift-diffusion simulations how surface recombination velocities above $10^3 \text{ cm}\cdot\text{s}^{-1}$ critically reduce V_{oc} and hence the power conversion efficiency of PSCs.

Furthermore, built-in voltages above 1.1 V and series resistances below $10 \text{ }\Omega\cdot\text{cm}^2$ were also recommended. Complementary, Wang et al.^[97] calculated the recombination velocities from different band alignments, depending on the selective contacts, by processing time-resolved photoluminescence decays.

Figure 7: Energy diagram band alignment effects on open-circuit voltage and recombination currents for different selective contact structures

(a) Energy diagram illustrating different band alignments towards the HTL. (b) Average V_{oc} of $p-i-n$ cells employing different conjugated polymers as HTLs and a C₆₀ ETL, compared to the average splitting of the quasi-Fermi levels (QFLS) of the corresponding HTL/perovskite bilayers (open circles), and of the $p-i-n$ stacks (stars). The QFLS of the perovskite/C₆₀ junction and of the neat perovskite on fused silica are shown in dashed lines. (c) Bulk and interfacial non-radiative recombination currents at open-circuit as obtained on samples with nearly flat chemical potentials. (d) Illustrates a solar cell as bucket with holes where the water level represents the V_{oc} of the cells.^[97]

Modified with permission from Stollerfoht et al.^[42] Copyright 2019, The Royal Society of Chemistry.

They also suggested the need of surface recombination velocities below $10 \text{ cm}\cdot\text{s}^{-1}$ in order to achieve $V_{oc} \approx 1.3 \text{ V}$.

In closing, interface recombination due to band alignment issues typically dominates over bulk recombination in PSCs. Particularly, most recent studies suggest that the hole transport material has a major influence. Interestingly, the interface recombination seems to be closely related with slow kinetic phenomena, most likely due to mobile ions.

V. Recombination and J-V hysteresis

One of the most debated issues in PSCs has been the dynamic evolution of the current-voltage characteristic, depending on the measurement conditions, as early noticed in 2014.^[101-103] A first concern on these phenomena was the need of validation of reported power conversion efficiencies (PCE). Hysteresis phenomena can make “bad” cells looking “good”. For instance, Figure 8a illustrate how sweeping voltages in different directions deliver a drastically different J-V curve. Particularly, for MAPbI₃-based devices the measurement in the direction from open-circuit (OC) to short-circuit (SC) delivers a much larger PCE than the opposite. Then some protocols for best practices are required,^[104-105] for example using the maximum power point tracking methods.^[106-107]

There is no evidence on the change of the generation rates under standard measurement conditions, and the $J-V$ hysteresis is also present in the dark.^[45, 93] This suggest that the hysteresis is actually the result of modifications in the recombination current mechanisms. Furthermore, the most accepted explanation for these phenomena indicate the presence of slow kinetic mobile ions.^[45, 62, 65, 108] Purposely, significant ionic conductivity has been reported by several authors,^[109-111] who also found a reduction in the ionic transport activation energy with the increase of the illumination intensity. Specifically, the study by Shao et al.^[112] evidenced a grain boundary dominated ion migration in MAPbI₃.

The nature of the ionic conductivity in MAPbI₃ was early reviewed by Yuan et al.,^[113] who concluded that both the MA⁺ cations and I⁻ anions are mobile, while the Pb₂⁺ ions are more difficult to move. Subsequently, several studies have given major importance to the iodine vacancies as predominant mobile

species in MAPbI_3 .^[114-116] Nevertheless, even the migration of extrinsic ions (e.g., Li^+ , Na^+ , Rb^+ , K^+ , H^+) has been pointed out as significant,^[117-118] which makes more challenging the analyses on the continuously evolving formulations of mixed perovskite compounds in PSCs.

The connection between interfacial recombination, ionic movement and hysteresis was purposely tackled by Pockett & Carnie^[119] in their study on $\text{TiO}_2/\text{MAPbI}_3/\text{spiro-OMeTAD}$ and $\text{PCBM}/\text{MAPbI}_3/\text{PEDOT:PSS}$ solar cells. They found the dominant recombination mechanism to occur at the TiO_2 /perovskite interface when the low-temperature TPV is measured over a period in which ions redistribute within the perovskite layer. The dynamic accumulation of ions towards the interfaces modifies the space charges creating preferential recombination pathways. Hence, the electrostatic and band alignment asymmetries may favor the recombination, e.g. near the ETL. Purposely, they also discarded significant impact of the recombination at the perovskite/HTL interface by performing TPV measurements using different laser wavelengths to probe different depths into the perovskite layer, as well as by changing the type of HTL which was used.

Predominant bulk or interface recombination were respectively correlated with hysteresis in J_{sc} or V_{oc} , from the drift-diffusion simulations by Xiang et al.^[120] A priori, this seems to be an effective method for evaluating recombination types: one can measure the $J-V$ curves in both directions (or a complete loop) and the larger modification around short-circuit or open-circuit informs on whether the recombination is predominantly bulky or interfacial, respectively. However, in practice the measurement conditions and polarization history of the sample can produce hysteretic artifact which may invalidate the use of this approach. In any case, the experimental reproducibility and compatibility with simulation parameters should be guaranteed.

Besides the $J-V$ hysteresis, the V_{oc} has also been found to evolve slowly after abrupt switch from dark to light.^[45] For instance, in the study by Walter et al.^[121] the V_{oc} relaxed during several minutes around 10% of the average V_{oc} value, with different monotonies depending on the perovskite composition. Such experimental behaviors were simulated by numerical drift-diffusion including the migration of both anions and cations in interaction with trap-mediated recombination in the bulk and/or at the surfaces of the perovskite absorber. Basically, while most of the V_{oc} is rapidly built by the electronic charge carrier generation, after the light is set, the

slower spatial redistribution of the ionic charge throughout the perovskite bulk evolves as the ions approach the new steady-state condition. During this longer period of “ionic readjustment” the SRH recombination dynamically corrects the local asymmetries of the electron–hole population and thus the V_{oc} . These experiments are very illustrative of what the $J-V$ hysteresis is: the dynamic evolution between electronic recombination and slow ionic charge distributions.

Similarly, at short-circuit, the space modifications on the recombination rate after different pre-biasing conditions were shown to explain the large hysteretic losses of J_{sc} ,^[62] as in Figure 8a. The drift-diffusion simulation concluded that the recombination rate after reverse-bias pre-conditioning is much larger than after forward-bias above flat-band preconditioning, as in Figure 8b. Particularly, in the vicinity of the interfaces the recombination rate drops around an order of magnitude, but in the bulk this difference can be up to eight orders.

Figure 8: Hysteresis and recombination effects in $J-V$ curve

(a) Current voltage curves of MAPbI₃-based devices with/without 2D capping layers towards the selective contacts. Inline arrows indicate the voltage sweep direction, the asterisks point where the pre-bias was set, and the vertical arrows highlight the losses of J_{sc} . (b) Space distribution of the recombination rate which explains the drop of J_{sc} after reverse pre-bias, as in (a). Adapted with permission from Almora et al.^[62] Copyright 2019, Elsevier B.V.

In addition, an interesting correlation was highlighted by Almora et al.^[34, 43] between the recombination resistance and the large low frequency capacitance C_{Lf} (see Figure 6a). This capacitance has been related with the hysteresis phenomena and slow ionic processes in PSCs.^[45, 65, 95-96] The general trend was $C_{Lf} \propto \exp[qV_{oc}/m_C k_B T]$ with $m_C \approx m$, as resulted from the recombination resistance in Figure 6c. This is the reason behind the constant characteristic times as in Figure 6d. Similarly, Yadav et al.^[122] correlated the light induced C_{Lf} with excess V_{oc} , and thus a reduction of recombination, manifesting $J-V$ hysteretic behaviors. Again, ionic charge accumulations redistribute the electronic charge carrier densities and respond slowly upon small bias or light perturbation. This ionic-electronic coupling connects in different timescales the pseudo-steady charge carrier densities, storing energy as a capacitor, with the dynamically evolving recombination processes, dissipating energy as a resistor.

On the whole, several studies suggest that the $J-V$ hysteresis in PSCs is due to the dual electronic-ionic conductivity of hybrid perovskites. This implies that recombination rates evolve with time for every field distribution due to the redistribution of the charge density profile. Note that, while not always explicitly, the ionic effects have always been present along all the previous sections and constitute a major defining feature for hybrid lead halide perovskites. This demands the revision of every formalism in order to discard measurement artifacts, which have been challenging for the understanding of the working principles of PSCs.

VI. Conclusions

In summary, hybrid lead halide perovskites present lower radiative recombination rates, which explain long charge carrier lifetimes in PSCs. This is one of the main factors contributing the exceptionally large power conversion efficiencies, compared with other solution-based photovoltaics. However, large SRH non-radiative recombination hinder the charge extraction. Particularly critical are some perovskite composition changes with respect to MAPbI₃ and the unfavorable band alignment at the interfaces with the selective contacts. In addition, the

presence of slow kinetic mobile ions seems to condition the charge carrier recombination under standard operational conditions. These are general guidelines for future investigations, which most likely may tackle the evolution of recombination pathways during degradation.

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