THEORETICAL STUDY OF MULTILAYER LUMINESCENT SOLAR CONCENTRATORS USING A MONTE CARLO APPROACH

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ABSTRACT: This work presents a theoretical study of luminescent solar concentrators (LSCs) based on a ray-tracing technique with a Monte Carlo approach. In particular, we focus on two systems: one in which the LSC is constituted of a slab and another in which the luminescent layer is sandwiched between two transparent layers. Our aim is to calculate the relation among the absorbed, re-emitted, and guided light as well as to calculate the generated photocurrent. The conversion efficiency is studied as a function of the LSC size and dye concentration. The combination of two or more kinds of dyes is discussed.

Keywords: Luminescent solar concentrator, photovoltaic, dye.

1 INTRODUCTION

One of the strategies to reduce costs of electrical power produced by solar cells is the use of solar concentrators, which collect sunlight over large areas and redirect it onto high-efficiency photovoltaic cells. This allows minimizing the amount of silicon whose cost is subject to highly volatile market. Solar concentrators usually make use of mobile mirrors able to track the sun. Another promising approach is the use of luminescent solar concentrator (LSC), in which the sunlight is absorbed by dyes dispersed in a waveguide and reemitted at lower frequencies into the guided modes of the structure. The Stokes shift between absorption and emission energies limits re-absorption and allows light to be collected by the solar cells located on the waveguide edges. Today, although the efficiency of LSC is typically of a few percent, we are witnessing a renewed interest in these devices, due to the possibility of reducing their costs by choosing new materials and geometries. A possible application for these devices could be as windows on buildings, because they generate electricity while a part of the visible spectrum pass through.

In this work we propose a theoretical study of a multi-layered LSC by means of a statistical approach. We start by defining the LSC geometry as a set of vectorial equations, describing the optical properties of each layer in terms of its refractive index as well as the absorption and emission spectra of the dyes embedded in the layer. We set the boundary condition by specifying whether photocells or mirrors are attached on the edges of the LSC or not. The main quantity that characterizes the LSC is its external conversion efficiency, which is the probability that a photon of energy E is converted in an electron-hole pair in the PV cells on the edges. This depends mainly on the photon collection probability, which can be calculated as the ratio between the photons collected on the LSC edges and those emitted by the dyes, provided a sufficiently large number of photons is considered. These are assumed to be emitted by the dyes randomly. As the dimension of each layer is typically larger than the wavelength, the optical path of each emitted photon can be calculated using ray optics arguments.

In this work we focus on the two structures shown in Figure 1: (a) a luminescent slab, and (b) a sandwich, in which the layer of thickness d containing the dyes (active

layer) is embedded in a waveguide of refractive index n_1 .

In particular, we compare the two structures, and we discuss the case in which the LSCs contain more than one kind of dye. Our aim is to determine the configuration that maximizes the conversion efficiency in terms of the structure geometrical parameters and the dye concentrations.





2 EFFICIENCY OF A SOLAR CONCENTRATOR

We define the LSC relative efficiency as

$$\eta_{rel} = \frac{J_{sc}(cell + LSC)}{J_{sc}(cell)},\tag{1}$$

where $J_{sc}(cell + LSC)$ is the short-circuit current generated by the photocells on the edges of the LSC, and $J_{sc}(cell)$ is that generated by the same photocell when directly illuminated. Thus, the LSC efficiency is

$$\eta = \eta_{cell} \cdot \eta_{re}$$

where η_{cell} cell is the efficiency of the bare photocell.

For a *photocell+LSC* system, the short-circuit current is

$$J_{sc} = e \int EQE(E) \ b_c(E) dE , \qquad (2)$$

where EQE(E) is the external quantum efficiency of the photocell considering an incident photon of energy E, *e* is the electron charge, and $b_c(E)$ is the flux of photons collected on the LSC edges.

The collected photon flux is given by

$$b_c(E) = P_c(E)b_e(E)$$
, (3)

where $b_e(E)$ is flux of photons emitted by the dyes, and $P_c(E)$ is probability of an emitted photons to be collected at the LSC edges. This fundamental quantity is computed using the Monte-Carlo approach presented in the next section.

In general, a LSC can contain more than one kind of dye in order to absorb the desired portion of the solar spectrum. If the dyes are embedded in the same layer the total emission flux $b_e(E)$ is given by the sum of the emission fluxes $b_{e,i}(E)$ associated to each dye type:

$$b_e(E) = \sum_{i=1}^n b_{e,i}(E),$$
 (4)

where *i* indicates the dye type, and the relation between the number of sun photons absorbed by the dye $N_{a,i}$, and that of emitted photons $N_{e,i}$ is

$$N_{e,i} = QE_i \cdot N_{a,i} = \int b_{e,i}(E) dE$$
(5)

where QE_i is the dye quantum efficiency.

The number of absorbed photons $N_{a,i}$ is given by

$$N_{a,i} = \int (1 - R(E)) P_{a,i}(E) b_s(E) dE$$
 (6)

where 1 - R(E) is the fraction of sun photons that pass through the LSC, and $P_{a,i}(E)$ is the absorption probability of the *i*-type dye, which depends on its concentration.

A fraction of the photons emitted by the dyes can be reabsorbed by other dyes due to the overlap between the absorption and emission spectra, and eventually, part of this re-absorbed light can be re-emitted. This re-emission effect is not included in the present calculations, and is left for future extensions. For this reason the short-circuit current calculated might result slightly underestimated.

3 THE COLLECTION PROBABILITY OF A LSC

To estimate the collection probability for a LSC, we use a technique based on arguments of geometrical optic and a Monte-Carlo approach. This approach consists in calculating a large number of the possible trajectories of light emitted within the layer containing the dyes. This is done including multiple reflections at the LSC surfaces (or interfaces if the LSC is a multilayer). At each interface, the trajectory is divided in two components: a reflected one and a transmitted one. The probability that a photon is reflected or transmitted is given by the Fresnel coefficients. The starting points are chosen randomly with a uniform spatial distribution, similarly, the initial direction is casual with an isotropic distribution.

Each trajectory is characterized by a certain amount of propagation losses. These are due to the following phenomena:

- i) **Absorption**. In each layer, the fraction of absorbed photons is given by $1 e^{-\alpha l}$, where α is the material absorption coefficient, and *l* is the length of the trajectory within that layer.
- Scattering. These losses are associated to multiple reflections at the LSC surfaces that are not covered by photocells or mirrors. Although for an ideally planar interface such losses are

null, in practice superficial roughness produces scattering. If *D* is the probability that a photon is scattered out of the LSC for a single collision. The total scattering probability is given by $(1 - D)^N$, where N is the number of collisions associated to the trajectory.

4 RESULTS

For this study we are considering two concentrators made of polymethyl-methacrylate (PMMA) of size $10 \text{ cm} \times 10 \text{ cm} \times 0.6 \text{ cm}$. In one case (slab) the dye is uniformly distributed in the entire LSC, in the other (sandwich) the emitting layer is 0.1 cm thick and located in the middle of the LSC (see Fig.1). Our goal is to compare these structures and to find the optimal dye concentration that maximizes the LSC efficiency in terms of the generated photocurrent.

The active layer is doped with two kinds of dyes whose absorption and reemission spectra are shown in Fig.2 along with the solar spectra and the EQE of typical silicon photovoltaic cell. These fluorophores have been chosen as they absorb light above 2eV and reemit it within a range [1.2eV, 3eV] in which Si solar cells are particularly efficient.



Figure 2: Absorption and emission spectra for A-dye and B-dye. Are also shown the solar spectrum and the quantum efficiency of a silicon photocell.

First we study the case in which only one dye type, either A-dye or B-dye, is embedded in the slab structures. In Fig.3 we show the calculated photon flux of the photons absorbed by the dyes (dashed line) and those reemitted and collected on the LSC edges (solid line). As is expected, the number of absorbed photons increases monotonically with the dye concentration and saturates at large concentrations. On the contrary, there exists an optimal dye concentration that maximizes the number of photons collected by the photocells on the LSC edges. Such a value is given by a trade-off between the number of absorbed sun photons and the absorption losses, which are due to the overlap between the absorption and emission spectra and increase with the dye concentration. For the slab, we found that the optimum concentrations are between 500-50000 ppmm for A-dye and between 100-200 ppmm for B-dye.



Figure 3:Photon flux: (i) absorbed from the sun, and (ii) collected on the edge, for two slabs of $10cm \times 10cm \times 0.6cm$; one doped with A-dye and another with B-dye.

A similar study has been done for the sandwich structure. A comparison between slab and sandwich is shown in Fig. 4 in the case of the A-type dye. The two curves are identical, but that of the sandwich is shifted at higher dye concentrations. The optimum concentration for the sandwich is around 1000 ppmm, and the exact maximum is obtained for a concentration that is exactly 6 times that required by the slab. In other words, in both cases the maximum number of collected photons depends only on the number of dyes embedded in the LSC, regardless whether uniformly distributed in the entire LSC or concentrated in a thinner layer. For this reason, we will show the results for the sole slab, as the same can be found at different concentration for the sandwich case.

A reason to use a LSC is to replace expensive photovoltaic materials (like silicon) over large areas. But the operating modes of them are different: a photovoltaic system converts (depending of QE of the photovoltaic material) the absorbed light over all its surface, whereas LSC converts only the light that is collected at its edges, where the photocells are located. Absorption and scattering losses set a limit to the maximum distance along with light can propagate, and this set an intrinsic limit to the maximum dimension over which a LSC is convenient. In Fig. 5 we report a study of the LSC efficiency as a function of the lateral dimension of the slab along with the number of absorbed and collected photons. We can see that the number of absorbed photons is increased when the LSC becomes larger. On the other hand, the efficiency decreases, as the reemitted light far from the edges is reabsorbed or lost by scattering without reaching the photocells. It is worth noticing that a more systematic study that we carried out as a function of both dye concentration and LSC lateral dimension has shown that the optimal concentration is nearly independent of the LSC size. This gives the advantage of studying small systems, which are easy to handle and characterize, to obtain the information to design larger LSC.

An advantage of combined dyes is the possibility of extending the portion of solar spectrum that can be converted. This required a careful search of the proper dyes that have to be able to work together without increasing the overall absorption losses of the system due to undesired overlaps between emission and absorption spectra of different dyes. For this reason, usually, different dyes are spatially separated in multi-layered structures. Nevertheless, here we want to study also the case in which two kinds of dyes coexist in the same active layer, as this structure might offer advantages in terms of costs and fabrication.



Figure 4: The absolute and relative efficiencies versus the B-dye concentration for the slab (orange) and a sandwich (blue).



Figure 5: Absorbed and collected photons (left scale), and corresponding efficiency (right scale) as function of the slab dimensions.

In Fig.6 we show the number of collected photons as a function of the concentration of both dye-A and dye-B. The graph shows a large plateau area in which the number of collected photons is nearly constant and close to the maximum value. It is also evident that, at least for the dye considered here, we do not observe a clear benefit with the combination of more than one dye. As the photon-electron conversion depends on the quantum efficiency of the photocell QE(E) (see the QE spectrum in figure 1), which is a quantity that depends on the energy of the collected photons, the sole number of photons that reaches the photocells is, in general, not sufficient to quantify the LSC efficiency. For this reason we calculate the photo-generated current and the corresponding LSC efficiency, which is shown in Fig.7. Here we consider silicon photocells (covering the whole lateral surface) that generate a short circuit photocurrent $J_{sc} = 35mA/cm^2$ under standard conditions (i.e. an irradiance of 100mW/cm2). We observe that the highest conversion efficiency is given in the presence of the sole B-dye with concentration between 100 and 200ppmm.

It is worth noticing that these results are strongly dependent upon the choice of our dyes. The main goal has been to derive the photocurrent and the conversion efficiency in the presence of several kinds of dyes. This has been partly accomplished, but effects related to the cross-re-emission deserve further investigation.



Figure 6: The collected photons on the slab edges, as function of the A-dye and B-dye concentration.



Figure 7: Absolute efficiency depending of the A-dye and B-dye concentrations for the slab.

5 CONCLUSIONS

In this work we have presented a systematic study of multilayered LSCs. In particular we focused on two configurations, namely slab and sandwich. This study has been carried on using a method that combines optical ray-tracing with a statistical approach (Monte-Carlo).

When one dye type is embedded in the concentrators, we found that the maximum conversion efficiencies for the slab and sandwich are identical, though they are obtained for different dye concentrations. We conclude that the efficiency does not depend on whether the dyes are dissolved everywhere in the slab or only in a thinner layer, rather it is simply proportional to the total number of emitters.

We have also studied the case in which two types of dyes are embedded in the same active layer. We showed that avoiding a large spectral overlap between absorption and emission spectra is essential to observe any benefit from the combination of two or more dyes.

6 REFERENCES

 M. Bendig, J. Hanika, H.Dammertz, J. C. Goldschmidt, M. Peters, M. Weber, "Simulation of fluorescent concentrators", Interactive Ray Tracing, 2008. RT 2008. IEEE Symposium on, pp. 93 – 98, ISBN: 978-1-4244-2741-3.

- [2] J. C. Goldschmidt, M. Peters, A. Bösch, H. Helmers, F. Dimroth, S. W. Glunz, G. Willeke, "Increasing the efficiency of fluorescent concentrator systems", Solar Energy Materials & Solar Cells 93, 176–182 (2009).
- [3] M. Kennedy, M. Dunne, S. J. McCormack, J. Doran, and B. Norton, "Multiple dye luminescent solar concentrators and comparison with Monte-Carlo ray tracing prediction", 23rd European Photovoltaic Solar Energy Conference, 1-5 September 2008, Valencia, Spain, pp. 390-393.
- [4] M. Kennedy, A. J. Chatten, D. J. Farrell, R. Bose, A. Büchtemann, S. J. McCormack, J. Doran, K. W. J. Barnham, and B. Norton, "Thermodynamic modelling and ray-trace modelling of luminescent solar concentrators: A comparison of the two approaches", Proceedings of the 23rd European Photovoltaic Solar Energy Conference and Exhibition, Sept 2008, Valencia, Spain.
- [5] W. Van Sark, K. Barnham, L. Slooff, A. Chatten, A. B,chtemann, A. Meyer, S. Mc.Cormack, R. Koole, D. Farrell, R. Bose, E. Bende, A. Burgers, T. Budel, J. Quilitz, M. Kennedy, T. Meyer, S. Wadman, G. van Klink, G. van Koten, A. Meijerink, and D. Vanmaekelbergh, "Luminescent Solar Concentrators - A review of recent results.", Opt. Express 16, 21773-21792 (2008).
- [6] Bose, R.; Farrell, D.J.; Chatten, A.J.; Pravettoni, M.; Buchtemann, A.; Quilitz, J.; Fiore, A.; Manna, L.; Barnham, K.W.J.; "Luminescent solar concentrators: Nanorods and raytrace modeling", Photovoltaic Specialists Conference, 2008. PVSC '08. 33rd IEEE, vol., no., pp.1-5, 11-16 May 2008
- [7] Lo C.K., Lim Y.S., Tan S.G., Rahman F.A. "A New Hybrid Algorithm Using Thermodynamic and Backward Ray-Tracing Approaches for Modeling Luminescent Solar Concentrators." Energies. 2010; 3(12):1831-1860.
- [8] Jana Bomm, Andreas Buchtemann, Amanda J. Chatten, Rahul Bose, Daniel J. Farrell, Ngai L.A. Chan, Ye Xiao, Lenneke H. Slooff, Toby Meyer, Andreas Meyer, Wilfried G.J.H.M. van Sark, Rolf Koole, "Fabrication and full characterization of state-of-the-art quantum dot luminescent solar concentrators", Solar Energy Materials and Solar Cells, Volume 95, Issue 8, Photovoltaics, Solar Energy Materials & Thin Films, IMRC 2009-Cancun, August 2011, Pages 2087-2094, ISSN 0927-0248.
- [9] Goldschmidt, J. C., Peters, M., Prönneke, L., Steidl, L., Zentel, R., Bläsi, B., Gombert, A., Glunz, S., Willeke, G. and Rau, U. (2008), "Theoretical and experimental analysis of photonic structures for fluorescent concentrators with increased efficiencies." physica status solidi (a), 205: 2811–2821.
- [10] Alan A. Earp, Geoff B. Smith, Jim Franklin, Paul Swift, "Optimization of a three-colour luminescent solar concentrator daylighting system", Solar Energy Materials and Solar Cells, Volume 84, Issues 1-4, International Solar Energy Society World Congress 2003, October 2004, Pages 411-426, ISSN 0927-0248.