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Photostable solar concentrators based on fluorescent glass films

Renata Reisfeld ^{a,*}, Dimitri Shamrakov ^a, Christian Jorgensen ^b

^a *Department of Inorganic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel,*

^b *Department de Chimie Minerale, Analytique et Appliquee, Universite de Geneve,
CH 1211 Geneva 4, Switzerland*

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Abstract

Efficient luminescent solar concentrators (LSC) were prepared by deposition of organically modified sol-gel films doped by photostable perylimide dyes on plexiglas substrates. The absorption spectra of these dyes extends from 420 to 620 nm covering the visible part of the solar spectrum and the emission is between 550 and 750 nm, close to the optimum response of silicon and gallium arsenide solar cells. The efficiency of this type of collector was calculated from the absorption coefficients, quantum efficiency of the fluorescence and the overlap between emission and absorption spectra by the method of Monte-Carlo and found to be close to 20%. Optimum concentrations are shown to be strongly dependent on the extent of overlap between the absorption and the emission spectra, which also appears to be the limiting factor in respect to the efficiency of the concentrator.

1. Introduction

There is no doubt that solar energy, which is clean and non-hazardous, could contribute considerably to a solution of the energy problem if appropriate methods were developed to collect, concentrate, store and convert solar radiation, which is diffuse and intrinsically intermittent [1]. At present, large-scale solar cell arrays are operating in inaccessible locations distant from conventional electricity plants. Previous estimates of price decreases to \$1/W–\$2/W which were obtained by making comparisons with the aluminium or electronic computers industry, may be slightly optimistic as the difficulties of preparing inexpensive silicon with a high

* Corresponding author.

photoelectric yield cannot be easily removed by increased production. One way of lowering the price of PV electricity is to concentrate the solar radiation, particularly that part which is most efficient in PV energy conversion, on high efficiency solar cells which are expensive, but their amount and cost can be considerably diminished by using concentrated solar light on their small areas. Recently, there has been a serious progress in technical development of solar cells [2]. Especially very high conversion efficiencies have been found in AlGaAs cells [3]. Thus, the light emitted as fluorescence from the edges of the concentrator can be matched to more than 50% efficiency of solar cells. Fig. 1 presents the standard solar spectrum AM 1.5 (curve 1) and spectral sensitivity of monocrystalline silicon cell (curve 2) and AlGaAs cell [3] (curve 3).

The operation of an LSC is based on absorption of solar radiation in a collector containing a fluorescent species in which the emission bands have little or no overlap with the absorption bands [4]. The fluorescence emission is trapped by

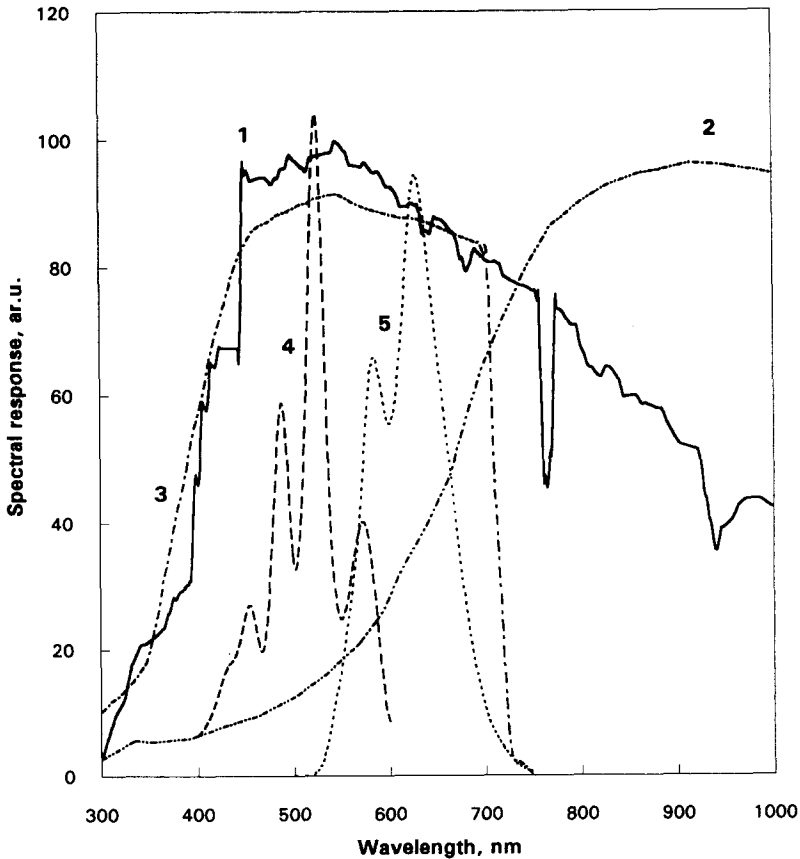


Fig. 1. (1) Solar spectrum, (2) sensitivity of silicon photovoltaic cell, (3) sensitivity of AlGaAs [3] photovoltaic cell, (4) absorption spectrum of LSC plate, and (5) emission spectrum from LSC's edge.

total internal reflection and concentrated at the edges of the collector which is usually a thin glass plate. LSC's have the following advantages over conventional solar concentrators: they collect both direct and diffuse light, there is good heat dissipation of non-utilized energy by the large area of the collector plate in contact with air so that essentially "cold light" reaches the PV cells, tracking the sun is unnecessary, and the luminescent species can be chosen to allow matching of the concentrated light to the maximum sensitivity of the PV cells. The main advantage is that the large area to be covered by the solar cell is reduced to the area of the edges.

The theory of LSC, which is based on internal reflection of fluorescent light which is subsequently concentrated at the edges, has been discussed in detail for inorganic materials [1,5,6] and organic dyes incorporated in bulk polymers [7,8]. A transparent plate doped by fluorescent species absorbs in the visible (part of the solar spectrum). The resulting high yield luminescence should then be emitted at the longer wavelength part of the spectrum. About 75%–80% of the luminescence is trapped by total internal reflection in the plate having a refractive index of about 1.5. Repeated reflections of the fluorescent light carry the radiation to the edges of the plate where it emerges in the concentrated form. The concentration factor is proportional to the ratio of the surface of the plate to its edges and the optical efficiency of the plate. Photovoltaic cells can be coupled to the edges and receive the concentrated light. Such an arrangement should substantially decrease the amount of photovoltaic cells needed to produce a given amount of electricity and thus reduce the cost of the system of photovoltaic cells.

The parameters determining the optical plate efficiency depend on the following factors:

- (1) The fraction η_{abs} which is the ratio of photons absorbed by the plate to the number of photons falling on the plate;
- (2) The quantum efficiency η_{F} , which is the ratio of the number of photons emitted to the number of photons absorbed;
- (3) The Stokes efficiency η_{s} which is the ratio of the average energy of emitted photons to the average energy of the absorbed photons and is given by

$$\eta_{\text{s}} = \nu_{\text{em}} / \nu_{\text{abs}}; \quad (1)$$

- (4) The fraction η_{t} of the light trapped in the collector given by

$$\eta_{\text{t}} = (1 - 1/n^2)^{1/2}, \quad (2)$$

where n is the refractive index of the light-emitting medium;

- (5) The transport efficiency η_{tr} which takes into account the transport losses due to matrix absorption and scattering;
- (6) The efficiency η_{self} due to losses arising from self-absorption of the colorants.

The optical efficiency of the plate, which is the energy coming out of the edges of the plate divided by the energy falling on the plate, including reflection is given by,

$$\eta_{\text{opt}} = (1 - R)\eta_{\text{abs}}\eta_{\text{F}}\eta_{\text{s}}\eta_{\text{t}}\eta_{\text{tr}}\eta_{\text{self}}, \quad (3)$$

where R is the Fresnel reflection coefficient and is about 4% for ordinary glass. The energy output, E_{out} , is given by,

$$E_{\text{out}} = E_{\text{in}} \eta_{\text{opt}} \eta_{\text{PV}}(\lambda), \quad (4)$$

where E_{in} is the energy falling on the plate and $\eta_{\text{PV}}(\lambda)$ is the efficiency of the PV cell at a wavelength λ .

The efficiency of PV cells can be increased from about 12% for the total solar spectrum to more than 50% at the emission wavelengths of the perylimide dyes, (cf. Fig. 1 curve 5). In addition, it is easier to prepare antireflective coatings for such a narrow wavelength range. Finally, the ratio of power from a PV cell attached to an LSC to the power from the same PV cell exposed directly to the solar radiation is

$$F = \eta_{\text{opt}} (A_{\text{surf}}/A_{\text{edge}}) (\eta_{\text{PV}}(\lambda)/\eta_{\text{solar}}), \quad (5)$$

where A_{surf} is the area of the collector, A_{edge} is the area of its edges to which the photovoltaic cells are coupled, and η_{solar} is the efficiency of the photovoltaic cells with respect to total solar spectrum. F also corresponds to the factor by which the solar cell area needed to produce a given power is reduced when it is attached to an LSC.

While a large number of papers have been published about luminescent plates in which the dye is incorporated in the entire bulk of the plate [8,9], the configuration in which the plate is covered by a thin film incorporating the colorant deposited in close contact with the plate is relatively new [4,10,11]. The advantage of doped thin films having optical contact with the transparent plate is that the luminescence emitted from the thin film is trapped in the plate while parasitic losses due to self-absorption and scattering from impurities can be greatly reduced as compared to bulk doped plates. A scheme of a thin film versus bulk LSC is shown in Fig. 2. In our previous paper [4] we have described a luminescent solar concentrator based on thin films of PMMA doped by one perylimide dye. Much better results can be obtained with the combination of photostable perylimide dyes, provided they can be introduced into the sol-gel system. Recently, we have indeed been able to introduce the dyes into a composite polymer/sol-gel glass system [12,13] and into a glass using the sol-gel procedure [14] for tunable solid state lasers in the visible. A combination of two dyes increases the overlap of absorption with the solar spectrum followed by an increase in optical efficiency.

In the current paper we present a new experimental procedure for preparation of photostable and mechanically resistant glass films doped with a combination of perylimide dyes for LSC applications.

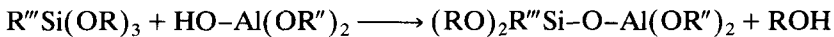
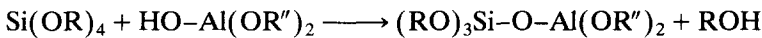
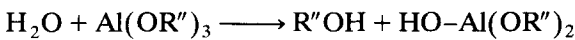
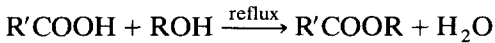
2. Experimental

The following reagents were used for synthesis (see formulae in Fig. 3): Tetramethoxysilane (I) (TMOS) (Fluka), Aluminium tri-sec-butylate (II) (Merck), 3-glycidoxypropyltrimethoxysilane (III) (OLYMO) (Aldrich), iso-propanol and ben-

tance of derived film coatings, which have to serve at the same time as a host matrix for light absorbing dye molecules and for mechanical protection of the supporting plexiglas plates.

The 3-glycidioxypropyltrimethoxysilane (GLYMO) was chosen as the ORMOSIL [15–17] component for the relatively high affinity of its organic substituent chain and derived organic network to completely non-polar perylimide dyes.

The chemically controlled condensation (CCC) technique [15] was employed for synthesis, when water necessary for precursor hydrolysis was formed slowly in the reaction mixture by esterification of alcohol and aliphatic acid according to the scheme:



The procedure for the sol preparation was as follows. In order to obtain the material with 7:2:1 molar ratio of $SiO_{1.5}R:Al_2O_3:SiO_2$, 3 ml (1.4×10^{-2} mol) of (GLYMO), 0.3 ml (2×10^{-3} mol) of TMOS and 1 ml (3.9×10^{-3} mol) of aluminium tri-sec-butylate were dissolved in 20 ml of iso-propanol. Under intensive stirring with a magnetic stirrer, 4.5 ml (0.06 mol) of propionic acid was dropped in slowly. Then stirring was continued for about 3 h under reflux. After cooling the mixture, 1 ml of water was added to complete the hydrolysis of precursors under stirring for another hour. Then either 0.11 g ($1.5 \cdot 10^{-5}$ mol) of *a* dye or 0.015 g (1.5×10^{-5} mol) of *b* dye were dissolved in the sol solution to yield 1×10^{-3} M content. Finally, 20 ml of pure benzene was added and then distilled out in order to remove the water as its benzene–alcohol azeotrope mixture. This last step is necessary to decrease the probability of non-polar dye molecules aggregating due to the presence of water in solution, which prevents maximal possible quantum efficiency values from being achieved.

Film coatings were developed by pouring the sol solution, which had been filtered through 0.1 μ m PTFE filter, onto the surface of levelled 3 mm thick plexiglas plates of 2×2 inches dimensions inside the dustless laminar box. After primary evaporation of solvents up to gelation of the solution, the plates were transferred into the oven in order to complete the aging process at 70°C. Plates coated on both sides were also prepared in this way. The films so deposited were of uniform thickness, which was varied by changing the ratio of the volume of initial solution per area to be coated in the range of 30–80 μ m. The film density reached 1.46 g/cm³.

Three types of LSC plates were prepared: plates coated with either *a* or *b* dye on one side, plates with both sides coated with a mixture of these two dyes, and plates with both sides coated with *a* and *b* dyes on different sides.

Absorption spectra of the composite films were measured on a Perkin-Elmer Lambda 5 spectrophotometer and emission spectra were measured on a Jasco-770

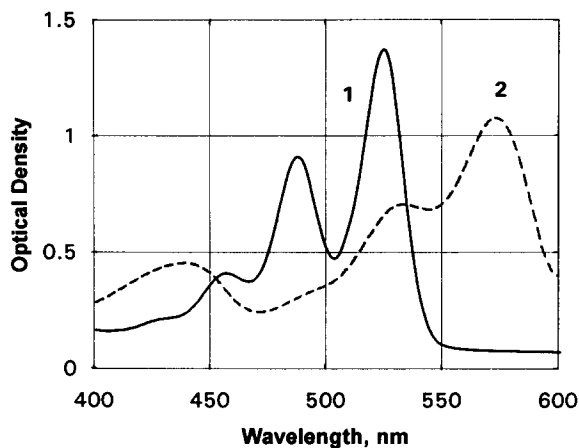


Fig. 4. Absorption spectra of solar concentrator plates: (1) one side *a* dye doped coating, and (2) one side *b* dye doped coating.

spectrofluorometer. The absorption and emission spectra are shown in Figs. 4 and 5. In Fig. 5. we can see a shift of the emission to the longer wavelength of the red dye as a result of trapping and reemission of light.

Lifetimes of the dyes in the composite films were measured using a PRA Nitrogen Laser (0.6 nsec FWHM, 10 Hz repetition rate), McPherson monochromator equipped with a Hamamatsu microchannel plate and a Tektronix digitizer (0.1 ns temporal resolution). The signals were passed to a PC computer where they

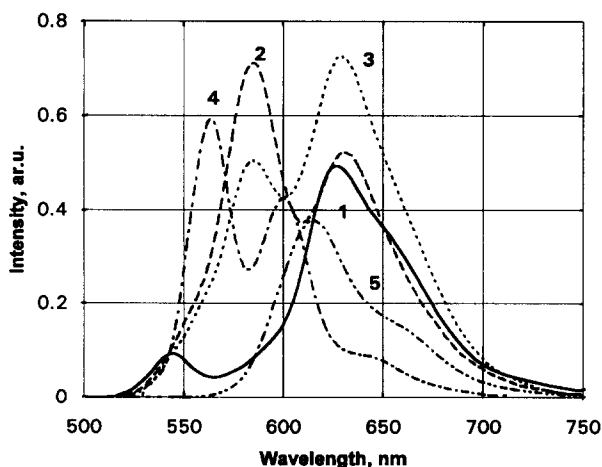


Fig. 5. Luminescence spectra of solar concentrator plates: (1) both sides *a* + *b* dyes doped coating, (2) *a* dye (yellow) on one side and *b* dye (red) on the other side with its yellow surface facing the light source, (3) the same plate with its red face turned towards the light source, (4) *a* dye doped coating on one side, and (5) *b* dye doped coating on one side.

rise in their photostability as shown under Nd:YAG (532 nm) irradiation with 16 MW/cm² peak power density [22].

3. Monte–Carlo calculations for optical efficiency

In order to calculate the optical efficiencies of LSC plates, which is the energy emitted from the edges divided by the solar energy falling on the plate, we have performed Monte–Carlo computer simulations. The input for these calculations consists of the solar spectrum at AM 1.5 (300–1100 nm), a combined absorption spectrum of the perylimide dyes and the emission spectrum of the dye *b*. The detailed calculation scheme can be found in [20]. Fig. 5 presents the spectra together with the response curves of two photovoltaic cells for comparison. The reason for only one emission spectrum shown is that the emission spectrum of the dye *a* is efficiently absorbed by the dye *b* already at low concentrations of the dyes used. On the other hand, the critical concentrations of the dyes for nonradiative energy transfer, given in Table 1, are too high to be effective at the practical concentrations used for the LSC. Therefore, the main contribution is due to radiative transfer.

First the solar photons are generated at wavelength intervals of 2 nm, each given the statistical weight according to the intensity of the solar spectrum at this interval. In the next step the impact solid angle is randomly generated between 0 and 2π . The photon is then refracted on the interface air–thin film according to Snell's law. The absorption probability and the free path of the photon in the solid medium is generated randomly from the absorption spectrum and Beer's law as follows:

$$\text{Absorption length} = -\log(1 - \text{Rnd}) / (e(\lambda)\text{Concentration}), \quad (7)$$

where Rnd is a random number between 0 and 1, generated by the computer and $e(\lambda)$ is the molar extinction coefficient of the combination of the two dyes at the wavelength λ . If the photon is absorbed, first the probability of emission is calculated, by comparison of the quantum efficiency of the dyes with a random number, then the wavelength of emission is generated, according to the statistical weight of the emission intensity at that wavelength [19]. The photon can be emitted in any direction, so the direction of emission is also generated randomly. The path of the photon is projected toward the nearest intersection with faces or edges of the plate and the length of this path is compared with the absorption path. If the photon reaches one of the faces of the plate without absorption, its impact angle is compared with the total reflection angle for this system. If the angle is smaller than the total reflection angle, the photon leaves the plate and is considered lost. Otherwise, the photon is reflected and the previous steps are repeated, until the photon is either reabsorbed, or reaches one of edges of the plate, where it is absorbed by photovoltaic cells. A typical calculation series counts 280000 solar photons penetrating the plate, which assures repeatability of the results to within about $\pm 2\%$. Except for the spectra and the refractive indices, which are experi-

mentally determined, other parameters, such as the size of the plate, thickness of the film, concentration of the dyes and number of photons tested are variables, allowing determination of the optimal set of these parameters for best performance of the thin film LSC's.

The output of the calculations shows that about 20% plate efficiency can be obtained with the plates of dimensions $30 \times 30 \times 0.3 \text{ cm}^3$ covered by a thin film of $50 \text{ }\mu\text{m}$ doped by a combination of the perylimide dyes *a* and *b* at concentrations ranging between 10^{-3} to 10^{-2} M. Such a practical device is now being constructed in our laboratory. Based on our previous studies we have good indications that the absorption and in some cases also emission of organic dyes can be increased by interaction with silver plasmons, created in the sol-gel glasses [23–25].

The interactions of the silver particles with the perylimide dyes *a* and *b* will be the subject of our future study, the results of which may increase the optical efficiency beyond 20%.

4. Summary

The solar concentrator plates covered by thin glass photostable and mechanically strengthened films were prepared. The perylimide colorants in the combined glasses have a good potential for applications on a larger scale.

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