Charge-carrier Diffusion and Radiative Efficiencies in Hybrid Metal Halide Perovskites

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The race for efficient, cost-effective photovoltaic cells

Best Research-Cell Efficiencies

- **Multijunction Cells** (2-terminal, monolithic):
  - LM = lattice matched
  - IMM = inverted, metamorphic
    - Three-junction (concentrator)
    - Two-junction (concentrator)
    - Four-junction (non-concentrator)
- Single-Junction GaAs:
  - Single crystal
  - Concentrator
  - Thin-film crystal
- Crystalline Si Cells:
  - Single crystal (concentrator)
  - Single crystal (non-concentrator)
  - Multicrystalline
  - Silicon heterostructures (HIT)
  - Thin-film crystal
- Thin-Film Technologies:
  - CIGS (concentrator)
  - CdTe
  - Amorphous Si:H (stabilized)
- Emerging PV:
  - Dye-sensitized cells
  - Perovskite cells (not stabilized)
  - Organic cells (various types)
  - Organic tandem cells
  - Inorganic cells (CZTSSe)
  - Quantum dot cells

**Multi-junction, crystalline inorganics**

**Single-junction, crystalline inorganics** (GaAs, Si)

**Solution-processed (or low-T evaporated) organics and DSCs**

**Hybrid Metal-Halide Perovskites**

http://www.nrel.gov/ncpv/images/efficiency_chart.jpg
"Planar heterojunction" solar cells
- Low exciton binding energy → mostly free charges at 300K
- High charge-carrier mobility and diffusion lengths → doping gradients or electron/hole-selective contacts suffice to collect charges effectively

Typical examples: crystalline silicon or GaAs solar cells
Features: highly efficient, but energy-intensive fabrication

"Excitonic" or "nanocomposite" cells
- High exciton binding energy → require energy offsets to induce charge separation
- Low charge-carrier diffusion lengths → must separate charges into different material components to inhibit recombination

Typical examples: Dye-sensitized solar cells (DSC), organic photovoltaics (OPV)
Features: lower efficiencies, cheap (low-temperature processing)
Excite MA-PbI$_{3-x}$Cl$_x$ film on which either electron (PCBM) or hole (spiro-OMeTAD) acceptor has been deposited

Model PL quenching as arising from diffusion of charge carriers to interface, assuming unity quenching efficiency

Extract charge-carrier diffusion length $L = \sqrt{D\tau}$ of $\approx 1\mu$m


Hybrid lead trihalide perovskites combine the best of both worlds: low-temperature processing yielding charge carrier diffusion lengths that exceed the optical absorption depth!
Hybrid metal halide perovskites have rapidly established themselves as new optoelectronic materials, allowing:

- solar cells with high PCE >20%
- varied range of processing protocols
- low-cost, abundant ingredients
- high absorption in the solar range
- long (micron) charge diffusion lengths allow for planar heterojunction designs
- light-emission/lasing reported

What are the mechanisms governing charge-carrier mobility, recombination and diffusion?
How are optoelectronic properties affected by composition?
Prototypical MA-PbI$_3$ & MA-PbI$_{3-x}$Cl$_x$: excellent optoelectronic properties!

- Shallow, low-density traps
- Non-Langevin Bimolecular recombination
- Strong radiative bimolecular transitions
- Decent charge-carrier mobility and long charge diffusion lengths
- Mostly homogeneous emission broadening

Other materials/properties?

Lead-free? MA-SnI$_3$

- Propensity towards tin vacancies gives rise to unintentional hole doping
- Rapid charge recombination

Tuneable materials for tandems?

A-Pb(Br$_x$I$_{1-x}$)$_3$

- Allows for perovskites with $E_g \sim 1.7$eV near the ideal band gap for tandem solar cells with silicon
- Problems with (photo-)stability
Charge recombination mechanisms in hybrid lead trihalide perovskites

**Non-radiative**
- Monomolecular
- Particularly detrimental in low-charge-density regime

**Radiative**
- For a direct semiconductor
- Hence to some extent required to achieve strong absorption

**Auger**
- Non-radiative
- Strong dependence on bandstructure, phonons, impurities (because of energy & momentum conservation)


*see e.g. Bolink, Adv. Mater. 27, 1837 (2015); Saba, Nat. Commun. 5, 5049 (2014)
Charge recombination mechanisms in hybrid lead trihalide perovskites

**Trap-mediated** ($k_1$)

**Bimolecular** ($k_2$)

**Auger** ($k_3$)

Rate equation governing the recombination dynamics:

$$\frac{dn}{dt} = G - k_1n - k_2n^2 - k_3n^3 = G - nR_T(n)$$

Temperature dependence of each rate constant to understand the different underlying mechanisms, and how each rate can be tuned!
Examine transient THz conductivity and photoluminescence (PL) decay dynamics following excitation with VIS light pulse:

- With increasing pump fluence, the decay dynamics become increasingly rapid.
- At low fluence, transients become mono-exponential with ~100ns lifetime.
- Can extract $k_1$, $k_2$, $k_3$ from such transients through global fits.
- Can obtain effective charge-carrier mobility from THz photoconductivity.

Analysis of temperature-dependent PL from solution-processed MAPbI$_3$ films, excited with low fluence so that monomolecular decay dominates:

- Mono-molecular charge recombination at low fluences in the photoluminescence transient tail
- Trap-related charge-carrier recombination becomes faster at higher temperatures

Trap-mediated charge recombination in MAPbI$_3$

**Increased trap-mediated recombination rate with increasing temperature:**

At high $T$, ionized, charged impurities may have larger cross-section for charge capture.

Activation energy crystal-phase specific, but mostly shallow traps at room-temperature

**Relevance to PV operation:**

- leads to decline in charge-carrier diffusion lengths $L_d$ (also because charge mobility declines with increasing $T$)
- But: still high $L_d \sim$1μm at 70°C.

What are the mechanisms governing bimolecular recombination in lead-halide perovskites?

**One possible model: Langevin theory**

- Electron moves in electric field generated by hole
- Capture and recombination occurs at distance $r_c$ where interaction energy is comparable to $k_B T$.
- Current into capture radius: $I = n e^2 \mu / \varepsilon_0 \varepsilon_r$ must be equal to rate of change of charge density through recombination: $dQ/dt = n e k_2$

\[
\frac{k_2}{\mu} = \frac{e}{\varepsilon_0 \varepsilon_r}
\]

<table>
<thead>
<tr>
<th>Material</th>
<th>Mobility</th>
<th>Measured $k_2/\mu$</th>
<th>$k_2/\mu : e / \varepsilon_0 \varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>evaporated MA-PbI$_{3-x}$Cl$_x$</td>
<td>$\Phi \mu = 33 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$</td>
<td>$k_2/\mu = 3.3 \times 10^{-12} \text{cm V}$</td>
<td>$3 \times 10^{-6} \varepsilon_r : 1$</td>
</tr>
<tr>
<td>Anthracene</td>
<td>$\mu = 2 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$</td>
<td>$k_2/\mu = 6 \times 10^{-6} \text{cm V}$</td>
<td>$3.3 : 1$</td>
</tr>
</tbody>
</table>


Ratio defies Langevin limit by $\approx 5$ orders of magnitude!
Photoconductivity dynamics in thin films of MAPbI$_3$ as a function of temperature $T$:

- Higher-order recombination becomes more prominent at lower temperature
- Extract bimolecular recombination rate constant $k_2$ as a function of $T$:
  - Expected from Langevin Theory: charge-carrier mobility increases with decreasing $T$
  - From band-structure picture: enhancements in band-edge transitions as thermal occupation of electron-hole states narrows

Auger charge-recombination in MAPbI$_3$:

dependence on temperature

Auger rate constants ($k_3$) in MAPbI$_3$:

- $k_3$ shows expected strong dependence on temperature
- Shows different temperature-dependences in different crystal structures
- Confirms strong dependence on bandstructure & phonons
- Allows tuning through structure/compositon modification

Relevance for devices:

- At room temperature: $k_3 \sim 10^{-28}$ cm$^6$s$^{-1}$
- $\sim 25 \times$ higher than that for GaAs ($4 \times 10^{-30}$ cm$^6$s$^{-1}$)
- Auger recombination contributes significantly for $n >> 10^{18}$ cm$^{-3}$, so not particularly relevant for PV, but highly important for lasers.

Charge-carrier mobilities in MAPbI$_3$

Are charge mobilities in high-quality lead iodide perovskite films near the intrinsic limit?

THz photoconductivity spectra are compatible with a Drude-response, i.e. only limited by momentum scattering.

The mobility increases with decreasing $T$ according to $T^{-1.5}$ in accordance with charge scattering off phonons.

- scattering off impurities and/or crystal boundaries can only play a minor role.
- At $T=300K$, $\mu \sim 30$ cm$^2$/Vs
- Unlikely to see increases by many orders of magnitude.

Can predict what will happen with charge diffusion if trap density is reduced!

Evaluate charge-carrier diffusion length $L_D$ in MAPbI$_3$ using:

$$L_D(n) = \left( \frac{\mu k_B T}{e R_T(n)} \right)^{\frac{1}{2}}$$

where $R_T = k_1 + nk_2 + n^2k_3$, and we assume $\mu=30\text{cm}^2/(\text{Vs})$, $k_2=10^{-10}\text{cm}^3\text{s}^{-1}$, $k_3=10^{-28}\text{cm}^6\text{s}^{-1}$

In the limit of ultra-low $k_1$, $L_D$ depends strongly on charge density $n$, approaching:

$$L_D=0.88 \mu m \times \sqrt{10^{18}\text{cm}^{-3}/n}$$

Meaningful values of $L_D$ can only be obtained with reference to the charge-carrier density present!
Calculating charge-carrier density present in MAPbI$_3$ under solar irradiance

Obtain spatially averaged value of the charge-carrier density $n_{AM1.5}$ present under solar illumination, non-charge extracting conditions (flat band, near $V_{OC}$)

**Step 1:** obtain charge-carrier generation rate under AM1.5 conditions:

\[
G(z) = \frac{(hc)^{-1}}{e} \int f_{\text{solar}}(\lambda) \alpha(\lambda) \exp(-\alpha(\lambda) z) \lambda d\lambda
\]

**Step 2:** solve cubic equation ($dn/dt=0$):

\[
\langle G \rangle = n k_1 + n^2 k_2 + n^3 k_3
\]

to obtain steady-state value of the charge-carrier density $n_{AM1.5}$ as a function of $k_1$ (assuming $k_2=10^{-10} \text{cm}^3\text{s}^{-1}$ and $k_3=10^{-28} \text{cm}^6\text{s}^{-1}$)

Can predict what will happen with charge diffusion if trap density is reduced!

Evaluate charge-carrier diffusion length $L_D$ in MAPbI$_3$ using:

$$L_D(n) = \left(\frac{\mu k_B T}{e R_T(n)}\right)^{\frac{1}{2}}$$

where $R_T = k_1 + n k_2 + n^2 k_3$, and we assume $\mu=30\text{cm}^2/(\text{Vs})$, $k_2=10^{-10}\text{cm}^3\text{s}^{-1}$, $k_3=10^{-28}\text{cm}^6\text{s}^{-1}$

At AM1.5 (arrows): values around 10µm cannot be exceeded for $\mu=30\text{cm}^2/(\text{Vs})$ because bi-molecular recombination sets a limit.

$L_D$ (y-axis) scales with $\mu^{0.5}$ therefore would need e.g.

$$\mu=9200\text{cm}^2/(\text{Vs}) \text{ for } L_D=175\mu\text{m}$$

Radiative efficiency $\Phi$ in MA-PbI$_3$ as a function of charge-carrier density $n$:

- Calculate $\Phi$ using

$$\Phi(n) = \frac{n k_2}{k_1 + n k_2 + n^2 k_3}$$

for different non-radiative trap-related recombination rates $k_1$, assuming radiative $k_2 = 10^{-10}$ cm$^3$s$^{-1}$, non-radiative $k_3 = 10^{-28}$ cm$^6$s$^{-1}$

- Onset of high $\Phi$ for $\tau = k_1^{-1} = 10$-100ns occurs at $1-10 \times 10^{18}$ cm$^{-3}$

  corresponds to excitation fluences 7-70$\mu$Jcm$^{-2}$ typically reported for ASE or lasing

- Onsets of ASE and efficient light emission at lower charge-carrier densities $<10^{15}$ cm$^{-3}$ will require trap-related lifetimes in excess of $\mu$s.

MA-SnI$_3$ on compact TiO$_2$ layer

For MA-SnI$_3$, monomolecular recombination is 3 orders of magnitude faster than in typical MAPbI$_3$.

Caused by sizeable p-doping through Sn$^{4+}$ which governs the charge dynamics:

$$\frac{dn}{dt} = -k_2 n (p + p_0) = -k_2 n^2 - k_2 p_0 n$$

photogenerated + doping hole densities

From fits: $k_1 = 8 \times 10^9$ s$^{-1}$ ($\tau = 110$ ps) yielding doping density: $\phi^{-1} p_0 = 5.8 \times 10^{18}$ cm$^{-3}$

[see e.g. J. Solid State Chem. 205, 39 (2013): $p_0 = 9 \times 10^{17}$ cm$^{-3}$]

But: decent effective charge-carrier mobility: $\phi \mu = 1.6$ cm$^2$V$^{-1}$s$^{-1}$

If unintentional doping and trapping in MA-SnI$_3$ can be controlled, long charge-carrier diffusion lengths are feasible.
MASnI$_3$: temperature-dependent PL spectra

- Phase transition at $\sim$110K from tetragonal to orthorhombic structure
- Full-width at half maximum of the PL emission suddenly narrows at the phase transition!
- Observe higher-lying emission peaks possibly originating from transitions involving higher-lying bands:

  - Can this excess energy be harvested?
Large (~200meV) Stokes shift between PL peak emission energy and absorption edge (for MAPbI$_3$ this is only at most a few tens of meV!)

- Sign of significant energetic disorder introduced by defects
- At T>110K temperature-dependence of emission FWHM is typical for charge-carrier scattering with ionized impurities
- Sharp drop in FWHM below 110K suggests that unintentional dopant carrier concentration drops significantly at the phase transition!
• Significant increase in PL lifetimes below 110K again suggests that unintentional dopant carrier concentration drops at the phase transition!
• Small changes in crystal structure seem sufficient to reduce background doping concentration!
• Can we replicate this effect e.g. through A-cation replacement?

Parrott, Milot, Stergiopoulos, Snaith, Johnston, Herz, JPC Letters 7, 1321 (2016)
Tunable mixed halide system: FAPb(Br$_{y}$I$_{1-y}$)$_{3}$:

- FAPb(Br$_{y}$I$_{1-y}$)$_{3}$ is a highly band-gap tunable material system that may allow applications in tandem cell.
- But: instability near the central region (0.3<y<0.5) where crystal structure switches from cubic to trigonal.
- Materials lose crystallinity (no peaks detectable in XRD) in this central region.


But: $\text{FAPb}(\text{Br}_y\text{I}_{1-y})_3$ is unstable under illumination, in particular for $0.3<y<0.5$

- Similar to observations by Hoke et al. for $\text{MAPb}(\text{Br}_y\text{I}_{1-y})_3$ (Chem. Sci. 6, 613 (2015))
- Materials segregate into iodide-rich and bromide-rich phases under illumination
- Pace of change depends strongly on irradiation intensity $I$:
  - $I=7.2\text{W/cm}^2$: rapid change over 5min
  - $I=15\text{mW/cm}^2$: fairly stable over 20h

Investigate optoelectronic properties of as-cast materials, at low excitation intensity and before light-induced changes have occurred.
Effect of disorder in FAPb(Br$_{y}$I$_{1-y}$)$_3$:

FAPb(Br$_{y}$I$_{1-y}$)$_3$ shows increase in disorder, trap density and decrease in charge-carrier mobility near the central region (0.3<y<0.5):

- Trap-related recombination rates ($k_1$) are highest for mixed-halide material.
- Increased FWHM of PL in central region indicative of higher energetic disorder.
- Mobility values dive between FAPbI$_3$ (27cm$^2$/Vs) and FAPbBr$_3$ (14cm$^2$/Vs) to values <1cm$^2$/Vs for y=0.4.
- Charge-carrier diffusion lengths under ∼AM1.5:

Photoconductivity dynamics in thin films of following VIS excitation:

- Higher-order recombination becomes more prominent for higher $y$
- Extract bimolecular recombination rate constant $k_2$ as a function of $y$:
  - $k_2$ increases with bromide fraction $y$
  - link with electronic bandstructure?
  - affected by exciton binding energy?

Auger charge-recombination in hybrid perovskites: dependence on bandstructure

Auger rate constants \( k_3 \) in FAPb\((Br_yI_{1-y})_3\):
- \( k_3 \) increases with increasing bromide \( y \) in FAPb\((Br_yI_{1-y})_3\)
- Confirms strong dependence on bandstructure
- Allows tuning through structure modification

Relevance for devices:
- at room temperature: \( k_3 \sim 10^{-28} \text{ cm}^6\text{s}^{-1} \)
- \( \sim 25\times \) higher than that for GaAs \((4\times10^{-30}\text{cm}^6\text{s}^{-1})\)
- Auger recombination contributes significantly for \( n>>10^{18}\text{cm}^{-3} \), so not particularly relevant for PV, but highly important for lasers.

Choose system A-Pb(Br\textsubscript{y}I\textsubscript{1-y})\textsubscript{3} that has the same structure for A-PbI\textsubscript{3} and A-PbBr\textsubscript{3}:

Optoelectronic properties of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb(Br}_{0.4}\text{I}_{0.6})_3$

- Band-gap at 1.74eV ideal for tandem with Si
- Good monomolecular lifetime: 157ns
- High stability under intense light illumination
- High charge-carrier mobility (21cm$^2$/Vs)
- Long charge-carrier diffusion length (~3µm)
- Low Urbach energy (16meV)
- 17% PCE in planar-heterojunction solar cell

Conclusions & Acknowledgements

- Charge-recombination in hybrid metal halide perovskites has contributions from
  1. Trap-related monomolecular rates depending on trap-density & depth
  2. Bimolecular electron-hole recombination that is strongly non-Langevin
  3. Auger recombination that depends on bandstructure and temperature

- At AM1.5 charge-carrier diffusion lengths in lead iodide perovskites with $\mu=30\text{cm}^2/(\text{Vs})$ will not exceed $\sim10\mu\text{m}$ even if all trap-related recombination is eliminated.

- Lowering the onset of efficient light emission into the intermediate charge-density regime ($<10^{15}\text{cm}^{-3}$) requires trap-related lifetimes well in excess of microseconds

- MA$_3\text{SnI}_3$: much faster monomolecular recombination due to tin vacancy (p-doping)

- A-Pb(Br$_y$I$_{1-y}$)$_3$: A=MA, FA exhibit stability gap in central region where the crystal structure changes, which can be overcome by use of mixed caesium/FA cations

Co-workers and collaborators:
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Physics, University of Oxford
3-year early stage researcher position available on new ITN network: "Interfaces in opto-electronic thin film multilayer devices" (INFORM).

**EC eligibility criteria:**

- Not resident in the UK for more than 12 months in the past three years
- No PhD Thesis submitted yet (could come as PhD student or first postdoc)
- no more than 4 years full time research experience

If interested & eligible, email or talk to me: laura.herz@physics.ox.ac.uk

Participating group leaders at Oxford: Laura Herz, Michael Johnston, Henry Snaith

Participating Institutions: Imperial College London, University of Oxford, Technion, University of Bayreuth, Humboldt Universität Berlin, TU Eindhoven, Holst Center, InnovationLab, Université de Fribourg, University of Cyprus, Universitat de Valencia