

IMPROVING THE EFFICIENCY OF LUMINESCENT SOLAR CONCENTRATORS

MASTER THESIS, 30 ECTS

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Abstract.

ABSTRACT

Luminescent solar concentrators (LSCs) are low cost photovoltaic devices, which reduce the amount of necessary semiconductor material per unit area of a photovoltaic solar energy converter by means of concentration. The device is comprised of a thin plastic plate in which luminescent species (luminophores) have been incorporated. The luminophores absorb the solar light and radiatively reemit part of the absorbed amount of energy. Total internal reflection traps most of the emitted light inside the plate and wave-guides it to a narrow side facet with a solar cell attached, where conversion into electricity occurs. The efficiency of such devices is as yet rather low, due to several loss mechanisms, of which reabsorption is of high importance [1]. It is generally expected, that spectral separation between absorption and emission influences the losses due to reabsorption [2]. Semiconductor nano-crystals with a quasi-complete separation of absorption and emission spectra (large Stokes' shift) may be good candidates to overcome reabsorption losses, however in practice their synthesis results in a drop in luminescence quantum efficiency [3]. The synthesis of highly luminescent nano-crystals with a small but not negligible spectral overlap promises to be less complicated [2], [4]. This work investigated the suitability of such quantum dots to circumvent the reabsorption problem in LSC devices by means of experimentally validated combined ray-tracing and Monte-Carlo simulations [2].

Combined ray-tracing and Monte-Carlo simulations is a widely used tool for efficiency estimations of LSC-devices prior to actual manufacturing. We have varied the LSC-size and luminophore concentration in the simulation for four different types luminophores: An hypothetical perfect luminophore, Lumogen Red 305 (the quasi-standard) and two different types of quantum dots, one with an almost complete absorption/emission-separation and one, where still a few percent of the light in the spectral region of emission is absorbed.

This thesis presents the simulation results of the LSC performance with four different luminophores under changing LSC-size and luminophore concentration. The work will present the impact of all the different loss processes. The simulations show that even the small absorption coefficients that overlap with the emission spectrum have a detrimental effect to the LSC by increasing the losses due to reabsorption.

It was found that semiconductor nano-crystals with a quasi-complete separation of absorption and emission spectra could be better luminophores as Lumogen Red 305. Only the absorption coefficients overlapping with the emission spectrum need to be negligible and the luminescent quantum efficiency needs to be at least 60%. However, it is demonstrated that a simple rectangle LSC geometry with PMMA as waveguide material is not economical viable.

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Introduction.

1. INTRODUCTION

The energy demand is growing and concerns of the environmental impacts by mankind's energy usage are increasing. Therefore alternatives to the use of fossil fuels have to be investigated. One of the alternatives is solar energy. The sun illuminates the earth's atmosphere with a power density of 1361 Wm⁻². This is, if converted, more than enough to meet mankind's energy demand. However, converting the energy of the sun in an efficient and especially an economically efficient¹ way remains an important goal within research [5].

Photovoltaic (PV) systems that convert light into electricity are one of the fastest growing power technologies of the last decades. Lots of research groups are working on increasing the performance of these systems. As illustration of the effort done within this field of science the PV cell efficiency breakthroughs over the last years are shown in Figure 1.



FIGURE 1: SOLAR CELL EFFICIENCY RECORDS [6].

The search to a better efficiency has led to a current world record of 44.7% energy efficiency (not in the chart yet) [7]. Still PV systems represent less than 1% of the total market share in energy production, indicating that there is still a lot to gain [8]. In the last few years the focus shifts from gaining maximum energy efficiency towards gaining electricity from sunlight in the most economically efficient way. One of these approaches is to concentrate the sunlight before it hits a solar cell.

¹ So that the energy converted from the sun can economically compete with the conventional energy sources.

Using concentrators within photovoltaics can be subdivided in two categories: high concentration photovoltaics and low concentration photovoltaics. Low concentration photovoltaics concentrate the sunlight up to 100 times the power of the sun. High concentration photovoltaics can even concentrate the sunlight up to 1000 times normal irradiation². Most concentrators are lenses based concentrators and they are expensive due the need of sun tracking systems. Another disadvantage of geometric based concentrators is that diffuse light cannot be concentrated with this method.

Within this thesis luminescent solar concentrators (LSCs) are explored. LSCs are concentrators based on a different working principle than lenses. An LSC uses luminescent particles to direct sunlight towards solar cells. Figure 2 presents an example of an LSC, showing incident rays transmitted on the waveguide, absorbed by the luminescent material, submitted at an angle to be trapped within the waveguide and guided towards solar cells at the edge of the LSC. Optical concentration is attained when the intensity of light reaching the solar cells is greater than the intensity of the solar radiation [9].



FIGURE 2: AN ILLUSTRATIVE DIAGRAM OF AN LSC THAT CONSISTS OF A SLAB OF TRANSPARANT MATERIAL DOPED WITH LUMINESCHENT MATERIALS. SOLAR LIGHT IS ABSORBED AND EMITTED AT LONGER WAVELENGTHS IN RANDOM DIRECTIONS. PART OF THE EMTTED LIGHT IS TRAPPED AND GUIDED TOWARD THE PV CELLS ATTACHED [10].

LSCs were originally proposed, in 1973 by Lerner [11], in an attempt to reduce the costs (€/kWh) of energy production by solar cells [12]. Until now however, LCSs have not become commercially viable due to too low efficiencies.

Even after 30-years of research there is no ideal luminescent material (luminophore) yet. The current available luminophores suffer from at least one shortcoming. These shortcomings are limited harvesting of light from the solar spectrum, large losses due to reabsorption events (see Chapter 2.3), low quantum efficiency and low photo-stability or low thermal-stability.

CdTe-CdSe Type-II core-shell quantum dots, a relatively new kind of luminophores, have interesting characteristics for the use in LSCs. CdTe-CdSe Type-II core-shell quantum dots offer the opportunity for a high Stokes shift, thereby reduce the likelihood for reabsorption, and broader absorption spectra, thereby increasing the possibility to harvest more light. The performances of using these quantum dots within LSCs were examined in this thesis.

² Up to concentrating to 100 times the power of the sun no active cooling is needed.

Introduction.

1.1. SCOPE OF THE THESIS

Regarding the search to the best performances for LSCs the ideal luminophore concentration and the ideal size of the LSC, using CdTe-CdSe Type-II core-shell quantum dots as luminophore, are not known. Within previous research towards an ideal concentration and/or ideal size of an LSC it is never mentioned that these two variables can be interdependent. It is expected that the ideal luminophore concentration is related to size of the LSC due to the effect on reabsorption of both size and concentration³. The relationship between these two variables is not known and it can be different for other kinds of absorption-emission spectra.

In this thesis research is conducted to investigate why the current LSCs exhibit (too) low system efficiencies, by using the modeling tool PVtrace. Also type-II quantum dots, relatively new luminescent materials, were investigated as luminescent material in LSCs. This research focused on the following question:

 Do CdTe-CdSe Type-II core-shell quantum dots provide a solution in achieving higher LSC efficiencies?

The following sub questions were derived from the research question:

- What is the relation between ideal size and ideal concentration?
- What are the maximum achievable performances for the different luminophores within the defined LSC?
- What are the important loss factors within LSCs using different luminophores?

This optimization study towards the ideal LSC size and luminophore concentration was performed to investigate the potential of the luminescent materials 'Lumogen Red 305' and two different Type-II core-shell quantum dots. In Chapter 2 the general theory of LSCs is explained along with the current developments within this field of science. Chapter 0 describes the methods used. Thereafter, the used simulation model is explained in Chapter 4. This is followed by Chapter 5 where the model validation is presented. In the Chapters 6, 7 and 8 are the results presented of the simulations with the different luminophores. Thereafter the discussion is presented in Chapter 9. And finally the conclusions are drawn in Chapter 10.

³ A larger LSC increases the average path length within the waveguide and thereby the likelihood for reabsorption. Higher luminophore concentrations will increase the absorption of light per area but will also increase the likelihood for reabsorption.

Background.

2. BACKGROUND

This chapter is to introduce the scientific field among LSCs and it supplies the knowledge to understand the problems within this technology. This chapter introduces the general concept of LSCs in Section 2.1. Secondly, a small historical overview of research in LSC technology along with a few of the achievements is described in Section 2.2. Then, the theory behind the different loss mechanisms is extensively elaborated in Section 2.3. Thereafter, the intersection of light with reflective interfaces, LSC simulations and the different luminophores are discussed in respectively Section 2.4, Section 2.5 and Section 2.6.

2.1. THE LUMINESCENT SOLAR CONCENTRATOR

The costs of photovoltaic (PV) solar cells are rapidly reduced over the last years [13]. Yet it still remains an expensive source of energy compared to competing energy sources. An LSC is usually a flat polymer plate into which luminescent materials (luminophores) are incorporated. Sunlight enters the LSC and photons are absorbed by the luminophores. The luminophores emit these photons with a longer wavelength and different direction. Differences in refractive indices permit that parts of this emitted light are trapped within the waveguide by total internal reflection (see Chapter 2.3.5). The light is concentrated towards an edge where a small PV solar cell is located (see Figure 3) [1], [12] and [14]. The ratio between the top surface of the waveguide are lower than the costs of solar cells, it may be possible to reduce the overall costs of photovoltaic electricity production.



FIGURE 3: A THREE DIMENSIONAL SCHEMATIC VIEW OF AN LSC. LIGHT IS INCIDENT ON THE TOP SURFACE. PHOTONS ARE ABSORBED AND EMITTED BY A LUMINOPHORE. PART OF THE LIGHT ESCAPES, THE OTHER PART IS GUIDED TOWARDS THE EDGE, WHERE A PV SOLAR CELL IS LOCATED.

The working principle of LSCs is based on the conversion of the solar spectrum to longer wavelengths at which PV cells exhibit higher external quantum efficiencies. Another advantage concerning this working principle for concentration is its applicability for both direct as diffuse light [15]. This can be considered as an important factor due to the high level of diffuse light within Northern Europe [16].

LSCs have not reached high efficiencies or high concentration factors yet [1]. This is caused by loss mechanisms, which are graphically shown in Figure 4. The most important loss mechanisms are: partial absorption by the luminophores, imperfect trapping of emitted light, reabsorption (which will

again subject the light to all loss mechanisms) and a low quantum efficiency. Waveguide losses (Figure 4, 5) are more important when LSCs scale up in size [14]. The loss mechanisms are further elaborated in Chapter 2.3.



FIGURE 4: A TWO DIMENSIONAL LSC WITH THE INDENTIFIED LOSS MECHANISMS. 1) LIGHT IS EMITTID WITHIN THE ESCAPE CONE. 2) REABSORPTION OF LIGHT. 3A) NOT ALL PHOTONS ARE ABSORBED. 3B) THE LUMINESCENT MATERIAL IS NOT STABLE. 3C) NO PERFECT QUANTUM EFIICIENCY. 4) PV SOLAR CELL LOSSES. 5A) EXTERNAL REFLECTION. 5B) ABSORPTION BY THE HOST MATERIAL. 5C) INTERNAL SCATTERING. 5D) SURFACE SCATTERING [12].

2.1.1. **DEFINITIONS**

Within different articles it is sometimes difficult to understand which efficiency is mentioned when. To avoid confusion a list of definitions, used in this thesis, is given below.

The energy entering the LSC is denoted as $energy_1$, this is the energy of the irradiation hitting the LSC. The LSC guides parts of the incoming irradiation towards the solar cell. The energy that reaches the solar cell is called energy₂. The solar cell converts this optical energy into electrical energy, which is called energy₃.

The optical efficiency η_{opt} is the efficiency of the LSC itself, so without taking into account the efficiency of the solar cell. The η_{opt} gives the efficiency of light reaching the solar cell compared to the incident light. The optical energy efficiency (see Eq. 1) has to be clearly separated by the optical flux efficiency (see Eq. 2). The flux efficiency gives photon-to-photon efficiency while energy efficiency gives the energy-to-energy efficiency

$$\eta_{opt_e} = \frac{Energy_2}{Energy_1} \cdot 100\%$$
 EQ. 1

$$\eta_{opt_f} = \frac{Flux_2}{Flux_1} \cdot 100\% \qquad \qquad EQ. 2$$

The concentration factor G is the energy intensity of irradiation hitting the PV cell per intensity of incident energy. See Eq. 3 for the calculation. Here is $area_1$ the incidental surface of the LSC and $area_2$ the surface of the solar cell. Whereby $area_1$ divided by $area_2$ is the geometrical concentration factor.

$$G = \frac{Energy_2}{Energy_1} \cdot \frac{Area_1}{Area_2}$$
 EQ. 3

The system efficiency η_{sys} is defined as the efficiency of the whole system, including the PV cell, see Eq. 4 for the formula.

$$\eta_{sys} = \frac{Energy_3}{Energy_1} \cdot 100\% \qquad \qquad EQ. 4$$

2.2. HISTORICAL DEVELOPMENT

The concept of trapping light within a transparent body by fluorescence is known since 1949 [17]. In 1970s the first proposal to use trapping of light by fluorescence with the mean of concentrating solar irradiance for energy conversion was proposed (an LSC). Through the 1980s extensive research was done within LSC technology until the limits of the fluorescent dyes available at that moment limited further development [11] and [18]. Friedman [19] achieved an efficiency $\eta_{sys} = 3.2\%$ with a Si solar cell connected to a thin film module of 14 x 14 x 0.3 cm³ with mixed dyes. When connected to a GaAs solar cell the efficiency reached $\eta_{sys} = 4.5\%$. An efficiency $\eta_{sys} = 4.0\%$ was reached by Wittwer et al. [20] for a two sheet 40 x 40 x 0.3 cm³ LSC. One of the sheets was connected to GaAs solar cells and the other to Si solar cells. The plates were separated by an air gap. More recently efficiencies of $\eta_{sys} = 7.1\%$ [21] and $\eta_{sys} = 6.7\%$ [22] were obtained by using respectively GaAs cells and GaInP cells. The higher efficiencies reached here were mainly a result of smaller waveguide sizes, the use of mirrors and diffuse reflectors and matching the spectral response of the solar cell with the emission spectrum of the luminophores. The maximum efficiency η_{sys} for large size LSCs was estimated at 8-10% [19].

The research within the field of LSC slowed down in the 1980s due to the limitations of the available luminophores and the drop of the energy price back then. Current increasing energy prices, new luminescent materials, new techniques to reduce the losses [23] and the development of new analyses tools renewed the interest in LSC development.

2.3. LOSS PROCESSES WITHIN THE LSC

Several loss mechanisms were mentioned in the description of the working principle of the LSC in Chapter 2.1. Minimizing these losses is a major challenge within the development of LSCs. The LSC efficiency can be expressed as the product of the efficiencies of all the different loss mechanisms⁴ present inside an LSC (see Eq. 5). The different loss mechanisms will be elaborated in the next sections.

 $\eta_{opt_e} = \eta_{Fresnel} * \eta_{Absorption} * \eta_{QE} * \eta_{Stokes} * \eta_{EC} * \eta_{Waveguide} * \eta_{Reabsorption}$ EQ. 5

⁴ The efficiency of a loss mechanism gives the efficiency of overcoming the loss process.

Goetzberger et. al. [24] proposed Eq. 5 with the corresponding values given in Table 1. Note that these different efficiencies are interdependent.

Efficiency component	Value
$\eta_{Fresnel}$	< 0.96
$oldsymbol{\eta}_{Absorption}$	~ 0.2 - 0.3
η_{QE}	> 0.95
η_{Stokes}	~ 0.8
η_{EC}	~ 0.75
$\eta_{Waveguide}$	~ 0.9
$\eta_{Reabsorption}$	~ 0.75
$\eta_{opt}{}_{e}$	0.11 - 0.07

TABLE 1: THE DETERMINED EFFICIENCIES OF THE EXPERIMENTAL LSC WITH SIZE 40 X 40 X 0.3 CM³ USING AN ORGANIC DYE AS LUMINOPHORE OF GOETZBERGER ET. AL. [24].

2.3.1. **REFLECTION** (η_{Fresnel})

A flat surface with a refractive index of 1.5^5 will reflect around 4% of the direct illumination. This 4% of the light will never enter the concentrator and is thereby considered as a loss. The Fresnel equations describe the proportions of light that refract and reflect by entering a medium with another refractive index. This theory assumes flat interfaces and homogeneous media. This theory is therefore applicable for all reflection processes within the LSC. The angles of reflected and refracted light can be calculated using Snell's law (elaborated in Chapter 2.3.5). The percentage of reflected light R is defined as the ratio of reflected intensity I_r and initial intensity I_i (See Eq. 6).

$$R = \frac{I_r}{I_i} \qquad \qquad EQ. 6$$

The percentage of transmitted light T is defined in a similar way (see Eq. 7). Eq. 8 has to hold because all the light is either reflected, refracted or absorbed (conservation of energy).

$$T = \frac{I_t}{I_i} \qquad \qquad EQ. 7$$

$$R+T+A=1$$
 EQ. 8

⁵ A refractive index of 1.5 is common for a PMMA plate [54].

A photon can have a polarized electric field either perpendicular to the plane (s-polarized) or parallel to the plane (p-polarized). The polarization of the electric field has influence on the probability of reflection. The Fresnel equations describe the probability of reflection of light for both polarizations using η_1 as host refractive index, η_2 as refractive index of the new media and θ_i as angle of incidence compared to the normal [25].

$$R_{s} = \left(\frac{n_{1}\cos\theta_{i} - n_{2}\sqrt{1 - \left(\frac{n_{1}}{n_{2}}\sin\theta_{i}\right)^{2}}}{n_{1}\cos\theta_{i} + n_{2}\sqrt{1 - \left(\frac{n_{1}}{n_{2}}\sin\theta_{i}\right)^{2}}}\right)^{2} \qquad EQ. 9$$

$$R_{p} = \left(\frac{n_{1}\sqrt{1 - \left(\frac{n_{1}}{n_{2}}\sin\theta_{i}\right)^{2}} - n_{2}\cos\theta_{i}}{n_{1}\sqrt{1 - \left(\frac{n_{1}}{n_{2}}\sin\theta_{i}\right)^{2}} + n_{2}\cos\theta_{i}}\right)^{2} \qquad EQ. 10$$

A graphical representation of the reflection probability for the different polarizations of the light entering the LSC is given in Figure 5.



FIGURE 5 : THE PROPORTIONS OF THE REFLECTED LIGHT FOR BOTH POLARIZATIONS PLOTTED VERSUS THE ANGLE OF INCIDENCE [25].

External reflection can be countered with rough surfaces. The downside of rough surfaces is the inability to guide photons to the edges. Therefore this is not an option in LSCs. Lowering the reflective index is also an option to reduce external reflection losses. A lower refractive index, unfortunately, has a negative effect on the trapping efficiency. This is elaborated in Chapter 2.3.5.

2.3.2. QUANTUM EFFICIENCY (η_{QE})

Not all absorbed photons are emitted as photons again. Part of them are lost as vibrations or heat due to non-radiative relaxation pathways [26]. The ratio between the emitted photons and the absorbed

photons, by the luminophores, is called the quantum efficiency (see Eq. 11). This efficiency is different for all kinds of luminophores.

$$\eta_{QE} = \frac{N_{emitted}}{N_{absorbed}} \qquad \qquad EQ. \ 11$$

High quantum efficiencies are essential for good performances within LSCs.

2.3.3. STOKES SHIFT (η_{Stokes})

The Stokes shift of an organic dye is the wavelength separation between the peak closest to the lowest energy of the absorption band and the peak nearest to the highest energy at the emission band [12]. Stokes shift losses are defined as the loss in energy between absorbed and emitted photons, only taking into account the photons that are emitted again. This energy loss is always present within the LSC and will be around $\eta_{\text{Stokes}} = 0.75$. This loss is not a major problem as long as the energy of the photons is still large enough to generate an electron-hole pair within the PV cell by overcoming its band gap. The energy lost due to Stokes shift would otherwise be lost within the PV cell, due to non ideal matching of the photons' energy and the band gap energy.

2.3.4. IMPERFECT ABSORPTION (η_{Absorption})

An LSC absorbs light with its luminophores. These luminophores have a given absorption spectrum. The strength of this absorption spectrum is luminophore concentration dependent. The more particles there are to react with, the higher the probability is for a photon to be absorbed. If there is no absorption event the photon will pass unabsorbed through the LSC. This can be due to low concentration of luminophores, short travel length or due to the mismatch of the photon energy with the absorption energy. Photons that have too little energy to excite an electron to a higher energy level cannot be absorbed by the luminophores.

The absorption of light by luminophores can be described with the Lambert-Beer law. The Lambert-Beer law states that the absorption of light by a given substance within a non-absorbing substrate is exponentially dependent on the concentration of the substance. The percentage of transmitted light (T) is calculated with Eq. 12, using molar absorptivity $\varepsilon(\lambda)$, path length *l* and the concentration c.

$$T = \frac{I_t}{I_0} = 10^{-\varepsilon(\lambda)lc}$$
 EQ. 12

So the absorbance A can be written as:

$$A = 1 - T = 1 - \frac{I_t}{I_0} = 1 - 10^{-\varepsilon(\lambda)lc}$$
 EQ. 13

Or

$$A = -\log_{10} \frac{I_t}{I_0}$$
 EQ. 14

A graphical presentation of this process is given in Figure 6.



FIGURE 6: ABSORPTION OF LIGHT WITHIN A SUBSTRATE [27].

A typical decay curve with increasing concentration or length is given in Figure 7.



FIGURE 7: THE TRANSMISSION OF LIGHT WITH INCREASING CONCENTRATION [28].

The molar absorptivity is a wavelength dependent constant. Within luminescent solar concentration this means that it is preferable to find a luminophore with a molar absorption spectrum that covers most of the solar spectrum to absorb as much as possible of the irradiating power. When there is a measurable absorption coefficient at a given wavelength photons will be absorbed as long as the concentration high enough or path length is long enough. These parameters are also important for the reabsorption problem described in Chapter 2.3.7.

To increase the absorption of light the search for luminophores with more ideal absorption spectra still continues. Also combinations of luminophores are used to combine the absorption spectra of each in so called multiple dye constructions [29].

2.3.5. TRAPPING EFFICIENCY (η_{EC})

Most of the absorbed photons emitted by the luminophores are directed to another direction than the incident one. Depending on the angle of emission the light escapes or is trapped in the waveguide. Snell's law describes the behavior of photons approaching an interface between two isotropic media. Snell's law states that the sine of the angle of incidence θ times the refractive index n stays constant over the different media (see Eq. 15).

$$\sin \theta_1 \cdot n_1 = \sin \theta_2 \cdot n_2 \qquad \qquad EQ. 15$$

When light travels from a medium with a higher refractive index to a medium with a lower refractive index Snell's law sometimes seems to require a $sin(\theta) > 1$. This is impossible. Therefore, light in such angles is completely reflected by the boundary by a phenomenon named as total internal reflection (TIR). The largest possible angle of incidence that is not total internal reflected is called the critical angle.

Al the photons emitted at angles equal or smaller than the critical angle are emitted within the escape cone (EC) and are not totally internal reflected. To calculate which proportion of the isotropically emitted photons is emitted into the EC a calculation follows given in Section 2.3.5.1.

2.3.5.1. CALCULATION FOR TRAPPING EFFICIENCY

In three-dimensional space angle θ_{crit} corresponds to half an apex of a cone. Photons that are emitted within this cone to the surface are not total internal reflected and thus escape.



FIGURE 8: THE SOLID ANGLE OF THE ASCAPE CONE WITH Θ CRIT = A, Ω AS THE ESCAPE CONE [30].

The efficiency of TIR η_{EC} is given by the probability of TIR and is thus one minus the solid angle of the escape cone Ω as fraction of the solid angle of all possible directions (see Eq. 16).

$$\eta_{EC} = 1 - P_{escape} = rac{\Omega}{4\pi}$$
 EQ. 16

The solid angle of the escape cone is calculated with a surface integral (see Eq. 17)

$$\Omega = \int_{0}^{\theta_{crit}} \int_{0}^{2\pi} d\varphi \sin \theta d\theta = 2\pi \left(-\cos \theta \Big|_{0}^{\theta_{crit}} \right) = 2\pi (1 - \cos \theta_{crit})$$
 EQ. 17

That can be written as Eq. 18 by substituting $\cos \theta_{crit}$ for $\sqrt{1 - \frac{1}{n^2}}$ using geometrics.

$$\Omega = 2\pi \left(1 - \sqrt{1 - \frac{1}{n^2}} \right)$$
 EQ. 18

So the probability of escaping through one surface of a rectangle is given by Eq. 19

$$P_{escape} = \frac{\Omega}{4\pi} = \frac{1}{2} \left(1 - \sqrt{1 - \frac{1}{n^2}} \right) = \frac{1}{2} \left(1 - \sqrt{1 - \frac{1}{1.5^2}} \right) = 0.127 \qquad EQ. 19$$

In a case of a rectangular LSC with 1 solar cell, attached to a side-surface, the efficiency of trapping is 0.363 as given by Eq. 20.

$$\eta_{EC} = 1 - P_{escape} = 1 - \frac{5\Omega}{4\pi} = 0.363$$
 EQ. 20

This trapping efficiency is disastrous for the efficiency of the LSC. Therefore the three remaining sidesurfaces are covered with mirrors, hereby increasing the trapping efficiency to a more acceptable value of 0.745. An attempt to further increase the trapping efficiency is the placement of a mirror or Lambertian mirror to the back-surface. Hereby preventing the escapement of photons through the back-surface of the LSC (with escape cone size Ω). Another advantage of this so called back-mirror is the increase of initial path length for absorption. The path length for absorption is doubled because the light needs to travel back and forth through the LSC before it leaves the LSC unabsorbed. This increases the likelihood for absorption. Experiments mentioned that the best performances were achieved with 'air-gap mirrors', i.e., an air-gap between the mirror and the LSC, attached to three sidesurfaces and an air-gap Lambertian mirror at the backside of the LSC [1]. An air-gap mirror is used because with direct contact between mirrors and the waveguide the TIR disappears. All photons would reflect with the reflection coefficient of the mirror. The air-gap mirror only reflects the photons inside the escape cone causing less photons to be lost due to no perfect reflection. This results in higher power conversion efficiencies.

2.3.6. WAVEGUIDE LOSSES (η_{Waveguide})

Naturally it is an advantage to produce LSC waveguides in the order of square meters in many applications. However, there are losses that are limiting the maximum size for the device. The drop in energy output by increasing size has been reported [31]. These transport losses are explained by reabsorption by the luminophores and by the waveguide losses.

At small size, waveguide losses are of little importance, while they are important at large sizes. These waveguide losses (or background absorption) consist of (parasitic) absorption of light by the host material. At visible wavelengths polymers and glasses, good candidates to be the material of the

waveguide, are highly transparent [32]. But polymers will strongly absorb the wavelengths in the near infrared (NIR) starting around wavelengths around 900nm [33]. Many polymers exhibit parasitic absorption at these wavelengths due to the harmonics and overtones of the C-H and C-O bond vibrations in the polymer [34].

Imperfections at the surface of the waveguide can lead to scattering. Also scattering points within the waveguide can lead to extra losses due to redirection of photons into the escape cone. Although at first sight internal scattering points could help to reduce the escape cone losses by redirecting the photons that would escape, this is not the case. Because of the longer lifetime of the trapped photons within the waveguide the likelihood of scattering these photons is significantly larger than of those that are not trapped.

The best background absorption coefficients achieved in PMMA are in the order of 0.5 m^{-1} [1] for light within the visible wavelengths. This value is measured and contains all the above loss mechanisms within the waveguide.

2.3.7. REABSORPTION LOSSES (η_{reabsorption})

Reabsorption is the absorption of photons that are emitted by the luminophores. Most luminophores emit photons in partially the same spectral region as that they absorb them. This spectral overlap between absorption and emission causes reabsorption. Although reabsorption itself is not a loss, the reabsorption events will expose photons again to other loss mechanisms [35]. Reabsorption events will submit a photon again to the quantum efficiency. Good quantum efficiencies are hereby even more essential. Also the measured EC losses can be higher than the calculated maximum due to reabsorption events. The Stokes shift losses also increase with reabsorption, each reabsorption event lowers the energy of the absorbed/emitted photon leading to a redshift in the emitted spectra by an increasing amount of reabsorption events. So, the reabsorption efficiency consists of the additional losses due to reabsorption events. The reabsorption efficiency is strongly related with the trapping efficiency and the quantum efficiency (calculated in fluxes). A changing η_{QE} has a direct effect on the $\eta_{reabsorption}$.

2.4. INTERACTION WITH A REFLECTIVE INTERFACE

When a photon hits a reflective interface it is reflected with the likelihood of the reflectivity of the surface. The new direction can be calculated using Snell's law. The surface can also be a scattering surface. A Lambertian surface is defined as the perfect scattering surface.

Sometimes there is confusion how a Lambertian surface reflects light. One statement states that a Lambertian surface reflects light equally into all directions. The other states that a Lambertian surface

reflects light with a cosine angular distribution. Figure 9 shows the images corresponding to these contradictory statements.



FIGURE 9: A SCHEMATIC REPRESENTATION OF THE TWO IMAGES CORRESPONDING TO THE TWO DESCRIPTIONS OF A LAMBERTIAN SURFACE [36].

However, both statements can be the correct one, depending on which measure is used. Each point of a Lambertian surface reflects light in a cosine pattern. When the surface is viewed with a finite field of view, the area of the surface seen is proportional to $1/cos(\theta)$ (geormety). The light measured comes from the intensity reflected from each point times the number of points seen, therefore being independent of θ . Thus the measured reflected radiance is independent of the viewing direction, which corresponds to the first statement.

2.5. SIMULATIONS

Modeling of LSCs is used tool to study and understand the LSC-system. Several groups have reported studies to LSCs with the use of modeling [15], [37], [38]. Two different approaches were used: i) The first model that is based on the radiative energy transfer between mesh points in the waveguide of the LSC. These thermodynamic models require minimal input data and respond with swift answers but are often limited to simpler geometries and limited luminescent species [1]. ii) The second model is a Ray-Tracing model in which every photon is tracked. Ray-tracing simulations offer a lot of freedom in device design and number of luminophores or other details. The downside of this approach is the high computational demand [12].

2.6. DISCUSSION OF THE DIFFERENT LUMINOPHORES

The different luminophores used in LSCs are categorized in three different categories: Organic dyes, rare earth metals and quantum dots. Each category is described below along with the impact of the luminophore properties on the LSCs.

Background.

2.6.1. ORGANIC DYES

Organic luminescent dyes are small π -conjugated organic molecules, where the core of the molecule is planar with all atoms of the conjugated chain lying in a common plane and linked by σ -bonds. Figure 10 shows some typical molecular structures of organic fluorescent dyes.



FIGURE 10: THE MOLECULAR STRUCTURES OF LUMOGEN F RED 305 (LEFT) AND LUMOGEN F ORANGE 240 (RIGHT) [39].

When an organic dye absorbs a photon it excites an electron from the ground electronic state S_0 to one of the vibrational levels of the first electronic state S_1 . Figure 11 shows the associated Jablonski energy level diagram of an organic dye. The excited electron decays non-radiatively to the lowest level in S_1 . From there it decays, by emission of a photon, to one of the vibrational levels in S_0 . The emitted photon has a lower energy due to the energy losses in this process and is emitted in a different direction than the absorbed photon.



FIGURE 11: THE JOBLONSKI ENERGY-LEVEL DIAGRAM FOR AN ORGANIC DYE [40].

Organic dyes offer high QE's, large absorption coefficients and high solubility and were therefore chosen as the first luminophores within LSCs. The main problems with organic dyes are the large reabsorption losses caused by a high overlap in the emission and absorption spectra, limited width of their spectral absorptions and limited photo-stability [12]. A typical absorption-emission spectrum for a luminescent organic dye is given in Figure 12. The Lumogen product group of BASF is used as reference dyes in LSCs [41].



FIGURE 12: THE NORMALIZED ABSORPTION AND EMISSION SPECTRA OF ORGANIC DYE 'F ORANGE 240' MEASURED BY Z. KRUMER.

2.6.2. QUANTUM DOTS

Quantum dots (QDs) are nanostructures from semiconducting material whose luminescence properties depend on their size. QDs offer broad spectral absorption, better stability than organic dyes and tunable spectra by changing the size. The main problem with QDs is the yet lower QE compared to organic dyes [12].

The impact of spatial confinement differs over different materials and/or different properties, as it depends on characteristic length scales of a given physical property, which are ultimately determined by the material's composition and structure. The relevant length scale in this case is the exciton Bohr radius which ranges from ~2 nm to ~50 nm. When the nano-crystal size approaches the Bohr radius confinement effects play a role on the wave function, including changes in the energy level separation. Increasing band gap (and the appearance of discrete energy levels) is caused by decreasing size [42].

The size (typically in the order of 10-20 nm) of QDs can be adjusted to confine the emission wavelengths to the maximum spectral response of the solar cell [31]. Quantum yields as high as 90% have been reported at laboratory scale [43]. QDs have a low chemical stability upon exposure to air. The used strategy to improve the stability is to coat the QDs with a shell of another semiconductor. Depending on the band gap of this semiconductor different types of quantum dots are distinguished.

2.6.2.1. TYPE-I

Type-I QDs are core-shell hetero-nanocrystals with a semiconducting shell material with a larger band gap than the core material (see Figure 13). Due to the band structure the offset of exited electrons and holes are directed to the core. Direct excitation takes place in the form of the radiative decay resulting in a lower energy for the exited photon than the energy absorbed in the shell material. However, the Stokes shift for type-I QDs is very small [42]. The efficiency of LSCs based on Type-I QDs is therefore

limited by self-absorption losses. A typical absorption-emission spectrum for Type-I QDs is given in Figure 14



FIGURE 13: SCHEMATIC REPRESENTATION OF THE THREE LIMITING CHARGE CARRIER LOCALIZATION REGIMES IN CORE-SHELL SEMICONDUCTOR HETERO NANO-CRYSTALS [42].



FIGURE 14: THE NORMALIZED ABSORPTION AND EMISSION SPECTRA TYPE-I CDTE QDS.

2.6.2.2. TYPE-I^{1/2}

Type-I^{1/2} QD's are QDs with only one charge carrier confined to a certain part of the hetero nanocrystal. The other charge carrier is delocalized over the whole nano-crystal. A schematic representation of a Type-I^{1/2} QD is found in Figure 13. The excitons radiative lifetimes were observed to be larger than those of Type-I QDs. The Stokes shift remains small (<20 meV) and is comparable with Type-I QDs

2.6.2.3. TYPE-II

Type-II QD's have a band structure with the preferable negative charge carrier position in the shell and the preferable positive charge carrier at the core. This spatial separation between the two energy carriers leads to a spatially indirect emission band gap. The results of this indirect band gap are a longer radiative lifetime and smaller overlaps between the absorption and emission spectra. The longer radiative lifetime has the negative consequence of decreasing quantum efficiency. Type-II QDs have been realized for a number of compositions as CdTe-CdSe and ZnSe-CdS [44]. Reabsorption is expected to be negligible due to the limited overlap between the absorption and emission spectra [45]. Reported QEs for Type-II QDs are typically between 0-10% [46] but recently high quality QDs of this composition became available. The high quality QDs have QE's around 50%, even a remarkably high

QE of 82% was reported [47]. A typical absorption-emission spectrum for Type-II QDs is given in Figure 15.



FIGURE 15 : THE NORMALIZED ABSORPTION AND EMISSION SPECTRA OF TYPE-II CDTE-CDSE QUANTUM DOTS MEASURED BY Z. KRUMER.

2.6.3. RARE EARTH METALS

Rare earth metals show great stability and a very large Stokes shifts. Due to the very large Stokes shifts the rare earth metal based LSCs experience almost no reabsorption. The QE of rare earth metals varies greatly depending on the host material and the concentration. The drawbacks of using rare earth metals as luminophore are an extremely low absorption coefficient and absorption spectra with numerous narrow absorption bands resulting in limited harvesting of the solar spectrum. See Figure 16 for a typical absorption- and emission spectrum for luminescent rare earth metals.



FIGURE 16: THE ABSORPTION AND EMISSION SPECTRA OF NDF3. FIGURE ADAPTED FROM [48].

Method.

3. METHOD

In this research project the qualities of CdTe-CdSe Type-II core-shell quantum dots as luminophores within LSCs were investigated. In Chapter 1 the research goal was defined. Chapter 2 presented the working principle, a historical overview of the technology and an extensive discussion of all the different loss mechanisms within LSCs. This research was performed through ray-tracing simulations with PVtrace. Different LSC set-ups with different luminophores were simulated. Section 3.1 introduces the different luminophores. Section 3.2 elaborates the simulation framework and Section 3.3 discusses the simulation variables. Section 3.4 describes the steps taken to gain the results from the simulations. Finally, Section 3.5 discusses the strategies chosen to lower the statistical error of the simulations in this research.

Within this research the simulation model **PVtrace** was used. PVtrace is a thoroughly validated Monte-Carlo ray-tracing model developed by Daniel J. Farrell [49]. This model was used to simulate several experiments. The model reported for every simulation all the steps of every photon in an SQL-file. Results were gain from analyzing the SQL-files of the different simulations. The model PVtrace is explained in Chapter 4.

3.1. THE LUMINOPHORES

In this research four different luminophores were researched (see Figure 17 for the corresponding spectra and QEs):

- A hypothetical perfect luminophore
- Lumogen Red 305
- Type-II CdTe-CdSe core-shell quantum dots (QD1)
- Different Type-II CdTe-CdSe core-shell quantum dots (QD2)

A hypothetical perfect luminophore was simulated to gain insight in the basic loss mechanism of the system. This perfect luminophore had no reabsorption. The analysis of simulations with a perfect luminophore gave insight to the maximum achievable efficiencies in the chosen system. The emission wavelength of the perfect luminophore was chosen at 900nm because this wavelength matched well with the absorption spectrum of a c-Si-solar cell and it does not experience any NIR waveguide absorption of PMMA.

Second, the luminophore Lumogen Red 305 was used in the simulations. Simulations with Lumogen Red 305 were performed to examine the performance of this current quasi standard luminophore. The analysis of these simulation results gave the efficiencies of the different loss processes within a realistic LSC. Moreover, several simulation results were compared with experimental results of

equivalent set-up. In this way the model was validated, using the experimental results of LSCs obtained by Z. Krumer [50].



FIGURE 17: THE ABSORPTION AND EMISSION SPECTRA OF THE USED LUMINOPHORES IN THE SIMULATIONS WITH THE USED QUANTUM EFFICIENCIES (QES).

Finally, simulations of LSCs doped with two different Type-II CdTe-CdSe core-shell quantum dots were performed. The main differences between the two different quantum dots that were important in this research were the spectral differences and the difference in quantum efficiencies. These simulations were compared with LSCs doped with the perfect luminophore and LSCs doped with Lumogen Red 305.

3.2. SIMULATION FRAMEWORK

The geometry of the waveguide of the simulated LSC was a rectangle with a thickness (height, Zdirection) of 1cm and a length-to-width ratio of 1:0.35 (X and Y direction respectively). The location of the PV cell was set at the smallest edge of the LSC (height x width). This resulted in a high ratio of

LSC-area to PV-cell area. The other three 'small edges' were covered with perfect air gap mirrors⁶. The air gap was set at 0.5mm. The refractive index was set at 1.5 and the waveguide losses (or background absorption) were set at 0.5m⁻¹, these values corresponded to PMMA of good quality. The starting positions of the photons were randomly spread over a rectangle of 'length times width' parallel to the LSC, but 5cm above it. The photons were randomly chosen from the AM1.5G flux spectrum (see Section 4.1). See Figure 18 for the graphical representation of this system.



FIGURE 18: A GRAPHICAL PRESENTATION OF A SIMULATED LSC WITH A LENGTH OF 10 CM. THE EDGE AT THE Y-Z INTERFACE IS THE SOLAR CELL, THE OTHER THREE SIDE SURFACES ARE COVERED WITH MIRRORS. THE FRONT SIDE IS THE APPENDURE SURFACE. THE BACKSIDE IS LEFT OPEN. THE LINE IS THE PATH OF A SIMULATED PHOTON.

The specific geometry (height of 1cm and a length-to-width ratio of 1:0.35) was chosen to be able to compare some of the simulation results with real experimental results⁷. The comparison between the simulated and experimental results was used for the validation of the model (see Chapter 5).

The absorption spectra, emissions spectra and the quantum efficiency of the luminophores were measured. See Appendix K for the steps taken in preparing the spectra for the use in PVtrace. The solar cell attached to the LSC, in the simulations, was a crystalline Si-solar cell with an efficiency of 18%.

3.3. VARIATION OF VARIABLES

The variables in the simulations were the luminophore concentration, the LSC size, the presence of a Lambertian air gap mirror at the backside and the presence of the loss mechanism 'background absorption'.

The variation of luminophore concentration was simulated as an increase in absorption coefficients. A linear dependency between luminophore concentration and absorption strength was assumed, based

⁶ The use of air gap mirrors instead of direct mirrors had been shown to have a positive effect on the total efficiency. Direct mirrors will abolish the TIR thereby exposing also the trapped photons to the reflection efficiency of the mirror. See Section 2.4 ⁷ The LSC within the experiments has geometry of 10 x 3.5 x 1cm³.

on the Lambert Beer law (see Section 2.3.4). There was assumed that the quantum efficiency was independent of the luminophore concentration. After that, the simulations with variation of luminophore concentrations were repeated at different LSC sizes.

To study properly the effects of the different loss mechanisms compared to changing luminophore concentrations or LSC size, multiple situations were simulated. Table 2 shows the four situations that were simulated for each luminophore. For each situation simulations series with different concentrations were performed at different sizes. The simulated lengths were: 1, 5, 10, 15, 20, 30, 40, 50, 60, 70, 85 and 100cm.

TABLE 2: AN OVERVIEW OF THE DIFFERENT 'SITUATIONS' SIMULATED PER LUMINOPHORE.

	Without Lambertian air	gap	With Lambertian air gap mirror
	mirror at the backside		at the backside
Without background absorption	Х		Х
With background absorption	Х		Х

3.4. ANALYSIS METHODS

Each step of every photon in all the simulations was saved in SQL-files using many different parameters (see Chapter 4 for more information). Therefore, these SQL-files contained a lot of information. This section describes the steps taken to gain information from these SQL-files.

With the analysis of the simulated systems the destination of the simulated photons was used. The knowledge of the destination of the photons, and its characteristics, was used to calculate the efficiencies of the LSC and the different loss mechanisms. The destination of the photons was found by using the unique characteristics to the creation of a new photon (the first step). By going back one line in the SQL-files after the first step (creation) of a photon, the last step of the previous photon is found. This searching principle made it possible to trace the final positions of all the photons, except for the last simulated photon. After finding all the destinations the unique characteristics of all possible destinations were used to identify the magnitude of the photons per destination. For further details for the used code and properties used to define the destinations of the photons see Appendix A.

The optical flux efficiency of the LSC was calculated using Eq. 21. Eq. 21 is an adapted version of Eq. 5 from Goetzberger et al. (see Section 2.3). Hereby $\prod_{reabsorption}$ replaced $F_{Reabsrption}$. This was because reabsorption is not an efficiency. Reabsorption enhances other loss mechanisms. In this research the enhancement of other loss mechanisms by reabsorption is reported as the reabsorption factor. Air gap losses are photons escaping through the air gap. Within Eq. 21 all the efficiencies are photon-to-photon efficiencies and calculated without reabsorption events. The additional losses caused by

reabsorption events were ascribed to the reabsorption factor. This resulted in a clear view of the impact of each loss process in LSCs.

$$\eta_{opt_f} = \eta_{Fresnel} * \eta_{Absorption} * \eta_{QE} * \eta_{air gap} * \eta_{EC} * \eta_{Waveguide} * F_{Reabsorption}$$
 EQ. 21

For the calculations used to calculate the different efficiencies within this research see Appendix H.

The system efficiency was calculated to compare the simulation results with real experiments. By calculating the η_{sys} the spectral response of the solar was taken into account. The spectrum reaching the solar cell through the waveguide was different than the spectrum of the photons reaching the waveguide, so the c-Si solar cell had a different efficiency for the incoming spectrum. The spectral response⁸ of a general c-Si-solar cell is given in Figure 19. The spectral response was linear adapted so that the spectral response matched with the efficiency of the solar cell. Solving Eq. 22 and Eq. 23 with R(λ) as the spectral response, f(λ) the AM1.5G energy spectrum and Z the solar cell efficiency gave the applicable spectral response. Y_Z is a constant so that R0.18(λ) gives the spectral response applicable for a c-Si solar cell with an efficiency of 18%.

$$Z = \frac{\int_0^\infty f(\lambda) * R_Z(\lambda) d\lambda}{\int_0^\infty f(\lambda) d\lambda}$$
 EQ. 22

$$R_Z(\lambda) = R(\lambda) * Y_Z$$
 EQ. 23



FIGURE 19: THE SPECTRAL RESPONSE OF A SI-SOLAR CELL. DATA TAKEN FROM PVEDUCATION.[51]

3.5. STATISTICAL ERROR

The Monte-Carlo ray-tracing model PVtrace relays on probability functions. Because there is always a finite number of photon simulated, there is always a statistical error. Two strategies were chosen to limit this statistical error:

⁸ The spectral response is the ratio of the current generated by the solar cell to the power incident on the solar cell.

i) The amount of simulated photons needed to be large:

The lengths '1cm till 15cm' were simulated with 50.000, '20cm till 50cm' with 75.000 and '60cm till 100cm' with 100.000 photons. The amount of photons simulated was assumed high enough to keep the statistical error small. The increase in simulated photons at larger sizes was done to let the density of simulated photons $[cm^{-2}]$ at acceptable densities

ii) The photons that could not provide information were not simulated:

The photons that would never take any part in the reaction were not simulated. This increased the performance of the simulations. It had no additional value to simulate the path of a photon with, for example, wavelength 1200. Even when it would reach the PV cell (by scattering effects) it would not react due to limited photon energy. All simulations were therefore truncated at 1150nm. This means that about 81% of the energy and 64% of the flux was simulated. Later in the analysis these factors were taken into account. The truncation of the solar spectrum could be seen as an increase in simulated photons, thereby decreasing the statistical error. While, actual, simulating the same amount of photons.
4. WORKING PRINCIPLES OF THE MODEL 'PVTRACE'

The simulations performed in this thesis were all performed with the model PVtrace. For insight and understanding of this model an explanation of the working principles follows here. PVtrace is a Monte-Carlo ray-tracing model that simulates photons and its paths. The path of the photon was determined by probability functions per option. The flow chart in Figure 20 shows the steps and loops within the model.



FIGURE 20: FLOW CHART OF PVTRACE. A SCHEMATIC REPRESENTATION OF THE 'CHOICES' AND STEPS A PHOTONS TAKES WITHIN A SIMULATION.

When a photon is launched photon data (location, direction and wavelength) is generated and saved in BOX1. In BOX2 three lengths are calculated: i) background absorption length, ii) absorption length and iii) length towards the next interface. The shortest length determines the next step within the model. If background absorption length is the shortest length then the photon is lost and a new photon

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is launched. If absorption length is the shortest length then the probability of emission is taken into account (QE) by re-emitting the photon. The data of the photon is updated by re-emission and the photon is going back to BOX 2. If the next interface is the shortest length there is checked if the photon reaches the solar cell. If 'yes' then a new photon is generated, if not than the angle of incidence and the refraction indices are used, within the Fresnel equations, to calculate new photon data. If the photon is still within the simulation zone⁹ the photon data is updated and send to BOX 2. This circle goes over and over again until the photon reaches the PV cell or is lost. The amount of launched photons is set as 'x'. When 'x' reaches the set limit the simulation stops. To overcome an internal ever going loop the variable 'z' is made. Every time the loop passes 'z' it raises with one. When the set limit is reached it kills the photon and launches a new one. After each step within in the program PVtrace saves many parameters. Some of these parameters saved are: absorption count, interaction count, in which object the photon is, which surface it reacts with, if it is going IN or OUT the LSC, wavelength, photon number, position (x,y,z), amount of steps of the photon and the amount of steps in the simulation. The generation of random numbers and the generation of all of this data makes this model computational demanding. The steps within the model are further described below.

4.1. LAUNCHING THE PHOTON

When launching a new photon, photon data is generated. The underlying processes of calculating this photon data and the choices made are explained here.

At the start of each simulation it was possible to set the start position of the photons. This could be a 3D figure in space, a 2D area or single point. When the dimensions were chosen, random numbers $\chi \in [0, 1]$ were generated to set a starting position per photon. χ was used to select specific points in space as starting position for each launched photon. Eq. 24, Eq. 25 and Eq. 26 were used to generate a random spread of the starting positions in a box¹⁰. The size of this box was set at the start of the simulation, as well as the starting point of the box in the XYZ-space (see appendix C for an example of spread emission from a rectangle). The direction of a photon was set at the start of each simulation with a vector in space (x,y,z) (see appendix C for an example).

$$location_{x-space} = \chi * Length$$
 EQ. 24

$$location_{y-space} = \chi * Width$$
 EQ. 25

$$location_{z-space} = \chi * Height$$
 EQ. 26

⁹ The simulation zone is determined as the zone where the direction of a photon at least interferes with one surface.

 $^{^{10}}$ χ will be recalculated so it is different every calculation.

To select the starting energy of the photons an AM1.5G spectrum was used as input. AM1.5G stands for Air Mass 1.5 Global. It represents the solar spectrum after sun light traveled 1.5 times the distance through the atmosphere compared to the vertical distance at the zenith. It is a good representable spectrum for the North hemisphere [52].

Figure 21 shows the AM1.5G energy spectrum and Figure 22 shows the AM1.5G photon flux spectrum. Eq. 27 was used to select the wavelength λ_{em} of the photon. With λ_{min} as the minimal wavelength and $f(\lambda)$ as the used spectrum. The flux spectrum was used within the simulations, instead of the mostly used energy spectrum. This was because photons were simulated here, so the relative photons amount matters and not the relative energy.



 $\chi = F_n(\lambda_{em}) = \frac{\int_{\lambda_{min}}^{\lambda_{em}} f(\lambda) d\lambda}{\int_{\lambda_{min}}^{\infty} f(\lambda) d\lambda} \qquad EQ. 27$

FIGURE 21: THE NORMALIZED PHOTON ENERGY AM1.5G SPECTRUM WITH ITS NORMALIZED INTEGRAL.



FIGURE 22: THE NORMALIZE PHOTON FLUX AM1.5G SPECTRUM WITH ITS NORMALIZED INTEGRAL.

4.2. CALCULATIONS IN BOX 2

After each interaction all the three distances were re-calculated. This means that all the lengths were re-calculated after each reflection. The model did not contain the background absorption code. The code, and the validation of the code, is found in Appendix D. The calculations used for calculating the absorption length, background absorption length and the length to the next interface are discussed in Section 4.2.1, Section 4.2.2 and Section 4.2.3 respectively.

4.2.1. ABSORPTION LENGTH

The absorption length l was calculated using the Lambert-Beer law. The Lambert-Beer law is given in Eq. 28.

$$A = 1 - T = 1 - \frac{l}{l_0} = 1 - 10^{-\varepsilon(\lambda)lc}$$
 EQ. 28

 $(\varepsilon(\lambda)^* c = a(\lambda))$ so

$$1 - 10^{-a(\lambda)l} = 1 - \frac{I}{I_0}$$
 EQ. 29

$$l = \frac{-\log_{10} \frac{l}{I_0}}{a(\lambda)} \qquad \qquad EQ. \ 30$$

The possibility to be absorbed at length '*l*' is I/I_0 , see Eq. 30. By replacing I/I_0 for χ a random length according to the absorption distribution could be generated, see Eq. 31.

$$l = \frac{-\log_{10} \chi}{a(\lambda)}$$
 EQ. 31

When a photon was located within the simulated LSC the wavelength dependent absorption coefficient $\alpha(\lambda)$ was extracted from the absorption spectrum and used within Eq. 31. The absorption coefficients are given in m⁻¹.

In the case of TIR the absorption length was recalculated after each reflection. Hereby the new absorption length is not calculated by subtracting the already travelled length from the first calculated absorption length, but recalculated using the same equation (Eq. 31). The validation of this approach is described in Appendix L.

To calculate the absorption length the natural logarithm was used in PVtrace, see Eq. 32.

$$l = \frac{-\ln(1-\chi)}{a(\lambda)}$$
 EQ. 32

To match the input data (emission coefficients in log10 dependency) with the method used the formula within the model was modified from Eq. 32 to Eq. 31. Adapting all input data to a natural logarithmic dependency would have been a correct modification as well.

4.2.2. BACKGROUND ABSORPTION LENGTH

The background absorption was calculated in the same way as the luminescent absorption length. The only difference was the different absorption coefficient within the calculations. Within this thesis $\alpha_{background}$ was assumed to be constant over all wavelengths. So, see Eq. 33 for the used formula.

$$l_{background} = \frac{-\log_{10} \chi}{a_{background,}}$$
 EQ. 33

4.2.3. NEXT INTERFACE DISTANCE

By calculating the next interface PVtrace imports all the interfaces in x,y,z space. By using linear algebra, vectors were calculated between the interfaces and the starting point along the direction of a photon. Simple algebra was used to get the length of this vector, see Eq. 34.

$$dv(v_1, v_2, v_3) = \sqrt{(v_1)^2 + (v_2)^2 + (v_3)^2}$$
 EQ. 34

4.3. QUANTUM EFFICIENCY AND RE-EMISSION

After the absorption of a photon, by a luminophore, the quantum efficiency was used to determine if the photon was (re-)emitted, by using Eq. 35. If Eq. 35 held then the photon was re-emitted. When a photon was emitted the wavelength was calculated by using Eq. 27, with the wavelength of the absorbed photon as λ_{min} and the emission spectrum as $f(\lambda)$. The limit λ_{min} was the physical limit. A photon cannot increase in energy by an absorption/emission event.

$$\chi \leq \eta_{QE}$$
 EQ. 35

4.4. INTERACTION WITH INTERFACES

The interaction of a photon with an interface depends on the characteristics of the interface itself. The photon could either have a reflective interaction (mirrors) or a Fresnel interaction with the interface.

4.4.1. INTERACTION WITH A NON-REFLECTIVE INTERFACE

When a photon hit a non-reflective interface a probability calculation with Fresnel's equations was performed to determine if the photon undergoes refraction or reflection. The new direction was calculated by using Snell's equation for either of the 2 possible options (reflection or refraction). The two Fresnel equations (Eq. 36 and Eq. 37) describe the likelihood for reflection for the two possible states of the electromagnetic field of a photon. It was assumed that both situations are present equally. So the average of both Fresnel equations was taken as the likelihood for reflection.

$$R_{s} = \left(\frac{n_{1}\cos\theta_{i} - n_{2}\sqrt{1 - \left(\frac{n_{1}}{n_{2}}\sin\theta_{i}\right)^{2}}}{n_{1}\cos\theta_{i} + n_{2}\sqrt{1 - \left(\frac{n_{1}}{n_{2}}\sin\theta_{i}\right)^{2}}}\right)^{2} \qquad EQ. 36$$

$$R_p = \left(\frac{n_1\sqrt{1 - \left(\frac{n_1}{n_2}\sin\theta_i\right)^2} - n_2\cos\theta_i}{n_1\sqrt{1 - \left(\frac{n_1}{n_2}\sin\theta_i\right)^2} + n_2\cos\theta_i}\right)^2 \qquad EQ. 37$$

The photon was reflected if Eq. 38 held.

$$\chi \le \frac{R_s + R_p}{2} \qquad \qquad EQ. 38$$

4.4.2. INTERACTION WITH A REFLECTIVE INTERFACE:

When a photon hits a reflective interface it was reflected with the likelihood of the reflectivity set. The reflective efficiency was calculated in the same way as the luminescent quantum efficiency. The new direction is simply derived from Snell's law. PVtrace also offers the option to insert a Lambertian surface. A Lambertian surface is a perfect scattering surface. PVtrace is ray-tracing model so the Lambertian scattering was calculated from a local point, so the cosine distribution is the method used (as earlier discussed in Section 2.4). For the code used to program the mirrors see Appendix B.

4.5. TECHNICAL REALIZATION

PVtrace wrote all relevant data in a SQL-lite database. This data was directly written on the hard disk, which is a time demanding step. To overcome this 'problem' the simulation was executed on a RAMdisk. Doing so, the SQL-database was then written into the memory, which is up to 25 times faster. The many simulations were performed using 20 different computers. Each computer ran series of simulations whereby, after each series of simulations, the results (the SQL-files) were collected. Results: Model validation.

5. RESULTS: MODEL VALIDATION

The model PVtrace, as used in this research, is elaborated in Chapter 4. This chapter is dedicated to the validation of this model. The results of real experiments, performed by Z. Krumer, were compared to the results of equivalent simulated experiments. Section 5.1 describes the experimental set-up. Section 5.2 describes the simulation framework and finally, Section 5.3 discusses the results of both the real experiments as the equivalent simulations.

5.1. EXPERIMENTAL SET-UP

The experiments were performed with an LSC doped with the luminophore Lumogen Red 305. The luminophores were dissolved in toluene and placed in a cuvette, made of quartz, with the dimensions of 10 x 3.5 x 1cm³. This cuvette was the waveguide of the LSC. The quartz walls of the cuvette had a refractive index of 1.46 and the toluene had a refractive index of 1.496 [53]. At one of the 1cm by 10cm surfaces a cylinder was attached with a length of 1.5cm and a radius of 0.4cm. This cylinder was used to fill the cuvette. A solar simulator was used as light source. A c-Si-solar cell, with an efficiency of 13%¹¹, was attached to the smallest surface of the cuvette (1cm by 3.5cm). All the other surfaces, except the front surface, were covered with a small air gap between the scattering surface had a reflectivity of 0.97 - 0.99 and was placed with a small air gap between the scattering surface and the walls of the cuvette. The luminophore concentration was the only variable in these experiments. Of every used luminophore concentration the absorption spectrum was measured (see Appendix L). The experiments were repeated several times to increase the reliability of the results.

5.2. SIMULATION FRAMEWORK

The simulation framework was discussed in Section 3.2. The dimensions, of the LSC, chosen were the same dimensions as in the real experiments $(10 \times 3.5 \times 1 \text{ cm}^3)$. The slight adaption made, in comparison with the simulation framework in Section 3.2, was the addition of a cylinder with a radius of 0.4cm and 1.5cm length, which has been placed on one of the 10 x 1cm² surfaces. The other three side surfaces were covered with perfect air gap mirrors. The backside was covered with a perfect Lambertian air gap mirror. See Figure 23 for the graphical representation. The simulated solar cell had an efficiency of 13% instead of 18% (which was used in the other simulations). This was to make a better comparison between the results of the simulations and the real experiments.

¹¹ A c-solar cell with an efficiency of 13% was used because this was the c-solar cell available. In the economical assessment (Section 9.2) a c-si solar cell with an efficiency of 18% was used. This efficiency is more common nowadays.

Results: Model validation.



FIGURE 23: VISUALIZATION OF A RUNNING PVTRACE SIMULATION RESEMBLING THE EXPERIMENTS WITH MIRRORS INCLUDED.

5.3. COMPARISON

The device efficiencies η_{sys} , defined as the ratio of the electrical energy delivered by the solar cell and the incoming radiative energy illuminating the LSC, are shown in the Figure 24.



FIGURE 24: AN OVERVIEW OF THE DEVICE EFFICIENCY UNDER DIFFERENT CONCENTRATION FOR BOTH THE SIMULATIONS AND THE EXPERIMENTAL RESULTS [50]. K IS THE CORRECTION FACTOR FOR THE LOSSES WITHIN THE ATTACHMENT OF THE SOLAR CELL.

The simulated results show reasonable alignment with the experimental results. The best results were gained by linear adapt the simulated results with a factor 0.78¹². In a try to explain this factor the differences and similarities between the simulations and the real experiments were investigated. First, the dimensions of the simulated waveguide and the experimental waveguide were the same. Only the

¹² The best results refer to the least square of the residue method.

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part of the waveguide that was doped with luminophores was slightly smaller in the experimental waveguide due to the quartz walls. The quartz walls were only 0.1cm, so this minor difference could not cause the difference of the factor 0.78. Second, the cylinder in the simulations was equivalent with the cylinder in the experiments and the simulated light source was the same as the one used in the experiments (AM1.5G). The only difference in the spectra used over the different luminophore concentrations were the slight errors in measuring the spectra. These errors were assumed to be negligible. Third, the mirrors used in the simulations had a reflectivity of 1 against a reflectivity of 0.97-0.99 in the experiments. Due to this difference few percent of the photons are less lost in the simulations compared to the experiments. But the difference of factor 0.78 cannot be explained by this. As fourth, the refractive index of 1.5 in the simulations slightly differs from the refractive index of 1.46 in the experiments. The higher refractive index results in a slightly higher trapping efficiency (using Eq. 19 and Eq. 20) but this was way too small to explain the factor of 0.78. The main explanation of the factor 0.78 difference between the simulations and the experiments was the use of a glue to connect the solar cell with the waveguide. The glue had a refractive index around 1.5 but happened to be not so transparent. This low transparency of the glue was assumed to cause a lot of the photons to be lost, due to parasitic absorption, even when the layer of glue was small (~0.1cm). The alignment between the simulations and the experiments gave enough reason to assume that the results of the simulated experiments were reliable.

Results: Perfect luminophore.

6. RESULTS: PERFECT LUMINOPHORE

As explained in Section 3.1, the perfect luminophore was simulated to examine the maximum efficiencies reachable within this defined luminescent solar concentrating system. This Chapter follows the methods described in Chapter 3. Section 6.1 shows the results of the simulations with a Lambertian air gap mirror at the backside and without the loss process of background absorption. Thereafter, Section 6.2 describes the results of the simulations without both a Lambertian air gap mirror at the background losses. Followed by Section 6.3, where the results are presented of the simulations with the loss process of background absorption and without the Lambertian air gap mirror at the backside. Finally the calculated impacts of the different loss processes are discussed in Section 6.4.

6.1. MIRROR AT BACKSIDE, NO BACKGROUND ABSORPTION

Figure 25 shows the absorption- and emission spectrum of the perfect luminophore. This luminophore had an absorption coefficient of 200m⁻¹ from a wavelength of 0nm till a wavelength of 899nm and it emitted all the photons at 900nm¹³. The absence of overlap between the absorption spectrum and the emission spectrum resulted in the absence of reabsorption events. The perfect luminophore was simulated with a quantum efficiency of 100%.



FIGURE 25: THE NORMALIZED ABSORPTION AND EMISSION SPECTRA OF THE PERFECT LUMINOPHORE (THE ABSORPTION SPECTRUM STARTS AT WAVELENGTH ZERO)

¹³ An absorption coefficient of 200m⁻¹ corresponds to an absorption of 99% of the photons, in the absorption spectrum, per cm.

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Table 3 shows the results of a simulation with the length of 10cm, using a perfect Lambertian air gap mirror at the backside without the loss process background absorption. The results were adjusted with the truncation factor as discussed in Section 3.5.

Destination	Photons	Energy
PV cell	29.10	27.65
Not absorbed	48.42	29.89
Fresnel	3.93	3.98
Air gap	3.79	3.64
EC	13.10	12.31
Stokes shift	0.00	20.98
Killed in simulation	1.66	1.56

TABLE 3: RESULTS IN % OF SIMULATED PHOTONS (CORRECTED WITH THE TRUNCATION FACTOR) WITHA SIMULATION WITH THE PERFECT LUMINOPHORE AT LENGTH = 10CM.

The most energy in this system was lost due to no absorption (30%), followed by the energy lost within Stokes shift (21%). Stokes shift is a loss process that is conceptual different from the others. There is a part of the energy of the photon lost and not photons itself. Therefore the Stokes shift losses were 0% if expressed in photon count. Besides, the conversion of photons to electricity within the PV cell causes this energy loss as well.¹⁴ It makes no difference where this energy is lost for the efficiency of the whole system. Furthermore, the Fresnel losses (external reflection) were around 4%, as expected (see Section 2.3.1). About 13% of the photons escaped through the EC and near 4% of the photons escaped through the air gaps. Finally, this system showed an η_{opt_e} of 27.65%, which contained 29.1% of the simulated photons (η_{opt_f}).

The simulations were performed over different sizes, as discussed in Section 3.3. Results of these simulations are found in Figure 26 and Figure 27. The Stokes shift losses (about 21%) and losses due to external reflection (4%) showed no dependency of the LSC size. All the other loss processes were saturating around a size of 20cm length. The percentage of not absorbed photon energy increased with size due to the decreased influence of the Lambertian mirror at the backside to 30-31%. The saturation was explained by the fact that photons that hit the Lambertian reflector, and thereby change direction, will have a higher probability of reaching the solar cell within a small LSC compared to a large LSC.

¹⁴ Under the assumption that the energy is large enough to cause a electron-hole pair with an equal likelihood.

Results: Perfect luminophore.



FIGURE 26: RESULTS IN ENERGY OVER INCREASING SIZE WITH THE PERFECT LUMINOPHORE ALREADY CORRECTED WITH THE TRUNCATION FACTOR.



FIGURE 27:. RESULTS IN PHOTONS AMOUNT OVER INCREASING SIZE WITH THE PERFECT LUMINOPHORE CORRECTED WITH THE TRUNCATION FACTOR

The EC losses increased with increasing size (till 13%) due to a decreased likelihood that a photon within the EC reached the solar cell before it could escape. The explanation of decreasing air gap losses by increasing size (to 5%) is that the ratio 'air gap to LSC' decreases and thereby the probability of a photon to escape there. An equivalent reasoning was used to explain the escape cone losses. By increasing size the likelihood that a photon within the EC reached the PV cell before it could escape decreases. This saturation was reached around a length of 10cm. The optical efficiency saturated to $\eta_{opt_e} = 26\%$ for large sizes, corresponding to $\eta_{opt_e} = 27\%$.

The calculated concentration factors are presented in Figure 28. The concentration factor increased almost perfectly linear with increasing size. The linear growth of the concentration factor was explained by the linear dependency between the surface area of the LSC (length * width = L^2 * 0.35cm²) and the surface area of the PV cell (height * width = L * 0.35 * 1cm²). No perfect linear increase in concentration factor is seen, by increasing size, due to the influence of the Lambertian air gap mirror at the backside and a random generator error within the simulations. The mirror gives advantages at small sizes, as discussed above, and the random generator caused a small error in the

calculated efficiencies. The concentration factor G correlated with the $G_{geometric}$ times η_{opt_e} (see Eq. 39).



FIGURE 28: THE CONCENTRATION FACTOR OF THE LSC AND THE GEOMETRICAL CONCENTRATION FACTOR PLOTTED AGAINST THE LENGTH.

$$G_{geometric} = \frac{Area_{LSC}}{Area_{PV}} = \frac{0.35 * L^2}{0.01 * 0.35 * L} = 100 * L$$
 EQ. 39

For a better understanding of the loss processes the different loss processes were expressed as percentage of absorbed photons. Figure 29 shows the destination of all absorbed photons. The percentage of absorbed photons that reached the solar cell saturated with increasing size to 60-61%. So, almost 40% of the photons escaped through escape cones, the only loss mechanism within this defined system. These escape cones were divided in escape cone losses (losses through the front and back surface) and air gap losses (losses through the no perfect closure of the air gap mirrors at the sides).



FIGURE 29: THE DESTINATION OF ABSORBED PHOTONS PLOTTED AGAINST SIZE.

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The air gap mirrors are not perfectly closing the escape cones at the edges. Part of the light still escaped through the side-surfaces, but this was significantly less than the 12.7% per edge that would escape without these mirrors (see Section 2.3.5). The Lambertian air gap mirror at the bottom scatters the light interacting with this mirror. The light enters the LSC again but it will always have an angle within the EC of the top-surface, else the photon was not able to enter the waveguide. This explains why the EC losses could reach a maximum of 25.5% (see Section 2.3.5), considering a refractive index of 1.5. However, the analyses are showing EC losses around 30%.

The physical explanation of this phenomenon is that photons were reflected from a 'side-mirror' to the Lambertian mirror at the bottom. The Lambertian mirror changed the direction of the photon until it entered the waveguide though the bottom surface. The photon direction was located within the EC of the top surface and escaped. Hereby were the EC losses with increased with recycled photons from the side mirrors resulting in a total measured loss of photons through the top surface of 30%. See Figure 30 for a graphical representation.



FIGURE 30: THE ROUTE OF A REEMITTED PHOTON THAT ESCAPED THROUGH THE TOP SURFACE BUT ORIGINALLY WOULD ESCAPE THROUGH THE RIGHT SURFACE. THERE IS A NORMAL AIR GAP MIRROR AT THE RIGHT AND A LAMBERTIAN AIR GAP MIRROR AT THE BOTTOM.

6.2. NO MIRROR AT THE BACKSIDE, NO BACKGROUND ABSORPTION

To support the above explanation and that it was no mistake within the model, the simulation results of the same system without the Lambertian air gap mirror at the backside are shown in Figure 31. The percentage of absorbed photons reaching the solar cell saturated with increasing size to 60-61%, just as in the situation with the Lambertian mirror. The EC losses were plateauing towards the expected and calculated maximum of 25.5%, showing thereby that the model calculated the EC losses in a correct way. The losses due to the not perfect closure of the escape cones by the air gap mirrors were around 13% of the absorbed photons, which was still a considerable loss. Reducing the air gap size reduced the losses through the air gap. This was done but due to limitations of the simulation software an air gap of 0.5mm was the minimum distance. A smaller air gap somehow increased the calculation time a lot, thereby making the calculations impossible due to limiting computational power.

Results: Perfect luminophore.



FIGURE 31: THE DESTINATION OF ABSORBED PHOTONS PLOTTED AGAINST SIZE WITHOUT A LAMBERTIAN MIRROR AT THE BACKSIDE.

The saturation to 60-61% of the absorbed photons that reached the PV cell within both the simulations with and without the Lambertian air gap mirror raised the question of the effect of this mirror. To examine the effects of the Lambertian air gap mirror the two simulation series were compared. Figure 32 shows the gain in optical energy efficiency by using a Lambertian air gap mirror at the backside.



FIGURE 32: OPTICAL EFFICIENCY GAIN OF THE LAMBERTIAN AIR GAP MIRROR BY INCREASING LENGTH

This increase in energy is mainly subscribed to the extra photons reaching the solar cell that would not be absorbed by the luminophore at all (see Figure 33).¹⁵ In real life, most of this photons would either be absorbed by the PMMA (NIR absorption) or not been absorbed by the solar cell. So the effect of the Lambertian back mirror would even be smaller than the simulations suggest. Figure 33 shows the emission spectra reaching the solar cell (in the case with a Lambertian backside mirror) in bins of 15nm. Figure 33a is at a length of 1cm, Figure 33b and Figure 33c were taken from the simulation data at a length of 50cm. Only Figure 33c was 'zoomed in' so it is visible that there were also incoming

¹⁵ The emission spectrum at the side surface of an LSC without a Lambertian mirror at the backside contains only photons of 900nm.

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wavelengths other than 900nm. The effect of the Lambertian air gap mirror at the backside was very limited as seen by the height of the bins in Figure 33.



FIGURE 33: EMISSION SPECTRA OF AN LSC SYSTEM WITH THE PERFECT LUMINOPHORE AND A LAMBERTIAN MIRROR AT THE BACKSIDE. THE BINS ARE 15NM.

6.3. NO MIRROR AT THE BACKSIDE, WITH BACKGROUND ABSORPTION

The above simulations were without the loss process of background absorption. To see the effect of these real life waveguide losses this process was simulated using the background absorption code. An absorption coefficient of 0.5m⁻¹ was used. This is one of the best-achieved absorption coefficients within PMMA in 2008. The results of the simulations are shown in Figure 34. These simulations were equivalent as the earlier presented simulations without a Lambertian air gap mirror at the backside, but with the additional background loss process.



FIGURE 34:. A) THE DESTINATION OF ABSORBED PHOTONS PLOTTED AGAINST SIZE WITH THE ADDED LOSS PROCESS OF BACKGROUND ABSORPTION. B) THE CORRESPONDING OPTICAL ENERGY EFFICIENCY.

The results show that the EC losses were nearly unaffected by the background absorption. This was because a photon that traveled at an angle in an escape cone reached the corresponding interface at such short distance that the likelihood of losing the photon to background absorption was almost zero. The air gap losses, instead, were decreasing with increasing length. These photons had longer path lengths before being lost through the air gap. So, with increasing length there was an increased likelihood for the photon to be lost as background absorption instead of being lost due to an air gap. The losses of photons that would have reached the PV cell increased also with size. Even 55% of the absorbed photons were lost at a length of 100cm due to background absorption.

Both the air gap losses as the photons that reached the PV cell decreased logarithmically with increasing size. This suggests a growth of the average path length. Figure 35 shows the trend line of background absorption against size. The background absorption increased logarithmically with size following the Lambert-Beer law.



FIGURE 35: BACKGROUND ABSORPTION LOSSES PER ABSORBED PHOTON OF AN LSC SYSTEM LOGARITHMICALLY PLOTTED AGAINST INCREASING SIZE. NO LAMBERTIAN AIR GAP MIRROR AT THE BACKSIDE

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A loss process that increases logarithmically with size has its influence on the concentration factor. Below, in Figure 36, is the concentration factor plotted against the length. The concentration factor saturated around G=8 with a perfect luminophore. These simulations showed the major effect of background losses on large scale causing the limit of G = 8 for this defined system.



FIGURE 36: CONCENTRATION FACTORS OF THE LSCS WITHOUT LAMBERTIAN MIRROR AT THE BACKSIDE.

6.4. IMPACT OF THE DIFFERENT LOSS PROCESSES

The size dependent loss mechanisms within an LSC were saturating around a length of 10cm with a perfect luminophore. The efficiencies shown in Table 4 were extracted from the data without the Lambertian mirror at the backside, using the equations in Appendix H. All this efficiencies are given as flux efficiencies. The perfect luminophore had an absorption efficiency of 48% and an optical efficiency of 12% at a length of 60cm. The efficiencies were limited by the η_{EC} , $\eta_{air gap}$ and (especially) at larger sizes by $\eta_{waveguide}$. The losses due to background absorption were dominant at larger sizes as seen in the reduction of optical efficiency from 23% to 12%. These were the maximum achievable efficiencies within the current defined system (so not within LSC at all). The only size dependent efficiency was the waveguide efficiency.

TABLE 4: THE DIFFERENT EFFICIENCIES CALCULATED USING THE SIMULATION SOFTWARE PVTRACE. ALL EFFICIENCIES ARE GIVEN IN PHOTON COUNT COMPARED TO THE SOLAR IRRADIATION OF AN AM1.5G SPECTRUM. THERE IS NO LAMBERTIAN MIRROR PLACED AT THE BACKSIDE.

	10cm	30cm	60cm
$\eta_{Fresnel}$	0.96	0.96	0.96
$oldsymbol{\eta}_{Absorption}$	0.48	0.48	0.48
η_{QE}	1	1	1
$\eta_{\scriptscriptstyle EC}$	0.75	0.75	0.75
$oldsymbol{\eta}_{Waveguide}$	0.82	0.60	0.42
$F_{Reabsorption}$	1	1	1
$oldsymbol{\eta}_{Air\ gap}$	0.83	0.83	0.83
η_{opt_f}	0.23	0.17	0.12

7. RESULTS: LUMOGEN RED 305

As explained in Section 3.1, Lumogen Red 305 was simulated to examine the performances of the current quasi-standard within this defined luminescent solar concentrating system. This Chapter follows the methods described in Chapter 3. Section 7.1 shows the results of the simulations with a Lambertian air gap mirror at the backside and without the loss process background absorption. Thereafter, Section 7.2 describes the results of the simulations without a Lambertian air gap mirror at the backside. Finally the calculated impacts of the different loss processes are discussed in Section **Error! Reference source not found.**

7.1. MIRROR AT BACKSIDE, NO BACKGROUND ABSORPTION

Lumogen Red 305 is the current quasi-standard luminophore within LSCs. The absorption and emission spectra of Lumogen Red 305 are shown in Figure 37.



FIGURE 37: THE NORMALIZED ABSORPTION AND EMISSION SPECTRA OF LUMOGEN RED 305.

A series of simulations with a varying concentration was performed. The LSC has a length of 10cm and the simulations contained a perfect Lambertian air gap mirror at the backside. Figure 38 shows the optical efficiencies of the LSC as result of the simulations. At the x-axis the absorption coefficient at 574nm was chosen as a proxy for the concentration. For comparison, around 60ppm is equivalent to an absorption peak of 200m⁻¹.



FIGURE 38 : THE OPTICAL EFFICIENCIES OF A LSC WITH SIZES 10 X 3.5 X 1CM³ WITH INCREASING CONCENTRATION.

The η_{opt_e} is higher than η_{opt_f} , this was explained by the fact that Lumogen Red 305 as luminophore has its spectra in a higher average intensity range of the solar spectrum than the perfect luminophore. The efficiency increased with increasing concentration until it saturated around absorption strengths of 200m⁻¹. For more insight why this saturation occurred, the effects of the loss processes were examined. Figure 39 shows the destination of the simulated photons.



FIGURE 39: SIMULATION RESULTS IN ENERGY OVER INCREASING CONCENTRATION WITH LUMOGEN RED 305.

The largest loss process was the not absorbed photons. The amount of not absorbed photons decreased with increasing concentration until it reached a limit. At this limit all the photons within the absorption spectrum were absorbed. This process followed the Lambert-Beer curve as seen in Figure

39. The losses due to external reflection were concentration independent (4%), just as the theory predicted. Also the air gap losses seemed concentration independent, which suggested that most of these photons were not absorbed photons. The escape cone and quantum efficiency losses were concentration dependent and increased with increasing concentration. The more photons absorbed, the more photons were lost through these routes. EC losses and QE losses were enhanced by reabsorption events. Figure 40 shows the spectra of photons reaching the solar cell at different concentrations, there was concluded that the red-shift of the spectra was the result of reabsorption. Also the effect of the scattering effect of the Lambertian air gap mirror was seen.

The valley in the emission spectra, which occurred at higher concentrations, around 700nm, was explained by the used absorption spectrum. The noise in measuring the absorption spectrum of Lumogen Red 305 was multiplied by increasing the absorption strength (within the simulations). Thereby absorption (multiplied noise) was also simulated within wavelength ranges where no actual absorption would occur. The multiplied noise started to show an effect around an absorption coefficient of 200m⁻¹ at 574nm. The spectrum was cut-off at 700nm, therefore there was a peak value after that specific wavelength (there was no reabsorption after this cut-off). For more information see Appendix F.



CONCENTRATIONS. THE LENGTH OF THE LSC WAS 10CM AND THE SYSTEM CONTAINED A LAMBERTIAN AIR GAP MIRROR AT THE BACKSIDE. THE BINS ARE 7NM EACH AND THE HEIGHT GIVES THE AMOUNT OF PHOTONS.

7.2. NO LAMBERTIAN AIR GAP MIRROR AT THE BACKSIDE

The Lambertian air gap mirror at the backside made analysis very difficult due to the scattering effect of this mirror. It scattered photons direct onto the solar cell, air gap losses were a mix of absorbed and not absorbed photons and the EC losses were difficult to analyze, as seen in the analysis of the perfect luminophore. Therefore a closer analysis of this system, without Lambertian air gap mirror, followed here. This analysis was performed to increase the understandability of the relationships between the loss processes and the concentration of the luminophore. Figure 41 shows the results of the simulations of the system described in Section 7.1, but without the Lambertian air gap mirror at the backside.



FIGURE 41 : THE OPTICAL EFFICIENCIES OF A LSC WITH SIZES 10 X 3.5 X 1CM³ AGAINST INCREASING CONCENTRATION.

The optical flux efficiency saturated at an efficiency of ~8%, about 3% lower than with the Lambertian air gap mirror. Also the plateau was reached at a higher luminophore concentration without the Lambertian air gap mirror at the backside than with. This happened due to the fact that the initial length to be absorbed, for a photon, at least doubled with a Lambertian air gap mirror at the backside. So, the profits of more absorption were reached at higher concentration without the mirror. The 3% difference in plateau value was explained by the scattering effect of the Lambertian air gap mirror. Parts of the scattered photons were directly directed onto the solar cell. Also the likelihood for a, by a luminophore, emitted photon, emitted in the escape cone, to reach the solar cell before reaching an escape cone was decreased by removing the backside mirror. These two effects were significant at this size, as seen in the flux spectra shown in Figure 40 and Figure 42.



FIGURE 42: THE SPECTRA OF PHOTONS REACHING THE SOLAR CELL FOR FOUR DIFFERENT CONCENTRATIONS. THE LENGTH OF THE LSC IS 10CM AND THE SYSTEM CONTAINS NO LAMBERTIAN AIR GAP MIRROR AT THE BACKSIDE. THE BINS ARE 7NM EACH AND THE HEIGHT GIVES THE AMOUNT OF PHOTONS.

Figure 43 shows the destination of the absorbed photons. The percentage of absorbed photons reaching the PV cell decreased with increasing luminophore concentration¹⁶. The increases of QE losses and EC losses by increasing concentrations were subscribed to the reabsorption effect. Reabsorption subjected the photons again to loss mechanisms as EC losses and QE losses causing an increase in the likelihood of losing photons.

¹⁶ The absolute value of absorbed photons increased with in increasing concentration. This is not shown in Figure 43.

Results: Lumogen Red 305.



FIGURE 43: THE DESTINATION OF ABSORBED PHOTONS (GIVEN IN PHOTON COUNT) PLOTTED AGAINST SIZE (LENGTH IS 10CM, WITHOUT A LAMBERTIAN AIR GAP MIRROR AT THE BACKSIDE).

The reabsorption loss factor is subtracted from this data. The quantum efficiency losses were 5% without reabsorption, so everything above 5% QE losses per absorbed photon is caused by again submitting a part of the photons to this loss mechanism (due to reabsorption). The escape cone losses were calculated at 25.14% at this size¹⁷. So, all the losses above 0.95 * 25.14% were subscribed to reabsorption losses as well. This is also explained in Appendix H.

The losses due to reabsorption increased with increasing concentration, as seen in Figure 44. The reabsorption losses were already causing 5% of the absorbed photons to be lost at very low concentrations. This is due to the high absorption coefficients in the overlapping part the emission spectrum (see Figure 37). The losses due to reabsorption increased to 13% of the absorbed photons at an absorption coefficient of 200m⁻¹ (at 570nm), and even to 18% at high concentrations. The height of the reabsorption loss plateau depends on the amount of reabsorption events, the escape cone losses and the quantum efficiency.



FIGURE 44: THE LOSS PROCESSES (PHOTON AMOUNT) PLOTTED WITH THE REABSORPTION LOSSES EXTRACTED FROM THE DATA.

¹⁷ The EC losses without reabsorption events are 25.14% at size length = 10 cm (the result within the simulation with the perfect luminophore)

The reabsorption losses were significant at an LSC length of 10cm, and were expected to reach higher values in larger sizes due to longer travel lengths. To study the relationships between size and ideal concentration simulations with changing concentration were performed for sizes between 1 and 100cm length.

In Figure 45 the destination of absorbed photons is shown for three different sizes with both with and without background absorption. These simulations were conducted without the Lambertian air gap mirror at the backside to be able to make better comparisons between the results. Figure 45 shows results for simulations at lengths of 10, 30 and 60cm. These simulations were conducted with 50.000, 75.000, and 100.000 photons respectively. Increasing luminophore concentration was causing increasing reabsorption losses with a saturation value around 23% of the absorbed photons (Figure 45c and Figure 45e). The figures without the background absorption show that at larger sizes about 35% of the absorbed photons reached the solar cell. The reabsorption losses could not be subtracted out of the simulation conducted with background absorption due to the interchangeability of the loss mechanisms.

At a length of 30cm the background absorption lowered the photon amount reaching the solar cell with a factor of ~0.62 to 25% of the absorbed photons. At a length of 60cm this factor changed to ~0.42 (that resulted in a percentage of 15% of the absorbed photons reaching the solar cell) making background absorption a dominant loss factor. The percentage of background losses decreased with increasing concentration due to the interchangeability of the loss mechanisms. When a photon is lost due to reabsorption it could not be lost as background absorption anymore.



a)



FIGURE 45: THE GRAPHS SHOW THE DESTINATION OF THE ABSORBED PHOTONS OVER INCREASING CONCENTRATION UNDER DIFFERENT LENGTHS. FIGURE A,C AND E ARE WITHOUT BACKGROUND ABSORPTION, FIGURE B,D AND E ARE WITH BACKGROUND ABSORPTION.

Figure 46 shows the concentration factors (G) that were reached without a Lambertian air gap mirror placed at the backside. A concentration factor around 2 was reached with Lumogen Red 305 within this defined system (with background absorption).



FIGURE 46: A 3D PRESENTATION OF CONCENTRATION FACTORS UNDER CHANGING SIZE AND CONCENTRATION WITHOUT LAMBERTIAN AIR GAP MIRROR. AC = ABSORPTION COEFFICIENT.

7.3. IMPACT OF THE DIFFERENT LOSS PROCESSES

The optical photon efficiency reached a plateau by increasing absorption strengths. This plateau started at absorption coefficients of $200m^{-1}$, at a wavelength of 574nm, (with a Lambertian air gap mirror at the backside) or $300m^{-1}$ (without the Lambertian air gap mirror). The concentration factor showed a limit around G=2. This limited performance was mainly caused by the low absorption efficiency. Escape cone losses and the reabsorption losses were considered as the most important loss mechanisms, but at larger sizes the background absorption losses (or waveguide efficiency) were the dominant loss factor.

The efficiencies for a LSC doped with Lumogen Red 305 with background absorption (waveguide losses) and without Lambertian air gap mirror were extracted from the above presented results. This is done at an absorption coefficient of $300m^{-1}$ at a wavelength of 574nm. This absorption coefficient correlates at the lowest concentration in the efficiency plateau reached with increasing the concentration. The calculated efficiencies are given in Table 5. The $\eta_{absorption}$ of 0.17 is low compared to the maximum $\eta_{absorption}$ of 0.48 of the perfect luminophore. That means that there is still a lot to win within the harvesting of photons with luminophores. The impact of reabsorption is a factor of 0.77 at a length of 10cm and it decreased to a factor of 0.6 at a length of 60 cm. The waveguide efficiency decreased from an efficiency of 0.81 to 0.42 by scaling up the LSC from 10cm length to 60cm length. The increase in length to 60cm resulted in a decrease of the optical efficiency from 6% (10cm length) to around 2%.

	10cm	30cm	60cm
$\eta_{Fresnel}$	0.96	0.96	0.96
$\eta_{Absorption}$	0.17	0.17	0.17
η_{QE}	0.95	0.95	0.95
η_{EC}	0.75	0.75	0.75
$\eta_{Air\ gap}$	0.83	0.83	0.83
$F(\eta_{QE}, \eta_{EC}, \eta_{Air\ gap})_{Reabsorption}$	0.77	0.65	0.60
$\eta_{Waveguide}$	0.81	0.62	0.42
η_{opt}_{f}	0.06	0.04	0.02

TABLE 5: THE DIFFERENT EFFICIENCIES WERE CALCULATED USING THE SIMULATION SOFTWARE PVTRACE. ALL EFFICIENCIES ARE GIVEN AS FLUX EFFICIENCIES COMPARED TO THE SOLAR IRRADIATION OF AN AM1.5G SPECTRUM AT THE LSC.¹⁸

¹⁸ For calculations see appendix H

Results: QDs.

8. RESULTS: QDS

Type-II core-shell quantum dots are a relative new kind of luminophores. The advantages of low reabsorption and a broad absorption spectrum are promising characteristics. As explained in Section 3.1, quantum dots were examined as luminophores. This Chapter presents the effects of the quantum dot characteristics on the LSC. This Chapter follows the methods described in Chapter 3 and investigates two different quantum dots. Section 8.1 shows the results of the simulations with QD1 as luminophore. Thereafter, Section 6.2 describes the results of the simulations with QD2 as luminophore.

8.1. QUANTUM DOT 1

Quantum dot 1 (QD1) is a CdTe-CdSe Type-II core-shell multipod. Figure 47 shows the normalized absorption and emission spectra of QD1. There is strong absorption in the high energy part of the spectrum. At wavelengths longer than 570nm the absorption coefficient reaches very low absorption coefficients towards zero at 800nm. This, so called, tail is characteristic in type-II QD absorption spectra. The simulations with QD1 were conducted with a QE of 48%¹⁹. The goal was to examine if these QDs provide better efficiencies within LSCs than Lumogen Red 305.



FIGURE 47: THE NORMALIZED ABSORPTION AND EMISSION SPECTRA OF QD1

8.1.1. MIRROR AT BACKSIDE, NO BACKGROUND ABSORPTION

A series of simulations with a varying concentration was performed. The LSC had size of $10 \times 3.5 \times 1$ cm³. The simulations contained a Lambertian air gap mirror at the backside and no background absorption. At the y-axis there was chosen for the absorption coefficient at 520nm.²⁰ Figure 48 shows the optical efficiencies with increasing concentration.

¹⁹ The measured QE of this specific QD was <10% but 48% can quite easily be reached with similar spectra.

²⁰ It is not known to which concentration this absorption strength correlates

Results: QDs.



FIGURE 48: THE OPTICAL EFFICIENCIES OF A LSC WITH SIZES 10 X 3.5 X 1CM³ WITH INCREASING CONCENTRATION.

The efficiency increased with increasing concentration until it reached a peak value around an absorption coefficient of 60m⁻¹. After the peak value the efficiency dropped again until it saturated. To get more insight into this peak value the effects of the loss processes were examined. The efficiency of the QD1 doped LSC showed a peak value against increasing luminophore concentrations. This peak value occurs because the loss processes increased more with increasing concentration than the increased harvesting of photons. Appendix G elaborates this phenomenon more extensively.

With QD1 as luminophore the largest losses were still the not absorbed energy, although more energy was absorbed than with Lumogen Red 305 (see Figure 49b). The QE losses were much larger than with Lumogen Red 305. This is due to the lower QE. Escape cone losses and QE losses increased with size due to the enhancement by reabsorption events. Figure 50 shows the spectra of photons that reached the solar cell at different luminophore concentrations. The red-shift of the spectra is the result of reabsorption. The effect of more absorption was seen in the decrease of photons reaching the solar cell within the absorption range of QD1.



FIGURE 49: A) SIMULATION RESULTS IN PHOTON AMOUNT OVER INCREASING CONCENTRATION WITH QD1. B) THE DIFFERENCE BETWEEN ABSORPTION OF THE AM1.5G SPECTRUM FOR LUMOGEN RED 305 AND QD1 WITH 574NM AND 520NM ABSORPTION COEFFICIENTS RESPECTIVELY.

A few photons with a wavelength shorter than 360nm reached the solar cell at an absorption coefficient of 287.15m⁻¹. This is because the absorption spectrum had only values starting at wavelength of 360nm, so the photons emitted at shorter wavelengths could not be absorbed within the simulation. So the photons that reached the solar cell with wavelengths shorter than 360nm were directly scattered from the Lambertian mirror onto the solar cell. In real life they would be absorbed because the quantum dots experience their highest absorption coefficients in that region. This is no catastrophic mistake because it only counts for 0.75% of the photon flux therefore the results are still valid.





a) 9.57 m⁻¹

b) 28.72 m⁻¹

Results: QDs.



FIGURE 50: THE SPECTRA OF PHOTONS REACHING THE SOLAR CELL FOR FOUR DIFFERENT CONCENTRATIONS. THE LENGTH OF THE LSC IS 10CM AND THE SYSTEM CONTAINS A LAMBERTIAN AIR GAP MIRROR AT THE BACKSIDE. THE BINS ARE 7NM EACH AND THE HEIGHT GIVES THE AMOUNT OF PHOTONS.

8.1.2. NO MIRROR AT THE BACKSIDE

To be able to extract the losses due to reabsorption simulations without the Lambertian air gap mirror at the backside were performed. Figure 51 shows the results of simulations of the same system described earlier but without the Lambertian air gap mirror at the backside.



FIGURE 51 : THE OPTICAL EFFICIENCIES OF A LSC WITH SIZES 10 X 3.5 X 1CM³ WITH INCREASING CONCENTRATION WITHOUT LAMBERTIAN AIR GAP MIRROR AT THE BACKSIDE.

The energy efficiency peaks at an absorption coefficient of 97m⁻¹ at 4.5% (2.5% lower than with the Lambertian air gap mirror). The 2.5% difference in peak value was attributed to the scattering effect of the Lambertian air gap mirror, part of the scattered photons were directly directed onto the solar cell. Also more harvesting of light by the luminophore caused an increase in efficiency. The significance of

the directly onto the solar cell scattered photons is seen in the flux spectra in Figure 50 and Figure 52. Also the advantage of a doubled absorption length is seen is Figure 50a and Figure 52a by the higher peak value of the emission spectrum.



FIGURE 52: THE SPECTRA OF PHOTONS REACHING THE SOLAR CELL FOR FOUR DIFFERENT CONCENTRATIONS. THE LENGTH OF THE LSC IS 10 CM AND THE SYSTEM CONTAINS NO LAMBERTIAN AIR GAP MIRROR AT THE BACKSIDE. THE BINS ARE 7NM EACH AND THE HEIGHT GIVES THE AMOUNT OF PHOTONS.

The percentage of absorbed photons that reached the solar cell, decreased by increasing absorption coefficients, as seen in Figure 53. The increase in percentage of QE losses and EC losses by increasing concentrations was subscribed to the reabsorption events.

Results: QDs.



FIGURE 53 : THE DESTINATION OF ABSORBED PHOTONS PLOTTED AGAINST SIZE. (LENGTH IS 10CM) WITHOUT LAMBERTIAN AIR GAP MIRROR AT THE BACKSIDE

The losses due to reabsorption are graphically shown in Figure 54. The quantum efficiency losses were set at 52%. The escape cone losses were calculated at 25.14% at this size. So everything above 0.48 * 25.14% was subscribed to reabsorption losses. The air gap losses were calculated to be 17% of the trapped photons, so everything different than 0.48 * 0.2514 * 0.17 was subscribed to the reabsorption effect as well. The reabsorption losses were very low at low concentration but increased to 20% of the absorbed photons at high concentration.



FIGURE 54: THE LOSS PROCESSES (PHOTON AMOUNT) PLOTTED WITH THE REABSORPTION LOSSES EXTRACTED FROM THE DATA.

The reabsorption losses were quite significant and are expected to cause more losses at larger sizes due to longer travel lengths. In Figure 55 the destination of absorbed photons is shown for three different sizes for both with and without background absorption. These simulations were conducted without the Lambertian air gap mirror at the backside. The simulations at the length of 10cm, length of 30cm and length of 60cm were conducted with 50.000, 75.000, and 100.000 photons respectively. Increased concentration resulted in larger reabsorption losses with saturation around 22% of the absorbed photons (Figure 55c and Figure 55e).

At a length of 30cm the background absorption lowered the photon amount reaching the solar cell with a factor of ~0.62 to 6% of the absorbed photons. At a length of 60cm this factor changed to ~0.42 (that resulted in that 4.5% of the absorbed photons reached the solar cell) making background absorption a dominant factor. The percentage of background losses decreased with increasing concentration due to the interchangeability of the loss mechanisms. When photons were lost due to reabsorption it could not be lost by background absorption anymore.



FIGURE 55: THE GRAPHS SHOW THE DESTINATION OF THE ABSORBED PHOTONS OVER INCREASING CONCENTRATION UNDER DIFFERENT LENGTHS. FIGURE A,C AND E ARE WITHOUT BACKGROUND ABSORPTION, FIGURE B,D AND E ARE WITH BACKGROUND ABSORPTION.

Figure 56 shows the concentration factors for different sizes at different luminophore concentrations. Figure 56a and Figure 56b are both results of simulations without the Lambertian air gap mirror at the backside. Figure 56c and Figure 56d are results of simulations with the Lambertian air gap mirror. There is a slight shift seen to higher absorption coefficients for the peak value of the efficiency (or concentration factor) at larger sizes. But, the most important conclusion is that no concentration factor above 1.0 was reached anywhere.



c)

FIGURE 56: (A,C) A 3D PRESENTATION OF THE RESULTING CONCENTRATION FACTOR S . (B.D) THE CORRESPONDING SURFACE PLOTS OF THE CONCENTRATION FACTORS. FIGURE A AND B ARE WITHOUT LAMBERTIAN AIR GAP MIRROR AT THE BACKSIDE, FIGURE C AND D ARE WITH. AC = ABSORPTION COEFFICIENT.

IMPACT OF THE DIFFERENT LOSS PROCESSES 8.1.3.

QD1 as luminophore never reached a concentration factor above 1 with a background absorption coefficient of 0.5 m⁻¹. The loss efficiencies for a LSC doped with QD1 with background absorption

(waveguide losses) and without Lambertian air gap mirror are extracted from the presented results. This is done at peak efficiency at an absorption coefficient of $60m^{-1}$ at a wavelength of 520nm.

As seen in Table 6, the quantum efficiency has a large effect on the total efficiency. Also the $\eta_{reabsorption}$ is lower than with Lumogen Red 305 as luminophore. This is remarkable because the absorption spectrum of QD1 is broader. The explanation is that due to the strongly increased reabsorption losses the ideal concentration was reached at levels where not all the light that could be absorbed actually was absorbed.

The waveguide efficiency was higher than with Lumogen Red 305 as luminophore. This implies that the average travelled length of the photons reaching the solar cell was less within the QD1 doped LSCs compared to the LSC doped with Lumogen Red 305. The reason for this is that the photons with the longer path lengths were already lost via other loss mechanism (reabsorption). Another reason can be the statistical error within the simulations caused by the limited amount of photons simulated.

Type-II quantum dots promised a larger Stokes shift that should have resulted in a higher $F_{reabsorption}$. In contrast to the expectations the reabsorption losses were larger with QD1. This is partially due to the lower QE, more percentage of photons was lost per reabsorption event, but even as important is the tail of the absorption spectrum of QD1. The very small absorption coefficients overlapping with the emission spectrum caused much reabsorption events at longer travel lengths and higher concentrations.

	10 cm	30 cm	60 cm
$\eta_{Fresnel}$	0.96	0.96	0.96
$\eta_{Absorption}$	0.16	0.16	0.16
η_{QE}	0.48	0.48	0.48
η_{EC}	0.75	0.75	0.75
$\eta_{Air\ gap}$	0.83	0.83	0.83
$F(\eta_{QE}, \eta_{EC}, \eta_{Air\ gap})_{Reabsorption}$	0.66	0.49	0.39
$\eta_{Waveguide}$	0.89	0.68	0.52
η_{opt}_{f}	0.03	0.02	0.01

TABLE 6: THE DIFFERENT EFFICIENCIES CALCULATED WITH THE SIMULATION SOFTWARE PVTRACE. ALL EFFICIENCIES FLUX EFFICIENCIES COMPARED TO THE SOLAR IRRADIATION OF AN AM1.5G SPECTRUM AT THE LSC.²¹
Results: QDs.

8.2. QUANTUM DOT 2

Quantum Dot 2 (QD2) is a Type-II dot-core/rod-shell nanorod with a size around 20nm in length. The simulated quantum efficiency was 60%²². The absorption- and emission spectrum looked a lot like those of QD1, only the absorption spectrum is a slightly broader and the absorption tail is less long. The emission spectrum is bit shifted to the red. The goal of the simulations with these spectra was to examine the possibilities to higher efficiencies with Type-II quantum dots. Figure 57 presents the normalized absorption- and emission spectrum of QD2.



FIGURE 57: NORMALIZED ABSORPTION AND EMISSION SPECTRA OF QD2

8.2.1. NO MIRROR AT BACKSIDE

A series of simulations with varying absorption coefficients was performed. The LSC had size of 10 x 3.5×1 cm³. A perfect Lambertian air gap mirror at the backside was used and 50.000 photons were simulated. At the y-axis there was chosen for the absorption coefficient at 520nm.²³ Figure 58 shows the optical efficiencies with increasing concentration without background absorption and without the Lambertian air gap mirror.



FIGURE 58: THE OPTICAL EFFICIENCIES OF A LSC WITH SIZES 10 X 3.5 X 1CM³ WITH INCREASING CONCENTRATION.

²² Measured QE=48%, but QE=60% are measured quantum efficiencies of other batches of Type-II QD's

²³ It is not known to which concentration this absorption strength correlates

The efficiency increased with increasing absorption coefficients until it reached a plateau (around 250m⁻¹). The optical efficiencies were comparable with Lumogen Red 305 doped LSCs. Figure 59 shows the losses without and due to reabsorption. The negative reabsorption losses seen at very low absorption coefficients were caused by the reabsorption of photons that else would be lost as air gap losses. The photons that would have escaped through the air gap needed to travel a relative long length before escaping. The likelihood for reabsorption was thereby larger than for other photon. Reabsorption saved these photons from escaping. But when the absorption coefficients became higher the additional losses toke over until about 5% of the absorbed photons were lost due to reabsorption.



FIGURE 59: THE LOSS PROCESSES (PHOTON AMOUNT) PLOTTED WITH THE REABSORPTION LOSSES EXTRACTED FROM THE DATA. QE=60%

Figure 60 shows that the reabsorption losses caused a 5% loss of absorbed photons at both 10cm, 30cm and 60cm length. At large sizes about 30% of the absorbed photons reached the solar cell, considering no background absorption. This value is comparable with Lumogen Red 305.





a)



FIGURE 60: THE GRAPHS SHOW THE DESTINATION OF THE ABSORBED PHOTONS OVER INCREASING CONCENTRATION UNDER DIFFERENT LENGTHS. FIGURE A,C AND E ARE WITHOUT BACKGROUND ABSORPTION, FIGURE B,D AND E ARE WITH BACKGROUND ABSORPTION.

Results: QDs.

8.2.2. IMPACT OF THE DIFFERENT LOSS PROCESSES

The shorter tail in the absorption spectra of QD2 reduced the reabsorption losses significantly to a factor of 0.86 at larger sizes, as seen in Table 7. The loss efficiencies for a LSC doped with QD2 with background absorption (waveguide losses) and without Lambertian air gap mirror were extracted from the presented results. This was done at the peak efficiency reached at an absorption coefficient of 250m⁻¹, at wavelength 520nm. The absorption efficiency of 0.24 was an improvement but still very modest compared to the maximum of 0.48.

TABLE 7: THE DIFFERENT EFFICIENCIES CALCULATED WITH THE SIMULATION SOFTWARE PVTRACE. ALL EFFICIENCIES FLUX EFFICIENCIES COMPARED TO THE SOLAR IRRADIATION OF AN AM1.5G SPECTRUM AT THE LSC.

	10 cm	30 cm	60 cm
$\eta_{Fresnel}$	0.96	0.96	0.96
$\eta_{Absorption}$	0.23	0.23	0.23
η_{QE}	0.60	0.60	0.60
$\eta_{\scriptscriptstyle EC}$	0.75	0.75	0.75
$\eta_{Air\ gap}$	0.83	0.83	0.83
$F(\eta_{QE},\eta_{EC},\eta_{Air\ gap})_{Reabsorption}$	0.92	0.87	0.86
$\eta_{Waveguide}$	0.85	0.62	0.45
η_{opt_f}	0.06	0.04	0.03

9. COMPARISON OF LUMINOPHORES

The results of the different luminophores, presented in the chapters 6, 7 and 8, are compared in this Chapter. The comparisons considered a system without Lambertian air gap mirror with the loss mechanism background absorption at the luminophore concentration, per luminophore, that resulted in the highest system efficiency. Section 9.1 discusses the equalities of the LSCs doped with the different luminophores. Thereafter, the differences of the LSCs doped with the different luminophores are discussed in Section 9.2. And finally a simple economical assessment is shown for the best (real) luminophore and the hypothetical perfect luminophore.

9.1. EQUALITIES OF THE DIFFERENT LUMINOPHORES

The LSCs doped with different luminophores showed some equivalent loss efficiencies. Table 8 presents these losses. At the bottom of this table the total impact of the equivalent loss mechanisms is presented. The escape cone losses were the most significant equivalent losses. Overall, all the LSCs, doped with different luminophores had in common that 40% of the energy was lost due to this 'fixed losses'.

	LR305	QD2	QD1	Perfect
$\eta_{Fresnel}$	0.96	0.96	0.96	0.96
$\eta_{\scriptscriptstyle EC}$	0.75	0.75	0.75	0.75
$\eta_{Air\ gap}$	0.83	0.83	0.83	0.83
Total impact	0.60	0.60	0.60	0.60

TABLE 8: AN OVERVIEW OF THE LOSS MECHANISMS WITH EQUIVALENT EFFICIENCIES OVER THE DIFFERENT LUMINOPHORES.

The equivalent loss mechanisms happened to be design dependent efficiencies. These loss mechanisms depended on the characteristics of the waveguide, the geometry of the waveguide and the placement of the air gap mirrors. They were independent from variables used in this research as: luminophore type, luminophore concentration and LSC size.

9.2. DIFFERENCES OF THE DIFFERENT LUMINOPHORES

The LSCs doped with different luminophores showed different efficiencies over some loss mechanisms. Table 9 presents these loss mechanisms with associated efficiencies per luminophore at a length of 10cm. The quantum efficiency was a set parameter and a property of the luminophore. The largest loss mechanism in the system was imperfect harvesting of the light in the waveguide. Perfectly 48% of the light could be captured. Lumogen Red 305, the current quasi-standard, captured 17% percent of the light. Surprisingly, QD1 showed lower absorption efficiency than Lumogen Red 305.

R.J.M. Reus, IMPROVING THE EFFICIENCY OF LUMINESCENT SOLAR CONCENTRATORS, Comparison of luminophores.

While quantum dots promised better harvesting of light due to the broader absorption spectra. The decreased absorption efficiency (to 16%) is explained by the lower ideal luminophore concentration used by QD1 compared to Lumogen Red 305. The lower ideal concentration of QD1 results in imperfect absorption over the absorption range of the solar spectrum. While Lumogen Red 305 absorbed (almost) all the photons in the absorption range of the spectrum. That resulted in higher absorption efficiencies for Lumogen Red 305 than for QD1, while the absorption spectrum of QD1 was broader. QD2 had broader absorption spectra than QD1. The characteristic tail of the absorption spectrum of QD1 started around 580nm while the tail of the absorption spectrum of QD2 started around 630nm. Also the ideal concentration of QD2 was higher than of QD1. This resulted in an approved absorption efficiency of 23%. The reabsorption losses were losses due to reabsorption events. These were dependable of the amount of reabsorption events, the size of escape cone and the quantum efficiency. The perfect luminophore had no reabsorption losses, Lumogen Red 305 had a reabsorption factor of 0.77, QD2 a reabsorption factor of 0.92 and QD1 a reabsorption factor of 0.66. The reabsorption factor of QD2 was higher while the losses per reabsorption event were also higher (due to lower quantum efficiency). This implied that an LSC doped with QD2 experienced way less reabsorption events. Another interesting finding was the difference in waveguide efficiency. The waveguide efficiency depended on the photon travel length and the background absorption coefficient. The background absorption coefficient was equal in all simulations. Therefore the travelled length per photon, reaching the solar cell, differed. Lumogen Red 305 doped LSCs had the longest travel length followed by the LSCs doped with the perfect luminophore. In the LSCs doped with the QD's part of the photons with the longer travel lengths were already lost before they could be absorbed by the waveguide. This resulted in an overall loss factor of 0.39 for the perfect luminophore, 0.10 for Lumogen Red 305, 0.11 for QD2 and 0.05 for QD1. This showed that QD2 doped LSCs were about 10% more efficient than Lumogen Red 305 doped LSCs at a waveguide length of 10cm.

	LR305	QD2	QD1	Perfect
$\eta_{Absorption}$	0,17	0,23	0,16	0,48
η_{QE}	0,95	0,6	0,48	1
$F(\eta_{QE},\eta_{EC},\eta_{Air\ gap})_{Reabsorption}$	0,77	0,92	0,66	1
$\eta_{Waveguide}$	0,81	0,85	0,89	0,82
Total factor	0,10	0,11	0,05	0,39

TABLE 9: THE LOSS MECHANISMS WITH DIFFERENT EFFICIENCIES OVER THE LUMINOPHORES AT LENGTH = 10CM

The next step in the comparison was to see how the efficiencies changed with increased waveguide size. Table 10 shows the efficiencies for the different luminophores at a length of 60cm. The absorption efficiency and quantum efficiency were unaffected by the waveguide size.

R.J.M. Reus, IMPROVING THE EFFICIENCY OF LUMINESCENT SOLAR CONCENTRATORS, Comparison of luminophores.

	LR305	QD2	QD1	Perfect
$\eta_{Absorption}$	0.17	0.23	0.16	0.48
η_{QE}	0.95	0.60	0.48	1
$F(\eta_{QE}, \eta_{EC}, \eta_{Air\ gap})_{Reabsorption}$	0.60	0.86	0.39	1
$\eta_{Waveguide}$	0.42	0.45	0.52	0.42
Total factor	0.041	0.053	0.016	0.202

TABLE 10: THE LOSS MECHANISMS WITH DIFFERENT EFFICIENCIES OVER THE LUMINOPHORES AT LENGTH = 60CM

The reabsorption factor for QD1 and Lumogen Red 305 decreased significantly with the increased waveguide size. While the reabsorption factor of QD2 did not increase significantly. Another important factor with increasing size was that the waveguide losses were dominant at a length of 60cm. This resulted in modest LSC efficiencies. The LSCs doped with QD2 performed about 30% better compared to the LSCs doped with Lumogen Red 305.

QD2 was a better luminophore than Lumogen Red 305 due to the better reabsorption losses and higher absorption efficiency. Still, the performances of this luminophores were about 25% of the maximum (perfect luminophore), so there is a lot to gain.

9.3. ECONOMICAL ASSESSMENT

A small economical assessment was performed to show the current market performances of the chosen LSC. A cost ratio [€/cm⁻²] of 4:1 for a c-Si-solar cell to a LSC plate was assumed²⁴. The simulations with and without Lambertian air gap mirror at the backside were economically examined. The loss process of background absorption was involved. This economical assessment was done for both QD2 as the perfect luminophore

The defined LSC system contained a c-Si-solar cell with an efficiency of 18%. The calculations of η_{sys} is therefore done with the spectral response spectrum $R_{0.18}(\lambda)$ (Eq. 22 and Eq. 23). The relative energy production of the LSC per \in compared to energy production per \in of a c-Si-solar cell were calculated with Eq. 40.

Relative energy production =
$$\frac{\eta_{sys_e} * E_{in}}{LSC_c + PV_{LSC_c}} / \frac{\eta_{cell} * E_{in}}{PV_c}$$
 EQ. 40

The waveguide costs LSC_c were the price per area times the area A. The area is length times width (= length² x 0.35). The PV_{LSC} area was height times width (=0.035 x length). So Eq. 40 was rewritten to Eq. 41, with X as the costs of PV cells per square meter.

²⁴ This value is based on 2013 market prices of Si-solar cells [55] and luminescent PMMA [56].

R.J.M. Reus, IMPROVING THE EFFICIENCY OF LUMINESCENT SOLAR CONCENTRATORS, Comparison of luminophores.

Relative energy production =
$$\frac{\eta_{sys_e} * 0.35L^2}{0.25X * 0.35L^2 + X * 0.0035L} * \frac{X * 0.35L^2}{\eta_{cell} * 0.35L^2}$$
$$= \frac{\eta_{sys_e} * L}{0.25L + 0.01} * \frac{1}{\eta_{cell}}$$
EQ. 41

Figure 61 shows a 3D plot, with associated contour plot, of the relative energy production per \in produced by a QD2 doped LSC compared to the energy production per \in of a c-Si solar cell. These results were of a system without a Lambertian air gap mirror at the backside. The economical comparison showed an optimal relative energy output of 0.3. This value was reached at a length around 10cm with an absorption coefficient of 250m⁻¹ (measured at 520nm).



Relative energy production

Relative energy production

FIGURE 61.THE RELATIVE KWH/€ OF A LSC SYSTEM COMPARED TO A SI-SOLAR CELL. A) THE 3D VIEW. B) THE CONTOUR-PLOT. AC = ABSORPTION COEFFICIENT. THE SYSTEM IS WITHOUT A LAMBERTIAN MIRROR AT THE BACKSIDE.

The analysis of the perfect dye (Figure 62) shows economical profitable LSCs at small sizes with a perfect luminophore. It was concluded that the simple LSC geometry, with PMMA, presented was not economical viable at this presented set-up. The background absorption losses had too much negative influence on the system.



FIGURE 62. THE RELATIVE KWH/€ OF A LSC SYSTEM COMPARED TO A SI-SOLAR CELL WITH A PERFECT DYE

Discussion.

10. DISCUSSION

This thesis was set out to assess the quality of CdTe-CdSe Type-II core-shell quantum dots as luminophores in LSCs. Also the impacts of the different loss mechanisms on the efficiency of the LSC were determined. This chapter discusses the results of the research in Section 10.1. The reliability of the results is discussed in Section 10.2. Finally, the implications of this research on the body of knowledge are discussed in Section 10.3.

10.1. THE RESULTS

The results in this thesis quantify that LSCs doped with QD2, CdTe-CdSe Type-II core-shell quantum dots, were 10% more efficient than LSCs doped with Lumogen Red 305, at a length of 10cm. The performances of LSCs doped with QD2 were even 30% better at a length of 60cm. Section 10.1.1 discusses the total impacts of these results and Section 10.1.2 put the results into broader context.

10.1.1. THE IMPACT OF THE RESULTS

The LSCs doped with CdTe-CdSe Type-II core-shell quantum dots (QD2) showed 10-30% better performances than the current quasi-standard LSCs (doped with Lumogen Red 305) within the simulations. The relative performances increased with increasing waveguide size. But the impact of this performance increase was modest. A 10% increase over an optical efficiency of 6% results in an optical efficiency of 6.6%. Therefore the impact on the optical efficiency was not even 1% at 10cm length. At a waveguide length of 60cm the relative performances of the ideal QD2 doped LSC were 30% better compared to the LSC ideally doped with Lumogen Red 305. A 30% increase over an optical efficiency of 2% results in an optical efficiency of 2.6%. Therefore the impact on the optical efficiency was also not even 1% at 60cm length. As comparison, the LSCs doped with the hypothetical perfect luminophore performed 290% and 390% better than the LSC's doped with Lumogen Red 305 for a waveguide length of 10cm and 60cm respectively. Furthermore became clear that the largest problem in scaling-up LSCs was not reabsorption but was the parasitic absorption of the waveguide.

10.1.2. THE CONTEXT OF THE RESULTS

Type-II core-shell quantum dots have promising characteristics as low overlap between the absorption and emission spectra and broad absorption spectra. This research investigated the performances of a few current state QD's as luminophores. The results of this research were all presented as optical efficiencies. But at the end the system efficiency is the most important efficiency. An increase in optical efficiency results in a lower increase in system efficiency. This made the small improvement of the change in luminophore even less significant.

The simulations showed that QD2 was a significant better luminophore than Lumogen Red 305 despite of the modest QE of 60%. It is expected that higher QE's will be reached in future research. There are already published articles that claim QE's of around 80%. The increase in QE will have a large impact on the optical efficiency of thereby making Type-II quantum dots an interesting option as luminophore. Care has to be taken to keep the overlap in the characteristic tail of the absorption spectrum and the emission spectrum to a minimum. Appendix I does contain a summary which explains this, already in Chapter 9 discussed principles in detail.

10.2. THE RELIABILITY OF THE RESULTS

First, this research was performed using the simulation tool PVtrace. The simulations come with statistical errors in the results due to the use of a random number generator. The two strategies chosen: 'high number of photons simulated' and 'truncation of the solar emission spectrum', as discussed in Chapter 3, resulted in a negligible random generator error.

Second, there was assumed that the QE of the luminophores was unaffected by the luminophore concentration. This statement is valid for the concentrations used with the luminophore Lumogen Red 305 because this was measured. However, this statement was not measured for the simulated values for the used quantum dots. But, the finding by Lumogen Red 305 gave enough certainty to make the same assumption for the used quantum dots.

Third, the multiplication of the measured noise in the absorption spectra were assumed to show influence at higher concentrations (high multiplication of the measured spectra), as shown in Section 7.1. The calculated efficiencies at these 'higher' absorption strengths were considered as less reliable due to these errors within the absorption spectrum (for Lumogen Red 305). At high simulated absorption coefficients the influence of the (multiplied) noise of the measured absorption spectrum was getting significant within the model. This resulted in more initial absorption and more reabsorption events in the simulation than in real life would be happened. Lumogen Red 305 started to show absorption in a range where it is not possible. Therefore these higher concentrations were not used in the calculation of efficiencies or the comparison section.

Overall could be concluded that the results were reliable, as demonstrated in Chapter 5 and Appendix D.1. Only the results in the plateau (of optical efficiency against luminophore concentration) of Lumogen Red 305 were considered less reliable.

10.3. IMPACT ON THE FIELD OF KNOWLEDGE

A lot of research was already done concerning LSCs (see Section 2). This research showed a working simulation model with validation. This was already been done by other research groups. But, this

thesis provides a clear format in classifying the photons under different loss mechanisms. Hereby insight was generated in loss mechanisms as reabsorption losses and waveguide losses. Also it was shown that the ideal concentration was only affected by the LSC size when the luminophore concentration against efficiency showed a peak value instead of a plateau. This was not found in the literature yet. Also the effect of a mirror at the backside of the waveguide was found to be negligible at large sizes. Also it was shown that quantum dots can already be better luminophores than Lumogen Red 305. And finally, the statement that an air gap mirror is principally better than a direct mirror was proven wrong. This is dependent of the reflection index of the mirror and the size of the air gap. These findings, used frameworks and methods thereby contribute to the body of knowledge.

Conclusion.

11. CONCLUSION

CdTe-CdSe Type-II core-shell quantum dots can provide a solution in achieving higher efficiencies within LSCs. The most important factors with the use of CdTe-CdSe Type-II core-shell quantum dots as luminophores were possibility of enhanced harvesting of light and less impact of losses due to reabsorption. This thesis assesses the quality of CdTe-CdSe Type-II core-shell quantum dots as luminophores and the LSC system in general. PVtrace was used as simulation tool in this thesis in order to answer the research questions. Section 11.1 presents the results to the research questions. Then, Section 11.2 presents the limitations of this study. Thereafter, the suggestions for further research are presented in Section 11.3. Finally, the final remarks are presented in Section 11.4.

11.1. ANSWERS TO THE RESEARCH QUESTIONS

This research sought answers to the following (sub) question(s):

What is the relation between ideal size and ideal concentration?

It has been shown that increasing concentration enhanced the harvesting of light, as described by law of Lambert-Beer, and it enhanced the amount of reabsorption events, thereby the reabsorption losses. The increase in concentration caused an increase in efficiency until the efficiency reached a plateau (Lumogen Red 305 and QD2) or increased until the reabsorption losses toke over (QD1), which resulted in a peak value. The ideal concentration showed a shift to higher concentrations for the luminophore with a peak value in efficiency by increasing LSC-lengths. The ideal concentration showed to be independent of the size when a plateau was reached for efficiency against increasing luminophore concentration.

What are the maximum achievable performances for the different luminophores within the defined LSC?

The maximum achievable performances simulated were, besides with the hypothetical perfect luminophore, with QD2. The optical efficiencies reached were 6.4% for an LSC-length of 10cm and 3.2% for an LSC-length of 60cm. These efficiencies were achieved without a Lambertian air gap mirror at the backside and at an absorption coefficient of $250m^{-1}$, at wavelength 520nm. With a QD2 doped LSC a relative energy production per \in of 0.3 was achieved compared to the energy production per \in by the same Si solar cell (of 18% efficiency) without an LSC attached. Also concentration factors around 2 were reached. LSCs doped with Lumogen Red 305 reached optical efficiencies of 6% and 2% for LSC lengths of 10cm and 60cm respectively. Also these efficiencies were achieved without a Lambertian air gap mirror at the backside. The absorption coefficient used to reach these efficiencies was $300m^{-1}$ at 574nm. The LSCs doped with the perfect luminophore showed efficiencies of 23% and 12% for LSC lengths of 10cm and 60cm respectively.

What are the important loss factors within LSCs using different luminophores?

The fixed loss factors, due to the simulation framework, were accountable for a factor of 0.6. This implies that 40% of the photons always were lost, no matter which luminophore was chosen. These fixed loss factors were EC losses (0.75), air gap losses (0.83) and losses due to external reflection (0.96). The EC losses and air gap losses were lower, than stated above, when the LSC length was reduced to 5cm and lower. The air gap losses were significant at the used air gap of 0.5mm, thereby showing that air gap mirrors does not necessary have to be better than direct attached mirrors. Furthermore, QE was a fixed luminophore dependent loss factor with a significant influence.

The impact of reabsorption was calculated. It was shown that the impact of reabsorption depended on the amount of reabsorption events and the likelihood of losing photons per such event. For Lumogen Red 305 the impact of reabsorption was a factor 0.6 at an LSC-length of 60cm. It was shown that QD2 suffered less reabsorption impact (0.82). This was due to the negligible absorption coefficients overlapping with the emission spectrum. This research showed that very small absorption coefficients overlapping with the emission spectrum largely enhanced the reabsorption impact. This is due to large photon travel lengths before reaching the solar cell compared to the small lengths in which photons (from the sun) could be initially absorbed.

Furthermore, the $\eta_{Waveguide}$ of PMMA was the limiting factor by increasing the LSC-size. The waveguide efficiency was already as low as 60% for LSC-sizes of 30 x 10.5 x 1cm³. Thereby was 40% of the optical efficiency lost, due to parasitic absorption, at a length of 30cm. In the ideal situation the waveguides should be as large as 1m. But with these background absorption losses this cannot be achieved.

<u>Main Question</u>: Do CdTe-CdSe Type-II core-shell quantum dots provide a solution in achieving higher LSC efficiencies?

Slightly higher optical efficiencies were already achieved at quantum efficiencies of 60% (with QD2). It is expected that future research will improve the QE of quantum dots. There are already quantum efficiencies reported for Type-II QDs around 80%. So, quantum dots provide a solution in achieving higher LSC efficiencies. But the background losses resulted in a limitation of the concentration factor for QD2 around G=2. For higher concentration factors the absorption spectra need to be broader, the QE higher and the background absorption lower.

11.2. LIMITATIONS OF THE STUDY

This study was limited to just a single geometry. This geometry was a height of 1cm, a length-to-width ratio of 1:0.35, a solar cell attached to a height times width surface and air gap mirrors attached to the other three smallest sides (with an air gap of 0.5mm). This thesis investigated this geometry and the impact of different luminophores with different concentrations on the system. Thereby was shown that

QD2 had better performances than Lumogen Red 305 independent from the geometry (see Section 9.1. and Section 9.2). However, a change in geometry is likely to influence the optical efficiencies and reached concentration factors. But that is another kind of study. With the economical assessment should be taken into account that a change in geometry can largely influence the assessment.

11.3. RECOMMENDATIONS FOR FURTHER RESEARCH

- Geometry study: The geometry is likely to influence the concentration factors and efficiencies within the system. A study towards the ideal geometry and ideal placement of the solar cells is therefore useful to study.
- 2) Different QDs: Chemical studies should try to make a quantum dot with a broad absorption spectrum and low overlap between the reabsorption spectrum and the emission spectrum. This is the first requirement for better performances. Thereafter the QE should at least be 60% to improve current state.
- **3) Different waveguides:** The waveguide showed to be the largest problem in scaling up the LSC. Research is necessary to improve the quality of the PMMA or to replace the waveguide for a different material like glass, fiberglass or even the liquid toluene.

11.4. FINAL REMARKS

This research aimed to compare current state Type-II core-shell quantum dots as luminophore with the current quasi-standard Lumogen Red 305. A solid method was used to calculate this. Thereby was the impact of every loss mechanism determined. The economical assessment showed that electricity generated by a QD2 doped LSC of length 60cm was four times as expensive as electricity generated by the same solar cell but without the waveguide. But by improving the waveguide, enhancing the QE to 85% and closing the air gaps this system can be economical viable²⁵.

	Real QD2 (60cm)	Improved system
$\eta_{Fresnel}$	0.96	0.96
$\eta_{Absorption}$	0.23	0.23
η_{QE}	0.60	0.85
η_{EC}	0.75	0.75
$\eta_{Air\ gap}$	0.83	1
$F(\eta_{QE},\eta_{EC},\eta_{Airgap})_{Reabsorption}$	0.86	0.90 ²⁶
$\eta_{Waveguide}$	0.45	0.90
η_{opt_f}	0.03	0.11

TABLE 11: AN OVERVIEW OF THE NECCESAIRY STEP TO MAKE LSCS ECONOMICAL VIABLE.

²⁵ Under the same economical assumptions of a waveguide-to-PV-cell cost ratio of 1:4.

²⁶ An improved QE results in an improved reabsorption factor

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APPENDIX A: METHODS TO EXTRACT DATA OUT OF THE SQL-LITE DATABASE

All the photon steps were saved within SQL-files. To find the destination of the photons, thereby the efficiency and the impact of all the loss processes, a code was written to find the correct data. In the SQL-files there was looked the last step of each photon (the destination). This 'last step' was found by searching to the creation of a new photon (everything is vacant) and then go one 'uid' (step counter) back into the database. A code looks a seen in Figure 63.

'SELECT photon.wavelength FROM photon WHERE uid IN (SELECT uid FROM state WHERE uid IN (SELECT uid-1 FROM state WHERE on_surface_obj="None" AND intersection_counter=0) AND container obj = "RAYBIN1" AND killed = 0)'

A)

'SELECT COUNT(*) FROM state WHERE uid IN (SELECT uid-1 FROM state WHERE on_surface_obj="None" AND intersection_counter=0) AND container_obj = "RAYBIN1" AND killed = 0;'

B)

FIGURE 63: A) A CODE USED IN SQL-FILES TO SEARCH ALL WAVELENGTHS OF THE PHOTONS REACHING RAYBIN. B) A CODE USED IN SQL-FILES TO SEARCH ALL THE AMOUNT OF THE PHOTONS REACHING RAYBIN.

The characteristics searched per destination are presented in Table 12 (with Lambertian mirror at the backside) and Table 13 (without Lambertian air gap mirror at the backside) and were all implemented in a code. When summarized, the total amount of photon destinations found was one minus the total amount of simulated photons. This is because the destination of the last simulated photon was not included, there was no new photon created after the last photon so this destination could not be tracked with this approach. This total gave also the conferment that all the photons were counted and none of them was double counted or missed.

TABLE 12: THE SEARCH VARIANTS USED IN FINDING THE DESTINATION OF THE SIMULATED PHOTONS WHILE THERE IS A LAMBERTIAN MIRROR AT THE BACKSIDE.

	Abs_co unt	Int_cou nt	Kille d	Container_o bj	On_surface _obj	Surface_id	Ray- direction- bound
--	---------------	---------------	------------	-------------------	--------------------	------------	-----------------------------

R.J.M. Reus, IMPROVING THE EFFICIENCY OF LUMINESCENT SOLAR CONCENTRATORS, Appendix A: Methods to extract data out of the SQL-lite database.

PV cell			0	Raybin			
Killed			1			None	
Not absorbed	0	>=2	0			Тор	Out
External reflection	0	=1	0			Тор	Out
Mirror losses			0	Face1 / Face2 / Face3 / Face4		Polygon	
Air gap Iosses			0	Bounds		Polygon / Far / Near / right / bottom	
EC losses	>= 1		0	Bounds	LSC	Тор	Out
QE losses			0	LSC	None	None	None
Background losses			0	Background			

TABLE 13: THE SEARCH VARIANTS USED IN FINDING THE DESTINATION OF THE SIMULATED PHOTONS WHILE THERE IS NO LAMBERTIAN MIRROR AT THE BACKSIDE.

	Abs_co unt	Int_cou nt	Kille d	Container_o bj	On_surface _obj	Surface_id	Ray- direction- bound
PV cell			0	Raybin			

R.J.M. Reus, IMPROVING THE EFFICIENCY OF LUMINESCENT SOLAR CONCENTRATORS, Appendix A: Methods to extract data out of the SQL-lite database.

Killed			1			None	
Not absorbed	0	>=2	0			Тор	Out
	0		0			Bottom	Out
External reflection	0	=1	0			Тор	Out
Mirror losses			0	Face1 / Face2 / Face3 / Face4		Polygon	
Air gap Iosses			0	Bounds		Polygon / Far / Near / right /	
EC losses	>= 1		0	Bounds	LSC	Top/Bottom	Out
QE losses			0	LSC	None	None	None
Background losses			0	Background			

APPENDIX B: HOW THE MIRRORS WERE PROGRAMMED

```
#Define Mirrors
reflectivity = 1
z = 0.0005 # the distance between the mirrors and the LSC
shape1=Polygon([(-z,-z,-z), ((L+z),-z,-z), ((L+z),(W+z),-z), (-z,(W+z),-z)])
shape2=Polygon([((L+z),-z,-z), ((L+z),-z,H),((L+z),(W+z),H), ((L+z),(W+z),-z)])
shape3=Polygon([(-z,-z,-z), ((L+z),-z,-z), ((L+z),-z,H), (-z,-z,H)])
shape4=Polygon([(-z,(W+z),-z), ((L+z),(W+z),-z), ((L+z),(W+z),H), (-z,(W+z),H)])
# lambertian status = True # (wether or not the surface is also a scatterar)
#mirror1
mirror1 = Coating(reflectivity, shape=shape1, refractive_index=1., lambertian=True)
mirror1.name = 'Face1'
#mirror2
mirror2 = Coating(reflectivity, shape=shape2, refractive index=1., lambertian=False)
mirror2.name = 'Face2'
#mirror 3
mirror3 = Coating(reflectivity, shape=shape3, refractive_index=1., lambertian=False)
mirror3.name = 'Face3'
# mirror 4
mirror4 = Coating(reflectivity, shape=shape4, refractive_index=1., lambertian=False)
mirror4.name = 'Face4'
```

An important fact about programming a polygon: the points needed to be programmed in a row. So, if you draw from point to point the lines may not cross. Else the program did not recognize the polygon as a surface. Also, PVtrace did not work with a reflectivity else than 1 for the polygon. Implementing a QE-like formula, in the polygon code in 'Materials', solved this limitation.

Appendix C: Example of input within pvtrace..

APPENDIX C: EXAMPLE OF INPUT WITHIN PVTRACE.

1	''' Simulation of a rectangular homogeneously doped LSC
2	Steps:
3	1) Define sizes
4	2) Create a light source
5	 Load absorption and emission data for orgnaic dye
6	4) Load linear background absorption for PMMA
7	5) Create LSC object and start tracer
8	6) Calculate statistics.
9	····
10	<pre>#sample = sys.argv[3]</pre>
11	
12	fromfuture import division
13	import numpy as np
14	<pre>from pvtrace.external import transformations as tf</pre>
15	<pre>from pvtrace import *</pre>
16	import sys
17	import os
18	import shutil
19	import glob
20	
21	
22	<pre>ph=int(sys.argv[1]) #amount of photons to be simulated</pre>
23	
24	# 1) Define some sizes
25	L = 0.100
26	H = 0.010
27	W = 0.035
28	
29	# 2) Create light source from AM1.5 data, truncate to 300 1150nm range
30	file = os.path.join(PVTDATA,'sources','AM1.5g-full.txt')
31	<pre>oriel = load_spectrum(file, xbins=np.arange(300,1150)) # range of spectrum</pre>
32	<pre>source = PlanarSource(direction=(0,0,-1), spectrum=oriel, length=L, width=W) # source size, direction</pre>
33	<pre>source.translate((0,0,H+0.01))</pre>
34	

Appendix C: Example of input within pvtrace..

```
35
36 # Collector Stopper Material
37
   abs2 = Spectrum([0,1000], [2,2])
38
    ems2 = Spectrum([500, 600], [0, 0])
   stop = Material(absorption_data = abs2, emission_data = ems2, quantum_efficiency = 0)
39
40 stop.refractive_index = 1.5
41
    # 5) Make the LSC and give it both dye and pmma materials
42
43
   lsc = LSC(origin=(0,0,0.000), size=(L,W,H))
44
45
    #CompositeMaterial([pmma, fluro red], refractive index=float(sys.argv[1]))
46 lsc.name = "LSC"
47
48 #Make Solar Cell (RAYBIN)
49 cellwidth = 0.001
    raybin1 = RayBin(bandgap=0, origin=(-cellwidth,0,0), size=(cellwidth,W,H))
50
51
    ravbin1.name = 'RAYBIN1
52
   raybin1.refractive index = 1.5
53
    raybin1.material = stop
54
55
   # Define Cylinder shape and position
    # cyl1= Geometry.Cylinder()
56
57
    # cyl1.radius = 0.004
    # cyl1.length = 0.015
58
59
    # cyl1.append transform(tf.rotation matrix(3*(np.pi/2),(1,0,0),(0,0,0)))
60
    # cyl1.append transform(tf.translation matrix(((L-0.005),W,(H/2))))
61
62
    #Define Mirrors
63
    reflectivity = 1
64
65
    z = 0.0005 # the distance between the mirrors and the LSC
66
67
    shape1=Polygon([(-z,-z,-z), ((L+z),-z,-z), ((L+z),(W+z),-z), (-z,(W+z),-z)])
     shape2=Polygon([((L+z),-z,-z), ((L+z),-z,H),((L+z),(W+z),H), ((L+z),(W+z),-z)])
68
     shape3=Polygon([(-z,-z,-z), ((L+z),-z,-z), ((L+z),-z,H), (-z,-z,H)])
69
     shape4=Polygon([(-z,(W+z),-z), ((L+z),(W+z),-z), ((L+z),(W+z),H), (-z,(W+z),H)])
72
   #mirror1
74
   mirror1 = Coating(reflectivity, shape=shape1, refractive_index=1., lambertian=True)
    mirror1.name = 'Face1'
76
   #mirror2
78
   mirror2 = Coating(reflectivity, shape=shape2, refractive_index=1., lambertian=False)
79
   mirror2.name = 'Face2'
81
    #mirror 3
82
   mirror3 = Coating(reflectivity, shape=shape3, refractive_index=1., lambertian=False)
83
   mirror3.name = 'Face3
84
85
    # mirror 4
   mirror4 = Coating(reflectivity, shape=shape4, refractive_index=1., lambertian=False)
86
87
   mirror4.name = 'Face4'
89 Edef delete():
        filelist = glob.glob("*.sql")
90
91 🛱
        for f in filelist:
92
           os.remove(f)
93
94 □def copy():
95
        source2 = os.listdir("F:\\python.pvtrace")
                                                                      #### WHERE TO FIND THE FILES ###
96
                                               #### WHERE TO MOVE THE FILES ###
97
98 自
99 目
        for files in source2:
           if files.endswith(".sql"):
               shutil.copy(files,destination)
```

Appendix C: Example of input within pvtrace..

100		
103	der	simulation():
104		
105		abs_1 = Toad_spectrum(Titet)
107		fluxe red = Material (abcountion data=abc f emission data=eme f emantum officiency=exective index=1.5)
100		filto_ieu - material(dostiption_data=dos_1, emission_data=emis_1, quantum efficiency-qe, ieriactive_index=1)
100		<pre># riuto_red = material_with_background(absorption_data-abs_1, emission_data-ems_1, background_absorption = 0, quantum_erriterency-de, refractive_index=1.5)</pre>
109		lsc.material = fluro_red
110		#make the cylinder luminecent
111		<pre># neck =LSC()</pre>
112		<pre># neck.shape = cyll</pre>
113		<pre># neck.material = fluro_red</pre>
114		<pre># neck.name= "bottleneck"</pre>
115		
116		
117		scene = Scene()
118		scene.add_object(lsc)
119		scene.add_object(raybin1)
120		# scene.add_object(neck)
121		scene.add_object(mirror1)
122		scene.add_object(mirror2)
123		scene.add_object(mirror3)
124		scene.add_object(mirror4)
125		
126		# Ask python that the directory of this script file is and use it as the location of the database file
127		pwd = os.getcwd()
128		dbfile = os.path.join(pwd, 'RG14b.sql') # < the name of the database file
129		
130		<pre>trace = Tracer(scene=scene, source=source, seed=8, throws=ph, database_file=dbfile, use_visualiser=False, show_log=False)</pre>
131		<pre>trace.show_lines = False</pre>
132		trace.show_path = False
133		import time
134		tic = time.clock()
135		trace.start()
136		<pre>toc = time.clock()</pre>

Note: background_absorption = 0 (line 108) should be background_absorption = Spectrum([0,4000], [x,x]) with x as absorption strength in m⁻¹, or an uploaded spectrum as the absorption spectrum of the dye.

```
# 6) Statistics
138
139
           print ""
140
           print "Run Time: ", toc - tic
          print ""
141
142
           print "Technical details:"
143
144
           generated = len(trace.database.uids_generated_photons())
145
146
           killed = len(trace.database.killed())
           thrown = generated - killed
          print "\t Generated \t", generated
print "\t Killed \t", killed
print "\t Thrown \t", thrown
147
148
149
           print "\t total photons in raybin1 \t", len(trace.database.endpoint_uids_for_object('RAYBIN1'))
151
# 3) Select aborption spectra
# dbfiles = [f for f in os.listdir(os.path.join(os.getcwd(),"data", "dyes")) if f.endswith('3 .abs.txt')]
155
156
157
     dbfiles = [f for f in os.listdir(os.path.join(os.getcwd(),"data", "dyes", "LR", "temp", 'select2')) if f.endswith('300.txt')]
      # seed number=1
158
159 pfor name in dbfiles:
160
161
162
           # print seed number
           destination = "C:\\Users\\robin\\Documents\\simulations"
163
           qe=1
164
165
           spec_a = str(name)
           file1 = os.path.join(PVTDATA, 'dyes', 'LR', 'temp', 'select2', spec_a)
166
           spec_e = 'emission_RG14.normalized'
           file2 = os.path.join(PVTDATA, 'dyes', spec_e+'.txt')
ems_f = load_spectrum(file2)
167
168
           simulation()
169
           copy()
           delete()
           # seed_number = int(seed_number) +1
```

The code in line 172 increased the seed with 1 every simulation. In this way it was possible to overcome random generator mistakes that could be possible when a low amount of photons was simulated.

Appendix D: The background absorption code.

APPENDIX D: THE BACKGROUND ABSORPTION CODE

0.05 5	
325 Ec.	ass Material_with_background(object):
520	A matching that the pathematic and the protons dependences, a proton is absorbed if a pathematic generated by sampling sense the pathematic law for the proton is less than the pathematic to escape the container. The emission occurs weighted by the quantum efficiency (a probability from 0 to 1). The emission
	wavelength must occur at a red-shifted value with respect to the absorbed photon. This is achieved by samping the emission spectrum from the photons
	wavelength upwards. The direction of the emitted photon is choosen uniformally from an isotropic distribution of angles."""
327	def
320	der _int(seit, absorbtion_data-wone, background_absorbtion=0., emission_data-wone, quantum_errictency=0.0, background_quantum_errictency=0.0, refractive index=1.0:
329	"""The required arguments are the absorption spectrum (a Spectrum object, with units 1/m/nm) and an emission spetrum (a Spectrum object with units
	1/nm). The quantum_efficiency is an optional argument with is the probablilty of emission. If quantum_efficiency is set to 0.0 the emission_spectrum
	is discarded and set to None."""
330	
331	<pre>super(Material_with_background, self)init()</pre>
333	å
334	- def spectrum from data source(data source):
335	
336 🛱	<pre>if isinstance(data_source, str):</pre>
337 白	<pre>if os.path.isfile(data_source):</pre>
338	data = np.loadtxt(data_source)
340	<pre>return spectrum(x=data[:,0], y=data[:,1]) alse:</pre>
341	raise IOError("File '%s' does not exist at this location, '%s' .") % (os.path.basename(data source), data source)
342	
343	<pre># Data is 'list-like'</pre>
344 白	<pre>elif isinstance(data_source, list) or isinstance(data_source, tuple) or isinstance(data_source, np.ndarray):</pre>
345	
340	ives, cuis - ip.snape(data_source) assert rows >1 "Pror processing the data file '%e' DVTrace data files need at least 2 rows and must have 2 columns "This data file has
01/	defines and de columns." & (data source, rows, cols)
348	assert cols == 2, "Error processing the data file '%s'. PVTrace data files need at least 2 rows and must have 2 columns. This data file has
	%d rows and %d columns." % (data_source, rows, cols)
349	<pre>return Spectrum(x=data_source[:,0], y=data_source[:,1])</pre>
350	
351	<pre># Data is already a spectrum alif ising according to the source of the source of</pre>
353	return data source
354	
551	
355 白	else:
356	raise IOError("PVTrace cannot process %s input given to the Material object. Please use the location of a text file (UTF-8 format) which
357	contains spectral data as 2 columns of increasing wavelength (col#1 is the wavelength; col#2 is data).)
358	*
359	
360	
361	
362	# Load absorption data
363 1	i background_absorption != None:
365	s leter factor absorption assorption from data source(background absorption)
366	<pre># self.background absorption = background absorption</pre>
367	<pre># self.background_absorption_data = Spectrum(x=[200, 4000], y=[background_absorption, background_absorption])</pre>
368	
369 白	elif background_absorption None:
370	# No data given make transparent material plb between d between the constraint of 0,0000 m (0,0000 m)
372	serr.background_absorption_data = spectrum(x=[0, 4000], y=[0., 0.])
373 日	if absorption data == None:
374	# No data given make transparent material
375	<pre>self.absorption_data = absorption_data</pre>
376	<pre>self.absorption_data = Spectrum(x=[0, 4000], y=[0, 0])</pre>
377	
378 É	elli absorption data != None;
380	<pre>seif.apsorption_data = spectrum_trom_data_source(apsorption_data)</pre>
381	# Load spectral emission data
382 🗉	if emission data None:
383	# Flat emission profile
384	<pre>self.emission_data = Spectrum(x=[200,4000], y=[1,1])</pre>
385	

Appendix D: The background absorption code.

1205			
200	L		
200	T		
1307			sell.emission_data = spectrum_from_data_source(emission_data)
388			
1209			+ Load quantum efficiency
390			assert 0 <= quantum_efficiency <= 1, "Quantum efficiency is outside the 0 to 1 range."
391			self.quantum_efficiency = quantum_efficiency
392			
393			# Load quantum efficiency
394			assert 0 <= background_quantum_efficiency <= 1, "Quantum efficiency is outside the 0 to 1 range."
395			self.quantum_efficiency = quantum_efficiency
396			
397			# Load refractive index
398			<pre>assert refractive_index >= 1, "Refractive index is less than 1.0"</pre>
399	-		self.refractive_index = refractive_index
400			
401	白	def	absorption (self, photon):
402			""Returns the absorption coefficient experienced by the photon."""
403	-		return self.absorption_data.value(photon.wavelength)
404			
405	白	def	absorption_b(self, photon):
406			""Returns the absorption coefficient experienced by the photon."""
407	-		return self.background_absorption.value(photon.wavelength)
408			
409	¢	def	<pre>emission_direction(self):</pre>
410			"""Returns a 3 component direction vector with is choosen isotropically.
411			NB. This method is overridden by subclasses to provide custom emission
412			direction properties."""
413			
414			# This method of calculating isotropic vectors is taken from GNU Scientific Library
415			LOOP = True
416	e -		while LOOP:
417			x = -1. + 2. * np.random.uniform()
418			y = -1, +2, * np.random.uniform()
419			$s = x^{*}2 + y^{*}2$
420	E .		if s <= 1.0;
421	F		LOOP = False
422			
100			
423		2	$= -1 + 2$, ~ 8
425			- = - = = = = = = = = = = = = = = = = =
426			· · · · · · · · · · · · · · · · · · ·
427	-	1	eturn no.array([x,v,z])
428			
429	¢.	def e	mission_wavelength(self, photon):
430			""Returns a new emission wavelength for the photon."""
431		+	The emitted photon must be red-shifted to consevration of energy
432		1	ower_bound = self.emission_data.probability_at_wavelength(photon.wavelength)
433	-	I	<pre>eturn self.emission_data.wavelength_at_probability(np.random.uniform(lower_bound,1.))</pre>
434			
435	T	del e	massion(serr, proton). ""Indates the obtain with a new wavelength and direction, assuming it has been absorbed and omitted """
437			opuaces the photon with a new wavelength and direction, assuming it has been absorbed and GMITEG."""
438			Indate wavelength
439		r	hoton.wavelength = self.emission wavelength(photon)
440		-	
441		+	Update direction
442		F	hoton.direction = self.emission_direction()
443	-	1	eturn photon
444			
445	- 中	def t	<pre>race(self, photon, free_pathlength):</pre>
446		1	"Will apply absorption and emission probabilities to the photon along its free path in the present geometrical container and return the result
		F	hoton for tracing. The free pathlength is the distance travelled in metres until the photon reaches the edge of the present container. It is for
		t	he calling object to decided now to proceed with the returned photon. For example, if the returned photon is in the volume of the container the
			ame tracing procedure should be applied. However, if the photon reaches a race, reflection, refraction calculation should be applied etc. If the becan is lest, the hostone pating instance priciples is not to Falce It is far the calling chieft to check this property and act accordingly a g
		r	Notion is lost, one photomic active instance variables is set to raise. It is for the calling object to check this parameter and act accordingly e.g. according to be lost photom and great a new photom to trace ""
447			containg the loss photon and great a new photon to trade.
448		+	Clear state using for collecting statistics
449		r	hoton.absorber_material = None
450		r	hoton.emitter_material = None
451			
452		+	Assuming the material has a uniform absorption coefficient we generated a random path length weigthed by the material absorption coefficient.
453		s	<pre>ampled_pathlength = -np.log10(1 - np.random.uniform())/self.absorption(photon)</pre>
454		k	ac%ground_pathlength = -np.log10(1 - np.random.uniform())/self.absorption_b(photon)
1455			

Appendix D: The background absorption code.



The code at line 486 was to rename the container.name to LSC. The containe.name was named 'Background' if photon.backgrounds turns to 6 (see line 461). This was done to make background absorption traceable within the SQL-files (else the characteristics were the same as with QE losses).

D.1 VALIDATION

To test the background absorption code experiments were conducted. The background absorption length was calculated separately from the absorption length. The shortest length was taken as next step for the particular photon. As test for the code the following principle was tested. Absorption coefficients can be summarized to calculate the transparency of a substance. So, the separately simulated absorption losses should give the same losses as an individual absorption coefficient of the summarized coefficients. Figure 64 presents the graphical representation.



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FIGURE 64: GRAPHICAL REPRESENTATION OF THE MECHANISM BEHIND MULTIPLE ABSORPTION COEFFICIENTS AT THE SAME WAVELENGTH.

$$T_x = 10^{-a_x(\lambda)l} \qquad \qquad \text{EQ. 42}$$

X = [1, 2, 3, 4]

In experiments 3 and 4 both the absorption materials of 1 and 2 were present in the host material. Only the way of calculating the likelihood for absorption is different. In situation 3 the absorption coefficients were summarized and in situation 4 both possibilities of passing through were calculated separately and combined afterwards.

Situation 3:

$$T_3 = 10^{-a_3(\lambda)l} = 10^{-(a_1(\lambda) + a_2(\lambda))l} = 10^{-a_1(\lambda)l} * 10^{-a_2(\lambda)l} = T_1T_2$$
 EQ. 43

$$A_3 = 1 - T_3 = 1 - T_1 T_2$$
 EQ. 44

Situation 4:

$$A_4 = A_1 + (1 - A_1)A_2 = A_1 + A_2 - A_1A_2$$
 EQ. 45

Using T + A = 1

$$A_4 = 1 - T_1 T_2$$
 EQ. 46

So, the mathematics forecast exactly the same results for both simulations. The simulation was performed with 50.000 photons. An absorption spectrum with an absorption coefficient of $2m^{-1}$ at every wavelength was chosen for both the background absorption as the luminescent absorption. The quantum efficiency was set to zero and the travelled length through the substance was set at 10cm. The expected amount of photons that reached the solar cell was hereby $10^{(-4^*0.1)} \times 50.000 = 19.905$. The results of the simulations are shown in Figure 65.

Appendix D: The background absorption code.



FIGURE 65: THE AMOUNT OF PHOTONS REACHING THE SOLAR CELL FOR BOTH THE COMBINED ABSORPTION COEFFICIENTS (BLUE DIAMONDS) AS THE SEPARATED ABSORPTION COEFFICIENTS (GREEN BULLETS).

As is seen in Figure 65 all the results were very close to the calculated value. There was no statistical difference between the two different ways of calculating the additive background absorption losses. Hereby was confirmed that the background absorption was programmed correctly. The advantage of separately calculating these lengths is not losing the knowledge of what caused the absorption event.



produced by PV)

PV)

APPENDIX E: LUMOGEN RED 305 WITH LAMBERTIAN BACK MIRROR



APPENDIX F: LUMOGEN RED, ABSORPTION SPECTRUM

FIGURE 66: THE NORMALIZED ABSORPITION AND EMISSION SPECTRA OF LUMOGEN RED 305



FIGURE 67: THE NORMALIZED ABSORPTION SPECTRUM OF LUMOGEN RED 305 F MULTIPLIED FACTOR 2500.

As seen in Figure 67 the noise after wavelength 630nm was multiplied with a factor of 2500 too, causing the value to increase to a significant absorption coefficient of $\sim 20 \text{ m}^{-1}$. The stronger absorption strengths used were only multiplied with a factor 1000 but still the relative low absorption coefficients between wavelength 630nm and 700nm were important for the reabsorption events. Thereby adding a bit of insecurity to the simulation results (more reabsorption losses, more initial absorption of light). To overcome this problem in the future a Gaussian curve could be plotted against the exponentially decay o the absorption coefficient.



FIGURE 68: THE SYSTEM ENERGY EFFICIENCY CALCULATED FOR A SYSTEM WITHOUT LAMBERTIAN AIR GAP MIRROR AT THE BACKSIDE.

APPENDIX G: PEAK AND NO PLATEAU

With increasing absorption strengths more photons were absorbed following the law of Lambert-Beer. This was seen as a profit process within harvesting of light.

With increasing absorption strengths the reabsorption events were stimulated, thereby exposing some photons again to already undertaken loss mechanisms. This resulted in a decrease of percentage of the absorbed photons reaching the solar cell. This process was seen as a loss process.

The losses due to reabsorption depend on the EC losses, QE losses and amount and strength of overlapping absorption and emission spectra (amount of reabsorption events). When the increase in percentage of losses, by increasing concentration, never overrules the increase in profits, the amount of photons reaching the solar cell increases to a plateau (as seen with Lumogen Red 305). When the increase in percentage of losses is large it overrules the extra increase in profits, thereby resulting in a peak value at a certain concentration.

Lumogen Red 305 already experienced a lot of overlap between absorption and emission spectra at low concentrations and the extra exposure to a QE of 95% has a quite modest effect resulting in this plateau value. QD1 experienced little overlap between absorption and emission spectra at low concentrations, but the extra exposure to the QE losses by reabsorption caused a lot of losses. The loss process overruled the extra absorption profits at a certain level. That resulted in a peak value by increasing concentration.

Figure 69 shows the efficiency of a 10cm by 3.5cm LSC, doped with Lumogen Red 305 with a QE of 50%. The loss process was hereby enhanced, thereby causing more additional losses than additional profits at a certain level. That resulted in a peak value for the efficiency. This simulation was performed with 50.000 photons and a Lambertian air gap mirror at the backside.



FIGURE 69: THE EFFICIENCY AT INCREASING ABSORPTION STRENGTHS FOR LUMOGEN RED 305 WITH QE=0.5.

APPENDIX H: CALCULATIONS OF EFFICIENCIES

This appendix presents the calculations for calculating the different efficiencies. The used amounts N_X were gained from the SQL-databases. N_x is the total amount of photons corresponding to process x (using of the search options given in Appendix A). $N_{total} = 1 - amount of simulated photons'. Eq. 47 up$ to Eq. 54 were all used for the simulations without background absorption.

 η_{Fresnel} presents the efficiency of photons entering the LSC waveguide. The η_{Fresnel} was calculated by using Eq. 47 where N_{Fresnel} is the amount of photons externally reflected.

$$\eta_{Fresnel} = \frac{N_{total} - N_{Fresnel}}{N_{total}}$$
 EQ. 47

 $\eta_{Absorption}$ presents the efficiency of absorption. The $\eta_{Absorption}$ was calculated by using Eq. 48 where N_{not absorbed} is the amount of photons leaving the LSC without being absorbed. N_{absorbed} was calculated by subtracting N_{not absorbed} and N_{Fresnel} from N_{total} (as given in Eq. 49).

$$\eta_{Absorption} = 1 - \frac{N_{not \ absorbed}}{N_{total} - N_{Fresnel}} \qquad \qquad EQ. \ 48$$

$$N_{absorbed} = N_{total} - N_{not \ absorbed} - N_{Fresnell}$$
 EQ. 49

The QE was set at the start of each simulation. η_{QE} was calculated using Eq. 50.

$$\eta_{QE} = \frac{QE}{100} \qquad \qquad EQ. 50$$

 n_{FC} presents the trapping efficiency of the waveguide under the assumption that photons could not escape through the side surfaces²⁷. η_{EC} was calculated using Eq. 51 where N_{EC} is the amount of absorbed photons escaped through the front surface²⁸ (with Lambertian air gap mirror at the backside) or escaped through the front and back surface (without Lambertian air gap mirror at the backside).

$$\eta_{EC} = 1 - \frac{N_{EC}}{N_{absorbed} * \eta_{QE}}$$
 EQ. 51

 $\eta_{air\,gap}$ presents the trapping efficiency of the waveguide under the assumption that photons could not escape through the front surface and back surfaces. $\eta_{air qap}$ was calculated using Eq. 52. These were the photons escaping through the air gap between the mirrors and the LSC.

 ²⁷ The side surfaces are the XZ and YZ surfaces of the LSC where no solar cell is attached.
 ²⁸ The front surface is the XY surface where the photons enter the LSC waveguide.

$$\eta_{Air\,gap} = 1 - \frac{N_{air\,gap}}{N_{absorbed} * \eta_{QE} * \eta_{EC}} \qquad EQ. 52$$

The F_{Reabsorption} are the additive losses due to reabsorption. So, the increase in observed losses compared to the calculated maxima. Reabsorption has no effect on the $\eta_{Absorption}$ and the $\eta_{Fresnel}$. The effects of reabsorption on the η_{QE} were the observed N_{QE} minus the calculated N_{QE} (using Eq. 50 and the known QE)²⁹. The effects of reabsorption on η_{EC} were the observed N_{EC} minus the calculated N_{EC} (using Eq. 51 and the escape cone losses without reabsorption). The effects of reabsorption on $\eta_{air gap}$ were the observed N_{air gap} minus the calculated N_{air gap} (using Eq. 52 and the air gap losses without reabsorption). This results in the N_{reabsorption} given in Eq. 53. The N_{reabsorption} was used in Eq. 54 to calculate the reabsorption factor.

$$N_{reabsorption} = \left(N_{QE} - N_{absorption} * (1 - \eta_{QE})\right) \\ + \left(N_{EC} - N_{absorption} * (1 - \eta_{QE}) * \eta_{EC_{perfect}}\right)$$

$$EQ. 53 \\ + \left(N_{air \ gap} - N_{absorption} * (1 - \eta_{QE}) * \eta_{EC_{perfect}} * \eta_{air \ gap_{perfect}}\right)$$

$$F_{Reabsorption} = 1 - \frac{N_{reabsorption}}{N_{reabsorption} + N_{PV}}$$
 EQ. 54

The $\eta_{waveguide}$ is the difference in photons reaching the solar cell with and without background absorption. Eq. 55 presents the used formula.

$$\eta_{Waveguide} = 1 - \frac{N_{PV \text{ without background absorption}} - N_{PV}}{N_{PV \text{ with background absorption}}} \qquad EQ. 55$$

This results in the formula given in Eq. 21 and this automatically equals with Eq. 56

$$\eta_{Waveguide} * F_{Reabsorption} * \eta_{Air\,gap} * \eta_{EC_{perfect}} * \eta_{Absorption} * \eta_{QE} * \eta_{Fresnel} = \frac{N_{pv}}{N_{total}} \qquad EQ. 56$$

 $^{^{29}}$ The calculated N_{QE} is η_{QE} times N_{absorbed}
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APPENDIX I: EFFECTS OF SELF-ABSORPTION IN TYPE-II QUANTUM DOTS WITH PARTIALLY OVERLAPPING ABSORPTION AND EMISSION SPECTRA EMPLOYED IN QUANTUM DOT LUMINESCENT SOLAR CONCENTRATORS

{QD1 is the same quantum dot as used in the thesis only the QE was enhanced to 60% to be able to make a good comparison with QD2]

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Luminescent solar concentrators (LSCs) are low cost photovoltaic devices, which reduce the amount of necessary semiconductor material per unit area of a photovoltaic solar energy converter by means of concentration. The device is comprised of a thin plastic plate in which luminescent species (fluorophores) have been incorporated. The fluorophores absorb the solar light and radiatively re-emit part of the absorbed amount of energy. Total internal reflection traps most of the emitted light inside the plate and wave-guides it to a narrow side facet with a solar cell attached, where conversion into electricity occurs. The efficiency of such devices is as yet rather low, due to several loss mechanisms, of which self-absorption is of high importance [1]. It is generally expected, that spectral separation between absorption and emission influences the losses due to self-absorption [2]. Semiconductor nano-crystals with a quasi-complete separation of absorption and emission spectra (large Stokes' shift) may be good candidates to overcome self-absorption losses, however in practice their synthesis results in a drop in luminescence quantum efficiency [3]. The synthesis of highly luminescent nanoparticles with a small but not negligible spectral overlap promises to be less complicated [2,4]. In this work we investigate the suitability of such nano-particles to circumvent the self-absorption problem in LSC devices by means of experimentally validated combined ray-tracing and Monte-Carlo simulations [2].

Combined ray-tracing and Monte-Carlo simulations is a widely used tool for efficiency estimations of LSC-devices prior to actual manufacturing. We have varied the LSC-size and luminophore concentration in the simulation for two different types of semiconductor nano-crystals: one with an

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almost complete absorption/emission-separation and one, where still a few percent of the light in the spectral region of emission is absorbed.

The simulations show that even the small absorption coefficients that overlap with the emission spectrum have a detrimental effect to the LSC. The results of the simulation have been compared with an experiment with fixed LSC-size and luminescent species and a variable concentration, where a reasonable agreement was found.

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LSCs are non-tracking solar concentration devices, with the capability to concentrate diffuse sunlight [5]. The incoming light reaches the luminescent particles, through the large facet of the device, where it gets absorbed and re-emitted. A large fraction of the absorbed light will be re-emitted at angle smaller than the critical angle for total internal reflection. This light will be wave-guided towards a small solar cell (Figure 1).



FIGURE 1: SCHEMATIC CONCEPT OF AN LSC

Current LSC-designs suffer from re-absorption, which enhances the loss-mechanisms present [6]. Self-absorption has shown to be correlated with spectral overlap [2]. We have compared the

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performance of LSCs based on two different luminophores: one with a slight spectral overlap (QD130) and an LQE of 48 % (Figure 2a) and one with almost no spectral overlap (QD231) and an LQE of 48 % (figure 2b). Even though sample QD1 had a somewhat smaller absorption width its performance was much worse at LSC-dimensions that are relevant for practical applications, clearly due to reabsorption. The reasons for this are that the average effective propagation length for trapped photons is longer than the thickness of the LSC plate and thus according to the law of Lambert-Beer the absorption is heavily amplified resulting in high self-absorption.



FIGURE 2A: THE ABSORPTION AND EMISSION SPECTRA OF A TYPE-II CORE-SHELL QD1.



Figure 2b: The absorption and emission spectra of a type-II core-shell QD2

We performed simulations on an LSC geometry with a height of 10 mm and a length-to-width aspect ratio 1:0.35. The illumination source emitted 50.000 photons from a rectangle of length times width precisely parallel to the LSC but 50 mm above it. The photons were sampled from the AM1.5G flux spectrum, however truncated after 1150 nm. This truncated spectrum contained 64 % of the photons within the full AM1.5G spectrum, which has been used to correct the results later. Thus, this truncation

³⁰ CdTe/CdSe Type-II multipods with a modified quantum efficiency [original <10 %], size unknown.

³¹ CdTe/CdSe Type-II dot-core/rod-shell nanorods, size ~20nm.

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omitted photons in the computation that neither could be absorbed by the luminophores nor by the solar cell, which leads to a reduced computation time. The refractive index of the modelled LSC has been chosen to be 1.5. The solar cell has been modelled by an object 35x10x1 mm3, which absorbs any photon hitting it. The other surfaces of the LSC have been covered with perfect mirrors with an air gap of 0.5 mm. The top facet has been left uncovered to define the aperture surface, also the bottom surface has been left open. The simulations have been performed using the emission spectra depicted in figure 2. We changed the length of the geometry in steps from 10 mm to 1000 mm and simulated different concentrations per length step. Figure 3 shows the efficiency change as a function of different concentrations for a length of 10 cm and 30 cm. QD2 (corresponding to the spectra in figure 2b) performs better than QD1 (corresponding to the spectra in figure 2a). The better performance of QD2 can be ascribed to the broader absorption spectrum but foremost by the (much) lower reabsorption losses (see figure 4). The reabsorption losses (combined additional QE and EC losses induced by reabsorption) are caused by the small absorption coefficients that overlap with the emission spectrum



FIGURE 3: OPTICAL EFFICIENCIES OF THE DIFFERENT QDS BY INCREASING CONCENTRATION FOR DIFFERENT LENGTHS.

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FIGURE 4: THE DESTINATION OF PHOTONS AS PERCENTAGE OF THE ABSORBED PHOTONS. QE = LOSSES DUE TO QUANTUM EFFICIENCY, EC = LOSSES DUE TO ESCAPE CONE, AIR GAP = LOSSES DUE TO ESCAPING THROUGH THE AIR GAP BETWEEN THE MIRROR AND LSC, PV = REACHING SOLAR CELL AND REABSORPTION = LOSSES DUE TO REABSORPTION (COMBINED ADDITIONAL QE AND EC LOSSES INDUCED BY REABSORPTION).

APPENDIX J: QD1 GRAPHS

In this appendix some graphics are shown of the efficiencies and concentration factors reached within LSC doped with the luminophore QD1. The concentration factor almost reached 1 with a Lambertian back mirror at the backside. The relative energy costs compared to the c-Si-solar cell are also shown, knowing that it will never be cheaper when there is a dilutor placed on top (LSC with a concentration factor below 1).













System eff





Relative kWh per €

CF

All without back mirror





Optical eff



System eff



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Relative costs

Relative kWh per €

APPENDIX K: PREPARATION OF THE SPECTRA

PVtrace takes an integral over the absorption and emission spectra. This could not work with negative absorption or emission coefficients. In practice it is also not possible to have negative absorption or negative emission coefficients. These values are due to the noise of the measurements.

Within this thesis the absorption and emission spectra were smoothed according the 'moving average' principle. A point was the average of the five surrounding points. So the absorption coefficient at 600nm was the average of the absorption coefficients measured at 598, 599, 600, 601 and 602nm. The absorption spectra were cut-off when only noise around absorption value 'zero' was measured. Lumogen Red 305 was cut-off at 700nm, QD1 was cut-off at 800 nm and QD2 was cut-off at 740nm.

Figure 70 shows why QD2 was cut-off at 740nm. The black line shows the measured absorption spectrum multiplied with a factor 1000 (without smoothening). Around 740nm only noise around zero is seen. The drop seen at 780nm was caused by the switch to another wavelength-zone (due to the machine measuring). After smoothening the curve with the moving average principle, the first point that was zero was at wavelength 740nm.



FIGURE 70: ABSORPTION SPECTUM OF QD2 AND THE 0-LINE (RED)

APPENDIX L: RECALCULATING ABSORPTION

The length of the red (dashed) arrow is equal to the total length of the blue arrows (Figure 71). The question is: 'is the likelihood of the reaching the end of the red arrow (assuming it is traveling through the LSC) the same as reaching the end of the blue arrows? So is it correct to re-stimulate absorption length after total internal reflection instead of subtracting the traveled length from the initial calculated length?



FIGURE 71: PATH LENGTHS OF A PHOTON REACHING THE SOLAR CELL.ONE WITH NO REFLECTIONS AT ALL, THE OTHER WITH THREE REFLECTIONS.

The length of the long blue arrows is L_{blue} . The total length of blue arrows is $3L_{blue}$. The length of the red arrow L_{red} equals $3L_{blue}$. The likelihood of reaching either the red (dashed) or the blue solar cell is calculated within Eq. 57 and Eq. 58.

$$P_{blue} = 10^{-a(\lambda)0.5L_{blue}} \cdot 10^{-a(\lambda)L_{blue}} \cdot 10^{-a(\lambda)L_{blue}} \cdot 10^{-a(\lambda)0.5L_{blue}} = 10^{-a(\lambda)3L_{blue}}$$

$$P_{red} = 10^{-a(\lambda)L_{red}}$$
EQ. 58

The correctness of the approach of recalculating the absorption length after every interaction is hereby proven.

Simulation experiment

The setup for the simulation experiment is as followed. The length of the simulated LSC is 10cm, the width 3.5cm and the hight is variable. The starting position of the photons is a point source at position [Length, Width/2, Heigth]. The direction (ϕ , θ) of the point source is (0, 0.25 π). The used absorption spectrum was 3.71m⁻¹ over the whole spectrum with a QE of 0. Per simulation 50.000 photons were simulated and the distribution of heights is chosen such that the number of TIRs is increased with one every new height. See Figure 72 for the grapical representation.



8 TIR occasions



5 TIR occasions





7 TIR occasions



4 TIR occasions





6 TIR occasions



3 TIR occasions



2 TIR occasions 1 TIR occasions 0 TIR occasions FIGURE 72: GRAPHICAL REPRESENTATIONS OF THE SIMULATED PHOTON PATHS CORRESPONDING TO THE DIFFERENT SIMULATION GEOMETRIES.

This simulation was conducted under seven different seeds³². Over all these simulations the highest percentage of photons that reached the Raybin was 29.919% and the lowest 29.736%. These values have a variation of ~0.5%, which can be subscribed to the statistical errors. See Figure 73 for all the results. Figure 73 also shows that the statistical error is small. That implies that the random number generator is of good quality and enough photons were used within the simulation.

³² The starting point within the random number generator



FIGURE 73: AN OVERVIEW OF THE AMOUNT OF PHOTONS REACHING THE SOLAR CELL UNDER DIFFERENT AMOUNTS OF TIR'S AND WITH DIFFERENT SEEDS. 50.000 PHOTONS WERE SIMULATED.