Review—Light Emission from Thin Film Solar Cell Materials: An Emerging Infrared and Visible Light Emitter

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In the last decade, there have been extensive studies on fabrication and physics of thin-film solar cell materials and devices. Many high-efficiency solar cell devices have been developed, and the knowledge gained in these studies can be used advantageously to produce bright light-emitting devices. In this review, we summarize recent luminescence spectroscopic studies on new solar-cell materials and discuss their photocarrier dynamics with respect to efficient light emission.

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Manuscript submitted July 27, 2017; revised manuscript received September 12, 2017. Published September 28, 2017. This paper is part of the JSS Focus Issue on Visible and Infrared Phosphor Research and Applications.

This special issue focuses on fundamental researches and applications for light emitters and phosphors in the infrared and visible spectral region. Here, we would like to introduce novel approaches, applying insights from thin-film solar-cell materials to the development of new light emitting materials. Recent progress in fundamental research on solar cells is remarkable as novel materials such as perovskite thin films, quantum dots, and colloidal nanocrystals being applied to fabrication of solar cells. Huge efforts in this fundamental research area lead to conversion efficiency improvements for many types of solar cells. There exist global demands and attention in establishments of affordable, flexible, lightweight and high conversion-efficiency devices.

The prerequisite as a light absorber for high-efficiency thin-film solar cells, is a direct band-gap semiconductor with large absorption coefficient and band-gap in the near infrared and visible spectral region. One of the best indicators of the intrinsic material quality of a semiconductor, which in turn directly determines the carrier loss in a device, is the internal luminescence quantum efficiency. Therefore, highly luminescent semiconductors are excellent light absorber materials for solar cells and allow for high open-circuit voltages. Reversely, excellent solar-cell light absorber materials could be excellent light-emitting materials. In fact, the electroluminescence (EL) measurement is a well-established and widely-used technique for characterizing solar cell devices. Furthermore, time-resolved photoluminescence (PL) spectroscopy based on modern laser techniques have revealed the charge carrier flow in bulk materials as well as in devices. PL and EL spectroscopy techniques are not limited to material characterization, but are also able to characterize devices. Taking account of these close relations, utilizing insights and understandings obtained from solar cell research is strategic for developments in novel luminescent materials and devices in the near infrared and visible spectral region.

In this short review, we briefly summarize luminescence properties for light emitters and discuss their photocarrier dynamics with respect to efficient light emission.

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Thin Film Solar Cell Materials and Luminescence Efficiency

First, we provide a brief introduction of the requirements for a solar cell with high conversion efficiency. The work by Shockley and Queisser in the year 1961 quantitatively discussed which semiconductors are suited light-absorber materials for high-performance solar cells. It was shown that for electric power generation through direct conversion of the white-light spectrum from the sun, an optimum bandgap energy \( E_g \) exists, which determines the absorption characteristics. From thermodynamic considerations, they derived a theoretical upper limit of slightly above 30% for the power conversion efficiency that can be obtained with a semiconductor providing an \( E_g \) of about 1.3 eV. This efficiency is an important reference value for actual devices, and is called Shockley–Queisser (SQ) limit.

The SQ limit can be reached if the internal luminescence efficiency of the light-absorbing semiconductor is 100%. The luminescence efficiency of the chosen semiconductor is directly linked to the solar cell efficiency. A good example is GaAs, which has been also used as light emitter in laser diodes. The high crystal quality of GaAs enabled fabrication of solar cells with 28.8% conversion efficiency, which is the highest efficiency that has been reached so far for single-junction solar cells and close to the theoretical SQ limit. However, excellent luminescence materials like GaAs are rare, and in almost all semiconductors the nonradiative recombination is dominant at room temperature, which means a lower luminescence efficiency and thus also an unavoidable drop in the solar cell conversion efficiency.

Recent theoretical calculations show that the solar cell conversion efficiency increases drastically in the vicinity of 100% luminescence efficiency. It has to be pointed out that this drastic increase is a result of the reabsorption of band-edge luminescence inside the material. Owing to the radiative recombination of carriers inside the crystal and following partial reabsorption due to overlapping emission and absorption spectra, the carrier generation is improved. Consequently, the absorption spectrum near the band edge is as important as the internal luminescence efficiency. If there exist a significant amount of localized states within the bandgap or a large band tail, the open-circuit voltage decreases and the conversion efficiency of the solar cell drops significantly. Semiconductors that have no states within the bandgap and provide a high luminescence efficiency enable ideal solar cells and are also appropriate for light-emitting diodes (LEDs). Here, note that many phosphors with luminescence centers such as transient-metal and rare-earth ions, show strong luminescence, but large Stokes shifts are observed. This characteristic is strongly different from those of materials usually used as light absorbers in solar cells. Phosphors that allow for wavelength conversion and other photon manipulation would be also very useful for solar cell technology. The knowledge about solar cell materials can be applied to the development of light emitters, and vice versa.
For cost-effective solar cells, only the semiconductor materials that provide a bandgap energy in the near-infrared and have a high-efficiency band-to-band luminescence can be used. Besides the commonly used semiconductors like Si, GaAs, and CdTe, the multi-ternary compounds are considered to be advantageous for thin-film solar cells. Promising representatives are CuIn_{1-x}Ga_xSe_2 (CIGS), Cu_2ZnSn(S,Se)_{1-x}I_x (CZTSSe), and CH_3NH_3PbI_3. These semiconductors exhibit direct band transitions, provide large absorption coefficients, and can be easily fabricated as a large-area polycrystalline structure on glass substrates. Furthermore, the chalcopyrite, kesterite, and perovskite structures, which are different from the 4-fold coordinated sp^3-hybrid structure, can be obtained by choosing an appropriate combination of the many possible constituting elements. The deep understanding of their optical properties is expected to support the development of new light-emitting materials.

**Multi-Ternary Semiconductors: CuIn_{1-x}Ga_xSe_2 (CIGS) and Cu_2ZnSn(S,Se)_{1-x}I_x (CZTSSe)**

In July 2017, the world record conversion efficiency for CIGS thin-film solar cells was 22.6%.\(^1,2^9\) It is interesting that this high efficiency was achieved with a polycrystalline CIGS absorber layer, because it is difficult to fabricate CIGS single crystals with low defect densities. A material that shows excellent photovoltaic properties even in polycrystalline thin films is very valuable for engineering purposes.\(^46-52\)

Moreover, CZTSSe is a multi-ternary semiconductor that contains no rare metals and no toxic heavy metals. However, compared to the CIGS solar cells, the CZTSSe solar cells’ efficiencies are drastically lower.\(^1\) Unfortunately, defects are formed easily within the bandgap of CZTSSe.\(^32\) Even in CZTSSe single crystals, a large band tail exists.\(^53\)

The detailed comparison between the fundamental optical properties of CZTSSe and CIGS is important for the practical implementation in polycrystalline thin film devices. We employed laser spectroscopy and investigated the various aspects of photocarrier dynamics in CIGS thin films and CZTSSe single crystals.

Figure 1a shows the optical absorption (blue curve) and PL spectra (red curve) of a CIGS thin film at room temperature.\(^2^3\) Two gentle step structures can be observed in the absorption spectrum, which reflect the band structure.\(^2^4-5^6\) To quantitatively assign the observed absorption structures, the first-order derivative of the absorption spectrum is shown in the top panel. Two peaks can be clearly observed at approximately 1.32 and 1.57 eV. The band structure obtained from first-principle calculations\(^5^7-5^9\) is illustrated in Figure 1b. The observed peaks are attributed to the onset of the absorption due to the allowed optical transitions from the v1 and v3 bands to the c1 band. The bandgap energy of CIGS depends on the Ga content, and was 1.32 eV for this sample.

Figure 1b shows that the PL spectrum of the CIGS thin film depends strongly on the laser excitation fluence.\(^5^4\) The PL spectra were obtained at room temperature, and for excitation we used a 300-fs pulsed laser with a photon energy of 1.75 eV. Under low excitation fluences, the PL is located about 0.3 eV below the bandgap energy, which is mainly attributed to the PL from the donor-acceptor (DA) band.\(^6^0,6^1\) By increasing the excitation fluence, a new PL peak emerges near the band edge, and under the highest excitation fluence a sharp high-energy PL peak becomes dominant. This latter PL peak is from the band edge, and exhibits a smaller spectral width due to stimulated emission. The above interpretation is supported by the time-resolved PL spectrum shown in Figure 2b. Even for low excitation fluences, a fast PL contribution comes from the band edge, followed by a slow PL signal from the localized states in the low energy region. This temporal change is due to the successive relaxation of carriers from the band edge to the localized states. The observation of the band-to-band PL indicates that the localized states in the polycrystalline CIGS thin film have only a low density. This is one of the reasons why CIGS has a high photovoltaic conversion efficiency.

By combining the time-resolved PL spectroscopy with transient absorption (TA) measurements, we were able to obtain the time constants for the various relaxation processes in the polycrystalline CIGS thin film, as illustrated in Figure 3.\(^5^4\) In the TA measurements, the probe light was tuned to the bandgap energy to investigate the dynamics of the relaxation of the carriers located at the band edge. From the decay time constants of each PL peak, we determined time constants of 10 and 0.1 ns for the DA band transition and band-to-band recombination processes, respectively. Based on the comparison of the PL rise time and the TA dynamics, we obtained a relatively fast time constant of about 10 ps for the trapping from the band to the localized states.

Although this material has such a fast relaxation from the band to the localized defect states, the TA revealed that the band-to-band relaxation is slow, and the electrons in the conduction band have a long lifetime on the order of nanoseconds.\(^5^4\) By employing broadband TA spectroscopy and by considering the band structure of CIGS (Figure 1b), we clarified that both the free electrons and holes have lifetimes of a few nanoseconds in their respective bands.\(^5^4 \text{ Such long lifetimes are possible due to the thermal activation of carriers that have been trapped in the shallow localized defect states. The long lifetime of electrons and holes enables a long diffusion, which is the reason why CIGS can be used in solar cells.\(^5^4\) For CIGS multi-ternary semiconductors, we clarified that long-lived electrons and holes exist in the bands and the localized states within the bandgap and the band edge fluctuation determine their optical responses.\(^5^4\) In the following, we investigate the influence
of localized states on the optical properties in CZTSSe single crystals. Figure 4a shows the PL and PL excitation (PLE) spectra for four samples with different S contents.62 The PL spectra can be fitted with a Gaussian function (Figure 4a; black broken curves), and the peak energy and spectral width are shown in the top and center panels in Figure 4b, respectively. We found that the PL peak energy and width increase for a larger S content. The PLE spectrum near the band edge in Figure 4a reflects the optical absorption coefficient. The gradually increasing curve in the low energy region evidences that many localized states exist within the bandgap. For higher photon energies above the bandgap energy, however, almost all photons are absorbed near the surface. Therefore, the decrease in the PLE intensity for higher energies means that nonradiative recombination centers exist near the surface.

The PLE curve in the energy region below the band edge can be expressed with the bandgap energy \( E_g \) and the tail width \( \gamma \). In the electrostatic potential fluctuation model, the absorption coefficient \( \alpha \) is a function of \( E_g \) and \( \gamma \), and the calculation result for \( \alpha \) is shown with the red broken curves in Figure 4a. The parameter \( \gamma \) and the Stokes shift are plotted in the lower panel of Figure 4b. Similar to the bandgap energy (top panel in Figure 4b) and PL width, the Stokes shift and the width of the absorption tail \( \gamma \) increase with higher S content. If the S dependence of the PL properties would be due to potential fluctuations as a result of alloy disorder (compositional disorder), \( \gamma \) should have its maximum at \( x = 0.5 \), which is not the case. However, if we assume that \( \gamma \) is determined by the fluctuation of charged defects, this experimental result would mean that the charged defects increase continuously with the S concentration. Therefore, the efforts to fabricate a wide-gap CZTSSe material with a higher S content cannot result in a large open-circuit voltage, which is one of the reasons why the CZTSSe solar cell efficiency is still low. Also from the viewpoint of the light-emitting materials, the high density of defects within the bandgap and the large Stokes shift suggest that an improvement in the luminescence efficiency with a higher S content cannot be expected.

The above discussion concluded that the defect density in CZTSe is smaller than that in CZTS. This is supported by the excitation fluence dependence of the CZTSSe\(_{1-x}\) PL spectra shown in Figure 5.62,66 In Figure 5a for the CZTSe (\( x = 0 \)) sample, a new peak becomes dominant at high excitation fluences, which is assigned to the PL from the band edge. The PLE and PL spectra for CZTSe show that the fluctuation of the band edge due to spatial electric fields is small (see Figure 4). For the CZTS sample (\( x = 1 \)) in Figure 5b, no peak is visible near the band edge even at high excitation fluences. This can be explained with a high density of localized states, and therefore a large Stokes shift is observed. The low PL energy is equivalent with a low chemical potential and thus a large voltage drop occurs, which is the reason why the CZTS solar cell’s efficiency is not increasing. On the other hand, the bandgap energy of CZTSe is well below the ideal value, which results in an impracticable low open-circuit voltage. As has been explained for the CIGS sample above, CZTSe emits PL from the band edge and contains only relatively few defects within the bandgap, and therefore is a good candidate for light emitters.

Figure 4. (a) Normalized PL (solid red curves) and PLE (solid blue curves) spectra of CZTSSe\(_{1-x}\) single crystals with different S contents (\( x = 0, 0.5, 0.8, \) and 1.0) obtained under weak photoexcitation. Excitation energies were 1.6 eV for \( x = 0, 0.5, 0.8 \) and 1.65 eV for \( x = 1 \). (b) Band-gap energy \( E_g \) (red circles), PL peak energy (blue circles), PL spectral width (cyan circles), Stokes shift (black triangles), and the average amplitude \( \gamma \) of the potential fluctuation (red triangles) as a function of the S concentration. Panels (a) and (b) adapted with permission from Ref. 62, American Physical Society.
The temperature dependence of the CIGS and CZTS PL decay times shown in Figure 6 evidences that the defects in CZTS are deeper than those in CIGS. Here, the effective carrier lifetime (nonexponential PL decays) is plotted as a function of the temperature. This temperature dependence provides the average activation energy of the localized states or the band tail states. It can be clearly seen that the localized states in CZTS (112 meV) are deeper than that in CIGS (33 meV).

The band-edge modulation due to charged defects is illustrated in Figure 7a. The reason why the carriers in CIGS have a relatively long lifetime is not due to a band-edge fluctuation induced by composition inhomogeneities, but due to a spatial separation of electrons and holes. This type of band-edge modulation also influences the intraband relaxation of hot carriers, as evidenced with the relaxation time constants in Figures 7b and 7c obtained from TA experiments. For CIGS (Figure 7b) the intraband-relaxation time constant is on the order of 0.5 to 1 ps, which is slow compared to that of the standard covalent semiconductors like GaAs. A similar slow relaxation was also observed for the CZTS single crystal (Figure 7c). We consider that the origin of the slow intraband relaxation is the existence of ionized defects, which are characteristic for CIGS and CZTS. By enhancing the lifetime of hot carriers, it should be possible to improve the charge separation efficiency because the excess energy can be exploited. If the electrons and holes are spatially separated through potential fluctuations, the recombination rate will be reduced. This is a disadvantage for light emitter applications. Although this separation reduces the usability for light emitters under weak excitation, it enables an excellent material for photocurrent (PC) generation. However, we note that under strong excitation, as is the case for LEDs with comparable dense carrier injection, an emission from the band edge occurs (Figure 2a). Consequently, the CIGS on top of a flexible substrate can be used for large-area elastic displays. The optimal elemental composition and doping for light emitters has to be found in future studies.

From the above discussion, we understand that it is extremely important to reduce the defect density within the bandgap region of the CIGS and CZTS materials. One possible approach is the alkali ion doping. Figure 8 shows that the CZTS material properties improve through Na ion doping. The strong drop in the PLE intensity for high-energy excitation of the undoped CZTS single crystal in Figure 8a (blue data) evidences that defects are formed near the surface, which reduces the photocarrier generation efficiency. The red data in Figure 8a indicates that the surface-related recombination centers are reduced by Na doping, which suggests that also the PC increases. However, the PL temperature dependence in Figures 8b and 8c reveals that even in the Na doped sample the improvement of lifetime and PL intensity is marginal. The large temperature dependence means that nonradiative recombination is dominant in CZTS. This indicates that compared to CIGS, a significant larger band tail or many localized states exist inside the CZTS sample.

### Organic-Inorganic Hybrid Perovskite: CH₃NH₃PbI₃

Since the first report of the all-solid-state perovskite solar cell in 2012, the halide lead perovskite AMX₃ [A = CH₃NH₃⁺ (MA⁺), CH₃NH₃PbI₃, CH₃NH₃PbBr₃, and CH₃NH₃PbIBr₃] became a highly anticipated novel solar cell material. A very active research community enabled a significant increase in the conversion efficiency and durability of the halide lead perovskite solar cells. By exchanging the halogen element (X), the bandgap energy can be tuned over a wide range, and by controlling the A site cation the durability can be improved dramatically. The halide lead perovskite is a good example for a material that has been originally developed for application in solar cells due to its appropriate band-edge properties, and recently started to receive much attention for use as a light-emitting material. Here we will pick up the organic-inorganic hybrid perovskites that have been investigated most intensively, i.e., CH₃NH₃PbI₃ and CH₃NH₃PbBr₃, and discuss their optical properties.

When a new semiconductor material is considered for applications, the assessment of its bandgap energy is the most important task. The accurate assessment from a single measurement often turns out to be difficult, and therefore a combination of several techniques is more reliable. We employed several techniques to characterize the CH₃NH₃PbI₃ thin film that is used in solar cell device structures. The experimental results of the PC, diffuse reflectance (DR), PL, PLE and TA spectroscopy are shown in Figure 9. By considering all spectra, we found that CH₃NH₃PbI₃ is a direct bandgap semiconductor and determined a room-temperature bandgap energy of 1.61 eV. We already mentioned that the fluctuation of the band edge and localized states limit the solar cell power conversion and luminescence efficiency. Interestingly, despite the simple fabrication of perovskites via solution
processing, the densities of impurities and defects are surprisingly low, and therefore a high luminescence efficiency can be reached. The low density of nonradiative recombination centers is reflected in the sharp onset of the absorption spectra.86

Figure 10 plots the PL spectra obtained at room temperature under resonant excitation for (a) CH$_3$NH$_3$PbI$_3$ and (b) lead-free CH$_3$NH$_3$SnI$_3$, i.e., the excitation laser energy is tuned to energies within the emission band, and with this data the PL origin can be discussed.83,87 We find that the PL spectral shape is very broad but independent of the excitation energy. The extremely strong anti-Stokes PL that occurs under low-energy excitation conditions suggests a strong electron-phonon interaction in both CH$_3$NH$_3$PbI$_3$ and

![Figure 7](image-url)

**Figure 7.** (a) Schematic band-edge structure of a multi-ternary compound semiconductor with electrostatic potential fluctuations. Rise time of the TA signal as a function of the excess energy in (b) a CIGS thin film and (c) a CZTSSe single crystal. Data taken from Refs. 54 and 68.

![Figure 8](image-url)

**Figure 8.** (a) PLE spectra for undoped (blue) and Na-doped (red) CZTS single crystals at room temperature. (b) PL decay dynamics for undoped (blue) and Na-doped (red) CZTS single crystals at different temperatures obtained under weak photoexcitation with 2.1 eV. The dashed lines are fits using a triple exponential function. (c) Steady-state PL spectra of undoped (blue) and Na-doped (red) CZTS single crystals measured between 12 K and 270 K. Panel (a) adapted with permission from Ref. 78, Japan Society of Applied Physics.
CH$_3$NH$_3$SnI$_3$ samples. Although the both spectra are very broad, we conclude that the PL width is intrinsic. In addition, the temperature dependence of the PL spectrum also reveals a strong coupling of electrons with phonons in CH$_3$NH$_3$PbI$_3$ perovskites. The PL efficiency of CH$_3$NH$_3$PbI$_3$ is extremely high compared to that of CH$_3$NH$_3$SnI$_3$. The organic-inorganic hybrid CH$_3$NH$_3$PbI$_3$ perovskite has high PL efficiency and no PL Stokes shift, which enable a high open-circuit voltage.

In contrary to the excitonic PL from organic molecules, the PL from this organic-inorganic hybrid material is due to a band-to-band recombination between free electrons in the conduction band and free holes in the valence band. The PL dynamics from a CH$_3$NH$_3$PbI$_3$ thin film at room temperature are shown in Figure 11. The power dependence in Figure 11a shows that the PL lifetime strongly depends on the excitation power. The experimentally obtained PL intensities and lifetimes are summarized in Figure 11b. The characteristic power dependence of the PL intensity and lifetime can be explained well with a rate equation system that considers the bimolecular radiative recombination and single carrier trapping (electrons in the present case). From the fitting we obtained an overall density of $10^{15}$ cm$^{-3}$ for the traps, defects and other non-radiative recombination centers. This value is extremely low, which explains the observed high luminescence efficiencies. Furthermore, from the shape of the absorption spectrum in the vicinity of the band edge, we determined an exciton binding energy of less than 10 meV at room temperature. These results support the conclusion that the PL dynamics in CH$_3$NH$_3$PbI$_3$ are governed by free carriers, rather than by the bound electron-hole pairs. Magneto-optic experiments also support the above conclusions.

The important reasons why the perovskite CH$_3$NH$_3$PbI$_3$ is an excellent material for solar cells are the low defect densities and long-lived free carriers. For practical applications, it is interesting to note that the radiative recombination rate of CH$_3$NH$_3$PbI$_3$ is comparable with that of GaAs. The sharp absorption edge and the high luminescence yield make the perovskite valuable materials for various light-emission applications.
device structures where the perovskite layer is sandwiched between the electron- and hole-transport layers. Since the photocarrier generation and light emission efficiencies depend on many processes,112,123 the most suited device design remains a critical issue for these emerging materials.

Conclusions

The light absorber materials used in high-efficiency thin-film solar cells provide strong luminescence even at room temperature. The perovskite materials and CIGS are highly anticipated as light emitters in the near-infrared and visible spectral region, because they provide useful characteristics such as efficient luminescence even if grain structures are present, and have a low formation probability of nonradiative recombination centers at the surface. They also exhibit material properties which were not available with the commonly used covalent semiconductors like GaAs and Si. The design of devices that take advantage of these properties is necessary. New strategies like the doping of these materials with luminescent centers are expected to lead to a significant progress in light emitter technology.

Acknowledgments

The content of this publication is a result of collaborations with many colleagues. We thank all contributors for their participation, in particular, H. Akiyama, K. Akimoto, S. Niki, A. Nagaoka, K. Yoshino, A. Wakamiya, T. Yamada, and T. Handa. This work was supported by CREST, JST (grant No. JPMJCR16N3), CREST, JST (Photovoltaics: 2011–2016), and The Sumitomo Electric Industries Group CSR Foundation.

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Figure 12. Transmission and PLE spectra (top) and one-photon excited PL (1-PL) and two-photon excited PL (2-PL) spectra (bottom) for CH3NH3PbBr3 single crystal. Figure adapted with permission from Ref. 97, Wiley-VCH.
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