Long-lived hot-carrier light emission and large blue shift in formamidinium tin triiodide perovskite
devices with efficiencies exceeding the Shockley-Queisser limit. Here, we report
photoluminescence from hot-carriers with unexpectedly long lifetime (a few ns) in for-
mamidinium tin triiodide. An unusual large blue shift of the time-integrated photo-
luminescence with increasing excitation power (150 meV at 24 K and 75 meV at 293 K) is
displayed. On the basis of the analysis of energy-resolved and time-resolved photo-
luminescence, we posit that these phenomena are associated with slow hot carrier relaxation
and state-filling of band edge states. These observations are both important for our under-
standing of lead-free hybrid perovskites and for an eventual future development of efficient
lead-free perovskite photovoltaics.
Hybrid organic–inorganic perovskites have attracted increasing interest for optoelectronic applications, including photovoltaics, lasers, light-emitting diodes, and sensors. The superior intrinsic photophysical properties such as high absorption cross-section, long charge-carrier diffusion length, low trap densities and facile solution processability, make them ideal candidates for cheap and efficient solar cells. Recently, the toxicity of the water-soluble lead-based materials has raised considerable concerns on the potential environmental impact of the large-scale use of these materials, driving the exploration of non-toxic, lead-free alternatives. Tin-based halide perovskites are a class of alternatives under the spotlight, which have direct band gap in the near infrared. Due to their narrower optical band gap (1.3 eV for MA SnI₃ and 1.32 eV for CsSnI₃) and broader solar spectrum absorption, the tin perovskites are potentially better candidates for high performance photovoltaic devices. These effective light harvesting materials have been recently employed in single junction solar cells with reported power conversion efficiencies larger than 8% and 9% in our group. By combining both the tin and lead perovskites in appropriate proportions, the tin-lead alloys with band gaps as low as 1.2 eV have been synthesized. Photovoltaic devices based on alloys such as FA₀.₇₅Cs₀.₂₅Sn₀.₅Pb₀.₅I₃ or perovskite-perovskite 4T tandem architecture have recently been reported to display high efficiencies, where the low efficiency of single junction tin-only-based solar cells seems not related to the intrinsic properties of the perovskite material, but to large losses in V_OC mainly due to trap assisted recombination.

It is known that when a semiconductor is excited with photons of energy higher than the band gap, hot carriers are generated and their excess energy is dissipated via phonon emission till they finally thermalize to the bottom of the band. This is a major loss channel in photovoltaics, and is partially responsible for the Shockley–Queisser efficiency limit. This limitation could in principle be circumvented if all the energy of the hot carriers could be captured, pushing in this way the efficiency up to 66%.

Recently, there have been intensive investigations on hot carrier relaxation in lead halide perovskites. Yang et al. and Price et al. observed a hot-phonon bottleneck in lead-iodide perovskites through femtosecond transient absorption measurements. Zhu et al. also reported hot photoluminescence (PL) emission at room temperature in lead bromide compounds, but showed that it disappears at 77 K. Yang et al., attributed the hot electrons in several hybrid perovskites to the hot-phonon bottleneck determined by the up-conversion of low-energy phonons. However, the thermalization of hot carriers reported so far typically takes place on a picosecond time scale or faster, making it very challenging or impossible to extract them before relaxation. Slowing down the hot carrier relaxation is the holy grail of third band gap shift, we can readily exempted at room temperature, because excitonic features are only-based solar cells seems not related to the intrinsic properties of the perovskite material, but to large losses in V_OC mainly due to trap assisted recombination.

Here, we demonstrate a very slow (nanosecond range) PL emission from hot carriers both at 293 and 24 K. Films of FASnI₃ were prepared on indium tin oxide (ITO) covered glass substrates by spin coating. The sample preparation is described in the methods section. The obtained FASnI₃ is confirmed by X-ray crystallographic data analysis (Supplementary Fig. 1). Optical absorption spectra measured at room temperature (293 K) till 24 K, and PL excitation spectra at 293 K and PL excitation spectra at 293 K are reported in the Supporting Information (Supplementary Fig. 2, Supplementary Fig. 3 and Supplementary Note 1). The absorption onset at 293 K is localized at around 1.43 eV (865 nm). Upon cooling down, it monotonically shifts towards lower energy 1.35 eV (916 nm) at 24 K, which is in agreement with the commonly observed anomalous Varshni trend in hybrid lead-based perovskites, with a positive thermal expansion coefficient of the band gap. Similar to the absorption spectra, the PL peak redshifts from 1.38 eV at 293 K to 1.24 eV at 24 K (Supplementary Fig. 4 and Supplementary Fig. 5). Both the PL and absorption spectra shift almost continuously towards low energy from 293 to 24 K. A slight change in the variation of the optical absorption spectrum which occurs at about 80 K is possibly in relation to a phase transition as is commonly observed in lead-based perovskites. Figure 1 shows the normalized PL spectra at 293 and 24 K under various excitation densities. The PL intensity at 293 and 24 K for a function of the pump power density are summarized in Figs. 1c, f, respectively. In general, the integrated PL intensity (I) is proportional to P², where P is the power of the exciting laser radiation. The PL intensity at room temperature increases linearly with excitation power up to about 2 μJ cm⁻², suggesting that the quantum yield in this range is constant (QY ≈ 6%). Two mechanisms are usually proposed to explain the linear dependence on the excitation intensity of the PL. The first is the radiative excitonic recombination. However, this possibility is readily exempted at room temperature, because excitonic features are not observed in the absorption spectrum, suggesting a very small exciton binding energy for this material. A second more suitable explanation is attributed to the recombination of photogenerated electrons with the hole density due to the unintentional doping in FASnI₃ (Supplementary Fig. 6 and Supplementary Note 1). However, when the excitation density is further increased (above 2 μJ cm⁻²), the slope of power-dependent PL intensity becomes sublinear, which is in contrast to what has been observed for lead-based perovskite that exhibits superlinear dependence on the injected carrier density. We attribute the slope variation at high excitation power in Sn-based perovskites to Auger losses (vide infra).

Interestingly, a blue shift of the emission is observed as the excitation density increases, both at 293 and 24 K. Figures 1b, e show the 2D pseudo-color plots of the normalized PL spectra. The blue-shifts of the PL peaks are as large as 75 and 150 meV at 293 and 24 K, respectively. To establish the possible origins of the band gap shift, we first consider the origins of band gap shifts in classical semiconductors and relate them to the perovskite semiconductor. The hypothesis related to excitation, such as exciton-exciton interactions or Coulomb screening of the excitation, can be readily excluded because there is no evidence for stable excitons in FASnI₃. Other two possible origins for FASnI₃ are photo-induced band filling and band gap renormalization, i.e., modification of band edge states self-energies by the screening due to photogenerated carriers. This second case can be ruled out because it gives rise to a red shift rather than the observed blue shift. In the first case, the blue shift of the optical band gap is a consequence of the dynamic free carriers filling of the densities of states, as schematically shown in Fig. 2a. Saturation in PL intensity is seen at high carrier densities (Fig. 1c; Supplementary Fig. 7). As a result, it is possible to fill band edge states, with a consequent blue shift of the transition energy and line-width broadening. Figure 2b, c show the peak shift in time-integrated PL spectra as a function of the photoexcited carrier density. The band filling is further validated by a good fit of the carrier
concentration dependent emission peak shift at time $= 0$ (Supplementary Fig. 8, and Supplementary Note III). From the fitting, we can estimate values for the reduced effective carrier mass of 0.121 $m_0$ at 24 K, and 0.214 $m_0$ at 293 K, where $m_0$ is the mass of the electron in vacuum. These values are in line with the previously reported value of 0.2 $m_0$ in MAPbI$_3$ obtained with a combined study of infrared reflectivity and Hall effect measurements.\(^{34}\)

**Energy-resolved and time-resolved photoluminescence.** To better understand the photoexcitation process and gain an insight into the charge-carrier dynamics in FASnI$_3$, we performed TRPL measurements as a function of the excitation density. TRPL was measured using a streak camera and exciting the sample with laser pulses of 3.08 eV and width of about 150 fs. When the excitation density increases, the emission peak extracted immediately after excitation shifts towards high energy. Figures 3a, b show pseudo-color plots of the typical TRPL spectra of FASnI$_3$ thin films measured at three different excitation densities for temperature at 293 and 24 K, respectively. The PL spectra clearly show an additional signal in the higher energy side of the spectra (PL from carriers with excess energy) when the excitation density is increased (Fig. 3c, d). By normalizing the PL spectra at the low-energy side, as shown in the inset of Fig. 3c, d, it is found that the contribution of this additional signal (high-energy tail) is increased at higher excitation. Interestingly, the ratio of the emission from the high energy tail is larger at 24 K than at room temperature under similar excitation. If this additional signal at the high-energy tail of the spectrum is assumed to come from hot carriers, then the emission from the hot carriers at 24 K is stronger than that at 293 K.

Recently, Manser and Kamat reported a blue shift in the transient bleach signal in thin films of methylammonium lead iodide\(^{37}\), which they attributed to band filling by free charge carriers. However, this effect has been reported to occur only at rather short delays (5 ps after excitation)\(^{26,37}\). Moreover, it appeared to be partially compensated by the band gap renormalization effect, thus contributing little to the PL. For a comparison, we investigated the properties of FAPbI$_3$, MAPbBr$_3$, and MAPbI$_3$ thin films. Figure 3e–g present TRPL spectra for FASnI$_3$, FAPbI$_3$, and MAPbI$_3$ at similar excitation conditions, showing that the FASnI$_3$ thin films show much stronger band-filling effect and prolonged hot carrier emission. The power-dependent PL with similar excitation conditions for those lead-based perovskites shows much smaller peak energy shifts as a function of the excitation power (17 meV for FAPbI$_3$ (Supplementary Fig. 9), 6.5 meV for MAPbI$_3$ (Supplementary Fig. 10), and 4 meV for MAPbBr$_3$ (Supplementary Fig. 11 and Supplementary Fig. 12) at room temperature compared to 75 meV for FASnI$_3$).

**Hot carrier emission.** The normalized emission under high excitation shows a large blue shift and a high-energy front living up to 1 ns after photoexcitation. This suggests that carriers do not reach the band edge immediately, and that luminescence from carriers with excess energy is present in the time dependent spectral evolution (Supplementary Fig. 13). This is an evidence that carrier cooling is inhibited by the filled states in tin-based...
perovskites; therefore, the dynamic band filling in FASnI₃ leads to a shift of the optical transitions towards high energy and to an unusually slow hot carrier relaxation time (more than 1 ns) towards the band bottom. This is especially noticeable when compared with lead-based perovskites, in which the carrier relaxation to the band edges is occurring in the picosecond regime or faster. This unique property of FASnI₃ may lead to the application of Sn-based perovskites in optoelectronic devices, such as wavelength tunable light-emitting diodes and lasers.

It was recently reported that the addition of SnF₂ in the active layer is critical in improving the efficiency of tin-based perovskite solar cells. For comparison, excess SnF₂ was added to the precursor solution for the fabrication of the FASnI₃ thin film (scanning electron microscope images and atomic force microscope images are presented in Supplementary Fig. 14 and Supplementary Fig. 15, respectively). Figure 4a shows TRPL spectra of a FASnI₃ film treated with SnF₂. The introduction of SnF₂ significantly increases the PL intensity (Supplementary Fig. 16) and the lifetime of the Sn-based perovskite (4 ns) in comparison to the one measured for films not treated with SnF₂ (0.3 ns). The longer lifetime of the PL confirms that SnF₂ suppresses the oxidation of Sn⁴⁺ and thus reduces the natural p-doping of FASnI₃. Similar to the pristine FASnI₃, blue-shifted emission at increased excitation density (Supplementary Fig. 17), and a broad PL high-energy tail extending up to 1.9 eV (Supplementary Fig. 18 and Supplementary Fig. 19) is observed at early times, which is attributed to radiative recombination of hot carriers. The emission peak red shifts as time elapses, reflecting the hot carrier relaxation dynamics and the reduction of the band filling as the photo-excited carriers recombine (Supplementary Fig. 20). The PL intensity decays are shown in Fig. 4b for emission energies of 1.65, 1.41, and 1.38 eV. The hot-carrier PL at the high-energy tail of the spectra (1.65 eV) shows an initial rapid cooling with a time constant of ₜ = 0.16 ns, followed by a significantly slower relaxation process taking up to 4.5 ns. In order to obtain the carrier temperature as a function of time, the PL spectra at different delay times are extracted. The spectra have a high-energy tail that decays exponentially with energy, whose line shape is approximated to be a modified Maxwell–Boltzmann distribution. The carrier temperature is obtained by fitting the high-energy tail of the spectra globally using PL spectra at each delay time (details of the fitting method is presented in Supplementary Note IV). In Fig. 4c, the hot-carrier temperature as a function of time is displayed. The carrier temperature rapidly decreases from ~1600 K after excitation to ~750 K at 0.2 ns after excitation. The cooling process then slows significantly down, showing a time constant of about 6 ns.

It is worth highlighting that such large blue shift is present in FASnI₃ also under continuous-wave excitation. The emission peak shift from around 1.4 eV under excitation of 0.027 kW cm⁻² (corresponding to 0.27 sun intensity), to 1.45 eV at 4.4 kW cm⁻² (44 suns intensity). Figure 5 shows the power-dependent PL of a FASnI₃ excited with a continuous-wave laser. Similar to the TRPL spectra, the spectra measured with CW excitation have a high-energy tail that decays exponentially with energy, which can be fitted with the modified Maxwell–Boltzmann distribution (red solid curves). The good fit of the high-energy tail confirms that it originates from the radiative recombination of hot carriers. Based on the normalized PL spectra, the contribution to total PL emission of the high-energy tail is estimated to be as high as 59% under 44 Suns. This strong emission from hot carriers, in continuous-wave operation, the mode of operation of solar
cells, is an important first step towards harvesting these hot carriers\textsuperscript{42,43}.

**Discussion**

The long-lived hot-carrier and the large contribution of them to the total PL signal raise questions about the reasons of this feature in FASnI$_3$. It is noted that FASnI$_3$ also shows very slow decaying hot PL and even larger PL blue shift at low temperature. This is in contrast to what was observed by Zhu et al.\textsuperscript{28}, which was explained by the protection afforded by molecular reorientations at room temperature, vanishing at low temperature due to the freezing of these motions. Obviously, such a mechanism can hardly explain the slow relaxation of hot carriers in FASnI$_3$, considering its persistence at low temperature. Phonon bottleneck effect may play an important role in decreasing the hot carrier population decay rate\textsuperscript{26,27,29,44}. Yang et al.\textsuperscript{29}, recently suggested that phonon up-conversion is essential for effective vibrational energy recycling in hybrid lead-halide perovskites, which prolongs the overall cooling period of the carrier–phonon system. Although interesting, this explanation does not provide a motivation for the difference between lead and tin compounds, as well as for the specific role of the FA cation by comparison to MA and Cs one.

Some alternative explanation could be related to a more fundamental difference between the electronic structures of tin and lead halide compounds. A first difference between lead and tin compounds might be related to the conduction band (CB). The spin–orbit coupling effect is indeed expected to be about 0.4 eV in tin compounds, that is about three times smaller than in their
excitation diode excitation. The solid lines.

Photoluminescence from FASnI3 thin film with addition of SnF2. a Semi-log plot of PL spectra at different delay time after excitation under an excitation fluence of 28 μJcm⁻². The high-energy tail of the PL spectra is fitted with $I_{PL} \propto \alpha(E) \exp(-\nu/kT)$, where $T_c$ is the carrier temperature, and $\nu$ is photon energy. b PL intensity decay at 1.65, 1.41, and 1.38 eV. The PL intensity has been normalized at the tail. c Extracted carrier temperature from the hot-carrier distribution as a function of the delay time. The fast component is fitted to be 0.14 ns, and the slow component is around 6 ns. The carrier temperature is obtained by fitting the high-energy tail of the PL spectra at each delay time (Supplementary Note IV).

Hot carrier contribution (%)

10
20
30
40
50
60

Normalized PL intensity (a.u.)

0
10
20
30

Energy (eV)

1.4
1.6
1.8

PL spectra of FASnI3 thin film with the addition of SnF2 under 405 nm laser diode excitation. The fitting of the carrier temperature is reported with red solid lines. b Hot carrier contribution to the photoluminescence and carrier temperature as a function of illumination intensities reported in term of sun (AM 1.5, 1 sun = 100 mWcm⁻²).
present not only upon pulsed excitation but also with CW one, which is essential for making the long-standing dream to use hot carriers in solar cells and other optoelectronic devices more realistic.

**Methods**

**Materials.** The glass substrates were sequentially cleaned using detergent, demineralized water, acetone, and isopropanol. The substrates were then baked in an oven at 140 °C for 10 min and treated with UV ozone for 20 min. FAESI precursor solutions were prepared by dissolving formamidinium iodide (FAI) and (II) iodide (SnI2) precursors with molar ratio of 1:1 in a mixed solvent of anhydrous N,N-dimethylethylformamide (DMF) and anhydrous dimethylsulfoxide (DMSO) in a volume ratio of 4:1 to form a 1 M solution and stirred overnight at room temperature in a nitrogen-filled glovebox. The perovskite solution was spin-coated on a glass substrate covered by ITO at 7500 rpm for 30 s. After cooling down at room temperature, the films were exposed to ambient air for 1 h and baked at 100 °C for 20 min. For the FAESI-treated samples, the required amount of SnF2 was added to the FAI/ SnI2 precursors to form the SnF2-treated FAESI precursor solution. For FAPbI3 thin films, FAI and PbI2 were dissolved in anhydrous N,N-dimethylethylformamide at a molar ratio of 1:1. 5 vol% hydriodic acid was added to the FAI and PbI2 solution. After spin coating at 3000 rpm for 60 s on a glass substrate and then drying at 160 °C for 40 min, perovskite films were formed. For MAPbI3 thin films, a precursor solution composed of an equimolar of CH3NH3I and PbI2 was spin-coated on top of cleaned glass substrate and then annealed at 100 °C in a nitrogen-filled glove box. MAPbBr3 thin films were made from a precursor solution composed of an equimolar of CH3NH3Br and PbBr2, which is dissolved in a mixed solvent of DMF and DMSO in a volume ratio of 4:1.

**XRD characterization.** The X-ray diffraction was performed at ambient conditions. The X-ray data were collected using the FEI Nova Nano SEM 650 with an accelerating voltage of 30 kV and a Lynxeye detector.

**Morphology characterization.** The AFM images were obtained using the Bruker NanoScope V in the ScanAsyst mode. Scanning electron microscopy (SEM) images were obtained using the FEI Nova Nano SEM 650 with an accelerating voltage of 15 kV.

**Optical measurements.** The thickness of the perovskite films were measured using a film thickness measurement method. The absorbance spectra of the films were measured in the range of 250–800 nm using a UV–vis spectrophotometer.

**Data availability.** The data that support the plots within this paper and findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

The project was conceived, planned, and co-ordinated by H.-H.F. and M.A.L. Samples are prepared by S.S. and S.A., and H.-H.F. measured PL and TRPL of the samples. S.A. performed XRD, AFM and SEM characterization. H.-H.F., J.E., and M.A.L. provided the interpretation of the results. H.-H.F. wrote the first version of the manuscript, and all authors contributed to the final version.

Additional information

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