Spectral-based analysis of thin film luminescent solar concentrators

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Abstract

We present a method to evaluate the parameters defining the efficiency of luminescent solar concentrators (LSCs). The light harvesting and self-absorption properties of thin film LSCs on glass substrates are determined by optical spectroscopy and the resulting optical efficiency is consistent with the directly measured photon flux gain.

Keywords: Lumogen F red 305, fluorescence, LSC, self-absorption

1. Introduction

The basic idea behind luminescent solar concentrators (LSCs) is to concentrate sunlight with an inexpensive polymer-based device (typically polymethylmethacrylate PMMA) onto efficient photovoltaic cells and thus reduce the price of solar electricity – a concept that can be traced back to the 1970s (Weber and Lambe, 1976; Goetzberger and Greubel, 1977; Goetzberger, 1978; Batchelder et al., 1979, 1981; Zewail and Batchelder, 1983). Light incident onto the face of the LSC plate is absorbed by a luminescent species dispersed within the plate and subsequently re-emitted at longer wavelength. With the refractive index of the plate being higher than that of the surrounding medium (typically air), a large part of the emitted photons is trapped in the plate by total internal reflection and waveguided toward the edges (Fig. 1). LSCs can be used under diffuse light and tracking of the sun is not required.

There is currently a renewed interest in this technology due to the availability of advanced materials (Ziessel et al., 2005; Currie et al., 2008; Mulder et al., 2009; Br"uhwiler et al., 2009; Earp et al., 2004) and sophisticated models to simulate the photon transport (Goldschmidt et al., 2008, 2009). Major obstacles to be overcome are: limited stability of the luminescent species, high self-absorption, and poor knowledge of the parameters governing the efficiency

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(Rowan et al., 2008). The lack of standard methods to quantify those parameters is a significant limitation in LSC development. Within this work we demonstrate a simple method that allows rapid assessment of LSC efficiency.

The capability of a LSC to concentrate light depends on the geometry of the plate, i.e., the ratio between the top (actual area covered with dye-doped polymer film, \( A_{\text{top}} \)) and the edge surface area (\( A_{\text{edge}} \)). Thus, the photon flux gain \( \Phi_{\text{opt}} \) is defined (Reisfeld and Jorgensen, 1982; Reisfeld et al., 1994; Reisfeld, 2002):

\[
\Phi_{\text{opt}} = \frac{A_{\text{top}}}{A_{\text{edge}}} \cdot \eta_{\text{opt}} \cdot \frac{\eta_{\text{PV}}(\lambda)}{\eta_{\text{PV}}(\text{solar})},
\]

(1)

where \( \eta_{\text{opt}} \) is the optical efficiency and \( \eta_{\text{PV}} \) is the efficiency of the photovoltaic cell at the emission wavelength of the LSC or under illumination with the full solar spectrum (excitation light source), respectively.

The optical efficiency \( \eta_{\text{opt}} \) is the energy output at the edges of the plate divided by the energy incident on the plate. The main processes involved are: (i) absorption of the incident light, (ii) re-emission of the absorbed photons, and (iii) photon transport to the plate’s edges. This corresponds to the product (Reisfeld and Jorgensen, 1982; Reisfeld et al., 1994; Reisfeld, 2002; Thomas et al., 1983; Zastrow, 1994):

\[
\eta_{\text{opt}} = \eta_{\text{LHE}} \eta_{\text{SA}} \eta_{\text{yield}} \eta_{\text{Stokes}} \eta_{\text{trap}} \eta_{\text{mat}} (1 - R),
\]

(2)

including the light harvesting efficiency (\( \eta_{\text{LHE}} \)), the self-absorption (\( \eta_{\text{SA}} \)), the luminescence quantum yield of the dye (\( \eta_{\text{yield}} \)), and the Stokes efficiency (\( \eta_{\text{Stokes}} \)), which is the ratio between the maxima of emission and absorption (in wavenumbers). The parameter \( \eta_{\text{trap}} \) represents the trapping efficiency defined by the refractive index of the matrix, \( \eta_{\text{mat}} \) comprises photon transport losses, such as scattering and parasitic absorption by matrix defects, and \( R \) is the Fresnel reflection coefficient of the LSC surface.

As a model system we employ thin film LSCs, where the photoactive component is dispersed in a PMMA layer on top of a transparent glass support (Reisfeld and Jorgensen, 1982; Reisfeld et al., 1994; Reisfeld, 2002). The perylene dye Lumogen F Red 305 (hereafter referred to as Red 305) is well suited for application in LSCs, as the absorption covers a large part of the visible range (Slooff et al., 2007; Kinderman et al., 2007; Slooff et al., 2008; Meyer and Markvart, 2009). Furthermore, Red 305 features a near-unity luminescence quantum yield (\( \eta_{\text{yield}} = 1 \)) (Ahn et al., 2007; Wilson and Richards, 2009) and good intrinsic stability (Seybold and Wagenblast, 1989; van Sark et al., 2008). High concentrations of Red 305 in PMMA can be achieved without aggregation (Al-Kaysi et al., 2006).

2. Experiments

2.1. Preparation of LSCs

PMMA (Aldrich, MW 120k) and Red 305 (BASF, used as received) were separately dissolved in CHCl₃ (Scharlau, HPLC grade). The two solutions
were mixed prior to the deposition of the films. Microscopy slides (Menzel, 
\( n = 1.512 \)) were used as substrates, and cleaned with acetone and oxygen 
plasma (Diener electronics, FEMTO). Scotch tape (3M) was used as spacer to 
define the film thickness and the area to be covered by doctor blading. The 
actually covered areas (approx 76x20 mm\(^2\)) are relevant in order to estimate 
the photon flux gain. Thin films with an excellent homogeneity were obtained 
after evaporation of the solvent in ambient conditions. The samples were dried 
to remove the remaining solvent (80\(^{\circ}\) C for 30 min).

2.2. Characterization

Absorption and emission spectra were recorded with a UV-vis spectropho-
tometer (Varian Cary 3 Bio) and a luminescence spectrometer (Perkin Elmer 
LS 50B). A fiber optic spectrometer (Ocean Optics USB4000) with a cosine 
corrector was used to measure the edge emission at a short edge of the fully il-
minated samples. The area of the Si solar cell (Silonex) attached on one short 
edge of the LSCs was 25x1 mm\(^2\). An air gap between LSC and the solar cell 
represents equal outcoupling conditions for all edges of the LSC, while silicon 
grease (\( n = 1.407 \)) was used to improve the index matching between LSC and 
the solar cell. A xenon lamp (Lot-Oriel 200 W, water filter) in combination with 
a KG5 filter (Schott) acted as excitation source (Fig. 2b).

3. Results and Discussion

The absorption and emission spectra of Red 305 dissolved in ethanol are 
shown in Figure 2a. Maxima are observed at 576 nm and 614 nm, respectively. 
The absorption spectra of a series of LSCs are given in Figure 2b. The optical 
density depends on the number of tape layers used as thickness template for 
the polymer-dye solution casting. All spectra resemble the solution spectrum 
in Fig. 2a, confirming the absence of aggregation.

The light harvesting efficiency depends on the light source’s emission spec-
trum (\( S_{SO} \)) and on the absorption spectrum of the respective LSC. Therefore, \( \eta_{LHE} \) can be expressed as the fraction of absorbed incident photons of the avail-
able photon flux:

\[
\eta_{LHE} = \frac{\int_0^\infty S_{SO}(\lambda) [1 - 10^{-A(\lambda)}] d\lambda}{\int_0^\infty S_{SO}(\lambda) d\lambda}.
\]  

The term \( (1 - 10^{-A(\lambda)}) \) describes the photons absorbed by the dye, where \( A(\lambda) \) 
is the absorbance at a wavelength \( \lambda \). Figure 3a shows \( \eta_{LHE} \) as a function of 
peak absorbance \( A_{max} \) at \( \lambda = 576 \) nm and an exponential fit revealing:

\[
\eta_{LHE} = 0.68 - 0.59 \exp(-1.31 \cdot A_{max}).
\]  
The achievable maximum for \( \eta_{LHE} \) lies below one, as a large fraction of the 
incoming photons (640 - 800 nm) is not absorbed by the LSC (Fig. 2b).
As a consequence of the overlap of absorption and emission spectra (shaded area in Fig. 2a), significant self-absorption occurs, altering the spectral shape of the edge emission. An increasing red shift of the emission maximum is observed with increasing thickness of the dye-PMMA films (Fig. 2c). In order to calculate $\eta_{SA}$, the observed edge emission of the LSC under full illumination ($S_{\text{edge}}$) has to be scaled to match the true emission spectrum of a dilute solution of Red 305 ($S_{\text{true}}$) in the long wavelength region (680 - 750 nm), where no self-absorption occurs (Ahn et al., 2007; Kittidachachan et al., 2007). The scaled edge spectrum $S'_{\text{edge}}$ represents the 'surviving' light and $\eta_{SA}$ is:

$$\eta_{SA} = \frac{\int_0^\infty S'_{\text{edge}}(\lambda)d\lambda}{\int_0^\infty S_{\text{true}}(\lambda)d\lambda}. \quad (5)$$

The result is shown in Figure 3a and can be fitted exponentially similar to $\eta_{LHE}$:

$$\eta_{SA} = 0.34 + 0.55\exp(-4.5 \cdot A_{\text{max}}). \quad (6)$$

Extrapolation to low absorption reveals $\eta_{SA}$ smaller but reasonably close to one, which would correspond to the absence of self-absorption. On the other hand, the LSC emission cannot be eliminated by self-absorption, but reaches a minimum of 0.36, as the absorbance becomes negligible in the long wavelength part ($\lambda > 650$ nm).

With the spectral shape being independent of the dye concentration in the films, $\eta_{\text{yield}}$, $\eta_{\text{Stokes}}$, $\eta_{\text{trap}}$, $\eta_{\text{mat}}$, and $R$ can be assumed constant. $\eta_{\text{Stokes}} = 0.94$ was calculated from the absorption and emission maxima. The trapping efficiency $\eta_{\text{trap}}$ can be determined with:

$$\eta_{\text{trap}} = \sqrt{1 - \frac{1}{n^2}} \quad (7)$$

and reveals 0.75 for $n \approx 1.5$ (PMMA and glass). Assuming perfect photon transport ($\eta_{\text{mat}} = 1$) and a Fresnel reflection coefficient $R$ of 0.04 (for PMMA and glass), the optical efficiency, $\eta_{\text{opt}}$, of the LSCs can be estimated. Hence, Fig. 3b shows the theoretical limit of the efficiency depending on the absorbance.

These values can now be used to calculate the achievable photon flux. According to eq. (1), the effective surface area of the polymer films, the whole edge area of the microscopy slides, and the efficiency of the attached solar cell have to be included – for $\eta_{\text{PV}}(\lambda)/\eta_{\text{PV}}(\text{solar})$ a value of 1.5 is assumed. To experimentally determine the photon flux gain, the LSCs (short edge) were attached to the solar cell either exhibiting an air gap or with the use of silicon grease for improved index matching. The photocurrent under the same photon flux was measured by direct illumination of the solar cell. These measured gain values are shown in Fig. 4 as a function of the gain expected from the spectroscopic analysis.

In case of an air gap between solar cell and LSC, the sample system exhibits equivalent conditions for the photon outcoupling at all edges of the LSC. This situation resembles the spectral-based analysis and a linear fit to the data points.
reveals a slope of 0.9 (blue line in Fig. 4). The overestimation of the expected gain by the spectral-based analysis is most likely associated with photon transport losses in the substrate ($\eta_{\text{mat}}$) and potential non-unit fluorescence quantum yield. Additional deviations might originate from scattering (loss) of light at the non ideal edges of the glass plates and from the back reflection at the solar cell, leading to a reduction of the electrically measured gain. Connecting LSC and solar cell by silicon grease leads to a significant increase of the observed gain values and a steeper slope of 1.5 (green data points in Fig. 4). This can be easily understood, as the critical angle is changed from 41° to about 68° by the improved index matching, advisable for future device realizations.

4. Summary

In conclusion, thin film LSCs were characterized, demonstrating a good agreement between spectral and electrical analysis, and the parameters governing the efficiency could be addressed separately. As light harvesting and self-absorption exhibit opposing dependence on the absorbance, a further increase of overall efficiency calls for approaches that spectrally separate absorption and emission processes.

Acknowledgments

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References


Figure captions

Figure 1: Photograph and principle of operation of a LSC based on a thin dye-doped polymer film. Re-emitted light is guided toward the edges by total internal reflection (yellow arrows).

Figure 2: Optical spectra. (a) Absorption and emission (red, excitation at 520 nm) spectra of Red 305 in ethanol. (b) Absorbance of LSCs prepared with different numbers of template layers (film thickness). A xenon lamp was used as excitation light source. (c) Comparison between the true emission spectrum (Red 305 in solution) and the scaled edge emission spectra of the LSCs.

Figure 3: Efficiencies derived by spectroscopy. (a) Independently determined values for the light harvesting and self-absorption efficiency of the thin film LSCs. The solid lines correspond to exponential fits to the data. (b) Optical efficiency $\eta_{\text{opt}}$ as a function of the maximum absorbance of the LSCs.

Figure 4: Measured photon flux vs. optically estimated photon flux. The solar cell was attached to the LSCs either exhibiting an air gap or by using silicon grease for an improved index matching.
Figure 1

Glass with dye-doped PMMA layer

Incident light

PV cell

Glass with dye-doped PMMA layer
Absorbance\(\text{arb. units}\) dissolved in ethanol:
- absorbance
- emission

Absorbance (arb. units)

Intensity (arb. units) xenon lamp
dye in PMMA (7.9 g/l)
(template layers)
- 1
- 2
- 3
- 4

Absorbance

Wavelength (nm)

Scaled PL (arb. units)
dye in PMMA (7.9 g/l)
(template layers)
- true emission (in solution)
- 1
- 2
- 3
- 4

Wavelength (nm)
Figure 3

(a) \( \eta (\text{LHE}) \)
(b) \( \eta (\text{SA}) \)

Efficiency vs. Absorbance
Figure 4

Gain estimated by spectroscopy
Electrically measured gain

- Air filled gap
- Silicon grease