Photophysics of lead-free tin halide perovskite films and solar cells

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ABSTRACT
The last five years have seen very active research in the field of environmentally friendly lead-free perovskite solar cells. Tin halide perovskites are certainly one of the most promising alternatives to lead-based perovskites, while the performance of present tin-based perovskite solar cells is still relatively low. Nevertheless, recent experiments on thin films with improved quality have indicated that tin halide perovskites can, in principle, provide a high device performance. In this Perspective, we summarize recent progress in the understanding of the fundamental photophysics of tin halide perovskite thin films. To identify the reason for the low performance of present devices, we discuss the energy loss mechanisms in solar cell structures from the viewpoint of photocarrier dynamics.

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I. INTRODUCTION
Metal halide perovskites are semiconductor materials that have been subject to investigations for a long time, and consequently, much knowledge regarding their physical and chemical properties has been accumulated. In the early stages of research, their phase transitions and structural properties were in the focus of investigations. In the 1990s, layered organic–inorganic hybrid perovskites received much attention and exciton photophysics at low temperatures were studied. In the year 2009, the first solar cell based on lead halide perovskite was reported. Then, after the report of the all-solid-state perovskite solar cell in 2012, halide perovskite solar cells started to become a very active research field all over the world. Presently, solar cells based on lead halide perovskites exhibit high power conversion efficiencies and are rapidly approaching the commercialization stage. At the same time, these perovskites themselves show unique luminescence properties. For example, even when lead halide perovskites are fabricated by simple and inexpensive low-temperature solution processes, they exhibit extremely high photoluminescence (PL) quantum efficiencies at room temperature. A photon recycling of both free-carrier and exciton luminescence has been observed in various halide perovskites because of their high PL quantum efficiencies. The high PL quantum efficiency is also considered to enable new optical functionality of perovskites as light-emitting and laser-cooling devices. Furthermore, the recent demonstrations of efficient high-order harmonic generation and light modulation in lead halide perovskites also suggest their utility for nonlinear optics applications.

Lead halide perovskites exhibit exceptional optoelectronic properties, but from the viewpoint of environmental issues, their lead content is considered problematic. To address the toxicity issue, the research on lead-free perovskite materials has become more active. Lead-free materials such as tin (Sn) halide perovskites, bismuth halides, germanium perovskites, and copper halide have been reported. In particular, the tin halide perovskites are attracting much attention because they have achieved relatively high solar cell efficiencies; 9.6% has been reported for tin iodide perovskite. However, this is still significantly lower than the conversion efficiencies of over 23% realized for lead halide perovskite solar cells. It is important to clarify whether the presently realized efficiencies are limited by the fabrication technology or the intrinsic material properties. Thus, large efforts have been devoted to the improvements of the film preparation method and also the device structure. On the other hand, until recently, the understanding of the optical properties of tin perovskites had not advanced much. Owing to recent improvements in the thin film quality, it has become possible to clarify the intrinsic optical properties of tin halide perovskites. The knowledge of these fundamental optical properties...
II. BANDGAP ENGINEERING AND FILM QUALITY IMPROVEMENT

Before we go into the detailed discussion of the optical properties, an overview of the structural properties of the perovskite material class is provided. The chemical formula of metal halide perovskites can be written as $ABX_3$ [Fig. 1(a)]. The A site contains an organic material [e.g., CH$_3$NH$_3$ (also called MA) or CH(NH$_2$)$_2$ (also called FA)] or an inorganic element (Cs) as a monovalent cation. The B site contains a divalent metal ion (e.g., Pb or Sn), and the X site is occupied by a halogen (Cl, Br, or I). The stability of the $ABX_3$ structure is determined by the tolerance factor and the octahedral factor, which are calculated from the ionic radii of the elements or molecules at A, B, and X sites. These sites can be occupied uniformly by a single element or molecule, or some combination of ionic species can be substituted into the lattice. The use of such mixed-cation or mixed-halide perovskites significantly improves the stability of device performance. By controlling the composition, their luminescence color can be tuned continuously over a wide wavelength range from the near-infrared to the blue. Figure 1(b) summarizes the bandgap energies of several perovskites suited for solar cell devices and their reported conversion efficiencies.

The bandgap energy ($E_g$) of a semiconductor is important when considering the application in solar cell devices since it determines the theoretical upper limit of the solar cell efficiency via the detailed balance principle. In order to achieve an efficient device, it is important to bear in mind that the optimum $E_g$ depends on the number of junctions and on the PL quantum efficiency of the used material. For example, if the PL quantum efficiency becomes smaller than unity, the optimum $E_g$ for the highest possible solar cell efficiency becomes larger. The PL quantum efficiency depends on the recombination dynamics of photocarriers in the material and is discussed in Sec. IV.

The narrowest bandgap of the lead-based perovskites is that of FAPbI$_3$, 1.48 eV. In case of a PL quantum efficiency of 100%, the optimum bandgap energy $E_g$ for a single-junction solar cell is 1.34 eV under AM 1.5G solar illumination as derived from the detailed balance theory. This $E_g$ cannot be obtained by lead-based perovskites. In this respect, tin halide perovskites are more suited because they can reach narrower $E_g$ than the lead perovskite counterparts. Furthermore, it has been reported that the $E_g$ of the Pb–Sn mixed perovskite APb$_{1-x}$Sn$_x$I$_3$ changes in a characteristic nonlinear manner with respect to the Sn content x. Figure 1(c) summarizes the reported $E_g$ values of APb$_{1-x}$Sn$_x$I$_3$ estimated from absorption spectra in the literature. It can be confirmed that $E_g$ reaches a minimum in the x range from about 0.5–0.75, and this trend is preserved even when different A-site cations are employed. As possible origins of this nonlinear change of the bandgap, the competition between spin–orbit interaction and the lattice distortion effect, the short-range order of the Pb–Sn configuration, and the atomic orbital mismatch between Pb and Sn have been suggested. While the similar trend can be seen among the different reports in Fig. 1(c), the absolute values of $E_g$ vary even for the same composition. The quality of the used thin film and the employed measurement methods can be considered as possible origins of the large difference in the reported values. Furthermore, in the tin halide perovskites, the onset of photoabsorption is very sensitive to the amount of doping. This issue is discussed in detail in Sec. III. In any case, the use of Sn results in a large bandgap tunability, and this is advantageous for the design of solar cell devices including multijunction cells.
Although tin halide perovskites are important in terms of their potential as lead-free materials and from the viewpoint of bandgap tunability, the present efficiencies of the lead-free tin-based perovskite solar cells are not as high as those of lead-based perovskite solar cells [Fig. 1(b)]. To understand what is needed to realize more efficient solar cells based on tin halide perovskites, we briefly summarize the optical properties of lead halide perovskites. Owing to the extremely large number of publications in the last decade, many exceptional properties of lead halide perovskites have been revealed, i.e., a large absorption coefficient in the visible region originating from direct band transitions,\textsuperscript{65–68} a sharp absorption edge with a low number of localized states within the bandgap,\textsuperscript{71–73} PL with almost no Stokes shift,\textsuperscript{71,72} a high PL quantum efficiency,\textsuperscript{74} an efficient electron–phonon interaction,\textsuperscript{75–78} anti-Stokes luminescence,\textsuperscript{79–80} a small exciton binding energy,\textsuperscript{81} and extremely long lifetimes and long diffusion lengths of photocarriers.\textsuperscript{82–84}

On the other hand, the understanding of the fundamental optical properties of tin halide perovskites had not progressed until very recently. The fabrication of high-quality samples is essential to understand intrinsic optical properties of a semiconductor material. However, the tin halide perovskites used in the early stages of research were strongly influenced by extrinsic factors, such as impurities, defects, and traps, preventing in-depth discussions of their intrinsic optical properties.\textsuperscript{85,86} Fortunately, recent improvements in film deposition techniques made the detailed discussions possible.

In the following, some details regarding the progress in preparation techniques are provided.

At first, it should be noted that the crystallization of tin-based perovskites is fast, and thus, the control of the crystal growth is difficult.\textsuperscript{87–89} Without careful preparation procedure, high-quality samples cannot be obtained. The reproducibility of the device performance was also reported to be low at the early stage of the research.\textsuperscript{90–91} Recent studies have clarified that a better film quality can be obtained via slower crystallization by utilizing an appropriate solvent\textsuperscript{92} and employing an antisolvent during the spin-coating process.\textsuperscript{93–94} By using these methods, thin films with better crystalline quality and improved coverage of the substrate can be achieved, which consequently leads to a better performance and reproducibility of solar cell devices. Recently, Ozaki \textit{et al.}\textsuperscript{95} reported the importance of the purity of the precursor, and they have developed highly-purified materials using tin halide complexes. Furthermore, as a simple but effective film deposition method, Liu \textit{et al.}\textsuperscript{96} have developed a hot antisolvent treatment (HAT). Instead of the room-temperature antisolvent, they dropped a 65 °C pre-heated antisolvent on the precursor solution during spin coating and succeeded in obtaining a perovskite film with improved coverage [see Figs. 2(a) and 2(b)].\textsuperscript{97} In the tin perovskite thin films prepared by the HAT method, an increase in the photocarrier lifetime was observed, which suggests suppression of nonradiative recombination centers [Fig. 2(c)]. Accordingly, by employing this HAT method, the device performance and reproducibility were improved [Fig. 2(d)]. These improvements in the fabrication of tin halide perovskite thin films have contributed to the recent progress in the understanding of the fundamental optical properties of tin halide perovskites.

III. OPTICAL ABSORPTION AND PHOTOLUMINESCENCE

A. Luminescence Stokes shift

In this section, the steady-state optical spectra near the band edge are elaborated. Figures 3(a) and 3(b) present the PL and absorption spectra of MASnI\textsubscript{3} and FA\textsubscript{0.75}MA\textsubscript{0.25}SnI\textsubscript{3} respectively. These thin films were prepared by adding SnF\textsubscript{2} to the precursor solution. The role of SnF\textsubscript{2} during the film fabrication is discussed in Sec. III B. For both MASnI\textsubscript{3} and FA\textsubscript{0.75}MA\textsubscript{0.25}SnI\textsubscript{3}, a sharp onset of the absorption is observed. This indicates a low number of defects within the bandgap. Less defect states imply less nonradiative recombination via processes like Shockley–Read–Hall recombination. Furthermore, it is noteworthy that almost no Stokes shift is observed between the PL peak and the absorption onset, neither for MASnI\textsubscript{3} (single A-site cation) nor for FA\textsubscript{0.75}MA\textsubscript{0.25}SnI\textsubscript{3} (mixed cation). The PL peak position is the effective upper limit of the open-circuit voltage (\(V_{oc}\)). The observation of a small Stokes shift and a steep absorption edge indicates small voltage losses within the bulk material.\textsuperscript{98–99} This is important not only for solar cells, but also for light-emitting diode (LED) operation. The \(E_g\) of MASnI\textsubscript{3} is 1.26 eV, while that of FA\textsubscript{0.75}MA\textsubscript{0.25}SnI\textsubscript{3} is 1.36 eV. The \(E_g\) of the latter material is close to the optimum \(E_g\) for a single-junction solar cell, which shows the importance of the development of the tin halide perovskites with mixed A-site cations and their small Stokes shifts. Here, note that the optimum \(E_g\) for which the highest conversion efficiency can be expected, depends on the PL quantum efficiency of the semiconductor material.\textsuperscript{33–35}

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**FIG. 2.** Scanning electron microscope images of FA\textsubscript{0.75}MA\textsubscript{0.25}SnI\textsubscript{3} films fabricated with (a) room-temperature (RT) chlorobenzene (Ph-Cl) and (b) preheated chlorobenzene at 65 °C. (c) PL decay curves of FA\textsubscript{0.75}MA\textsubscript{0.25}SnI\textsubscript{3} films and (d) I–V curves under 1-sun illumination of FA\textsubscript{0.75}MA\textsubscript{0.25}SnI\textsubscript{3} solar cells prepared with room-temperature (blue line) or 65 °C preheated chlorobenzene (red line) as antisolvent. Adapted with permission from Liu \textit{et al.}, Angew. Chem., Int. Ed. \textbf{57}, 13221 (2018). Copyright 2018 Wiley-VCH.
In tin halide perovskites, hole doping and band-filling effects play crucial roles for the optoelectronic responses and, consequently, also for the device performance. Figures 3(a) and 3(c) show the PL and absorption spectra of the MASnI$_3$ thin films prepared with and without the SnF$_2$ additive, respectively. It has been reported that, in tin halide perovskites, spontaneous hole doping easily occurs, and that the addition of SnF$_2$ effectively reduces the hole density in the films mainly due to the suppression of the formation of tin vacancies and/or oxidation of Sn$^{2+}$ to Sn$^{4+}$. It is found that the absorption onset of the thin film prepared without SnF$_2$ is located at 1.26 eV, whereas the sample prepared with 10 mol. % SnF$_2$ is shifted to 1.27 eV. The PL peak energy of the MASnI$_3$ film prepared with 10 mol. % SnF$_2$ is also shifted to 1.27 eV, which is in agreement with the absorption spectra. The PL peak positions of both samples are almost the same. The narrow PL FWHM width at half-maximum (FWHM) values. The narrow PL FWHM (85 meV at room temperature) verifies that a high-quality sample can be obtained by employing a mixed solution of dimethyl sulfoxide and chlorobenzene as solvent. As the temperature decreases, the PL peak energy shows a less steep absorption spectrum near the onset. On the other hand, the states near the top of the valence band is occupied by holes. Therefore, light absorption occurs for photon energies slightly larger than the fundamental bandgap energy. In contrast, PL is emitted by the recombination between the photogenerated electrons that have relaxed to the bottom of the conduction band and the holes from the unintentional background doping. Thus, the PL peak positions of both samples are almost the same. The more gradual absorption onset is caused by increased structural disorder in the sample without SnF$_2$ due to the large number of Sn vacancies.

A further interesting example of exploiting the large background doping concentration in tin-based perovskites is the following: by intentionally replacing some Pb atoms by Sn inside a lead-based perovskite, it becomes possible to control the charging inside a perovskite nanoparticle layer and to increase the LED efficiency. The consideration of doping and ionization is particularly important for the application of halide perovskites due to their ionic nature. Most parts of the above discussion of the doping are about p-type tin halide perovskites. By using a different crystal growth technique, the fabrication of n-type tin iodide perovskites with high electron mobilities has been reported as well. In comparison, the doping of lead perovskites is relatively difficult, which can be considered as the other aspect of the usually advantageous defect tolerance of this material. The doping effect is one of the most important topics for tin halide perovskites and also influences the physical properties discussed hereafter.

C. Electron–phonon interaction in tin halide perovskites

In halide perovskite crystals with the polar nature, the electron–phonon interaction plays a critical role for their optical and charge transport properties. Thus, intensive studies have been performed to clarify the electron–phonon interaction, and its possible relation to the optical properties in lead halide perovskites have been discussed. Recently, it has become possible to obtain tin halide perovskite films with better quality owing to improved fabrication techniques, e.g., the use of SnF$_2$ additives or the HAT method. Therefore, the width of the PL spectrum can now be used to discuss the intrinsic physical properties. Below, the results of recent investigations on the electron–phonon interactions in tin perovskite MASnI$_3$ are provided.

Figures 4(a) and 4(b) show the PL spectra of a MASnI$_3$ thin film for different temperatures and the corresponding PL full width at half-maximum (FWHM) values. The narrow PL FWHM (85 meV at room temperature) verifies that a high-quality sample is obtained by employing a mixed solution of dimethyl sulfoxide and chlorobenzene as solvent. As the temperature decreases, the PL peak energy shows a further interesting example of exploiting the large background doping concentration in tin-based perovskites is the following: by intentionally replacing some Pb atoms by Sn inside a lead-based perovskite, it becomes possible to control the charging inside a perovskite nanoparticle layer and to increase the LED efficiency.
a redshift. This tendency is opposite to that of typical inorganic semiconductors such as GaAs and Si. A similar tendency has also been observed for lead halide perovskites, lead chalcogenides, and CuCl. In the lead halide perovskites, the electron–phonon interaction, and the temperature-induced change in the overlap between the p orbital of iodine (I) and the s orbital of Pb (which form the valence band in APbI3 perovskites), have been considered as possible origins of this tendency. In the temperature region below 120 K, MASnI3 exhibits a complex PL response whose details are discussed in Ref. 134.

The temperature dependence of the PL FWHM can be described by the intrinsic electron–longitudinal-optical (LO) phonon coupling. By fitting the temperature-dependent FWHM values using a model considering the electron–LO phonon coupling [black solid line in Fig. 4(b)], \( h\omega_{LO} = 21.6 \text{ meV} \) and \( T_{1} = 54 \text{ meV} \) are obtained for the LO phonon energy and the coupling constant in MASnI3, respectively. From the low-energy tail of the PL spectrum, the steepness parameter \( \sigma \) (defined by \( E_{U} = k T/\sigma \), where \( E_{U} \) is the Urbach energy) can be estimated. It is clarified that the temperature dependence of \( \sigma \) can be well explained by the contribution from the above-mentioned phonon with an energy of 22 meV [black solid line in Fig. 4(c)]. Furthermore, the same phonon energy has also been obtained from different samples fabricated using a different method. Such a confirmation of reproducibility is important when characterizing intrinsic physical properties of tin perovskites. The temperature dependence of \( \sigma \) in Fig. 4(c) supports that the Urbach tail of the MASnI3 thin film is the intrinsic tail determined by the intrinsic electron–phonon interaction, but is not due to static impurity levels or other extrinsic factors. Actually, from \( \sigma(300 \text{ K}) = 2.19 \), the Urbach energy of MASnI3 at 300 K is calculated as \( E_{U} = 12 \text{ meV} \). This is a remarkably small value that is comparable to the \( E_{U} \) of the lead perovskite MAPbI3, where the small \( E_{U} \) is considered as one reason for the observed high \( V_{oc} \) of the MAPbI3 solar cells.

As shown above, even in the tin halide perovskites, the broadening of the optical transitions is governed by the intrinsic electron–optical phonon interactions if films with good quality are investigated. This feature is very similar to that observed in lead halide perovskites. Note, however, that the values of their LO phonon energies are different; recently, the LO phonon energies of the lead halide perovskites MAPbX3 (X = Cl, Br, I) have been directly determined by using THz spectroscopy. The reported value for MAPbI3 is \( h\omega_{LO} = 16 \text{ meV} \). From this reported value for MAPbI3 and the results for MASnI3 in Fig. 4, we find that the optical phonon frequency shifts toward higher energies upon replacing Pb by Sn. In qualitative terms, this can be understood as the effect of inserting the lighter Sn atom.

It is known that in the lead halide perovskites, the effective electron–LO phonon coupling leads to an intrinsic broadening. In order to explore this feature, the results of resonant PL measurements on MASN3 and MAPbI3 are shown in Figs. 5(a) and 5(b), respectively. In both samples, the shape of the PL spectra does not depend on the excitation energy. This is consistent with the absence of a notable Stokes shift of the PL (Fig. 3) and also the temperature dependence of the PL FWHM (Fig. 4). Furthermore, even when the excitation energy is below the PL peak energy, a strong anti-Stokes luminescence signal appears. The observation of anti-Stokes luminescence suggests an upconversion mechanism inside the material, presumably by the assistance of phonons. Importantly, in the lead halide perovskites, the strong anti-Stokes luminescence coupled with a high luminescence quantum efficiency can be implemented to achieve efficient laser cooling. In Ref. 26, one can find detailed discussions on laser cooling, including the relation between laser cooling and photon recycling and the observation of anti-Stokes luminescence in optically thick samples.

### D. Charge carrier mobility and exciton binding energy

The effective mass of charge carriers is an important physical parameter for transport properties and many other physical properties. First-principle calculations have shown that the tin iodide perovskite possess a more dispersive band and smaller effective mass than its lead perovskite counterparts. The smaller effective masses indicate higher carrier mobilities in tin halide perovskites; actually, carrier mobilities on the order of 100 cm2/(V s) have been reported in thin films and polycrystalline samples of tin iodide perovskites (MASnI3, FASnI3, and CsSnI3). These values are larger than the reported mobilities of lead halide perovskites, which possess carrier mobilities in the range from a few to few tens of cm2/(V s).

The exciton binding energy is also important when considering the recombination kinetics of photogenerated carriers and their transport processes. Recently, by low-temperature magnetospectroscopy, the exciton binding energy in the Sn-dominant MASN3 has been measured to be 16 meV. This is almost the same as that of MAPbI3, in which the room-temperature optical responses are governed by free-carriers. Thus, similar free-carrier like photoresponses are expected for tin iodide perovskites, and this can be confirmed by the absorption spectra with no excitonic peak (see Fig. 3).
As described above, the optical spectra obtained from MASnI\textsubscript{3} and MAPbI\textsubscript{3} thin films under steady-state excitation conditions are very similar. Therefore, both seem to be suited for various optoelectronic applications. However, as mentioned at the beginning of this Perspective, the conversion efficiencies of tin- and lead-based perovskite solar cells differ strongly. This indicates that dynamic properties of photocarriers including carrier lifetimes, diffusion, and other recombination kinetics are strongly different. In fact, the dynamic behaviors of photocarriers govern the photovoltaic properties as shown below.

**IV. PHOTOCARRIER DYNAMICS AND ENERGY LOSS PROCESSES**

**A. Energy losses in solar cells**

First, the energy losses in a tin perovskite solar cell are briefly analyzed through the PL and absorption spectra for a thin-film sample and the current–voltage (I–V) curve of a solar cell device (Fig. 6). This plot intuitively explains the energy loss processes.\textsuperscript{3,4,14-16} The I–V curve in Fig. 6(a) is obtained for a regular-structure solar cell comprising a glass/fluorine-doped tin oxide (FTO)/compact TiO\textsubscript{2}/mesoporous TiO\textsubscript{2}/MASnI\textsubscript{3}/poly(triaryl amine) (PTAA)/Au structure.\textsuperscript{34} Due to the narrow bandgap of MASnI\textsubscript{3} and a thick absorber layer of 500 nm, a relatively high short-circuit current density ($J_{sc}$) of 26.1 mA/cm\textsuperscript{2} is obtained. While this value exceeds the current density obtained in lead-based perovskite solar cells, it is only 67% of the upper limit that can be determined by the $E_{g}$ of MASnI\textsubscript{3}, indicating a large current loss. Note that, in a MAPbI\textsubscript{3} solar cell, a $J_{sc}$ of 91% of the theoretical upper limit has been obtained,\textsuperscript{124} and also in other types of semiconductor solar cells, the current loss is usually small.\textsuperscript{122} The figure also shows the presence of large losses in $V_{oc}$ and the fill factor (FF).

Recent works have shown that the voltage losses in tin-based perovskite solar cells can be suppressed by using an inverted architecture.\textsuperscript{152,153,155-157} Figure 6(b) shows the I–V curve of an inverted planar-structure solar cell, comprising a glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS)/FA\textsubscript{0.75}MA\textsubscript{0.25}SnI\textsubscript{3}/C\textsubscript{60}/bathocuproine (BCP)/Ag layer structure.\textsuperscript{152} By applying the inverted structure, the $V_{oc}$ drop reduces and also the FF improves; a $V_{oc}$ of 0.55 V and an efficiency of 7.2% are obtained.\textsuperscript{36} However, the $J_{sc}$ value still stays at only 54% of the limit expected from $E_{g} = 1.36$ eV. One advantage of tin-based perovskites is the possible high current density due to their narrow bandgap. However, the $J_{sc}$ values achieved so far in tin-based perovskite solar cells are well below the theoretical $J_{sc}$ determined by $E_{g}$. In other words, the advantage of this material system has not yet been fully exploited. The improvement in $J_{sc}$ is indispensable for the efficiency improvement of tin-based perovskite solar cells.

**B. Photocarrier recombination and transport dynamics**

Time-resolved PL measurements enable a detailed investigation of operating mechanism of solar cells including photocurrent loss processes.\textsuperscript{152,153,156-160} Figure 7 summarizes the photocarrier density dependence of the PL lifetimes of the FA\textsubscript{0.75}MA\textsubscript{0.25}SnI\textsubscript{3} thin film (prepared using SnF\textsubscript{2}), the MAPbI\textsubscript{3} thin film, and the solar cell devices based on these films.\textsuperscript{153} In the MAPbI\textsubscript{3} thin film [Fig. 7(a); blue filled circles], the PL lifetime is long under weak excitation and becomes shorter for higher excitation fluences. This dependence can be explained by the bimolecular radiative recombination of free electrons and holes.\textsuperscript{153} The long lifetime under weak excitation indicates the low density of nonradiative recombination centers. On the other hand, the PL lifetime of the FA\textsubscript{0.75}MA\textsubscript{0.25}SnI\textsubscript{3} thin film [Fig. 7(b); blue filled circles] is extremely short and shows almost no reduction even under high excitation fluences. This indicates that the PL lifetime of the FA\textsubscript{0.75}MA\textsubscript{0.25}SnI\textsubscript{3} film is mainly determined by nonradiative recombination via a large number of defect states, probably originating from the formation of tin vacancies and/or the oxidation of Sn\textsuperscript{2+}. We note that the PL lifetime of tin perovskite films is further shortened by more than one order of magnitude if SnF\textsubscript{2} is not added to the precursor solution.\textsuperscript{154,162} The use of a stronger reducing agent that more effectively suppresses the vacancy formation and/or tin oxidation could lead to longer carrier lifetimes.

When the above perovskite layers are incorporated in solar cell devices, the PL lifetimes become much faster than that of the bare thin films [Figs. 7(a) and 7(b); red filled circles]. This is a result of the carrier extraction from the perovskite layer to the transport layers, which cause a faster reduction of the photocarrier density in the absorber layer.\textsuperscript{161,162} Note that the data shown with red in Fig. 7(a) are obtained for a regular mesoporous

![Fig. 6](image_url)
The fusion length in the FA device is dominated by the fast nonradiative bulk recombination in the interfaces under strong excitation conditions. This means that long-lived carriers are generated in the absorber layer and the Fermi-level shifts strongly. Such a prolonged carrier lifetime is observed for increased excitation fluences [Fig. 7(a)].

In Fig. 7(b), a similar tendency can be seen for the FA0.75MA0.25SnI3 solar cell, a significantly prolonged PL lifetime in the thin film [Fig. 7(d)]. Furthermore, the observed EQE is less than ηvat in about 20%, due to the dominant nonradiative recombination within the absorber layer and the large transmission loss (due to the thin absorber thickness) should be improved to obtain a better Voc.

Finally, the Voc losses are discussed. Even in the tin perovskite solar cell with the inverted architecture, the large Voc loss still exists [Eq. 9]. For example, it has been pointed out that the valence band maximum of the tin iodide perovskites is higher than the highest occupied molecular orbital (HOMO) of the existing hole transport materials, which prevents efficient carrier extraction. Other mechanisms may exist as well. For example, it has been reported that the high-efficiency MAPbI3 solar cells are extremely small, Voc measured = 0.88 eV, which approaches the detailed balance limit. Also, in the Pb–Sn mixed-type perovskites, relatively small Voc losses have been reported. One of the losses responsible for the drop from the detailed balance limit Voc limit is the loss through nonradiative recombination.

In the tin perovskite thin films, the PL quantum efficiency is only about 3%-10%, and the EQE of a LED device operated under a current density similar to that of solar cell operation is 0.72%. The corresponding nonradiative voltage loss can be calculated as [KT/q ⋅ ln(ηLED)] ḕ 0.13 eV for T = 300 K. Obviously, this is not enough to fully explain the observed Voc deficit. The additional loss, Voc limit − Voc measured = [KT/q ⋅ ln(ηLED)], is about 0.4 eV. This large value suggests that the influence from interface recombination is large, rather than bulk-like recombination. Other mechanisms may exist as well. For example, it has been pointed out that the valence band maximum of the tin iodide perovskites is higher than the highest occupied molecular orbital (HOMO) of the existing hole transport materials, which prevents efficient carrier extraction.

Energy levels for tin iodide perovskites and typical hole transport materials are compiled in Ref. 94. This data would suggest that hole transport materials with a higher HOMO level, such as PEDOT, could be beneficial for the Voc improvement. A more detailed discussion on the Voc losses may be achieved by using electroluminescence measurements.

V. SUMMARY AND OUTLOOK

This Perspective summarized the intrinsic optical properties and the energy loss mechanisms in tin halide perovskites by considering the steady-state optical spectra and the photocarrier dynamics. It was shown that the steady-state optical properties of tin halide perovskites are very similar to those of lead halide perovskites,
i.e., a PL with almost no Stokes shift, an efficient electron–phonon interaction, and a sharp Urbach tail were observed. However, from the viewpoint of the recombination kinetics of photocarriers, an increase of the carrier lifetime is essential for the improvement of the conversion efficiencies of tin-based perovskite solar cells. The relation between the carrier dynamics and the device properties was discussed to provide possible solutions for the low conversion efficiencies.

While the explanations in this Perspective laid emphasis on the solar cell operation, tin halide perovskites can also be considered as materials for various other optoelectronic devices, such as lasers, LEDs, and transistors. The intrinsic optical properties summarized in this work are essentially important for these optoelectronic applications.

At present, the PL quantum efficiencies of tin halide perovskites are still low due to the large number of nonradiative recombination centers. On the other hand, the steady-state PL data verified that they possess a high potential for application in optoelectronics. A better film quality through improvements in film deposition techniques or developments of other processing steps is essential for further progress. If the PL quantum efficiency and carrier lifetimes can be increased, tin halide perovskites can be considered as a powerful alternative to the lead-based perovskites.

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