



Supporting Information

for *Adv. Funct. Mater.*, DOI: 10.1002/adfm.201802803

Interplay of Structural and Optoelectronic Properties in
Formamidinium Mixed Tin–Lead Triiodide Perovskites

*Elizabeth S. Parrott, Thomas Green, Rebecca L. Milot,
Michael B. Johnston, Henry J. Snaith, and Laura M. Herz**

Supporting Information

Title: Interplay of structural and optoelectronic properties in formamidinium mixed tin-lead triiodide perovskites

*Elizabeth S. Parrott, Thomas Green, Rebecca L. Milot, Michael B. Johnston, Henry J. Snaith, Laura M. Herz**

Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford
OX1 3PU, UK
E-mail: laura.herz@physics.ox.ac.uk

Contents

1. Additional Figures

- 1.1 Temperature Dependent PL Spectra
- 1.2 Room temperature measurements for additional compositions
- 1.3 Temperature dependent PL decays
- 1.4 Recombination Mechanisms for Sn= 87.5%
- 1.5 Results from two fabrication methods

2. Notes on Fitting Data

- 2.1 Absorption spectra and Tauc plot analysis
- 2.2 Temperature dependent PL intensity
- 2.3 Band-gap Bowing Parameter
- 2.4 Instrument Response Function Correction
- 2.5 Stretched Exponential Fitting

3. PL decay dynamics

- 3.1 Bimolecular recombination
- 3.2 Shockley Read Hall Recombination
- 3.3 Carrier Trapping

4. PLQE for transient measurements

1 Additional Figures

1.1 Temperature Dependent PL Spectra

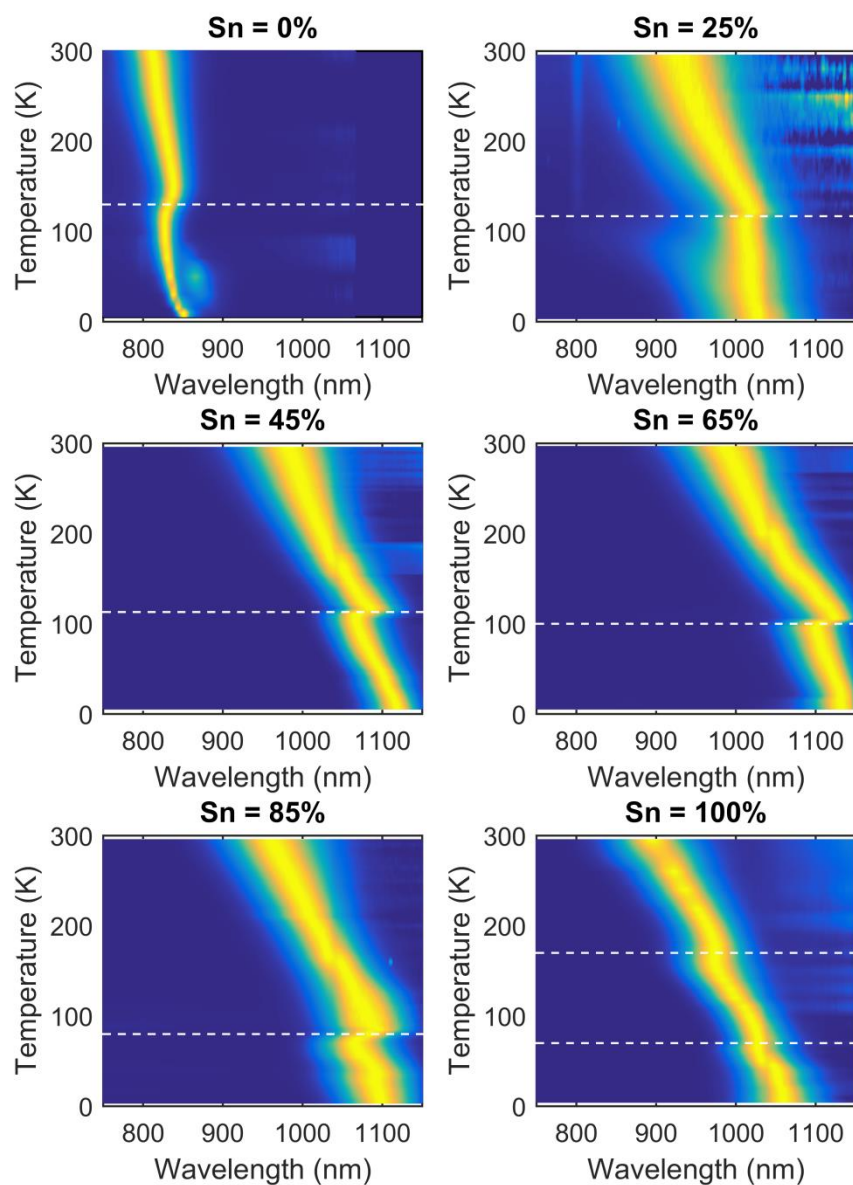


Figure S1. Color plots of normalized PL intensity (yellow/lightest = 1, blue/darkest = 0) for $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$ where x is given as a percentage above each figure. Samples were excited at 400 nm, 1 W cm^{-2} . Discontinuities in the PL are marked with white dashed lines and assumed to be phase transitions.

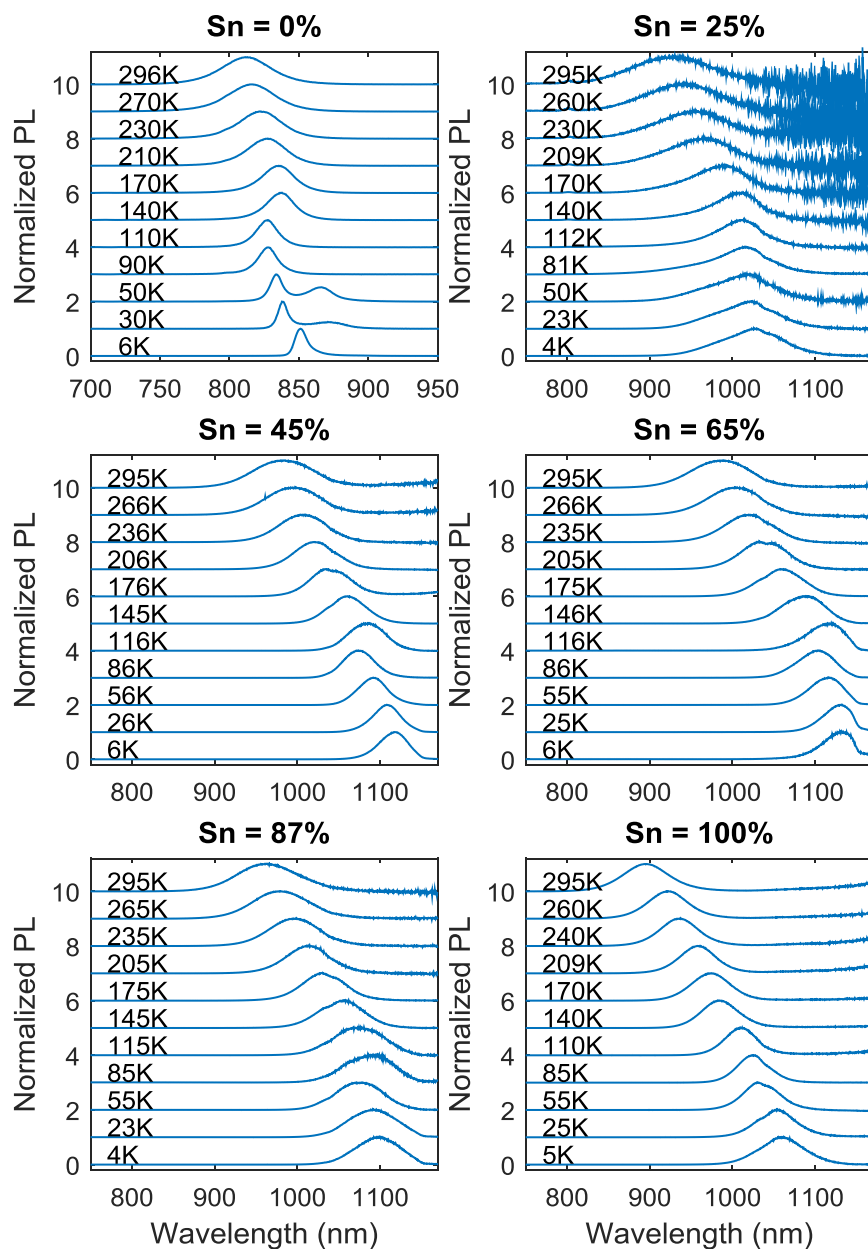


Figure S2. Examples of PL spectra at different temperatures for each composition of $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$, normalized and offset for clarity.

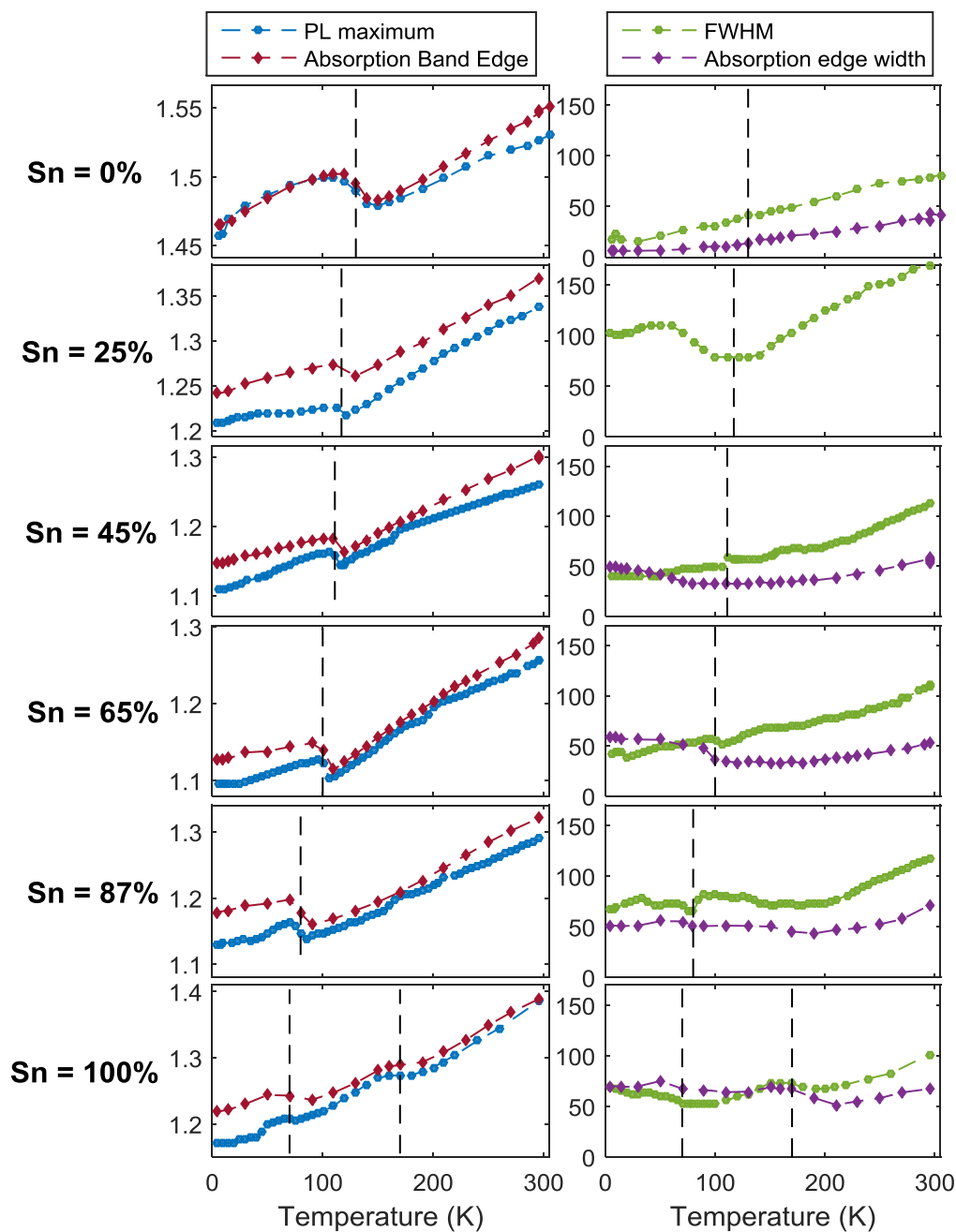


Figure S3. Left: Optical band-gap determined from PL peak and absorption edge energies for each composition of FASn_xPb_{1-x}I₃. PL spectra were recorded for excitation at 400 nm, 1 Wcm⁻². Right: PL linewidth and absorption edge width (could not be determined for 25% Sn). The black dashed lines show the phase transitions.

We measured the relative PL intensities of the 6 samples used for temperature dependent measurements. This enabled us to scale the temperature-dependent PLQE measurements in Figure 5d of the main text by comparing the values at 295 K to the values measured here. We could not do this directly from our temperature-dependent measurements since any change in alignment when mounting the cryostat with a new sample would result in a different measured intensity. The results match with our results for the 12 compositions tested in the main paper (Figure 3), although the intensity of the 100% lead sample is a little higher.

We also calculated the Stokes shift from the difference in PL maximum and absorption onset as shown in Figure S3. The mean of the values corresponding to the high and low temperature phases for each composition are shown in Figures S4(b-c).

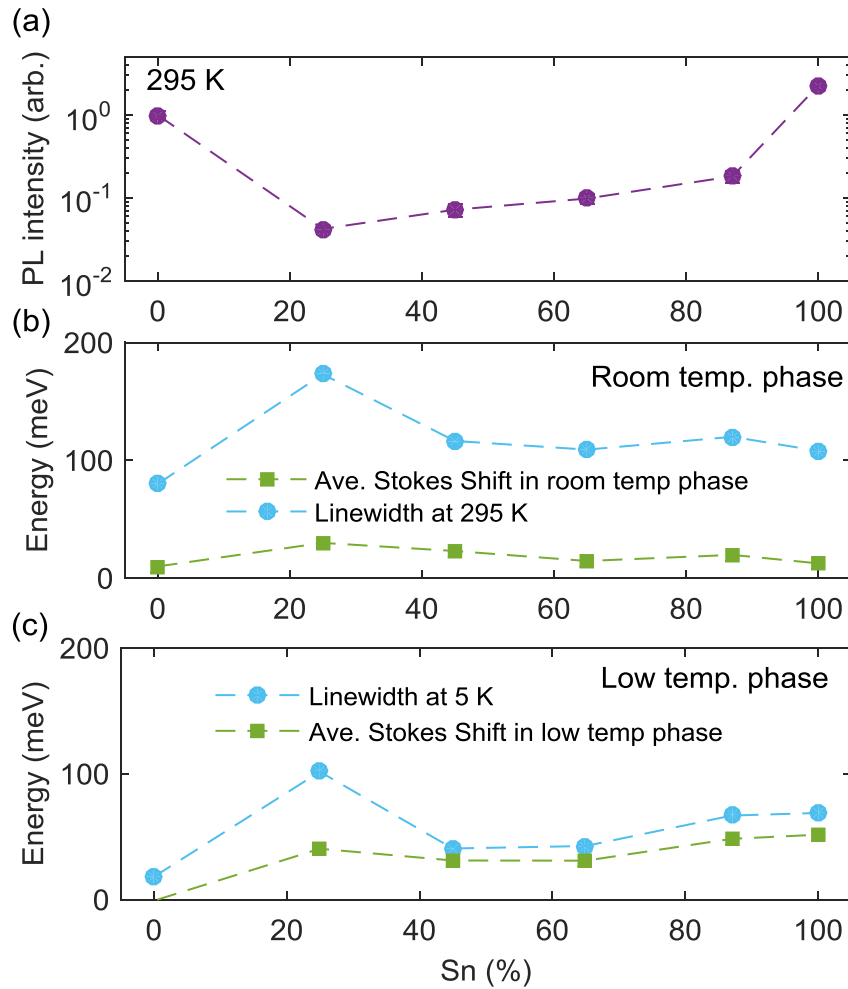


Figure S4. (a) Relative intensity of the PL at room temperature across 6 compositions of FASn_xPb_{1-x}I₃. (b) PL linewidth (FWHM) at room temperature (295 K), and the Stokes shift averaged over the room temperature phase. (c) PL linewidth (FWHM) at low temperature (5 K), and the Stokes shift averaged over the low temperature phase.

1.2 Room temperature measurements for additional compositions

We determined PL peak and absorption edge energies for 12 compositions (those used in section 2.3 of the main text) at room temperature shown in Figures S5. The PL at 14 nJ cm^{-2} and absorption edge were used to calculate the Stokes Shift in Figure 3b of the main text. The PL linewidth from Figure 3a is reproduced in Figure S5c for ease of comparison. All compositions, except the 12.5% Sn sample, have absorption edges which approximately fit a parabola with a band-gap bowing parameter of 0.74 eV, which is within the error of the room-temperature value of 0.73 eV calculated in the main text (Figure 2). The 12.5% Sn sample also has a high FWHM and absorption onset width suggesting inhomogeneity. When the intensity is increased from 1 to 110 W/cm^2 , a blue shift and an increase in FWHM is expected as states available for charge-carriers are filled. However the 12.5% Sn material shows a narrower FWHM at high power, suggesting that only sub-band-gap states are contributing to the PL at low powers. The inhomogeneity may be due to the presence of the yellow δ -phase. The Goldschmidt tolerance factor is 1.001 for FAPbI_3 and 0.998 for FASnI_3 ^[1], suggesting that the formation of the δ -phase, which is thought to be stable for tolerance factors greater than 1,^[2] is more likely for lead-rich perovskites, suggesting that alloying with tin may be beneficial in achieving a stable perovskite phase. However since material processing routes have a large influence on the formation of the δ -phase, we do not consider this to be an intrinsic property of the material. Annealing at a higher temperature may potentially eliminate the δ -phase.

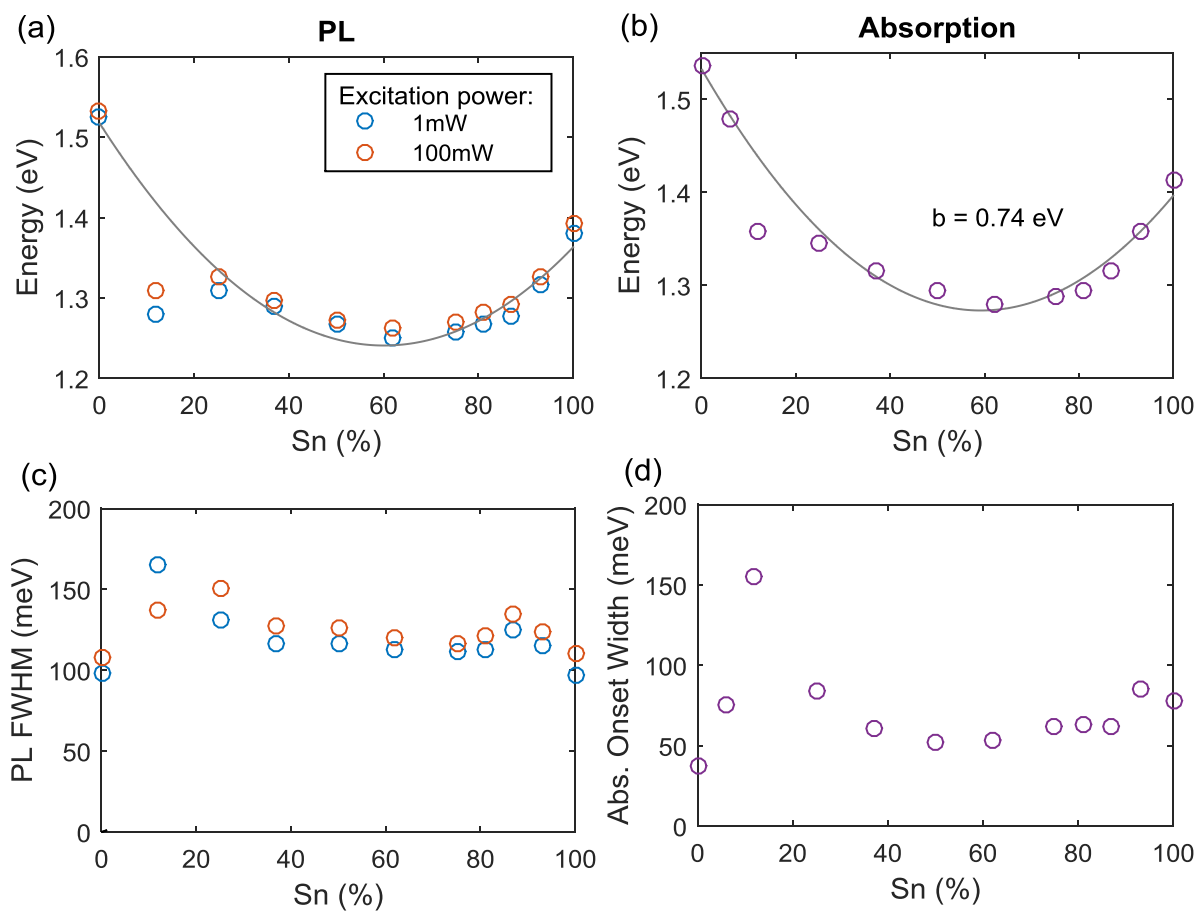


Figure S5. (a) PL peak energy for 12 compositions of $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$, measured for 400-nm laser excitation intensities of 1 W/cm^2 (blue circles) and 110 W/cm^2 (orange circles). The grey line is a fitted parabola. (b) Absorption onset energy (purple circles) and a fitted parabola (grey line). (c) PL linewidth for an excitation intensity of 1 W/cm^2 (blue circles) and 110 W/cm^2 (orange circles). (d). Absorption onset width determined from fitting a Gaussian to the differential of the absorption.

Here we show TCSPC data fitted with a stretched exponential to determine the lifetimes and stretch factors in Figure 4b and 4c respectively.

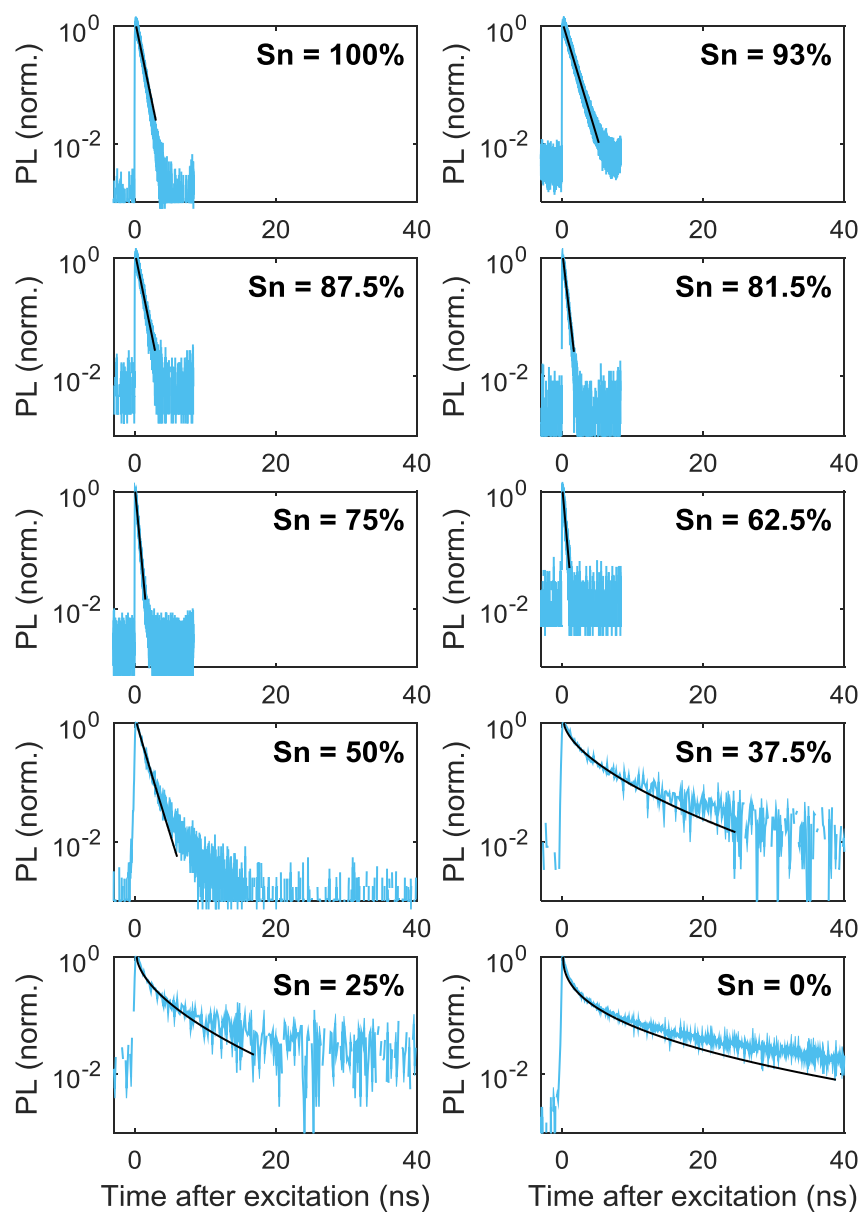


Figure S6. PL decay curves for a range of $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$ compositions, excited at 400nm, with 14 nJ/cm^2 per pulse. Stretched exponential fits are shown by black lines.

Two of the compositions luminesce too weakly to have their PL decay measured under the above conditions. Below are the PL decay curves collected at higher intensity excitation. Even at higher power, the exponential is considerably stretched, and the PL exhibits a fairly long lifetime, similar to the other compositions with <50% Sn content.

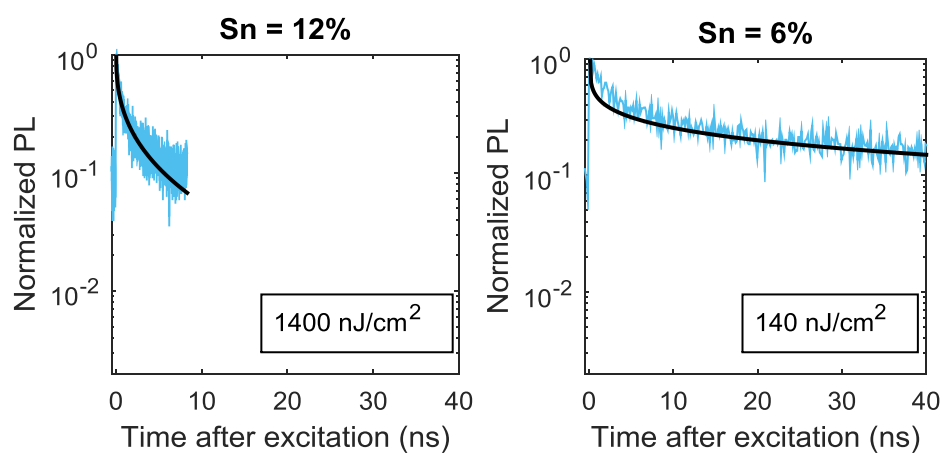


Figure S7. PL decay curves for two $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$ compositions, excited at 400nm, with a fluence of 1400 nJ/cm^2 and 140 nJ/cm^2 per pulse respectively. Stretched exponential fits are shown by black lines.

1.3 Temperature dependent PL decays

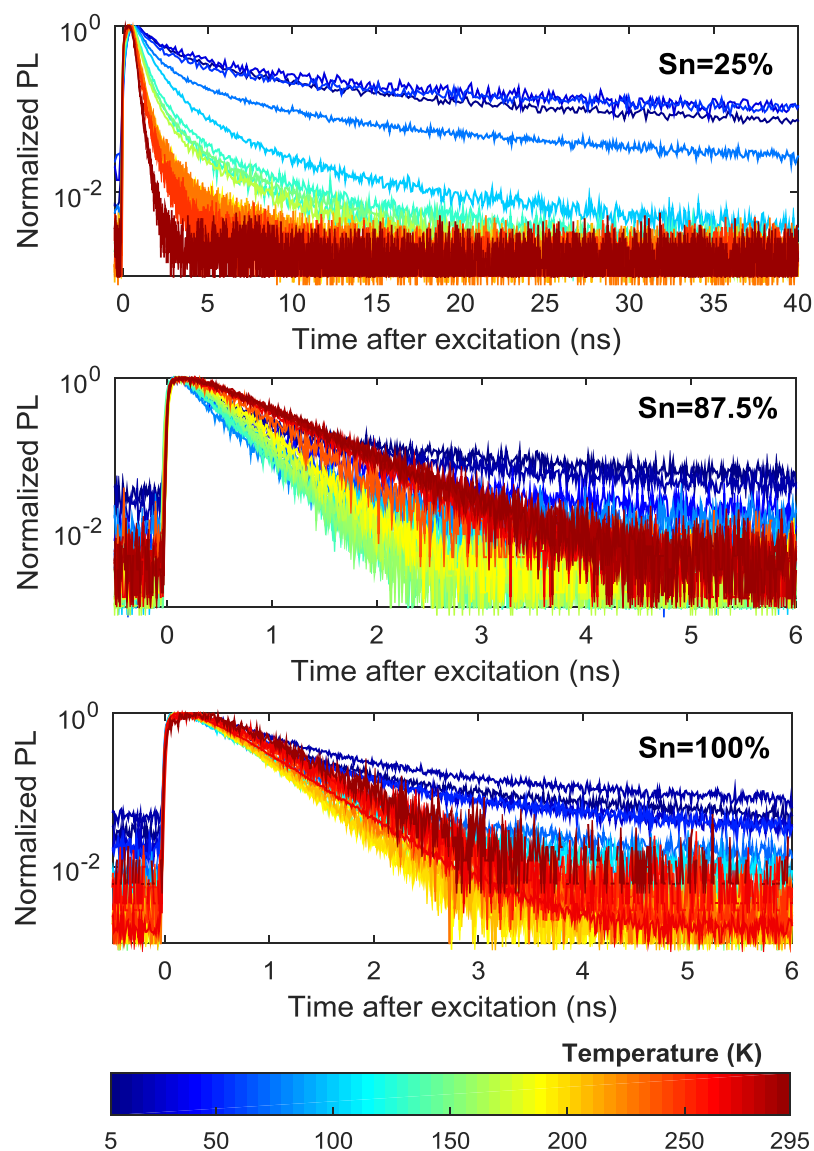


Figure S8. Temperature dependent PL decay curves for three $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$ compositions, excited at 400nm with a fluence of 1400 nJ/cm^2 . The temperature is indicated by the corresponding color on the color bar.

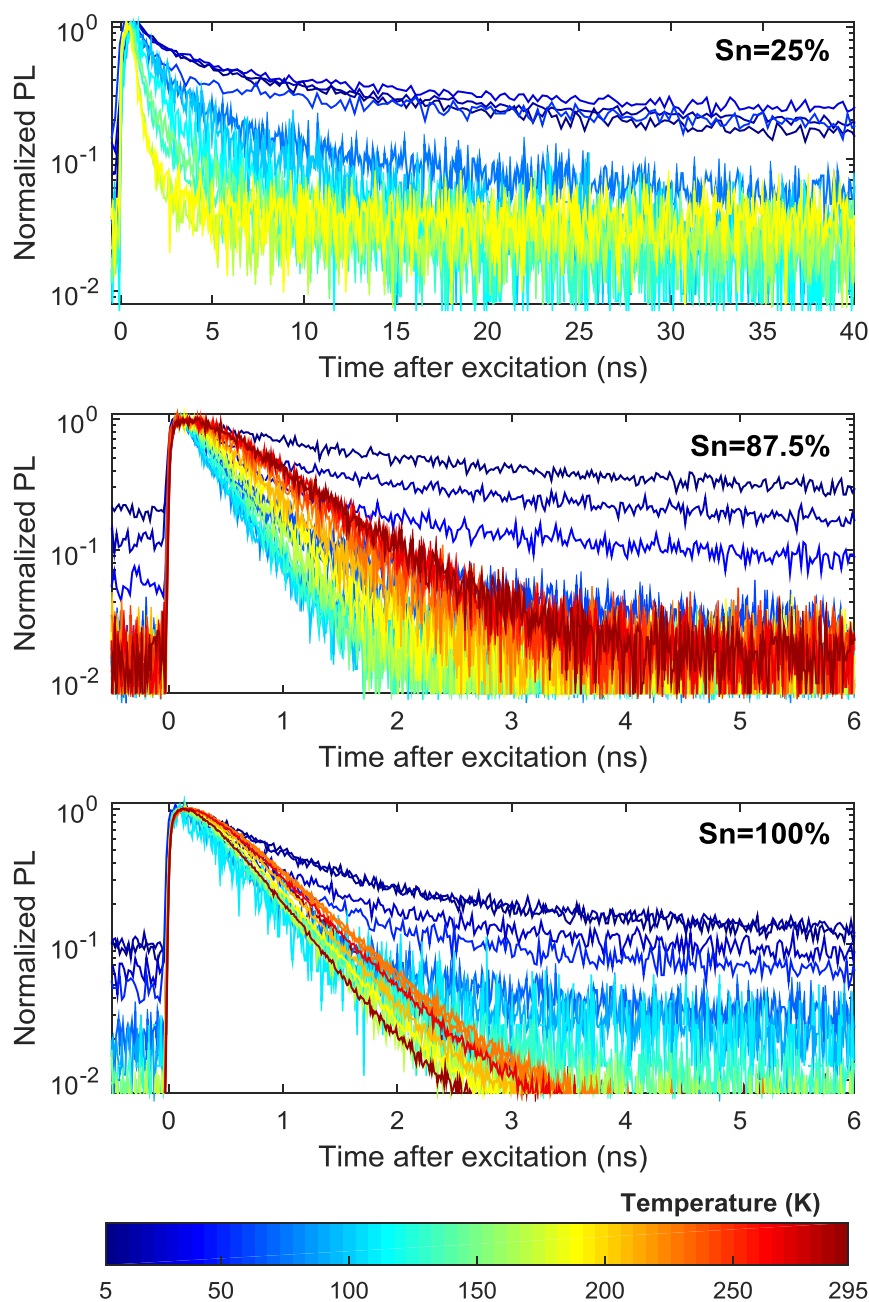


Figure S9. Temperature dependent PL decay curves for three $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$ compositions, excited at 400 nm with a fluence of 14 nJ/cm^2 . The temperature is indicated by the corresponding color on the color bar.

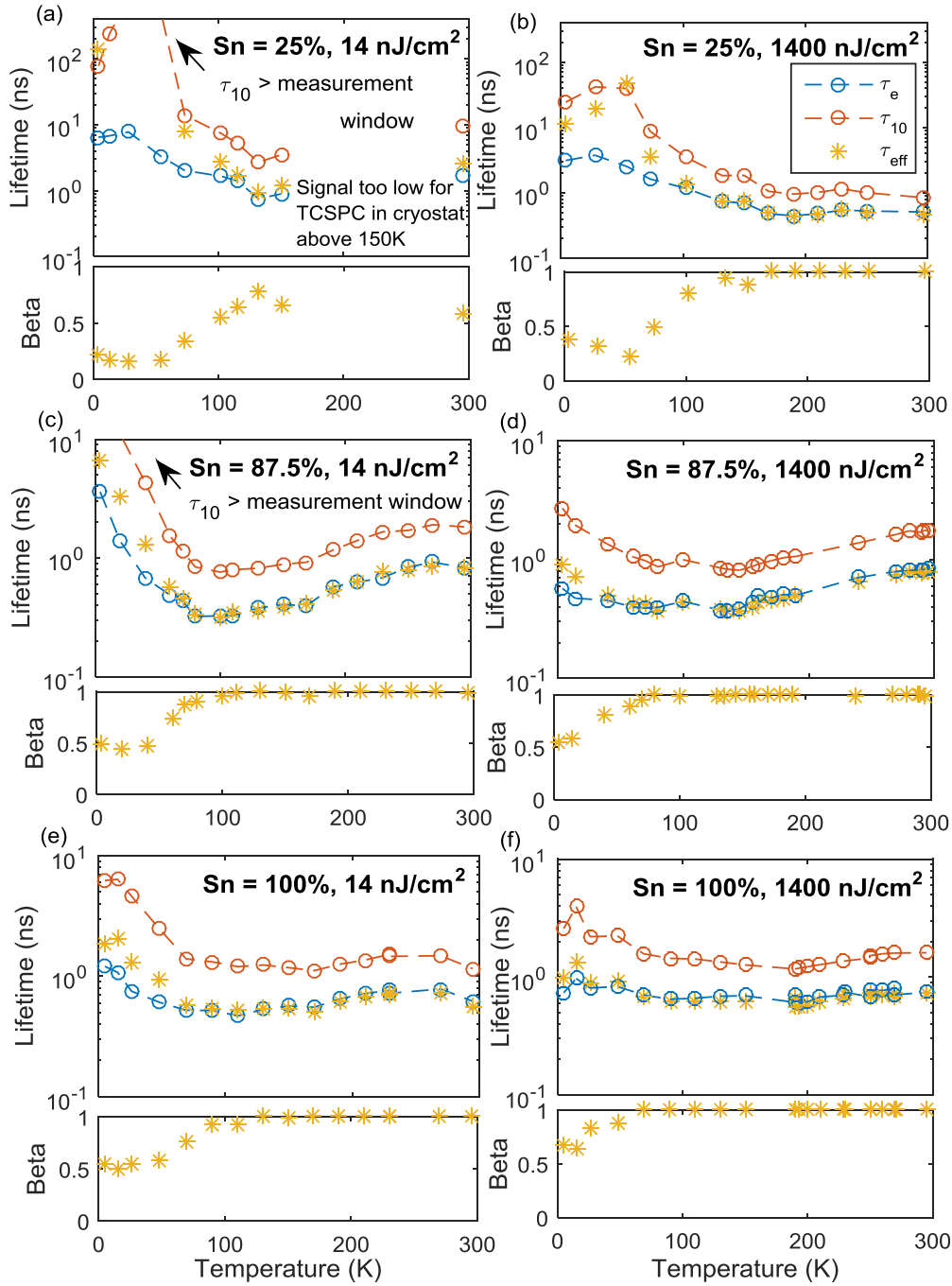


Figure S10. Temperature dependence of the PL lifetime for three FASn_xPb_{1-x}I₃ compositions, excited with a low power (14 nJ/cm²) or high power (1400 nJ/cm²) pulse at 400nm. τ_e and τ_{10} are the time taken for the PL intensity to decay to 1/e and 1/10 of its initial value respectively. τ_{eff} is the effective lifetime ($\tau_{eff} = \tau/\beta \Gamma(1/\beta)$) based on a stretched exponential fit ($I = I_0 \exp(-(t/\tau)^\beta)$), where β is the stretch parameter.

1.4 Recombination Mechanisms for Perovskite with Sn= 87.5%

We show relative PLQE values as a function of temperature T for the 87.5% Sn composition in Figure S11 and PL lifetimes in Figure S10c and S10d. At low T , there is an initial drop in the intensity with increasing T , followed by a gradual increase, with a discontinuity at the phase change, in contrast to the behaviour for 25 and 100% Sn perovskites which do not appear to be affected by the phase transitions. This zig-zag shape, which is repeatable, may be the result of several mechanisms with opposite temperature dependencies competing. The PL lifetime shows the same general trend, dropping steeply and gradually recovering as the temperature is increased, which suggests this behaviour is mainly due to a change in non-radiative recombination.

1.5 Results from two fabrication methods

To investigate whether removing the anisole dipping step affects PL, we measured the temperature dependent PL of two 87.5% Sn samples where, prior to annealing, the film was either dipped in anisole and then blow-dried with nitrogen (anisole method), or blow-dried with nitrogen whilst still spinning (N_2 method).. The PL peak energy and FWHM were the same. The PL intensity is the most sensitive to the change, but shows the same trends, as shown in Figure S11.

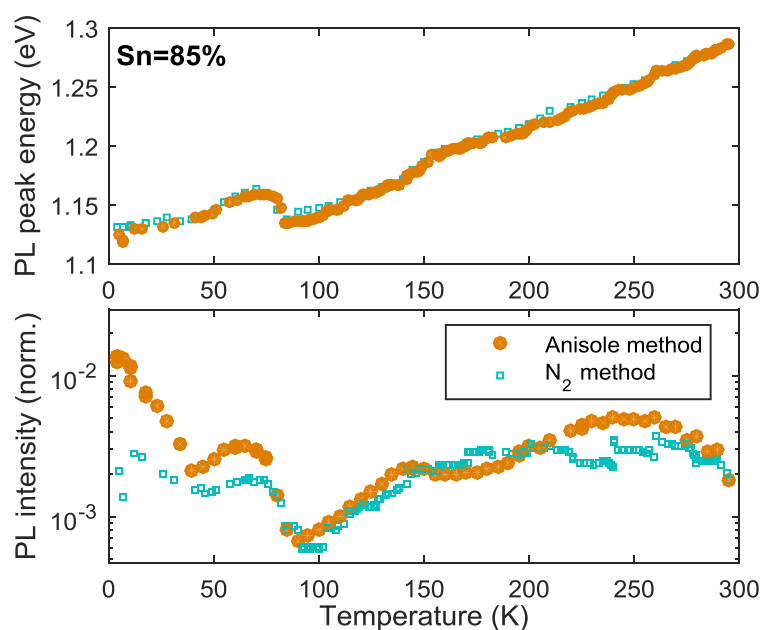


Figure S11. Temperature dependence of the PL intensity of $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$ with $x=0.875$, made by dipping in anisole and then blow-drying with nitrogen (anisole method), or by blow-drying with nitrogen whilst still spinning (N_2 method).

2 Notes on Fitting Data

2.1 Absorption spectra and Tauc plot analysis

We calculated the absorbance (A), which is equal to the absorption coefficient (α) times the sample thickness (z), from our measurements of the transmission and reflection of our sample using Beer's law, rearranged to give

$$A = \alpha z = -\ln\left(\frac{T}{1-R}\right) \quad (\text{S1})$$

where T is the fraction of transmitted light and R is the fraction of reflected light.

In the main article, we displayed a value for the absorption edge energy extracted from the point of steepest gradient near the onset of the absorption spectrum. Here we compare these results with those obtained from a Tauc plot method, which is more widely used in the literature.^[3,4] For direct band-gaps, the band-gap (E_g) is determined by plotting $(\alpha E)^2$ against E and finding the intercept with the x-axis (where α is the absorption coefficient and E is the photon energy). However, this method does not take into account the influence of excitons on the shape of the absorption onset. Not only do excitons introduce discrete energy levels, they also enhance the absorption of the continuum states, such that attempting to find E_g from a Tauc plot, which assumes α to be proportional to $\sqrt{E - E_g}$ (where E is the photon energy), is meaningless and will lead to misleading results. The correct way to determine the band-gap is to fit the full Elliot theory formula which includes the enhancement from excitons.^[5,6] However, to apply this method correctly requires very “clean” absorption data which has been corrected for reflection and scatter, which is difficult for these tin-lead perovskites. We therefore recommend the 'steepest gradient' method used in the main article as a more practicable alternative.

Although the steepest gradient method does not accurately determine the true band-gap, it gives a more meaningful quantitative result allowing comparison of absorption onsets and is less sensitive to a number of problems encountered with Tauc plots which are illustrated in Figure S12. Firstly, a change in the strength of the exciton absorption will change the gradient of the 'straight line section' which influences the intercept, as shown for the Sn=0% sample. Secondly, since we did not use an integrating sphere, diffuse scatter from the sample can give an offset for the rougher samples which will also influence the intercept, as shown for the 87.5% sample. Finally, since the expectation of a straight line is not physically grounded, there is not always an unambiguous straight line section to fit to, with either no straight line at

all or several straight sections, as shown for the 25% sample where two portions are fitted, one in black and one in grey.

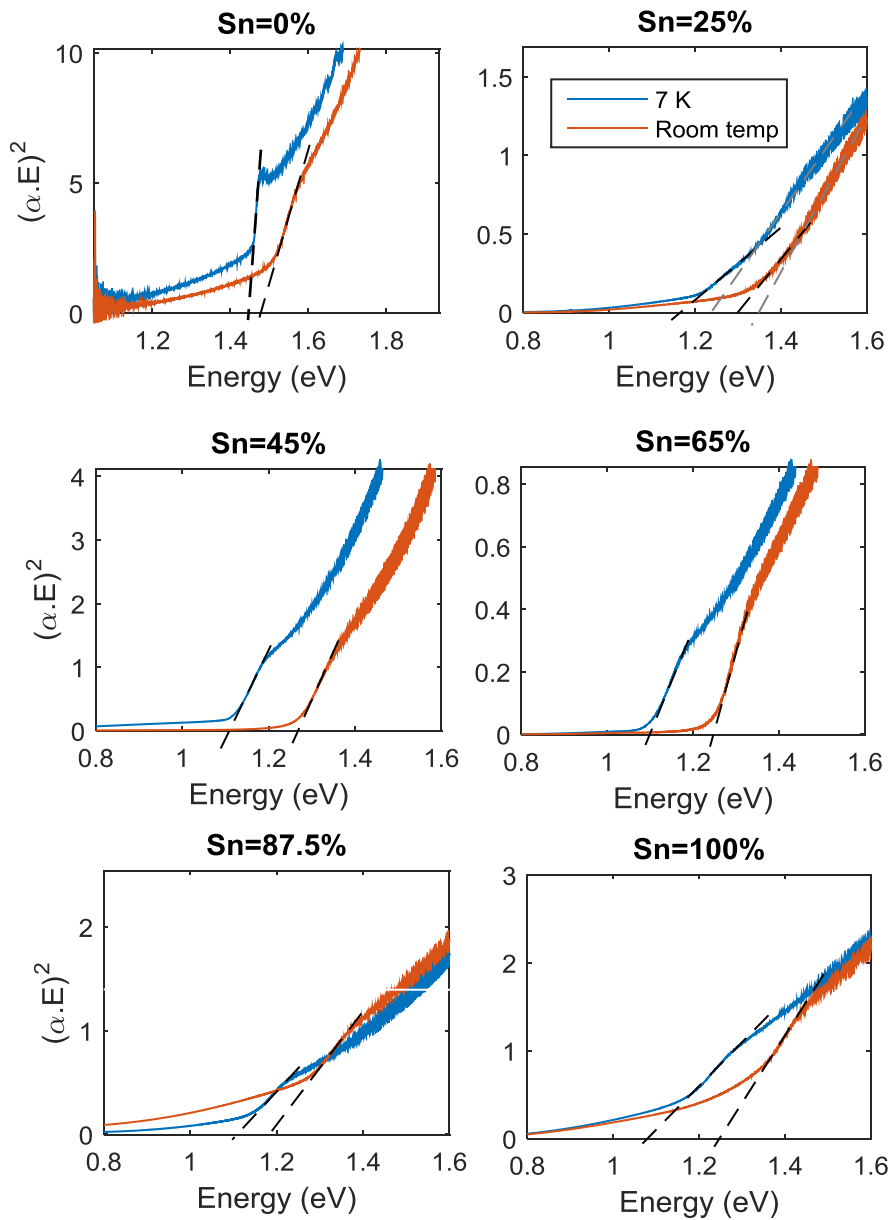


Figure S12. Tauc plot from absorbance of each composition of $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$ at a room temperature of 295 K (orange) and low temperature of 5-10 K (blue). The dashed lines show fits to the straight-line portions of the curves, giving the optical band-gap at the intercept.

To illustrate the difference in the measured band-gap between the Tauc plot and our gradient method of determining the absorption onset, we have re-plotted the band-gap bowing at high and low temperature in Figure S13. The data no longer fits to a single bowing parameter and gives the impression of a composition dependent bowing parameter. Some of

the discrepancy in the degree of bowing found in the literature may be as a result of different methods for determining band-gap from absorption data, rather than being caused by differences in the material itself.

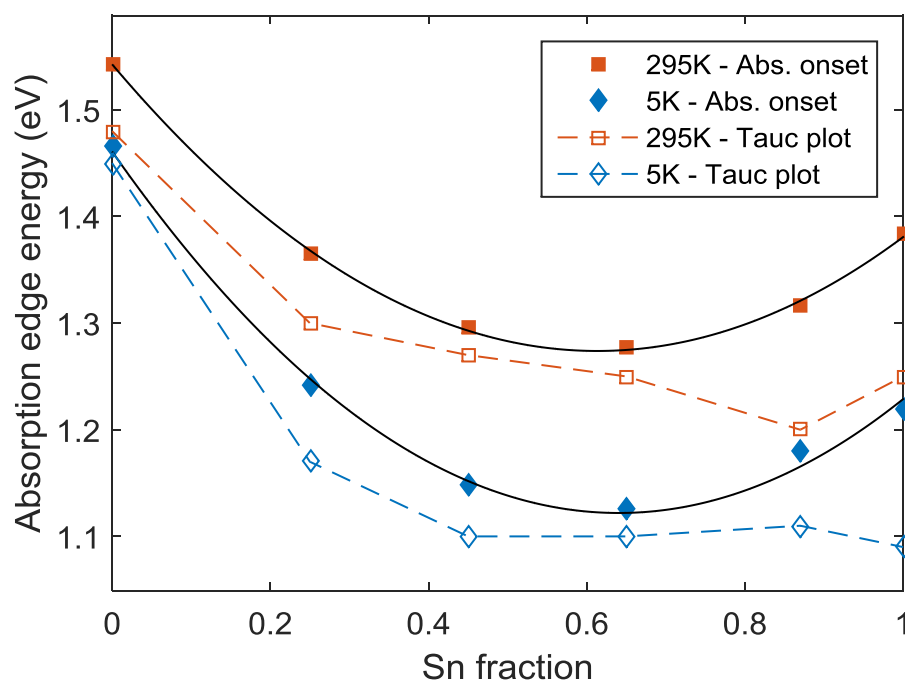


Figure S13. Optical band-gap of $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$ determined by the absorption onset (filled points) and by a Tauc plot (empty points) at 295 K (orange) and 5 K (blue) temperature. Black lines show parabolic fits to the absorption onset data, and dashed lines are guides to the eye for the Tauc plot data.

2.2 Temperature dependent PL intensity

A common approach^[7–11] to characterizing temperature dependent PL intensities is to fit the equation

$$I(T) = \frac{I(0)}{1 + A \exp\left(-\frac{E_a}{k_B T}\right)} \quad (\text{S2})$$

where E_a is an activation energy. Following this approach, we fit equation S2 to the temperature-dependent PLQE data for the 25 and 100% Sn compositions. We find a characteristic activation energy of 41.2 meV for 25% Sn and 0.5 meV for 100% Sn. The fitting parameter A is 1.34×10^4 for 25% Sn and 44.2 for 100% Sn.

This activation energy has typically been interpreted as an exciton binding energy,^[9–11] since thermal dissociation of excitons reduces the rate of exciton-mediated electron-hole recombination. However from the PL lifetimes shown in Figure 5 of the main text, we know that the increase in PLQE at low temperature is due, at least in part, to a substantial reduction in non-radiative recombination. In addition, radiative recombination in perovskites is thought to be dominated by band-to-band recombination of free charges, not of excitons.^[12] This band to band recombination is also strongly temperature dependent in perovskites, as recently shown by Davies et al.^[6]

Equation S2 is derived from the formula for PLQE in steady state, i.e. the ratio of the number of charge-carriers recombining radiatively to the number of charge-carriers generated

$$\phi(T) = \frac{U_{rad}}{G} = \frac{U_{rad}}{U_{rad} + U_{SRH}} = \frac{1}{1 + R(T)} \quad \text{S3}$$

where U_{rad} is the radiative recombination rate and U_{SRH} is the non-radiative recombination rate, where both are dependent on the charge-carrier density n and the temperature T . G is the generation rate, which is equal to the total recombination rate, and R is the ratio U_{SRH}/U_{rad} , which is equal to $A \exp(-E_a/kT)$ in equation S2. We discuss an analogous approach for pulsed-excitation in section 4. To correctly apply this formula requires measurement of the absolute PLQE, and correction for PL self-absorption. However, we will use it here to investigate a suitable interpretation of the characteristic activation energy we have found from equation S2.

In metal halide perovskites, radiative recombination is thought to follow $U_{\text{rad}} = k_2'(p_0 + \Delta n) \cdot \Delta n$ as written in equation 2 of the main text, whilst for multi-phonon assisted recombination, $U_{\text{SRH}} \sim \exp(-B/kT)$ where B is the activation energy for multi-phonon assisted recombination. In MAPbI_3 ,^[6] $k_2' \sim \exp(C/kT)$. The ratio R therefore gives $R \sim \exp(-(B+C)/kT)$, and the characteristic energy of 40 meV from the fit to the PLQE data for the 25% Sn composition can be interpreted as an upper limit to the multi-phonon activation energy.

A better fit is obtained at low temperature for the 25% Sn PLQE data by including a T^2 term, such that $R = A \exp(-E_a/kT) + DT^2$. The activation energy is fixed at 41.2 meV and A and D are fitted to give $A = 1.1 \times 10^4$ and $D = 9.3 \times 10^{-4}$ as shown in Figure S14. This could either be due to a low temperature deviation of k_2' from $\exp(C/kT)$, or an additional non-radiative recombination process which is only important at low temperature such as a spatial distribution of traps, which has recently been observed in FAPbI_3 .^[13]

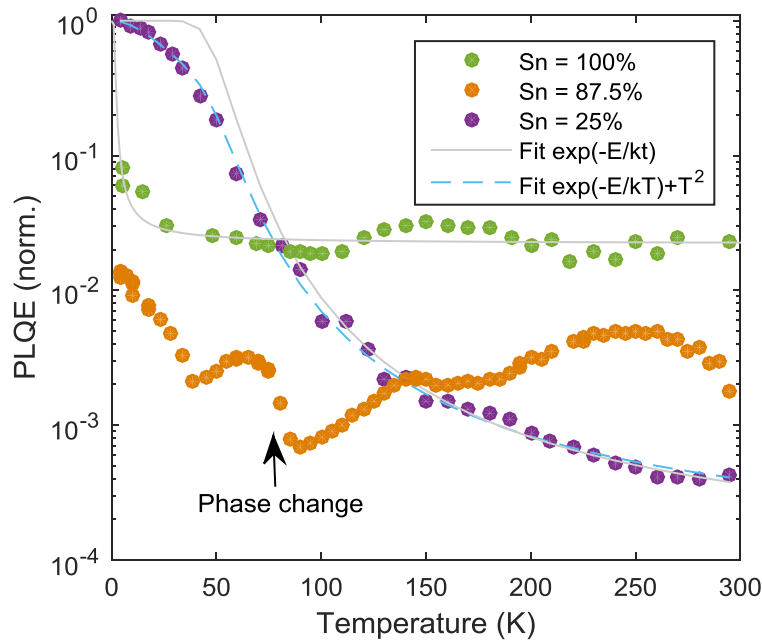


Figure S14. Temperature dependence of the PL intensity of three $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$ compositions, for excitation with 14 nJ/cm^2 at 400 nm . The two curves are scaled with respect to each other to match the relative PLQE at room temperature, as shown in Figure S4.

2.3 Band-gap Bowing Parameter

The band-gap bowing parameter was determined by fitting a parabola to the optical band-gap as determined from the absorption onset energy (extracted via the steepest-gradient method). The 95% confidence limits are shown in Figure S15. To determine whether the bowing parameter is actually changing with temperature, we averaged b outside of the phase transition zone. The average value for the low-temperature region lies outside the confidence limit in the high-temperature region, meaning it is highly likely that the bowing parameter does have a different value in the two regions.

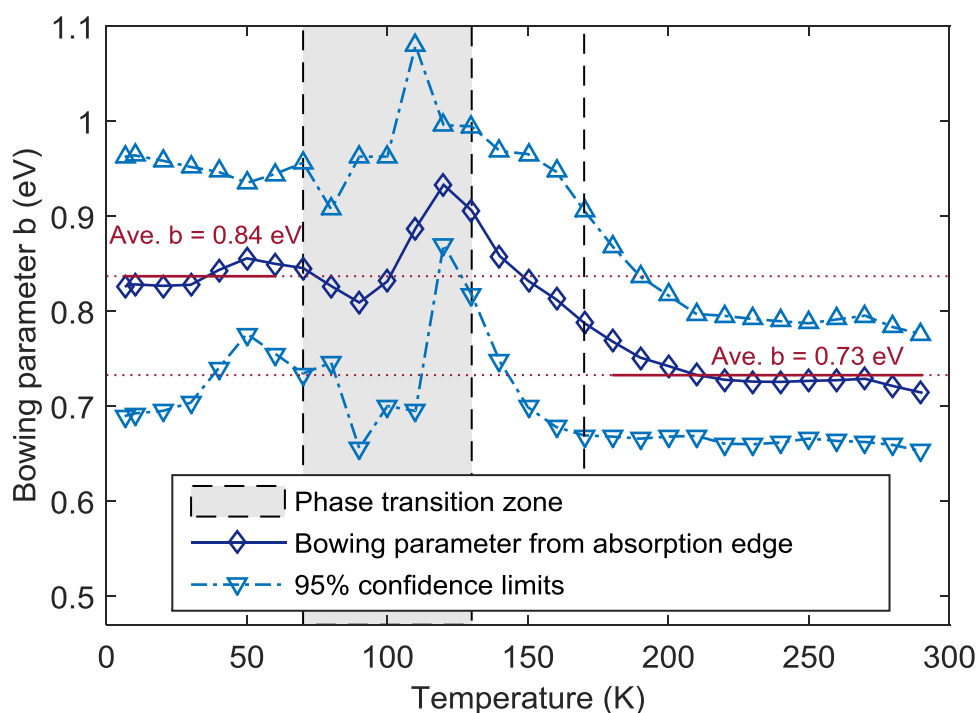


Figure S15. Band-gap bowing parameter determined from fitting a parabola to the optical band-gaps across the $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$ composition range (dark blue diamonds). The 95% confidence limit of the fit is also shown (light blue triangles). The average values for the bowing parameter b in the high and low temperature phase are shown in red.

2.4 Instrument Response Function Correction

To check the extent to which the instrument response function (IRF) influences the fitted lifetime, we fitted the PL transients taken for the compositions with Sn>50% with a single exponential function convolved with the instrument response function. The true PL lifetime is 0.1 ns lower than the uncorrected lifetime. When the lifetime is above 1 ns, the IRF does not make a significant difference to the measured lifetime.

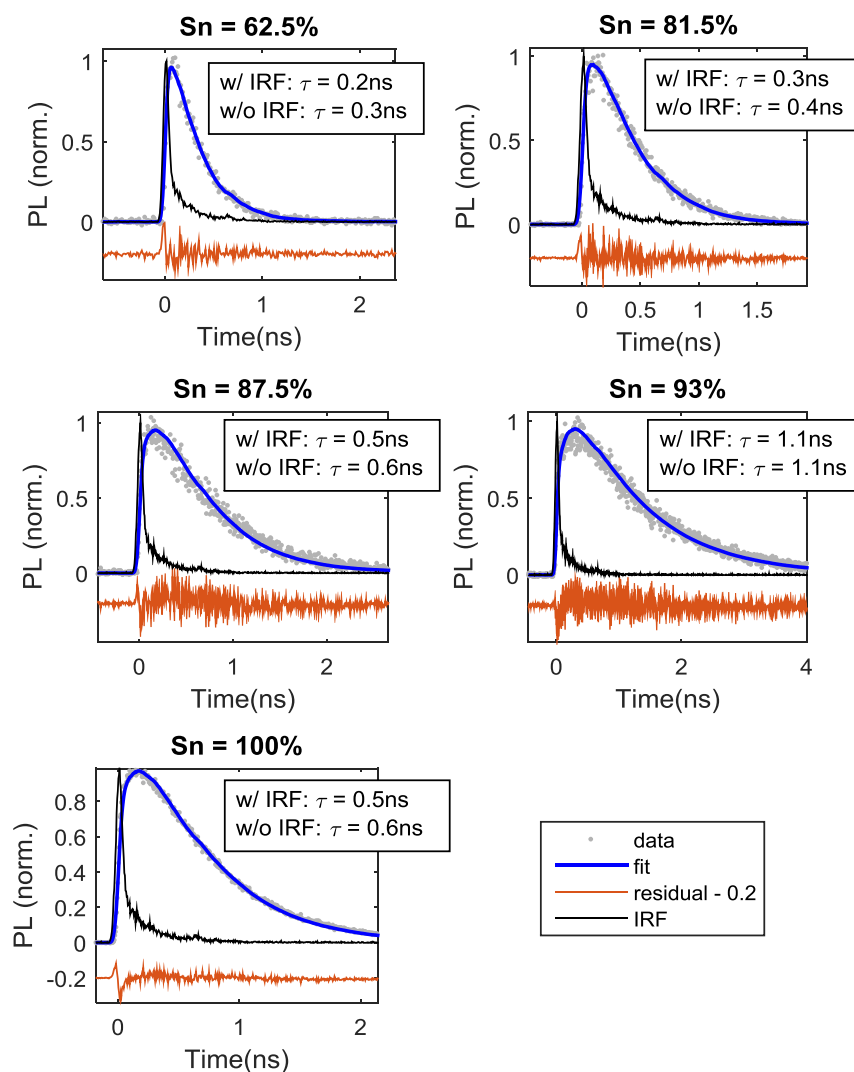


Figure S16. PL decay curves for two FASn_xPb_{1-x}I₃ compositions, excited at 400nm, 14 nJ/cm². Mono-exponential curves convolved with the instrument response function (IRF) are shown in blue. The residual of the fit is shown underneath in orange, offset by -0.2.

2.5 Stretched Exponential Fitting

To fit the curves we determined the time taken for the PL to drop from the maximum (initial) intensity I_0 to either I_0/e or $I_0/10$, yielding values for τ_e and τ_{10} , respectively. This approach is illustrated in Figure S13. These values were used to pick initial parameter values for a stretched exponential fit, which gives the effective lifetime τ_{eff} and the stretch parameter β . All of these values are plotted for each temperature, intensity and composition in Figure S10.

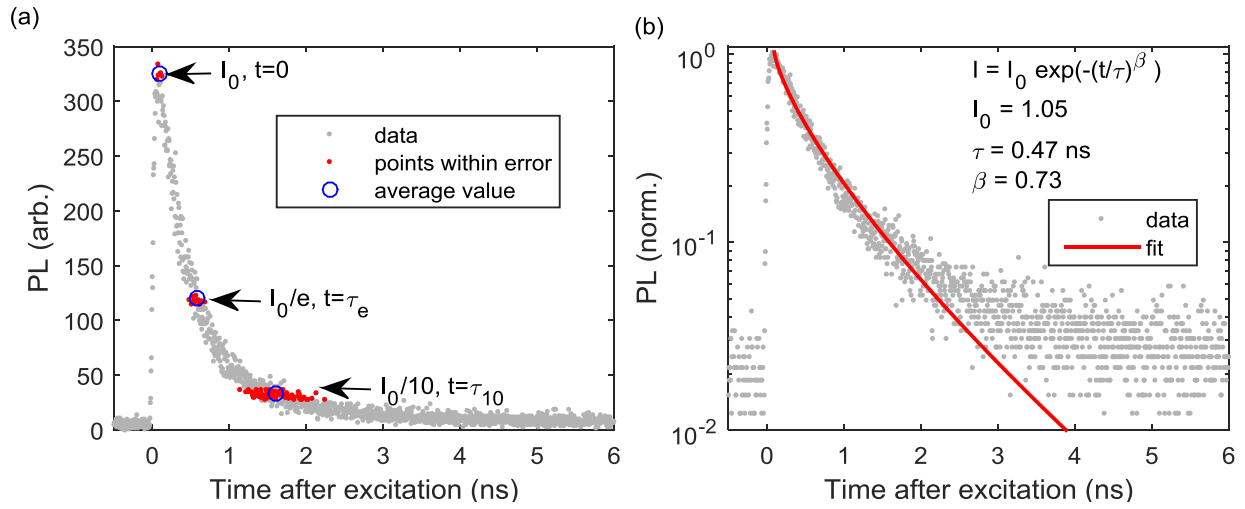


Figure S17. Example of (a) determination of parameters τ_e and τ_{10} and (b) stretched exponential fit for $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$ with $x=0.875$, excited at 14 nJ/cm^2 power, 400 nm wavelength at a temperature of 60 K .

3 Considerations for interpreting PL transients

3.1 Bimolecular recombination

A general rate equation for charge-carrier recombination, which can include radiative and non-radiative contributions to the mono- and bi-molecular terms, is given by

$$\frac{d\Delta n}{dt} = -(k_1^{nr} + k_1^r)\Delta n - (k_2^{nr} + k_2^r)\Delta n^2 \quad S4$$

the solution to which is given by:

$$\frac{\Delta n(t)}{\Delta n_0} = \frac{K}{(K+1)e^{k_1 t} - 1} \quad S5$$

where $K=k_1/(k_2\Delta n_0)$ is a dimensionless parameter and k_1 and k_2 include the radiative and non-radiative contributions.

The PL intensity will be proportional to $k_1^r\Delta n + k_2^r\Delta n^2$, which complicates the fitting of equation S5 to our data. We have therefore chosen to parameterise our measured decay curves with a stretched exponential $I = I_0 \exp(-[t/\tau]^\beta)$ and extract τ_{eff} , the effective lifetime and β , the stretch parameter.

Figure S18 shows a comparison between a stretched exponential function fitted to equation S5, with $k_2 \gg k_1$, where the charge carrier density $\Delta n \sim t^{-2}$. Whilst the fit will never be perfect, it does provide a useful way to parametrize the decay, with mono-exponential decay giving $\beta=1$, and here the fit gives $\beta=0.4$.

Figure S19 shows the charge-carrier density n over time after excitation with a laser pulse. The relative values of k_1 and k_2 determine how 'stretched' the curve is, as discussed above. For a typical radiative bimolecular recombination value of $k_2 = 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, an initial carrier density of 10^{19} cm^{-3} would be needed to see an effect on this time scale. This is much larger than our maximum value of 10^{17} cm^{-3} , suggesting that the decay is not stretched due to radiative bimolecular recombination, and the inclusion of a non-radiative bimolecular term k_2^{nr} may be necessary. This could originate from Shockley Read Hall recombination as detailed in section 4.2.

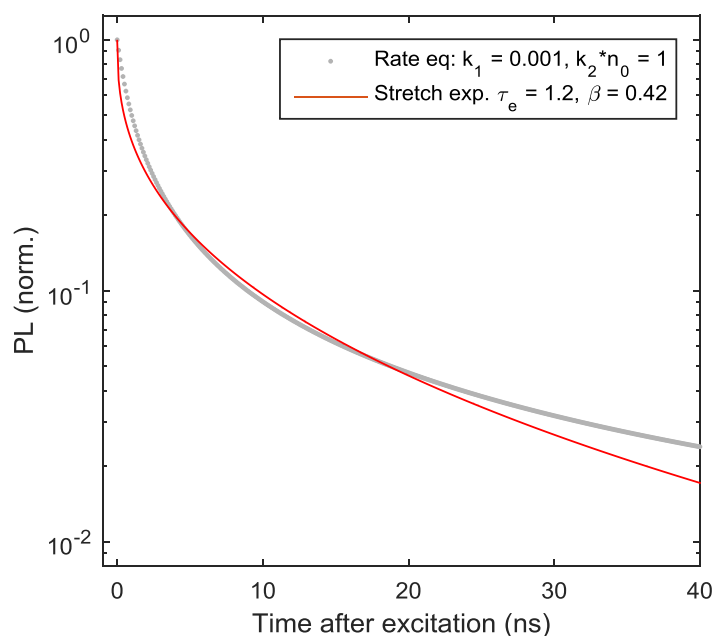


Figure S18. Grey line shows a simulated PL decay with the carrier density determined by equation S5, with $K \ll 1$ (i.e. the bimolecular term in equation S4 dominates). The red line is a stretched exponential fit to the simulated data.

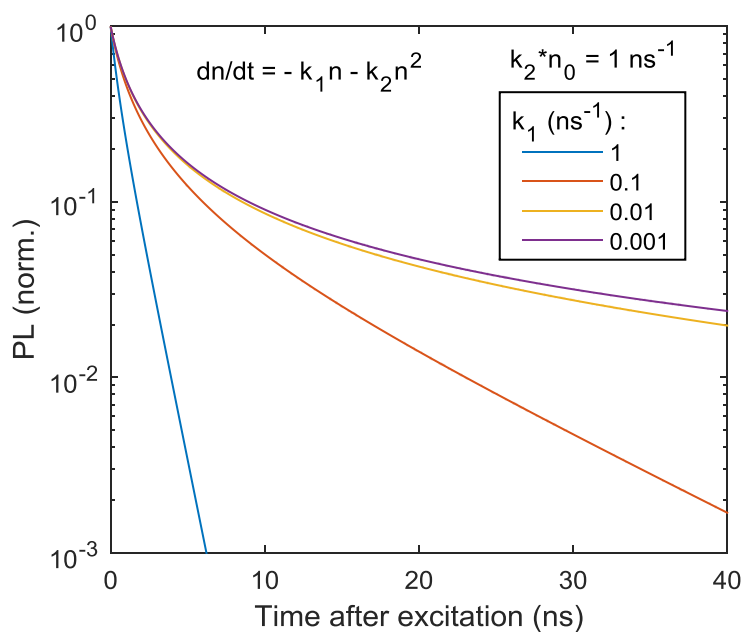


Figure S19. Simulation of the charge carrier density decay curves for a range of values of k_1 . For a typical value of $k_2 = 10^{-10} \text{ ns}^{-1} \text{ cm}^3$, a high carrier density of $n_0 = 10^{19} \text{ cm}^{-3}$ is required to give $k_2 n_0 = 1 \text{ ns}^{-1}$

3.2 Shockley Read Hall Recombination

The Shockley Read Hall recombination rate is the rate at which electrons and holes recombine via traps,^[14,15] and is given by

$$U_{SRH} = \frac{(p_0 + n_0 + \Delta n)}{\tau_n(p_0 + \Delta n + p_1) + \tau_p(n_0 + \Delta n + n_1)} \cdot \Delta n = k_1 \cdot \Delta n \quad (S6)$$

where Δn is the photogenerated charge-carrier concentration, n_0 and p_0 are equilibrium electron and hole concentrations (from doping), n_1 and p_1 are the electron/hole concentrations in the conduction/valence band when the Fermi level is equal to the energy level of the trap, and τ_n and τ_p are the minority carrier lifetimes. This expression (S6) assumes that the density of electrons in the traps remains in thermal equilibrium, which is valid either in steady state or when one of n_0 , p_0 , n_1 or p_1 are large compared to the total trap density.^[14,16] The case when this is not valid is discussed in section 3.3. Equation S6 can be used to describe the decay of the photogenerated charge density Δn after an initial excitation of a semiconductor by a laser pulse, even for large excitation, provided the condition for thermal equilibrium is met. Clearly equation S6 implies that k_1 is not, in general, independent of Δn and therefore should not strictly be referred to as a constant, however in many scenarios Equation S6 can be simplified. For example, in an intrinsic semiconductor, Δn is usually the largest term, such that $k_1 = 1/(\tau_n + \tau_p)$. Alternatively, in a p-doped semiconductor, p_0 is largest, giving $k_1 = 1/\tau_n$.^[14] One example of k_1 not being a constant is when the traps are close to the conduction or valence band, making n_1 or p_1 large. If the trap is near to the conduction band,

$$U_{SRH} = \frac{\Delta n}{(\tau_n + \tau_p)\Delta n + \tau_p n_1} \cdot \Delta n \quad (S7)$$

Whilst Δn may initially be larger than n_1 directly after photoexcitation of the semiconductor with a laser pulse, after some time it will have decreased such that n_1 dominates, giving a monoexponential decay $\Delta n \sim \exp(-k_1 t)$ at early times and tending towards $\Delta n \sim t^{-2}$ at later times.

To demonstrate this behaviour more clearly we have solved the rate equation

$d(\Delta n)/dt = -U_{SRH}$ numerically for several scenarios, shown in Figure S20.

For all the following scenarios, the SRH lifetimes were taken to be $\tau_n = \tau_p = 1$ ns. The initial photoexcited carrier density was set as $\Delta n_0 = 10^{14} \text{ cm}^{-3}$ and the intrinsic carrier density was taken to be $p_0 = n_0 = 10^5 \text{ cm}^{-3}$ for both holes and electrons, calculated from

$$n_0 = N_c \exp((E_F - E_g)/kT), \quad p_0 = N_v \exp(-E_F/kT) \quad (\text{S8})$$

setting zero energy at the top of the valence band, with $N_c = N_v = 10^{15}$, $E_F = 0.6$ eV, $E_g = 1.2$ eV and $T = 300$ K.

The scenarios are as follows:

Heavily p-doped:

$p_0 = 10^{16} \text{ cm}^{-3}$. First case: Mid-gap trap state which gives $p_1 = n_1 = 10^5 \text{ cm}^{-3}$. Second case: very shallow traps with $n_1 = 5 \times 10^{14} \text{ cm}^{-3}$ (both these scenarios give the same result).

The solution is equivalent to a mono-exponential decay with $k_1 = 1/\tau_n$.

Moderately p-doped:

$p_0 = 10^{14} \text{ cm}^{-3}$. Mid-gap trap state which gives $p_1 = n_1 = 10^5 \text{ cm}^{-3}$.

k_1 changes from $1/(\tau_n + \tau_p)$ to $1/\tau_n$ as time goes on and Δn decreases.

Intrinsic:

$p_0 = n_0 = 10^5 \text{ cm}^{-3}$. Mid-gap trap state which gives $p_1 = n_1 = 10^5 \text{ cm}^{-3}$.

The solution is equivalent to a mono-exponential decay with $k_1 = 1/(\tau_n + \tau_p)$.

Shallow trap:

Intrinsic doping. Trap level $E_t = 0.1$ eV below conduction band which gives $n_1 = N_c \exp((E_t - E_g)/kT) = 7 \times 10^{13} \text{ cm}^{-3}$, $p_1 = N_v \exp(-E_t/kT) = 0 \text{ cm}^{-3}$.

The decay is no longer exponential and appears 'stretched', since k_1 depends on Δn .

Very shallow trap:

Intrinsic doping. Trap level 0.05 eV below Fermi level which gives $n_1 = 5 \times 10^{14} \text{ cm}^{-3}$, $p_1 = 0 \text{ cm}^{-3}$.

The lifetime of the decay is increased for shallower traps.

Very shallow trap with moderate doping:

$p_0 = 10^{14} \text{ cm}^{-3}$. Trap level 0.05 eV below Fermi level which gives $n_1 = 5 \times 10^{14} \text{ cm}^{-3}$, $p_1 = 0 \text{ cm}^{-3}$.

The solution becomes exponential again, but the lifetime is longer than for deep traps.

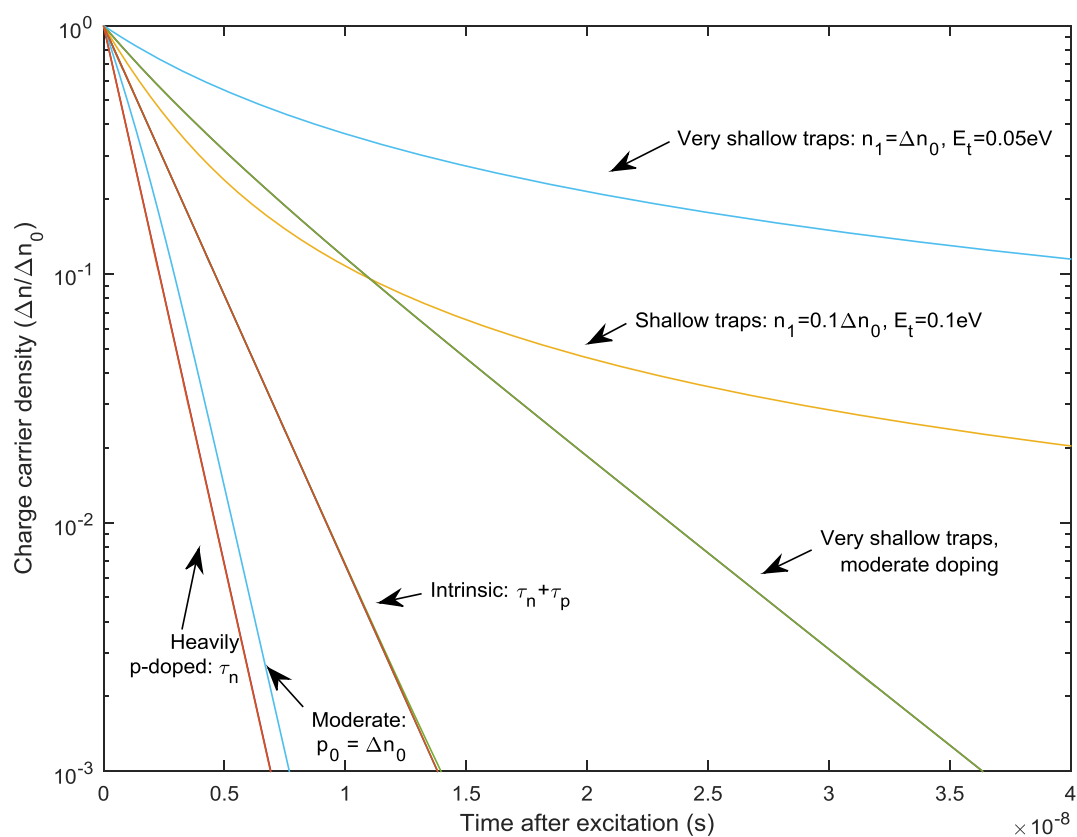


Figure S20. Simulation of the charge carrier density decay curves for SRH recombination under a range of conditions.

3.3 Carrier Trapping

Here we describe the case of charge-carrier dynamics when the trapped electron density does not remain in thermal equilibrium with the free charge-carrier density. This is the case when the system is not under steady state conditions and the total trap density is large compared with n_0 , p_0 , n_1 and p_1 . In this case the PL transients may initially be determined by the rate at which traps are populated, rather than the rate of recombination, until the free and trapped populations reach thermal equilibrium. This creates an imbalance in free carrier densities, eg. if electrons are trapped much faster than holes, Δn will be depleted as electrons populate traps, whilst Δp initially remains approximately constant, thereby photodoping the semiconductor. The trapping lifetime (dominated by fast electron trapping) is then much shorter than the SRH recombination lifetime (dominated by the slower hole trapping) and it is this that limits the PL lifetime, whereas in a solar cell in steady state conditions it will be the longer SRH recombination lifetime that is relevant.^[17]

For small photoexcitation, the free charge-carrier density follows a bi-exponential decay, with the shorter lifetime corresponding to the filling of traps and the longer lifetime corresponding to recombination. However if the photoexcited free electron density is large enough ($\Delta n > n_0 + n_1 + N_0$ where N_0 is the density of empty traps) the decay will not be exponential.^[16]

4 PLQE for transient measurements

Equation S3 for the PL quantum efficiency assumes a constant carrier density, however we measured PLQE with a pulsed laser, such that the carrier density decays to zero between each pulse.. Here we investigate whether it is valid to use an average carrier density from a transient measurement, in the PLQE formula for steady state.

For pulsed measurements, the carrier density, and therefore the recombination rates, are time dependent. Equation S3 must therefore be integrated over the measurement time, or equivalently, the time between excitation pulses. The PLQE is then given by

$$\varphi = \frac{\int U_{rad} dt}{\int U_{rad} + U_{SRH} dt} \quad S9$$

where U_{rad} is the radiative recombination rate and U_{SRH} is the non-radiative recombination rate, as in equation S3. This is equivalent to the number of charge-carriers recombining radiatively divided by the total number of photoexcited charge-carriers. Assuming the carrier density decays entirely within the pulse window, the bottom of the equation above is equal to Δn_0 , the initial photoexcited charge-carrier density.

To perform the integrals in equation S9, we need to know how the recombination rates depend on charge-carrier density Δn and also how Δn changes with time. We assume that equation S4 gives a suitable rate equation for the charge-carrier density, the solution to which is given by S5.

We can now integrate the top of equation S9, with U_{rad} given by

$$U_{rad} = k_1^r \Delta n + k_2^r \Delta n^2 \quad S10$$

Integrating the terms of equation S10 over the time between laser pulses, t_p , gives

$$\int_0^{t_p} \Delta n dt = \Delta n_0 \frac{K}{k_1} \log \left(\frac{K+1-e^{-k_1 t_p}}{K} \right) \quad S11$$

$$\int_0^{t_p} \Delta n^2 dt = \Delta n_0^2 \frac{K^2}{k_1} \left[t_p k_1 - \frac{1}{x} - \log \left(\frac{x}{K} \right) + \frac{1}{K} \right] \quad S12$$

where $K=k_1/(k_2 \Delta n_0)$ is a dimensionless parameter as in equation S5 and $x=(1+K)\exp(k_1 t_p) - 1$

Assuming the charge carrier density effectively decays to zero within the pulse window, we can let t_p tend to infinity:

$$\varphi_{pulse} = \frac{1}{\Delta n_0} \int_0^\infty U_{rad} dt = \frac{1}{\Delta n_0} \int_0^\infty k_1^r \Delta n + k_2^r \Delta n^2 dt \quad S13$$

$$\varphi_{pulse} = \frac{k_1^r}{k_1} K \log \left(\frac{K+1}{K} \right) + \frac{k_2^r}{k_2} \left[1 - K \log \left(\frac{K+1}{K} \right) \right] \quad S14$$

Expressing the steady state PLQE in terms of k_1 and k_2 gives

$$\varphi_{steady} = \frac{k_1^r}{k_1} \frac{K}{K+1} + \frac{k_2^r}{k_2} \frac{1}{K+1} \quad S15$$

To use this simpler steady state equation for pulsed measurements, we need to choose a suitable carrier density to use in $K=k_1/(k_2\Delta n_{ave})$.

To make the steady state and pulsed expressions for PLQE equivalent, the average carrier density must be chosen to be

$$n_{ave} = \frac{\int \Delta n^2 dt}{\int \Delta n dt} \quad S16$$

which for a simple exponential decay is equal to $n_0/2$. The average value can approach n_0 if the lifetime is long with respect to the pulse window, and can be less than $n_0/2$ if the decay is stretched, which will change with temperature for our measurements. However, since we are more concerned about the order of magnitude of the PLQE than the precise value, we consider the use of the steady state formula with an average carrier density of $n_0/2$ to be a suitable approximation. An example is shown in Figure S21 showing that the approximation of a constant n_0 diverges as k_2 is changed, however, the bottom panel shows on a log scale that this difference is negligible.

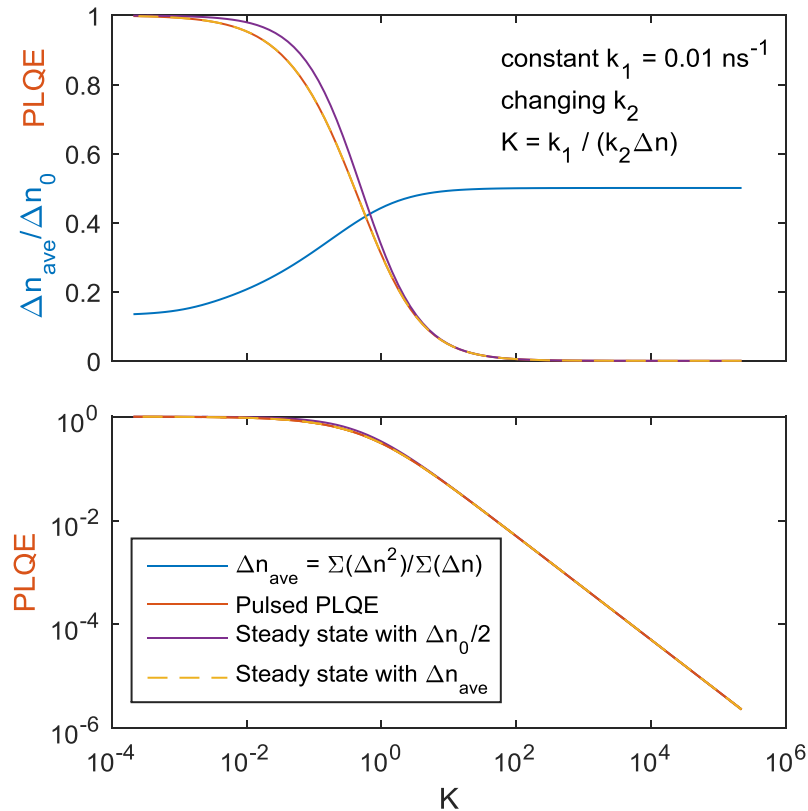


Figure S21. Simulation of the PLQE under pulsed and steady state excitation, showing that a correct choice of the carrier density can make the expressions equivalent.

References

- [1] G. Kieslich, S. Sun, T. Cheetham, *Chem. Sci.* **2015**, *6*, 3430.
- [2] Z. Li, M. Yang, J. S. Park, S. H. Wei, J. J. Berry, K. Zhu, *Chem. Mater.* **2016**, *28*, 284.
- [3] B. Zhao, M. Abdi-Jalebi, M. Tabachnyk, H. Glass, V. S. Kamboj, W. A. Nie, J. Pearson, Y. Puttisong, K. C. Gödel, H. E. Beere, D. A. Ritchie, A. D. Mohite, S. E. Dutton, R. H. Friend, A. Sadhanala, *Adv. Mater.* **2016**, *29*, 1604744.
- [4] T. Bin Song, T. Yokoyama, C. C. Stoumpos, J. Logsdon, D. H. Cao, M. R. Wasielewski, S. Aramaki, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2017**, *139*, 836.
- [5] M. A. Green, A. Ho-Baillie, H. J. Snaith, *Nat. Photonics* **2014**, *8*, 506.
- [6] C. L. Davies, M. R. Filip, J. B. Patel, T. W. Crothers, C. Verdi, A. D. Wright, R. L. Milot, F. Giustino, M. B. Johnston, L. M. Herz, *Nat. Commun.* **2018**, *9*, 293.
- [7] M. Leroux, N. Grandjean, B. Beaumont, G. Nataf, F. Semond, J. Massies, P. Gibart, *Phys. Status Solidi Basic Res.* **1999**, *216*, 605.
- [8] H. Fang, F. Wang, S. Adjokatse, N. Zhao, J. Even, M. A. Loi, *Light Sci. Appl.* **2016**, *5*, e16056.
- [9] S. Sun, T. Salim, N. Mathews, M. Duchamp, C. Boothroyd, G. Xing, T. C. Sum, Y. M. Lam, *Energy Environ. Sci.* **2014**, *7*, 399.
- [10] T. J. Savenije, C. S. Ponseca, L. Kunneman, M. Abdellah, K. Zheng, Y. Tian, Q. Zhu, S. E. Canton, I. G. Scheblykin, T. Pullerits, A. Yartsev, V. Sundstro, *J. Phys. Chem. Lett.* **2014**, *5*, 2189.
- [11] K. Wu, A. Bera, C. Ma, Y. Du, Y. Yang, L. Li, T. Wu, *Phys. Chem. Chem. Phys.* **2014**, *16*, 22476.

- [12] A. Miyata, A. Mitiglu, P. Plochocka, O. Portugall, J. T.-W. Wang, S. D. Stranks, H. J. Snaith, R. J. Nicholas, *Nat. Phys.* **2015**, *11*, 582.
- [13] A. D. Wright, R. L. Milot, G. E. Eperon, H. J. Snaith, M. B. Johnston, L. M. Herz, *Adv. Funct. Mater.* **2017**, *27*, 1700860.
- [14] W. Shockley, W. T. Read, *Phys. Rev.* **1952**, *87*, 835.
- [15] R. N. Hall, *Proc. IEE - Part B Electron. Commun. Eng.* **1959**, *106*, 923.
- [16] G. K. Wertheim, *Phys. Rev.* **1958**, *109*, 1086.
- [17] T. Leijtens, G. Eperon, A. Barker, G. Grancini, W. Zhang, J. Ball, A. R. Srimath Kandada, H. Snaith, A. Petrozza, *Energy Environ. Sci.* **2016**, *9*, 3472.