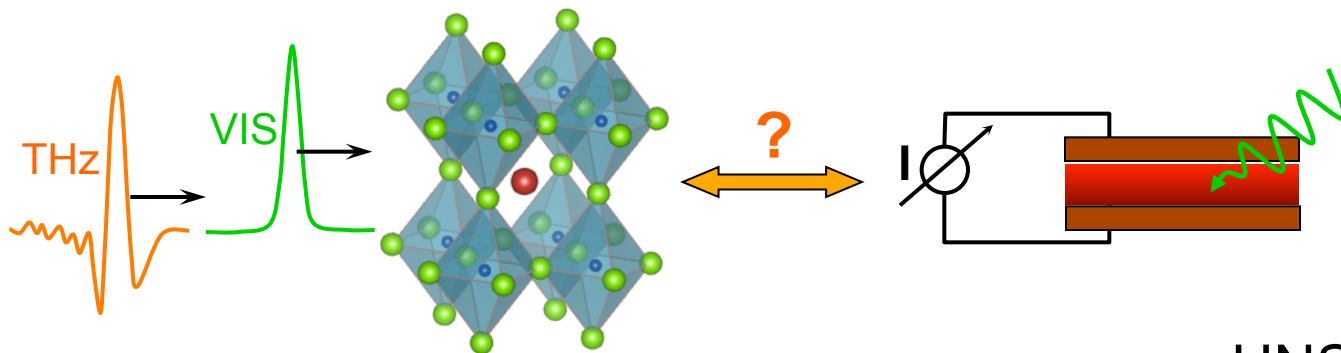


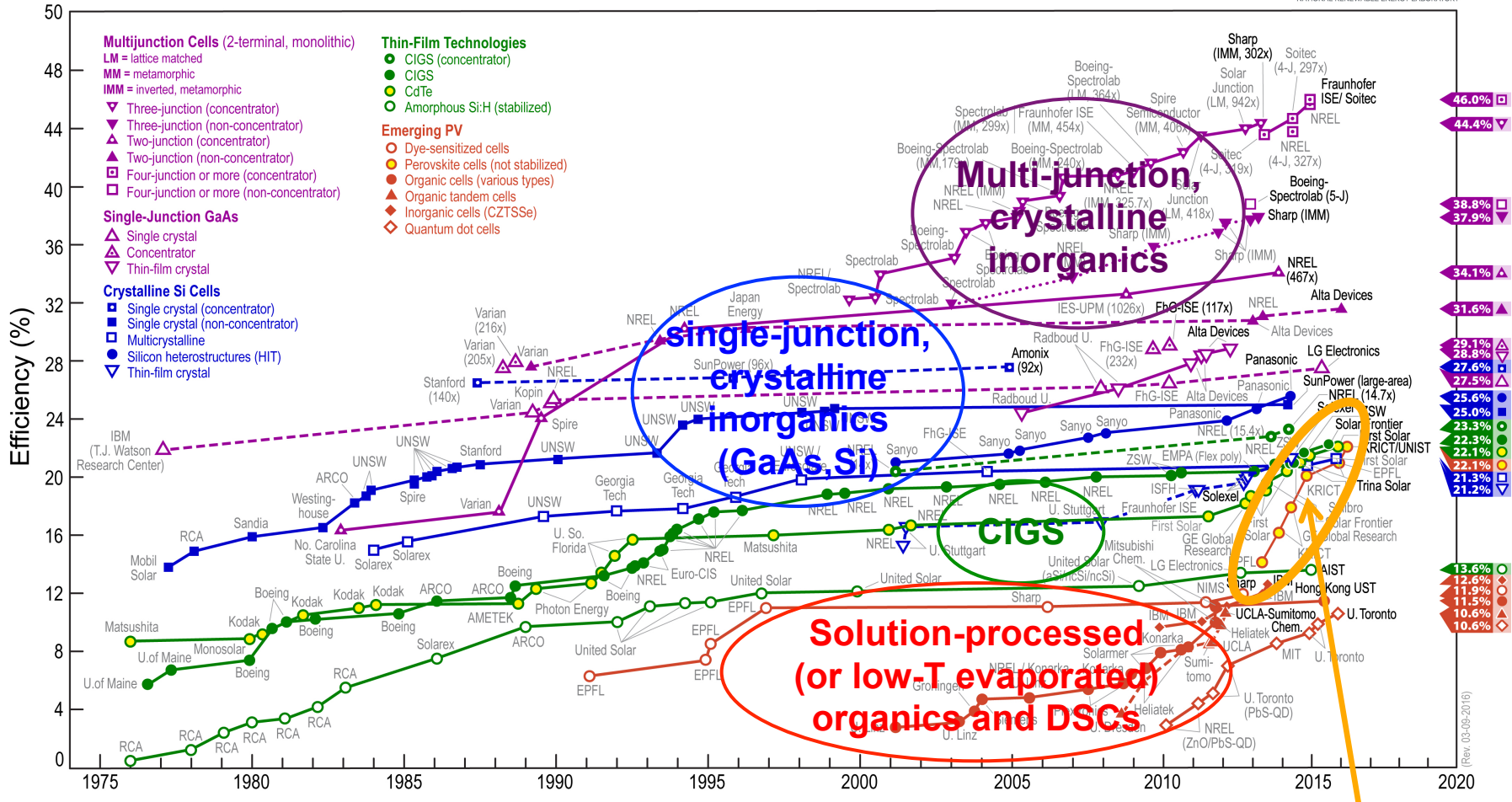
Charge-carrier Diffusion and Radiative Efficiencies in Hybrid Metal Halide Perovskites

Prof Laura Herz

Clarendon Laboratory, University of Oxford



Best Research-Cell Efficiencies

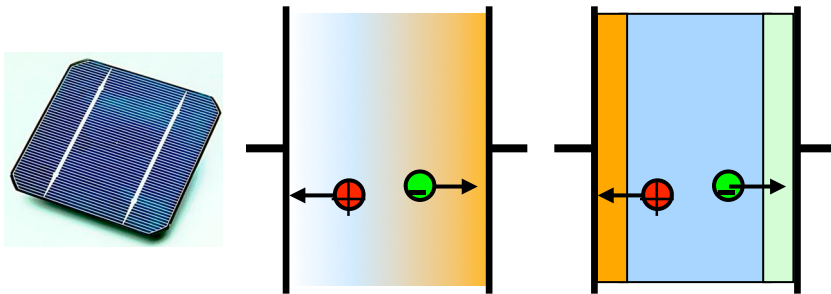


http://www.nrel.gov/ncpv/images/efficiency_chart.jpg

Hybrid Metal-Halide Perovskites

“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

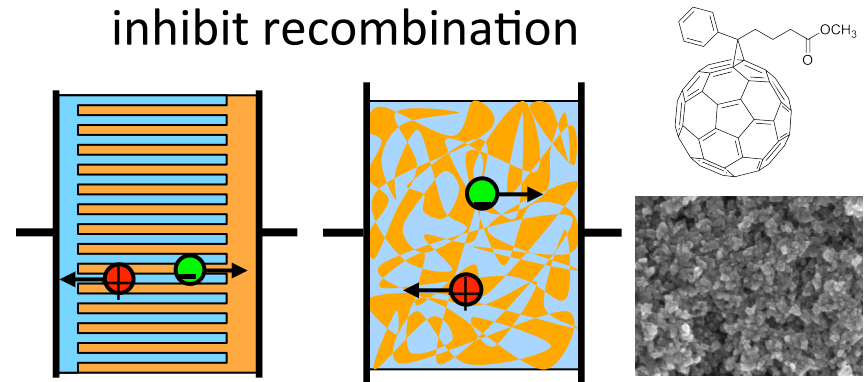


Typical examples: crystalline silicon or GaAs solar cells

Features: highly efficient, but energy-intensive fabrication

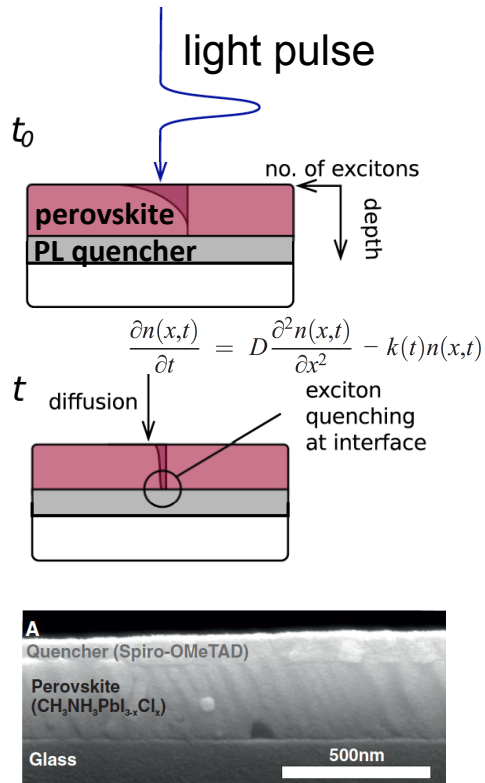
“Excitonic” or “nanocomposite” cells

- 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



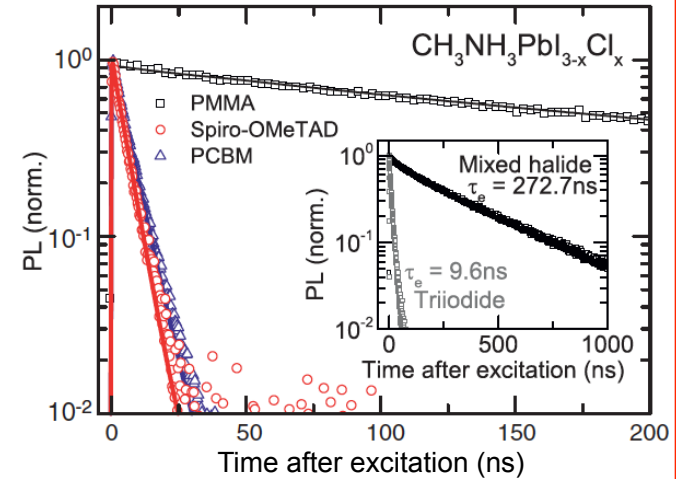
Typical examples: Dye-sensitized solar cells (DSC), organic photovoltaics (OPV)

Features: lower efficiencies, cheap (low-temperature processing)



Excite $\text{MA-PbI}_{3-x}\text{Cl}_x$ 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



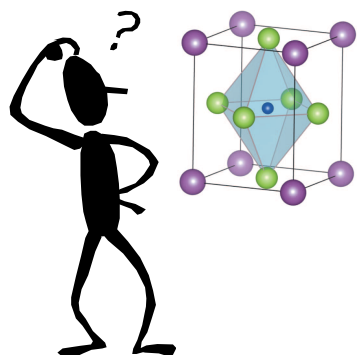
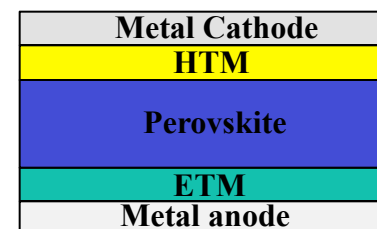
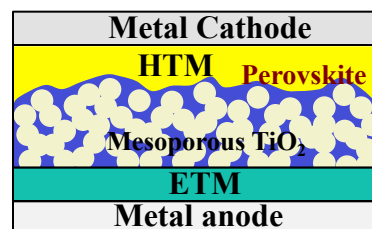
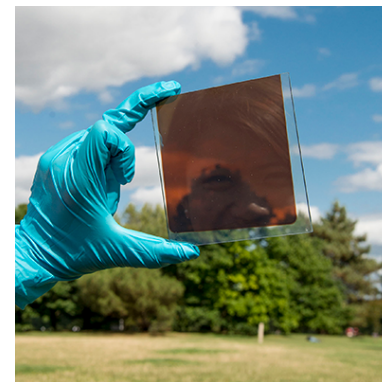
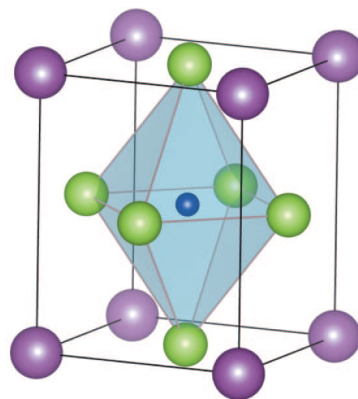
Extract charge-carrier diffusion length $L = \sqrt{D\tau}$ of $\approx 1\mu\text{m}$

Stranks, Eperon, Grancini, Menelaou, Alcocer, Leijtens, Herz, Petrozza, Snaith, Science 342, 341 (2013).

Hybrid lead trihalide perovskites combine the best of both worlds: low-temperature processing yielding charge carrier diffusion lengths that exceed the optical absorption depth!

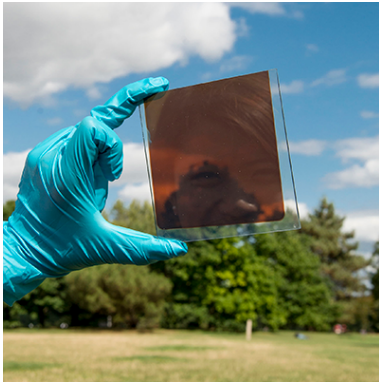
Hybrid metal halide perovskites have rapidly established themselves as new optoelectronic materials, allowing:

- 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-PbI₃ & 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-SnI₃

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

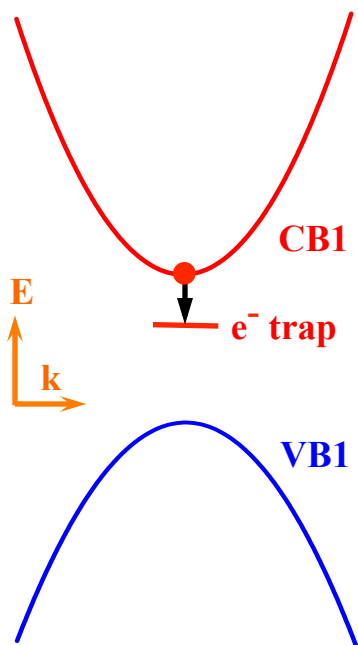
Tuneable materials for tandems?

A-Pb(Br_xI_{1-x})₃

- Allows for perovskites with $E_g \sim 1.7\text{eV}$ near the ideal band gap for tandem solar cells with silicon
- Problems with (photo-)stability

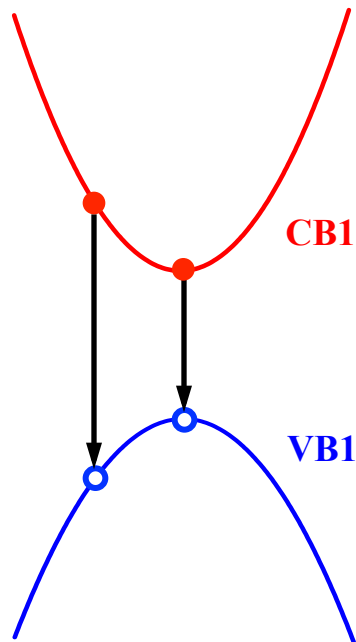


Trap-mediated (k_1)



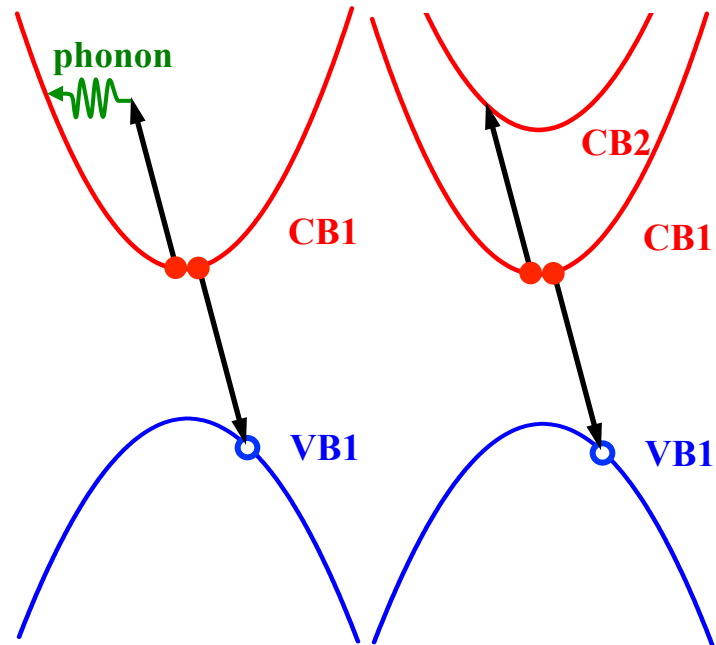
non-radiative*
 monomolecular
 particularly detrimental
 in low-charge-density
 regime

Bimolecular (k_2)



radiative*, for a direct
 semiconductor
 hence to some extent
 required to achieve
 strong absorption

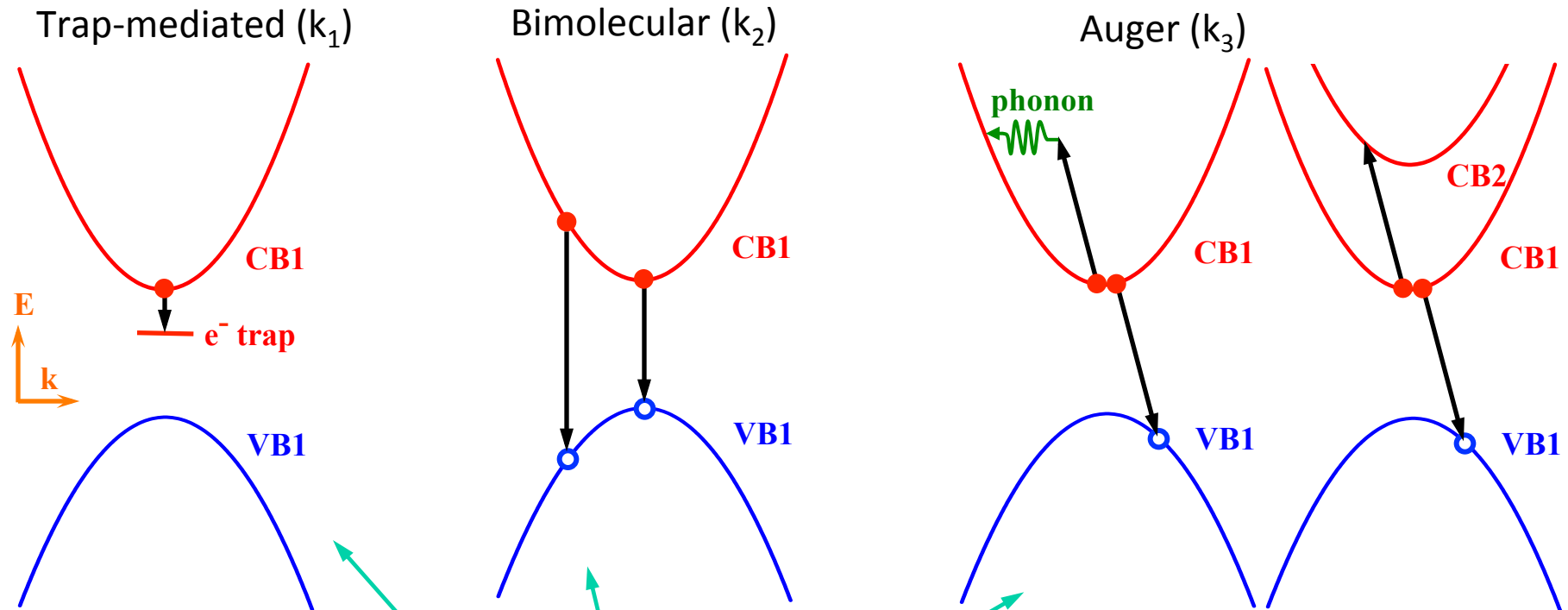
Auger (k_3)



non-radiative*
 strong dependence on
 bandstructure, phonons,
 impurities (because of energy &
 momentum conservation)

Herz, *Ann. Rev. Phys. Chem.* **67** (2016) DOI:10.1146/annurev-physchem-040215-112222

*see e.g. Bolink, *Adv. Mater.* **27**, 1837 (2015); Saba, *Nat. Commun.* **5**, 5049 (2014)

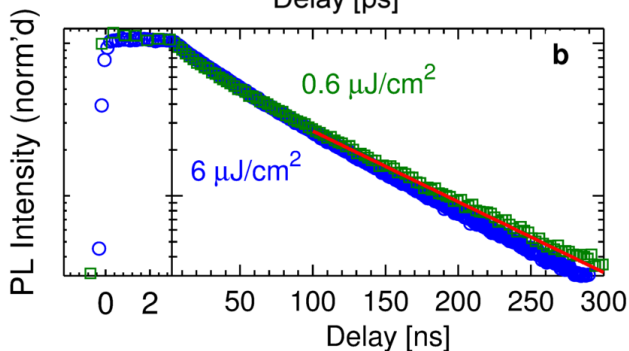
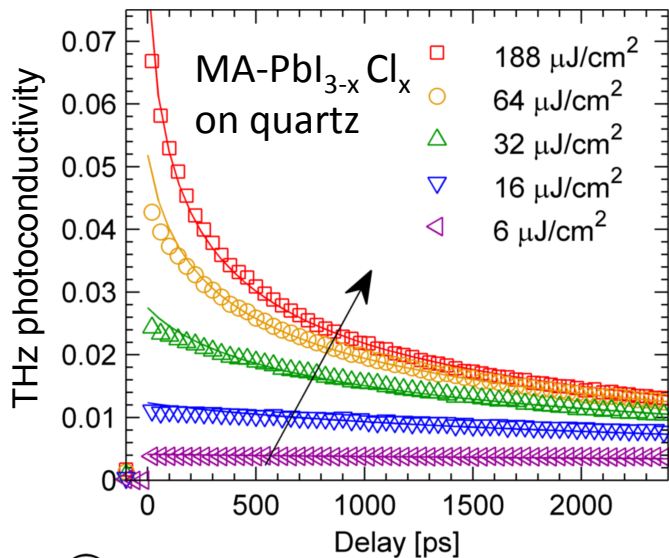
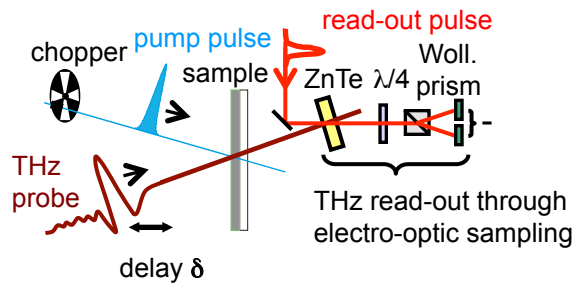


$$\frac{dn}{dt} = G - k_1 n - k_2 n^2 - k_3 n^3 = G - n R_T(n)$$

Rate equation governing the recombination dynamics

$$R_T = k_1 + nk_2 + n^2k_3$$

Examine temperature-dependence of each rate constant to understand the different underlying mechanisms, and how each rate can be tuned!



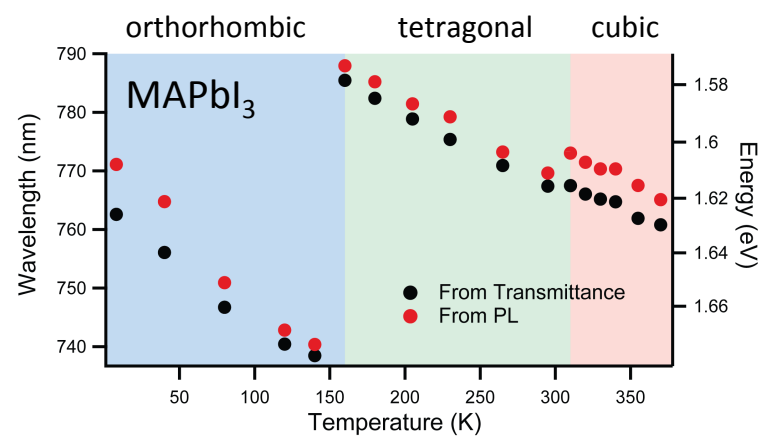
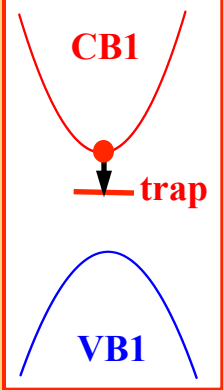
Examine transient **THz conductivity** and **photoluminescence (PL) decay dynamics** following excitation with VIS light pulse:

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

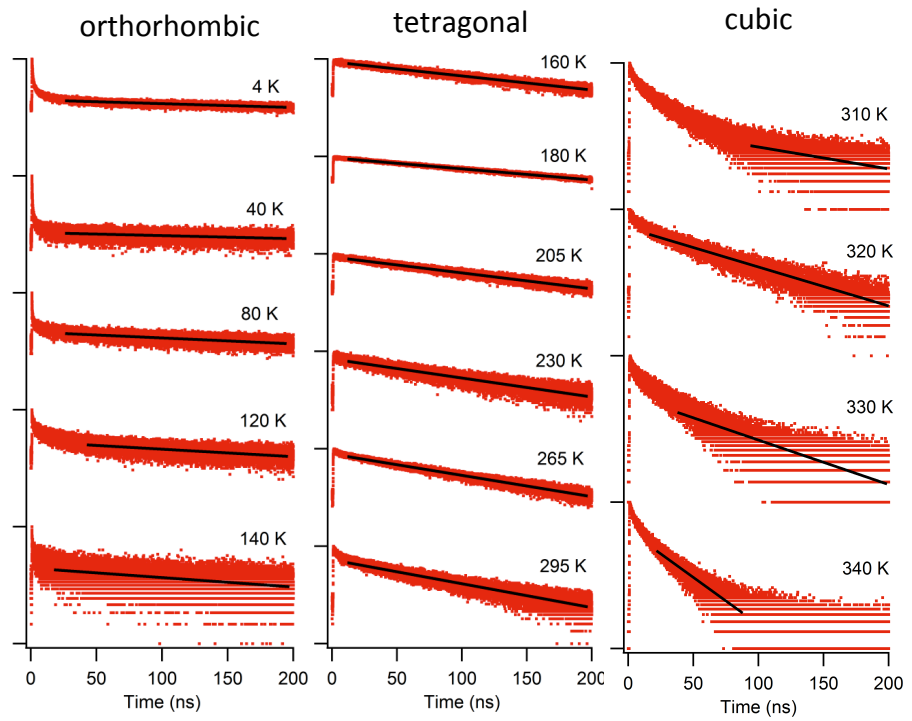
Wehrenfennig, Liu, Johnston, Snaith, Herz,
Energy Env. Sci. 7, 2269 (2014)
J. Phys. Chem. Lett. 5, 1300 (2014)

Analysis of temperature-dependent PL from solution-processed MAPbI₃ films, excited with low fluence so that monomolecular decay dominates:

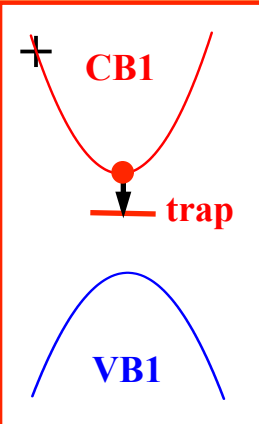
PL peak •
 and absorption onset •
 energies as a function of T:



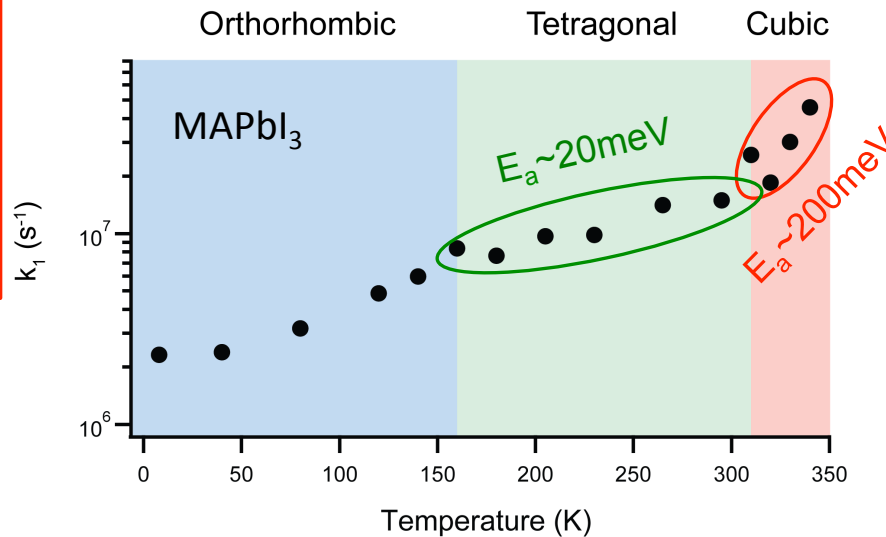
PL transients:



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



Increased trap-mediated recombination rate with increasing temperature:

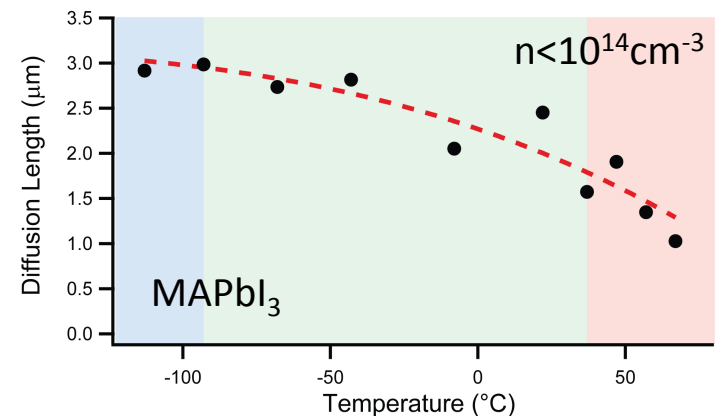


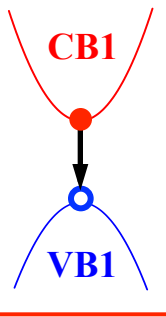
At high T, ionized, charged impurities may have larger cross-section for charge capture.

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

Relevance to PV operation:

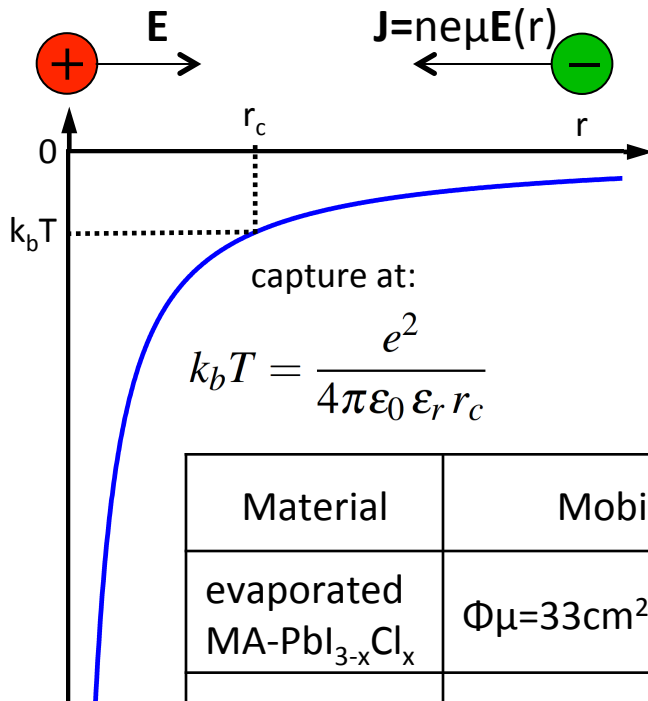
- leads to decline in charge-carrier diffusion lengths L_d (also because charge mobility declines with increasing T)
- But: still high $L_d \sim 1\mu\text{m}$ at 70°C.





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

One possible model: Langevin theory

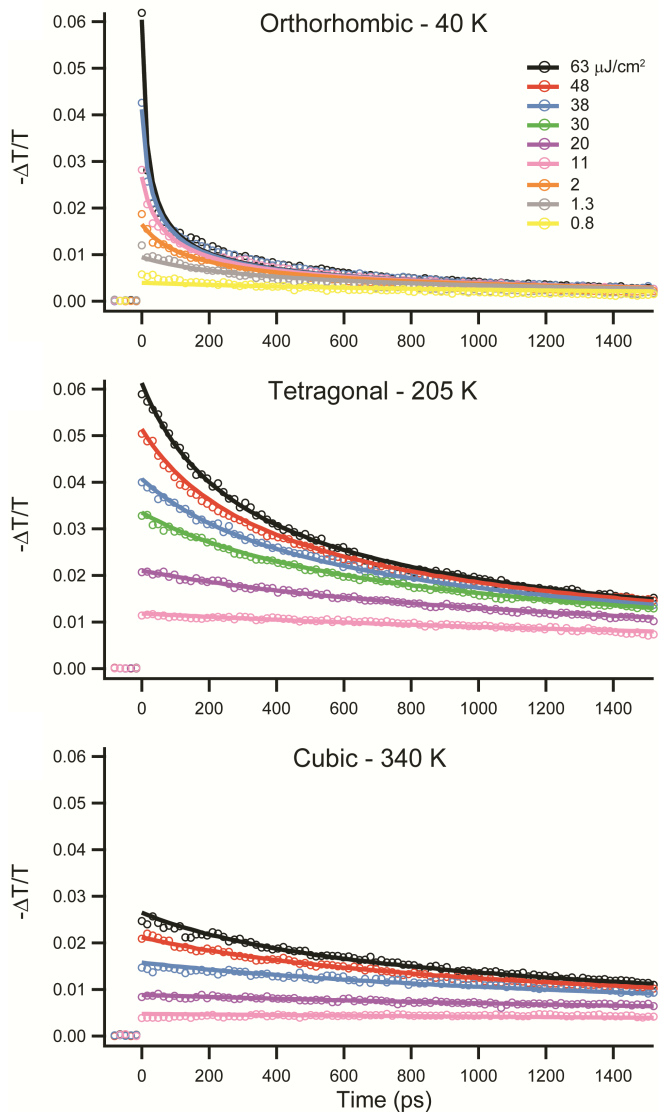
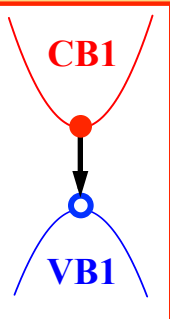


- Electron moves in electric field generated by hole
- Capture and recombination occurs at distance r_c where interaction energy is comparable to $k_b T$.
- Current into capture radius: $I = ne^2\mu/\epsilon_0\epsilon_r$ must be equal to rate of change of charge density through recombination: $dQ/dt = nek_2$

$$\frac{k_2}{\mu} = \frac{e}{\epsilon_0 \epsilon_r}$$

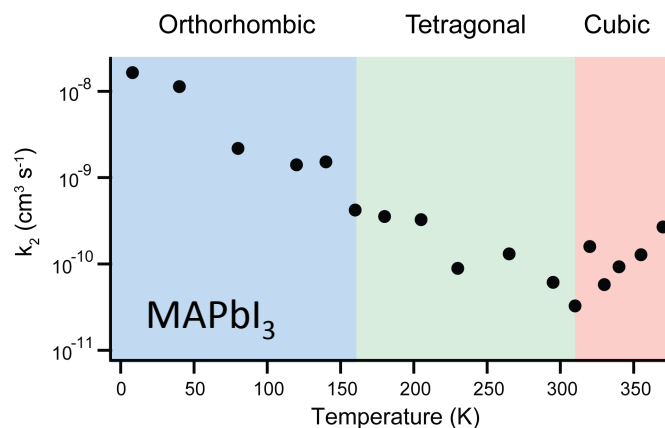
Material	Mobility	Measured k_2/μ	$k_2/\mu : e/\epsilon_0\epsilon_r$
evaporated MA-PbI _{3-x} Cl _x	$\Phi\mu = 33 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$k_2/\mu = 3.3 \times 10^{-12} \text{ cm V}$	$3 \times 10^{-6} \epsilon_r : 1$
Anthracene	$\mu = 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$k_2/\mu = 6 \times 10^{-6} \text{ cm V}$	3.3 : 1

Ratio defies Langevin limit by ≈ 5 orders of magnitude!

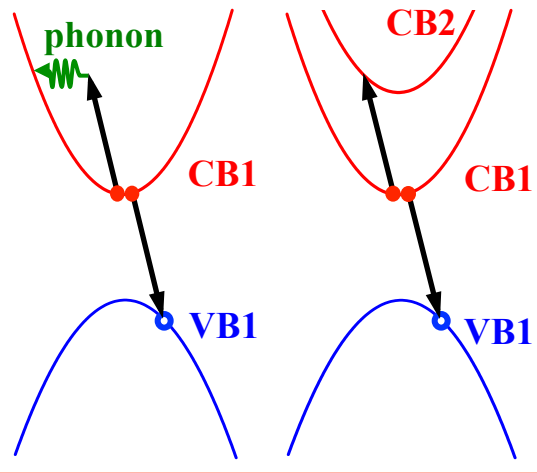


Photoconductivity dynamics in thin films of MAPbI₃ as a function of temperature:

- 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

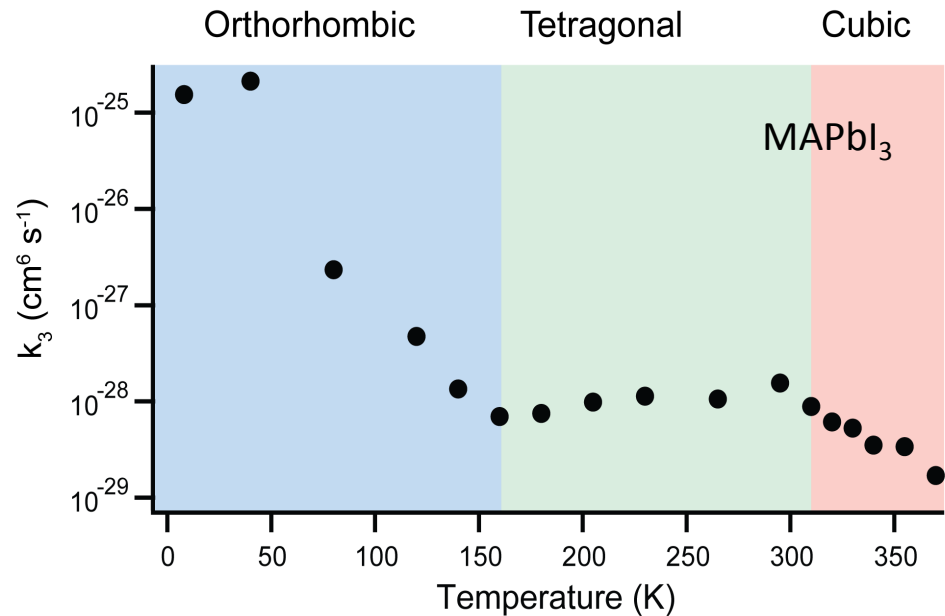


Auger rate constants (k_3) in MAPbI₃:

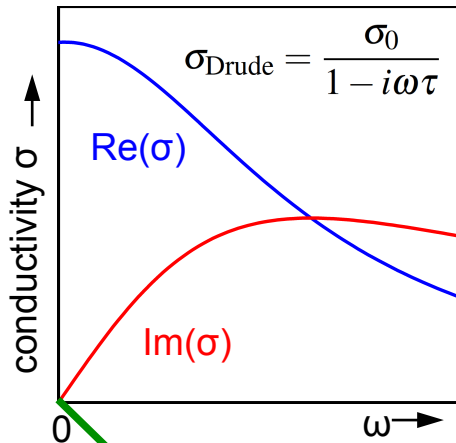
- k_3 shows expected strong dependence on temperature
- shows different temperature-dependences in different crystal structures
- Confirms strong dependence on bandstructure & phonons
- Allows tuning through structure/composition modification

Relevance for devices:

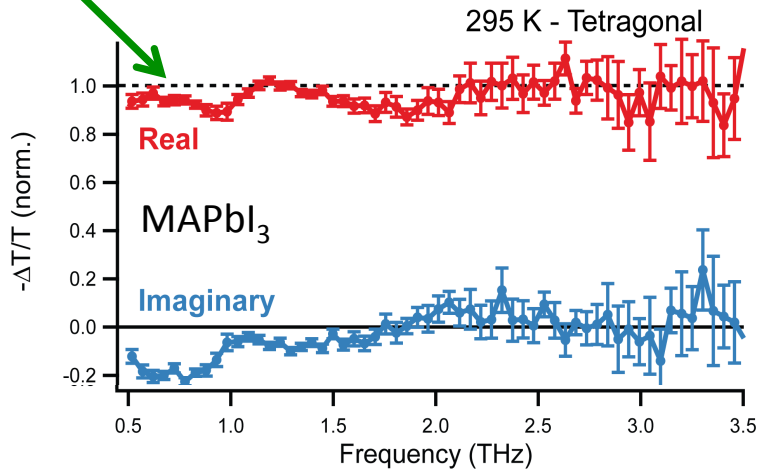
- at room temperature: $k_3 \sim 10^{-28} \text{ cm}^6 \text{ s}^{-1}$
- $\sim 25\times$ higher than that for GaAs ($4 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$)
- Auger recombination contributes significantly for $n \gg 10^{18} \text{ cm}^{-3}$, so not particularly relevant for PV, but highly important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



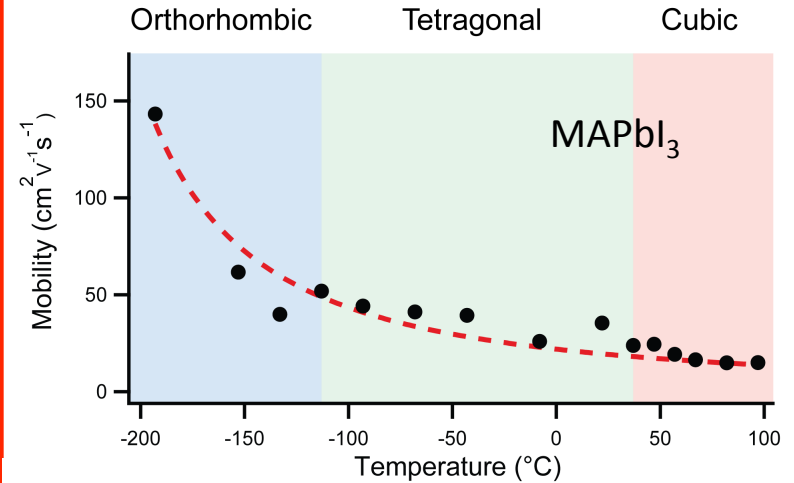
Are charge mobilities in high-quality lead iodide perovskite films near the intrinsic limit?



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



En. Environ. Sci. **7**, 2269 (2014)
 Adv. Func. Mater. **25**, 6218 (2015)



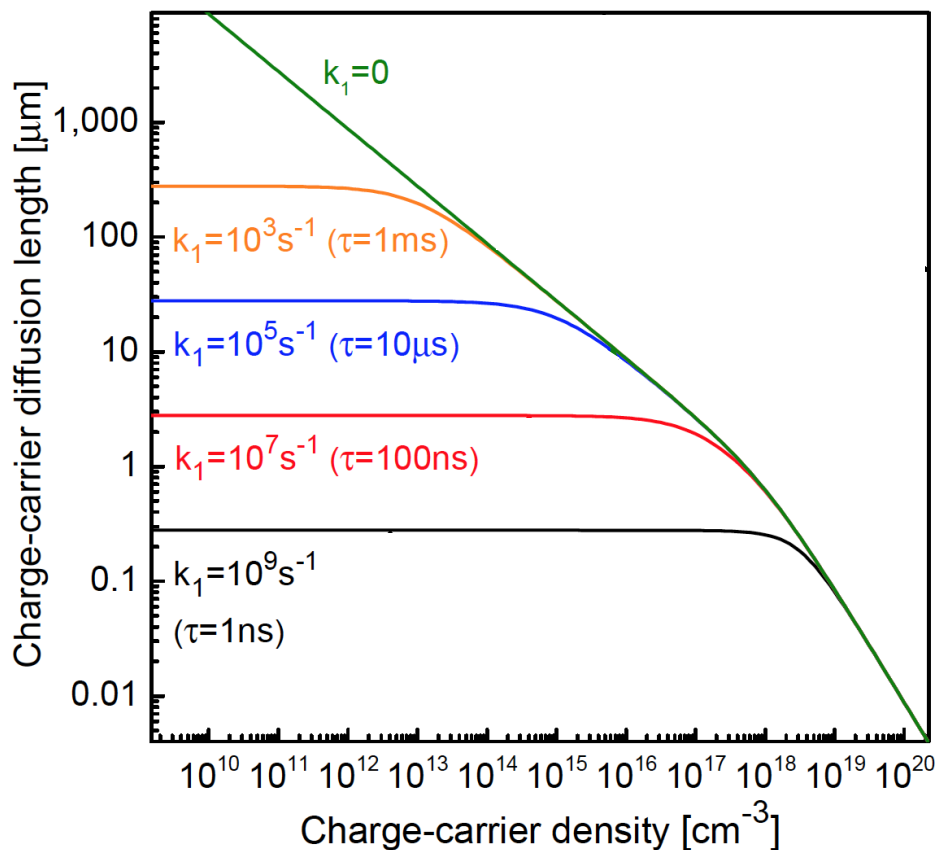
The mobility increases with decreasing T according to $T^{-1.5}$ in accordance with charge scattering off phonons

➔ scattering off impurities and/or crystal boundaries can only play a minor role.

➔ At $T=300\text{K}$, $\mu \sim 30 \text{ cm}^2/(\text{Vs})$

➔ Unlikely to see increases by many orders of magnitude

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



Johnston & Herz, *Acc. Chem. Res.* **49**, 146 (2016)

Evaluate charge-carrier diffusion length L_D in MAPbI₃ 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 $\mu=30\text{cm}^2/(\text{Vs})$, $k_2=10^{-10}\text{cm}^3\text{s}^{-1}$, $k_3=10^{-28}\text{cm}^6\text{s}^{-1}$

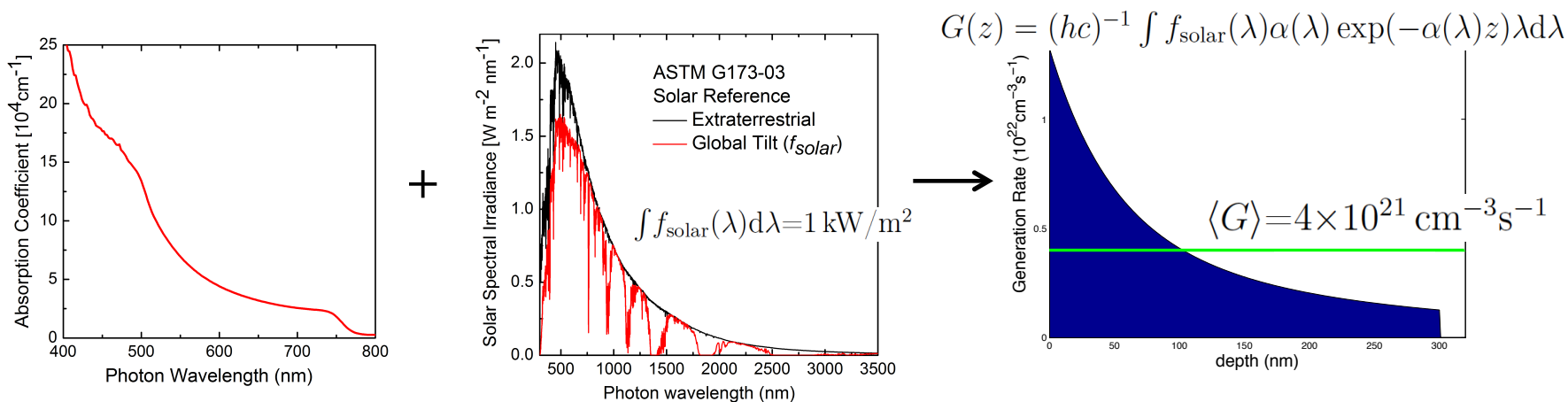
In the limit of ultra-low k_1 , L_D depends strongly on charge density n , approaching:

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

Meaningful values of L_D can only be obtained with reference to the charge-carrier density present!

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})

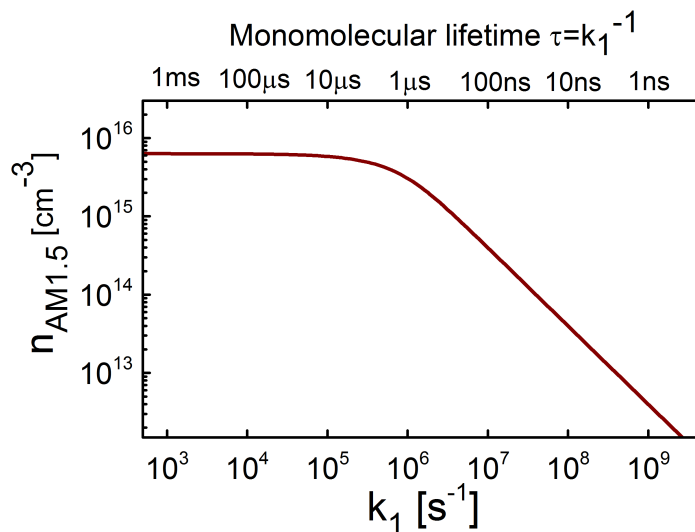
Step 1: obtain charge-carrier generation rate under AM1.5 conditions:



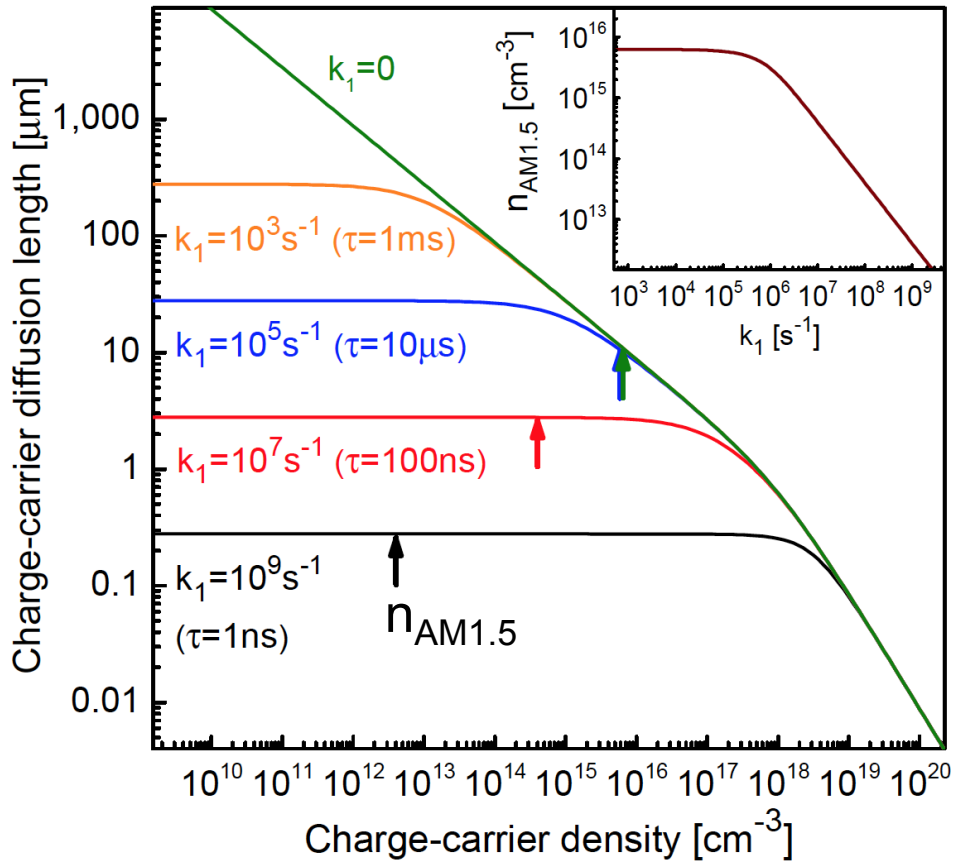
Step 2: solve cubic equation ($dn/dt=0$):

$$\langle G \rangle = nk_1 + n^2k_2 + n^3k_3$$

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!



Johnston & Herz, Acc. Chem. Res. **49**, 146 (2016)

Evaluate charge-carrier diffusion length L_D in MAPbI₃ using:

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

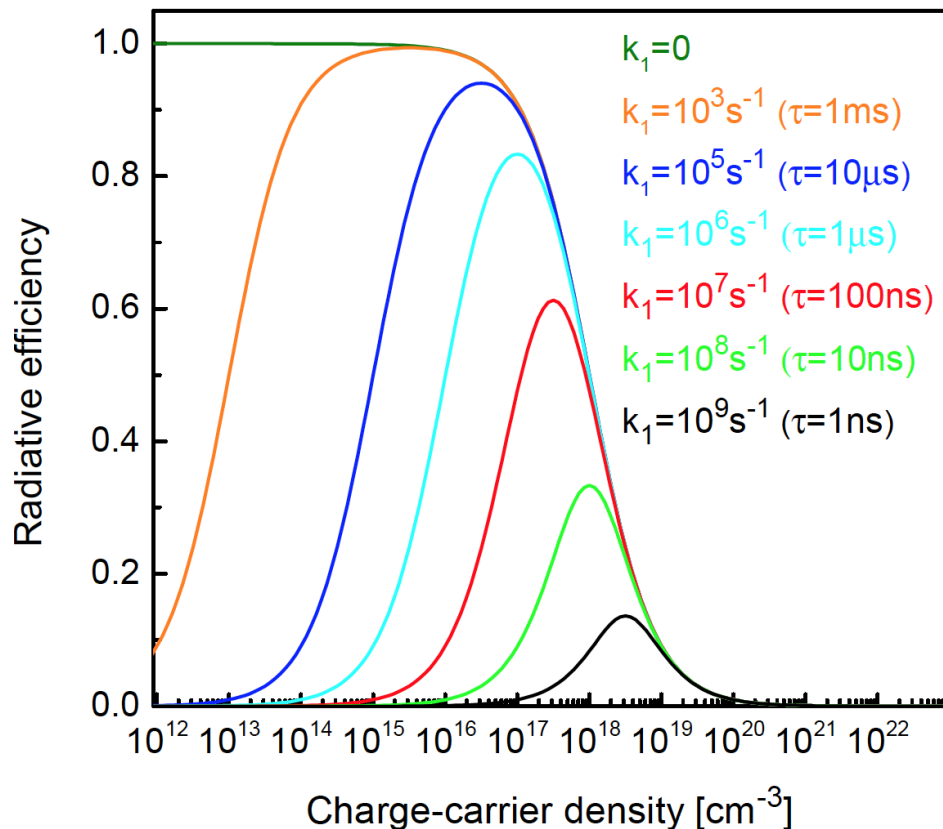
where $R_T = k_1 + nk_2 + n^2k_3$, and we assume $\mu=30\text{cm}^2/(\text{Vs})$, $k_2=10^{-10}\text{cm}^3\text{s}^{-1}$, $k_3=10^{-28}\text{cm}^6\text{s}^{-1}$

At AM1.5 (arrows): values around $10\mu\text{m}$ 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 Φ in MA-PbI₃ as a function of charge-carrier density n :



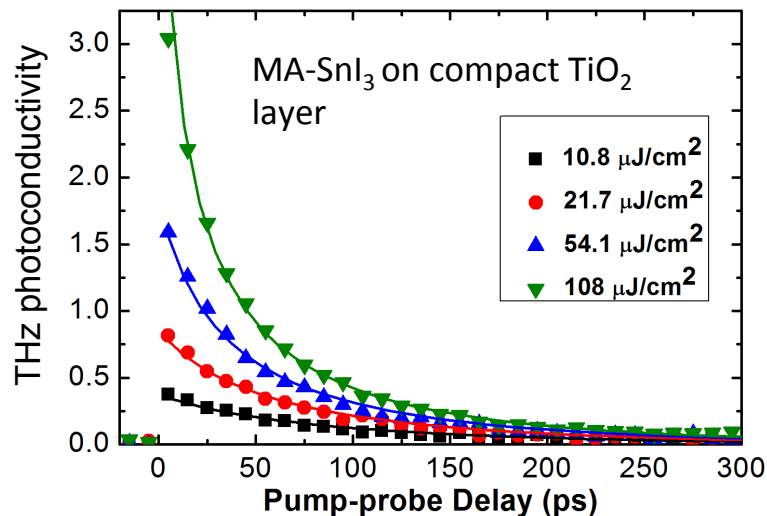
Johnston & Herz, Acc. Chem. Res. **49**, 146 (2016)

- Calculate Φ using

$$\Phi(n) = \frac{nk_2}{k_1 + nk_2 + n^2k_3}$$

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

- Onset of high Φ for $\tau=k_1^{-1}=10\text{-}100\text{ns}$ occurs at $1\text{-}10 \times 10^{18}\text{cm}^{-3}$ corresponds to excitation fluences $7\text{-}70\mu\text{Jcm}^{-2}$ typically reported for ASE or lasing
- Onsets of ASE and efficient light emission at lower charge-carrier densities $<10^{15}\text{cm}^{-3}$ will require trap-related lifetimes in excess of μs .



Energy Environ. Sci. **7**, 3061 (2014)

- From fits: $k_1 = 8 \times 10^9 \text{ s}^{-1}$ ($\tau = 110 \text{ ps}$) yielding doping density: $\phi^{-1} p_0 = 5.8 \times 10^{18} \text{ cm}^{-3}$ [see e.g. J. Solid State Chem. **205**, 39 (2013): $p_0 = 9 \times 10^{17} \text{ cm}^{-3}$]
- But: decent effective charge-carrier mobility: $\phi \mu = 1.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

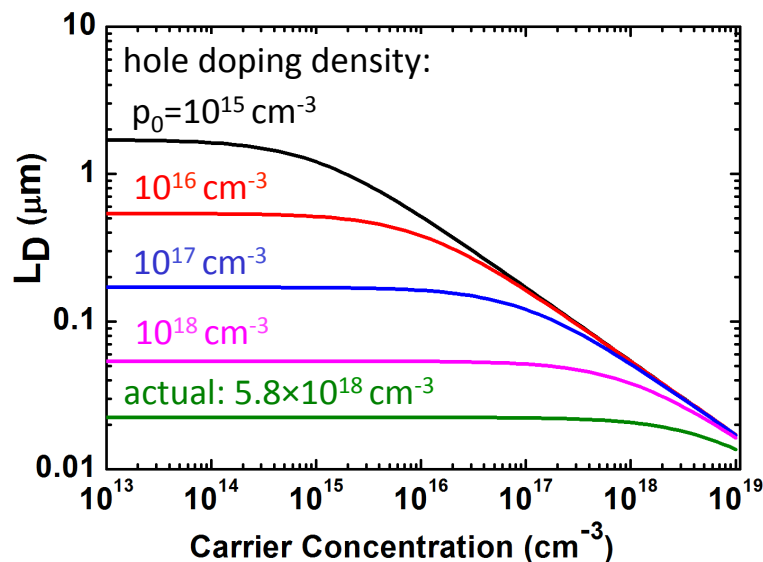
If unintentional doping and trapping in MA-SnI_3 can be controlled, long charge-carrier diffusion lengths are feasible

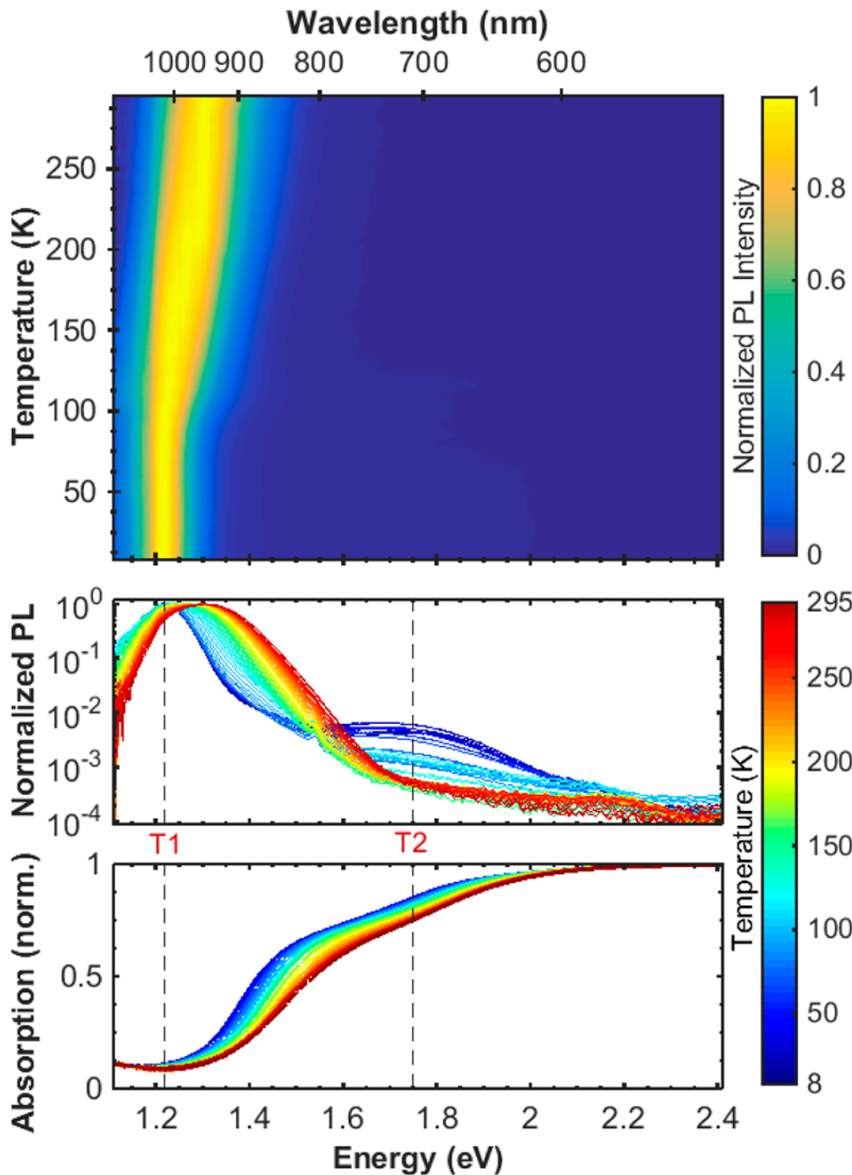
For MASnI_3 , monomolecular recombination is 3 orders of magnitude faster than in typical MAPbI_3 .

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

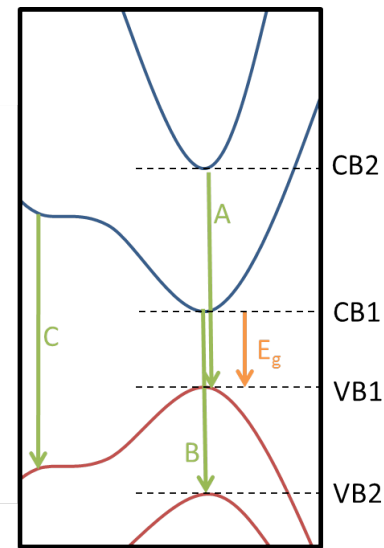
$$\frac{dn}{dt} = -k_2 n (p + p_0) = -k_2 n^2 - \underbrace{k_2 p_0 n}_{k_1}$$

↑ ↑
 photogenerated + doping
 hole densities

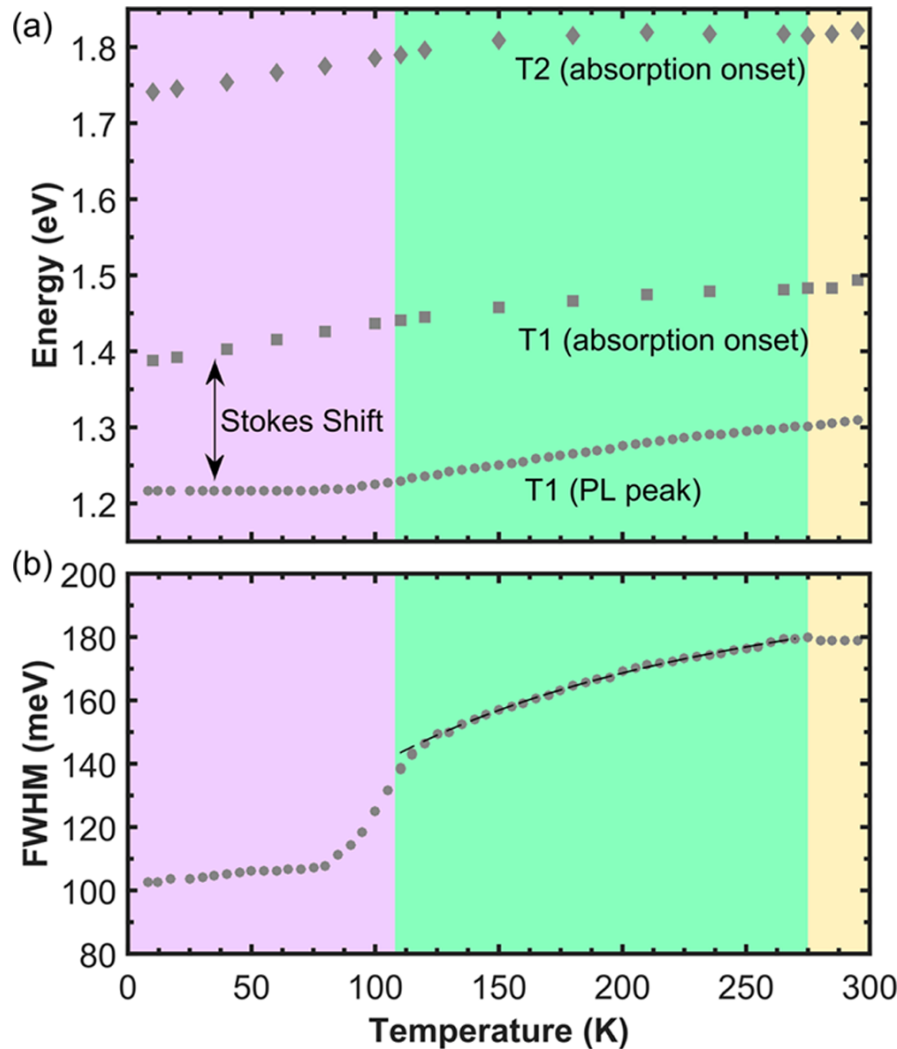




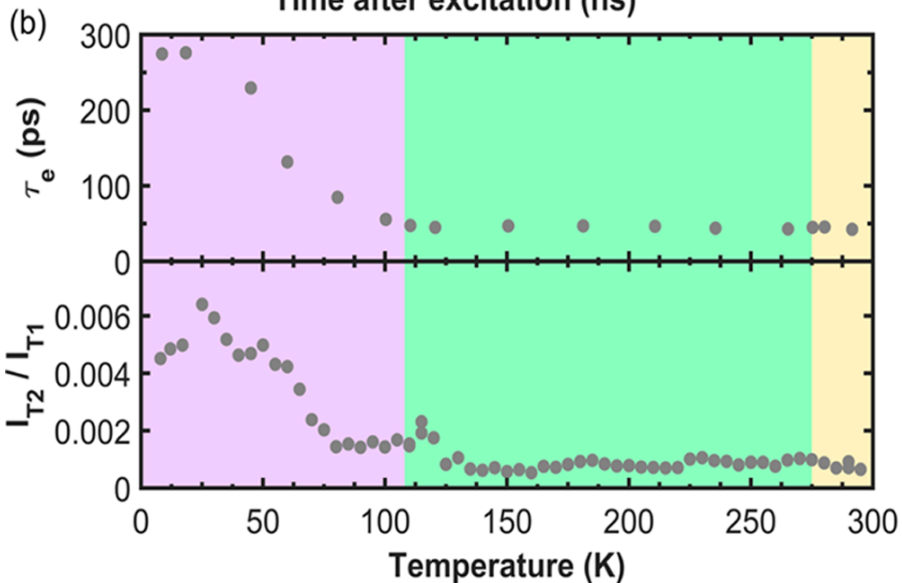
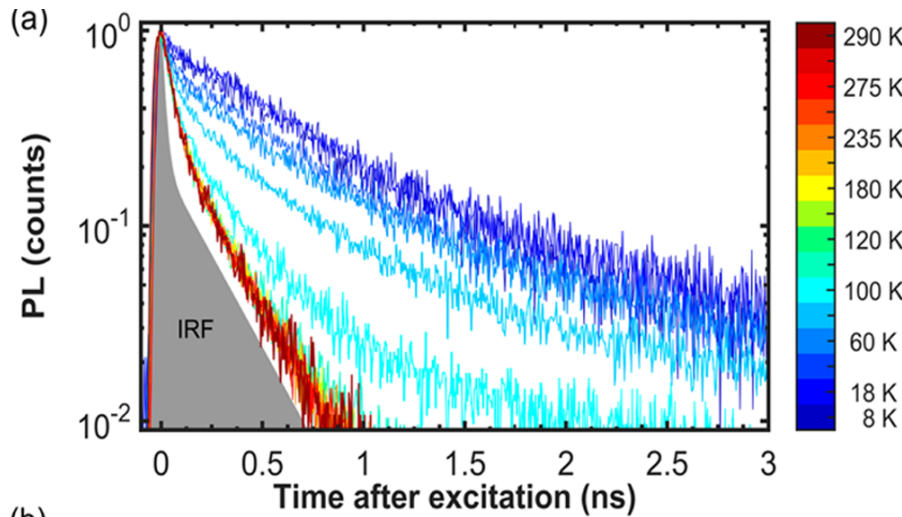
- Phase transition at $\sim 110\text{K}$ from tetragonal to orthorhombic structure
- Full-width at half maximum of the PL emission suddenly narrows at the phase transition!
- Observe higher-lying emission peaks possibly originating from transitions involving higher-lying bands:



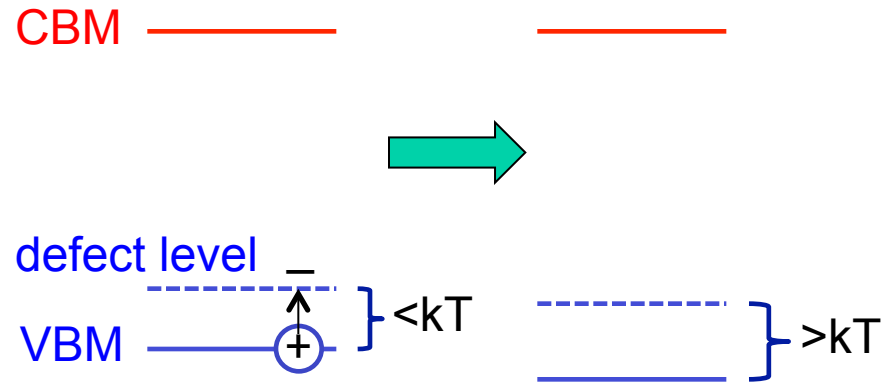
- Can this excess energy be harvested?



- Large (~200meV) Stokes shift between PL peak emission energy and absorption edge (for MAPbI₃ 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!

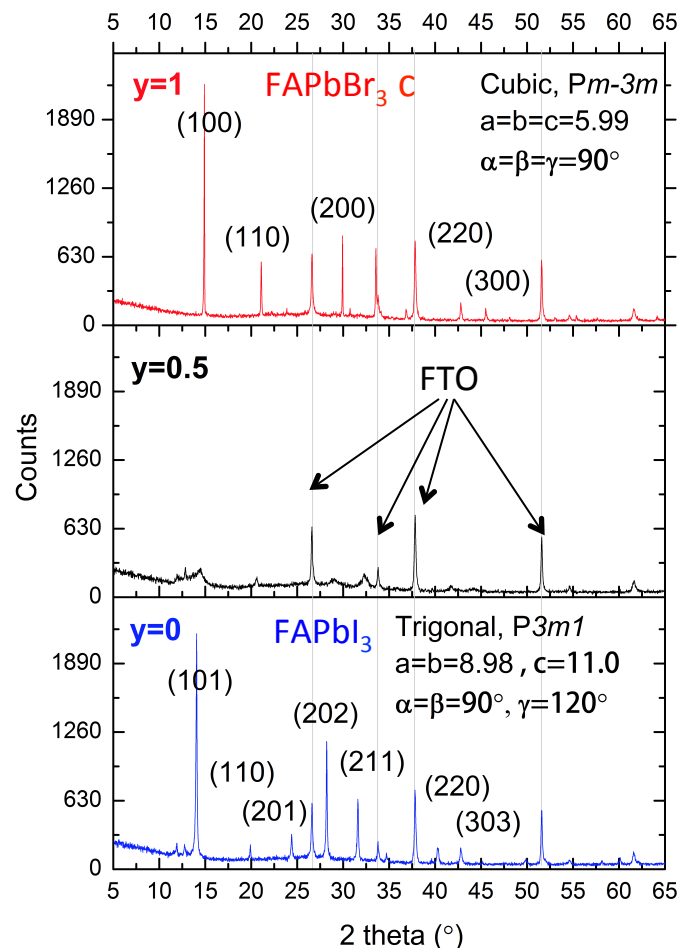
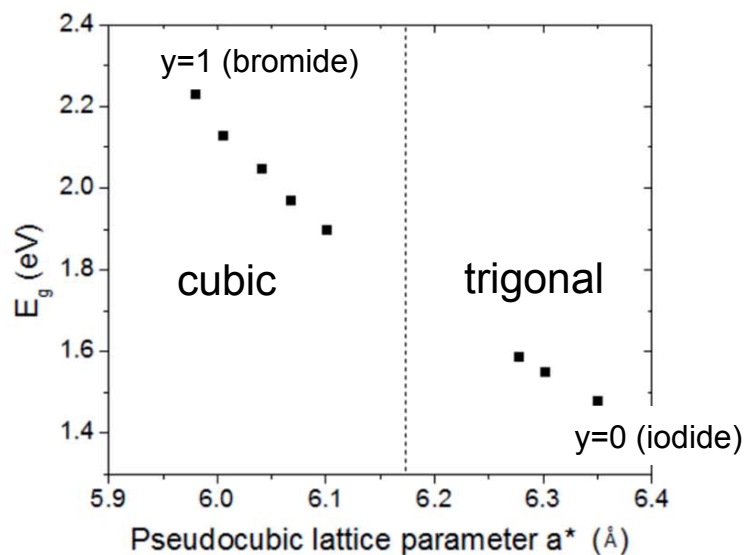


- Significant increase in PL lifetimes below 110K again suggests that unintentional dopant carrier concentration drops at the phase transition!
- Small changes in crystal structure seem sufficient to reduce background doping concentration!



- Can we replicate this effect e.g. through A-cation replacement?

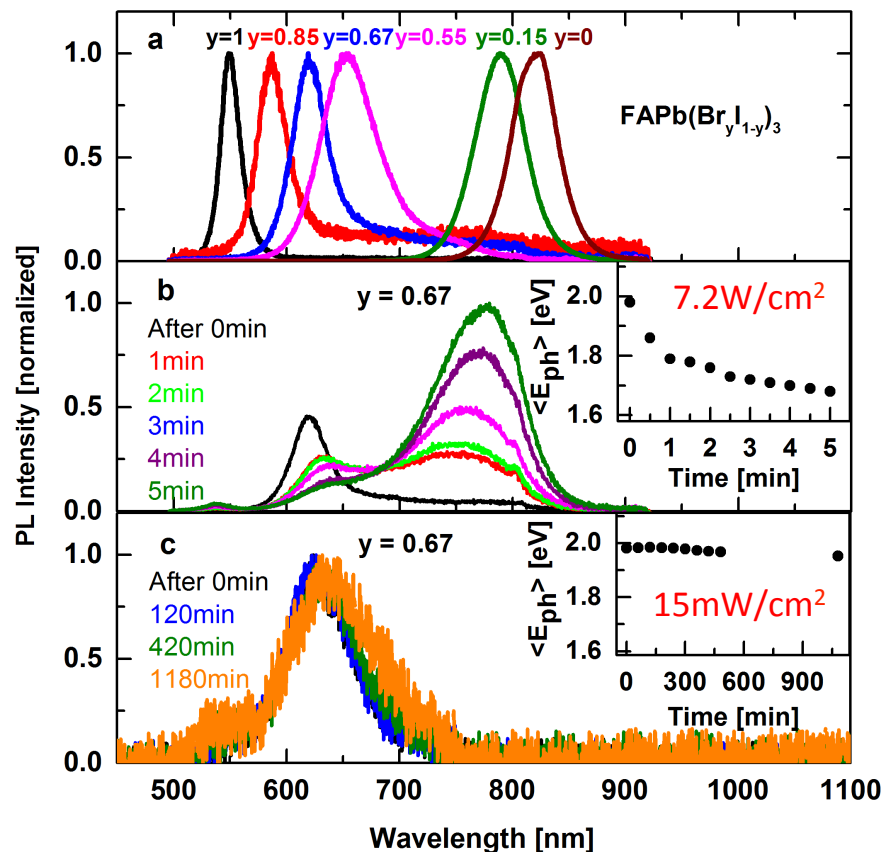
- $\text{FAPb}(\text{Br}_y\text{I}_{1-y})_3$ is a highly band-gap tunable material system that may allow applications in tandem cell
- But: instability near the central region ($0.3 < y < 0.5$) where crystal structure switches from cubic to trigonal
- materials loose crystallinity (no peaks detectable in XRD) in this central region



Eperon, Stranks, Menelaou, Johnston, Herz, Snaith
 Energy Environ. Sci. **7**, 982 (2014)

Rehman, Milot, Eperon, Wehrenfennig,
 Boland, Snaith, Johnston, Herz,
 Adv. Mater. **27**, 7938 (2015)

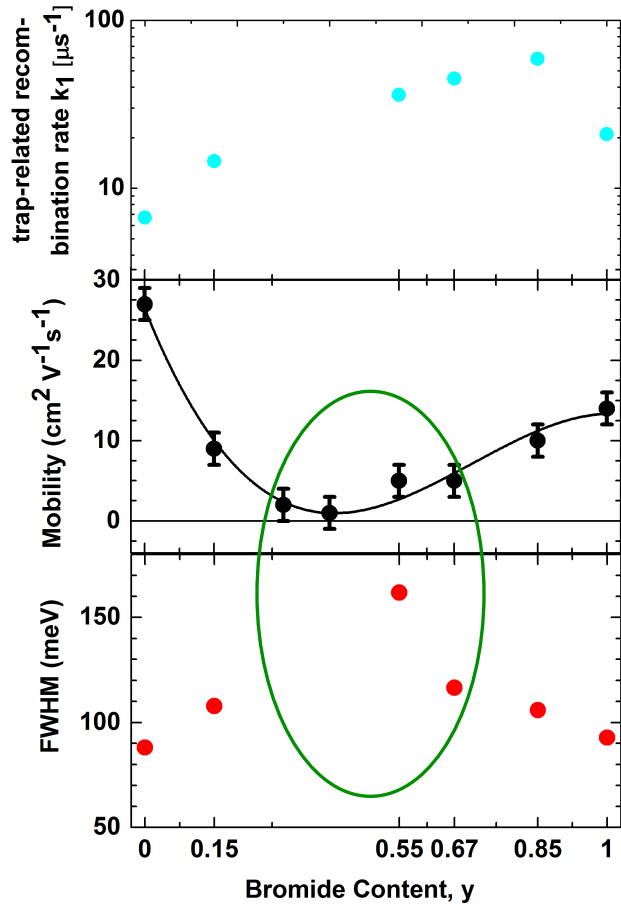
But: $\text{FAPb}(\text{Br}_y\text{I}_{1-y})_3$ is unstable under illumination, in particular for $0.3 < y < 0.5$



- 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

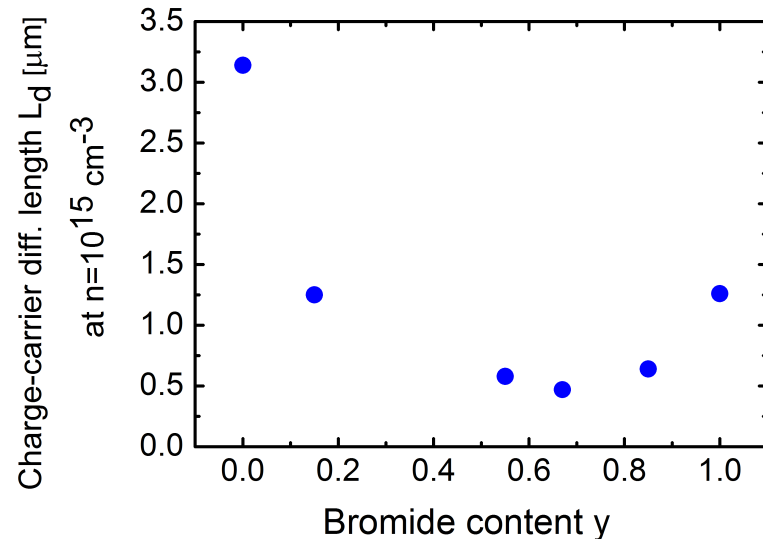
Investigate optoelectronic properties of as-cast materials, at low excitation intensity and before light-induced changes have occurred.

Rehman, Milot, Eperon, Wehrenfennig, Boland, Snaith, Johnston, Herz, Adv. Mater. **27**, 7938 (2015)

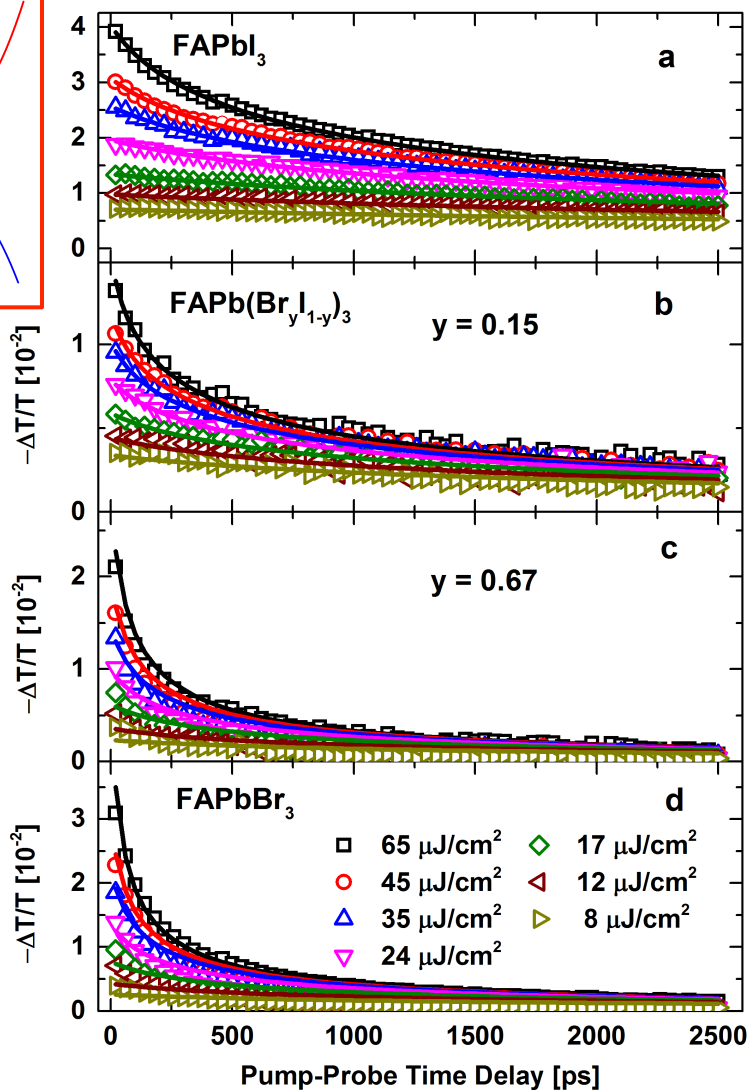
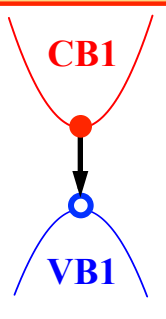


$\text{FAPb}(\text{Br}_y\text{I}_{1-y})_3$ shows increase in disorder, trap density and decrease in charge-carrier mobility near the central region ($0.3 < y < 0.5$):

- 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 ($27\text{cm}^2/\text{Vs}$) and FAPbBr_3 ($14\text{cm}^2/\text{Vs}$) to values $< 1\text{cm}^2/\text{Vs}$ for $y=0.4$
- Charge-carrier diffusion lengths under $\sim\text{AM1.5}$:

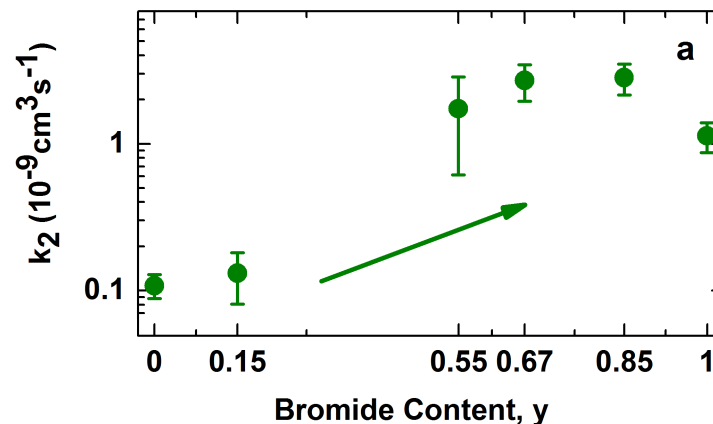


Rehman, Milot, Eperon, Wehrenfennig, Boland, Snaith, Johnston, Herz, Adv. Mater. **27**, 7938 (2015)

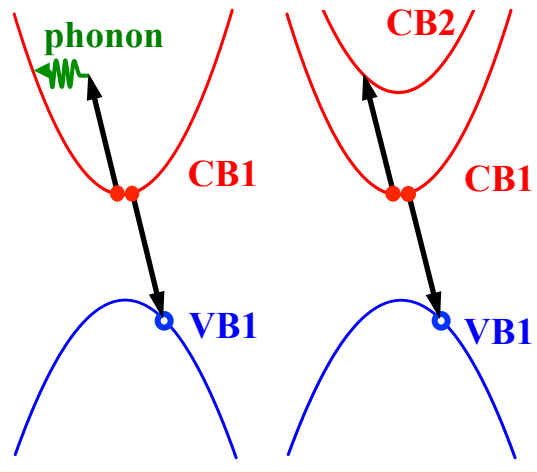


Photoconductivity dynamics in thin films of following VIS excitation:

- 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?

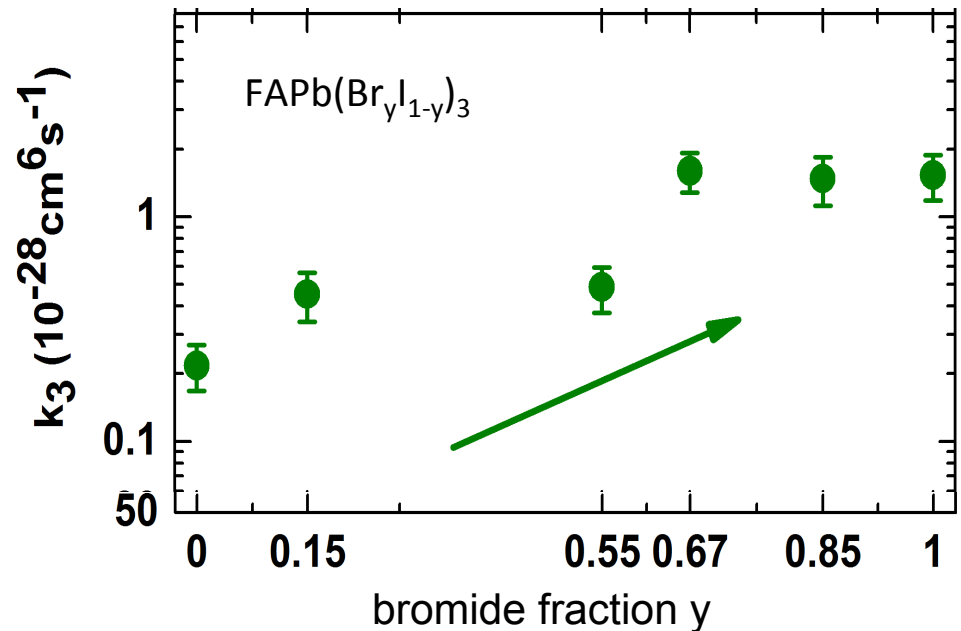


Auger rate constants (k_3) in $\text{FAPb}(\text{Br}_y\text{I}_{1-y})_3$:

- k_3 increases with increasing bromide y in $\text{FAPb}(\text{Br}_y\text{I}_{1-y})_3$
- Confirms strong dependence on bandstructure
- Allows tuning through structure modification

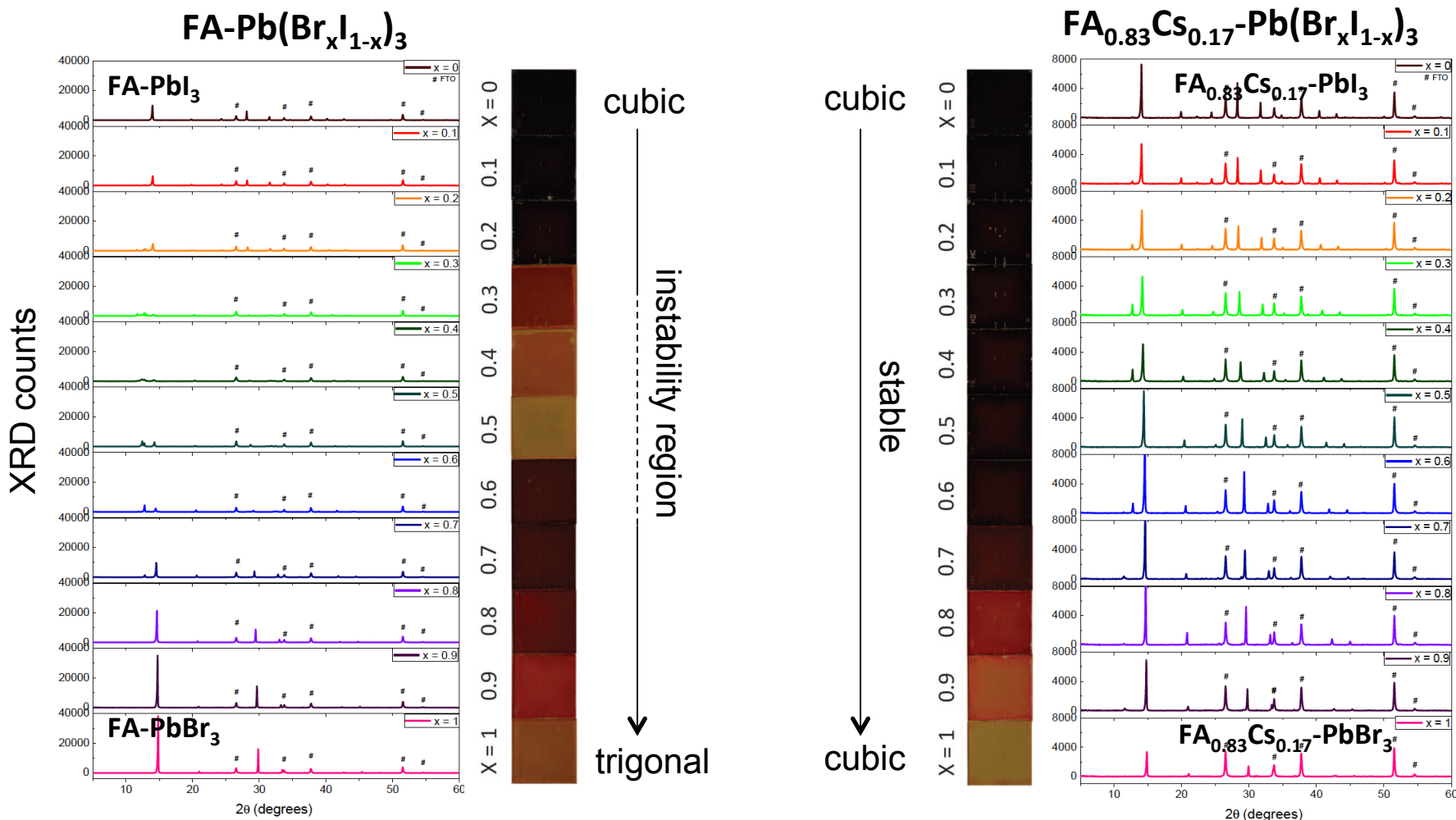
Relevance for devices:

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



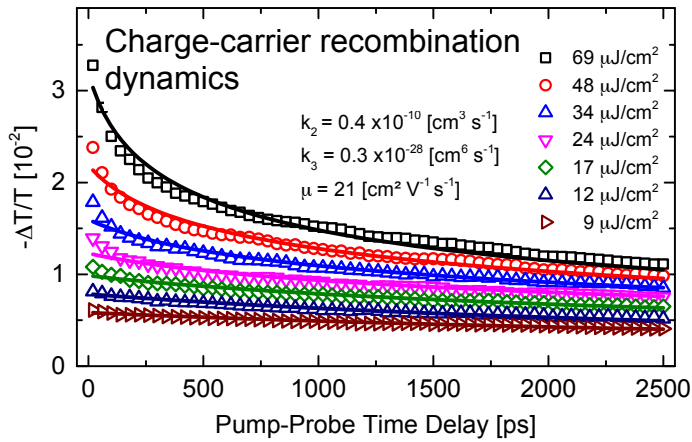
Rehman, Milot, Eperon, Wehrenfennig,
 Boland, Snaith, Johnston, Herz,
 Adv. Mater. **27**, 7938 (2015)

Choose system $A\text{-Pb}(\text{Br}_x\text{I}_{1-x})_3$ that has the same structure for $A\text{-PbI}_3$ and $A\text{-PbBr}_3$:

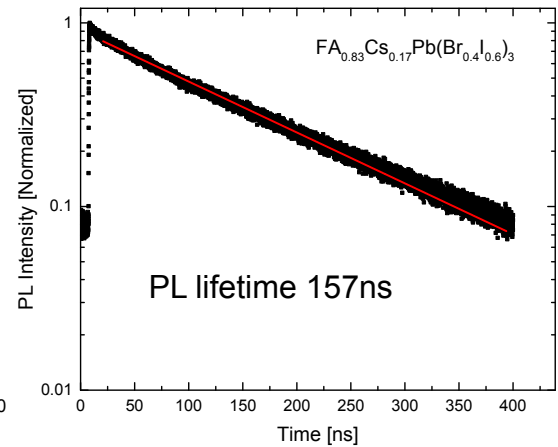
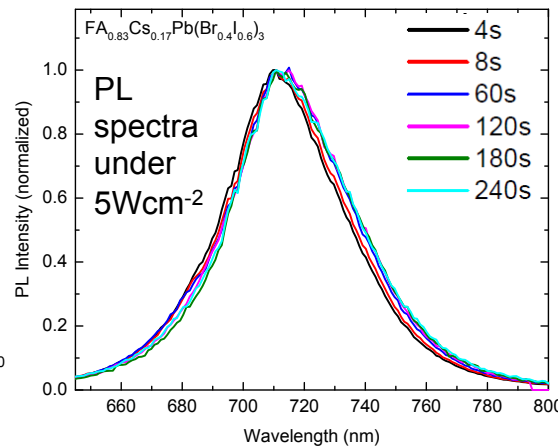
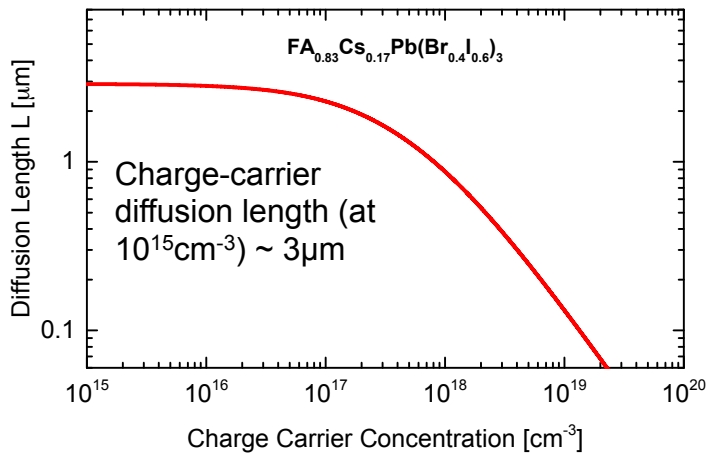


McMeekin, Sadoughi, Rehman, Eperon, Saliba, Hörantner, Haghighirad, Sakai, Korte, Rech, Johnston, Herz, Snaith, Science **351**, 151 (2016)

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



- Band-gap at 1.74eV ideal for tandem with Si
- Good monomolecular lifetime: 157ns
- High stability under intense light illumination
- High charge-carrier mobility (21cm²/Vs)
- Long charge-carrier diffusion length (~3μm)
- Low Urbach energy (16meV)
- 17% PCE in planar-heterojunction solar cell



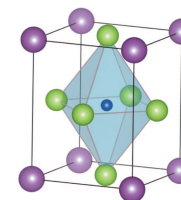
McMeekin, Sadoughi, Rehman, Eperon, Saliba, Hörantner, Haghighirad, Sakai, Korte, Rech, Johnston, Herz, Saith, Science **351**, 151 (2016)

- 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 $\sim 10\mu\text{m}$ 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-SnI₃**: much faster monomolecular recombination due to tin vacancy (p-doping)
- **A-Pb(Br_yI_{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:

Rebecca Milot, Waqaas Rehman, Christian Wehrenfennig, David McMeekin, Beth Parrott, Ming Zhen Liu, Giles Eperon, Chris Menelaou, Michael Johnston, Henry Snaith

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, Universite de Fribourg, University
of Cyprus, Universitat de Valencia**

