Quantum yield measurements of high-efficiency dyes for luminescent solar concentrators

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Introduction

Luminescent solar concentrators (LSCs) [1]-[4] provide a means of reducing the silicon requirements for an electricity-generating solar panel. Although the principle was demonstrated more than 30 years ago, development has been hindered by the poor quantum yield and photostability of the fluorescent dyes used in the concentrator sheet.

A range of visible fluorescent dyes (Lumogen F) has been developed by BASF specifically for LSC use [5]. The five dyes cover a wide range of absorption and emission wavelengths and have high quantum yields.

The absorption and emission spectra of the five dyes from the Lumogen F range were measured, as were their quantum yields. A small LSC module was constructed using laser-grooved solar cells and the performance measured.

Dye spectra

In order to correctly predict and model the performance of an LSC, it is essential to measure the absorption and emission spectra of the dye in the host material used which in this case is PMMA (Perspex).

Absorption spectra were measured in a standard UV/VIS spectrophotometer. A piece of clear, undoped PMMA sheet was used as a reference sample to eliminate the effects of the PMMA host absorption on the measured spectra.

Fluorescence spectra were measured in a Horiba Jobin-Yvon Fluromax 3 spectrofluorimeter. To minimise the effects of self-absorption (caused by the overlap of dye absorption and emission spectra) an extremely low concentration of dye was used in the sample (peak optical density for the 2mm thick sample was typically 0.02). Additionally, the sample was excited near the edge and fluorescence was collected from the edge as shown in Fig. 1. This minimises the pathlength of the fluorescence light inside the sample.

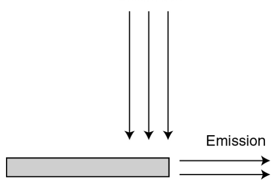

Fig. 1: Measurement of fluorescence

The absorption and emission spectra for five dyes in the Lumogen F range are shown in Fig. 2. Both absorption and emission spectra have been normalized to 1.

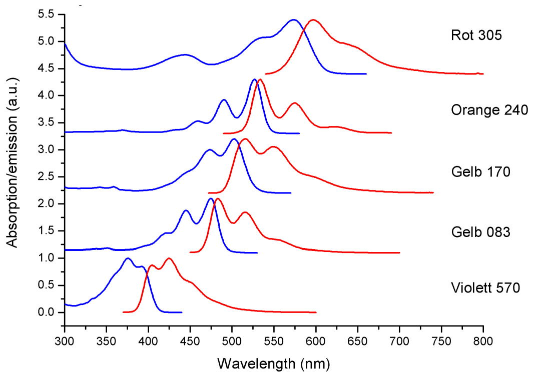

Fig. 2: Absorption and emission spectra of Lumogen F dyes in PMMA

It is possible to absorb all of the incident solar radiation up to about from 350-600nm using a combination of up to four of these dyes.

Dye quantum yield

All of the Lumogen F dyes have a small Stokes shift and therefore there is a high probability of reabsorption of the emitted fluorescence. Also, in a mixed-dye LSC, fluorescence emission from one dye will be absorbed by another dye[6].

Because of these multiple emission-reabsorption events, it is important to measure the fluorescence quantum yield (FQY) of the dyes in order to determine what the effective FQY of the dyes will be inside the LSC host polymer.

Initially, a thermal-lens technique was tried for measuring FQY [7]-[10]. In it, a piece of PMMA containing the dye under study is illuminated by a laser beam. The amount of power absorbed is measured optically and the amount of heat generated is determined from the magnitude of the thermal lens formed inside the sample. Although the thermal-lens technique has apparently been widely used, it was found extremely difficult to get it to work reliably and to give sensible results.

Instead, an integrating sphere technique was used for FQY measurements [11]-[14]. The basic principle is to measure both the amount of light absorbed by the sample and the amount of fluorescence light emitted. From this the FQY can be calculated.

As shown in Fig. 3, the sample is placed at the center of a sphere made from a PTFE with a high diffuse reflectance. Excitation light is focussed on to the sample through the entrance port and fluorescence emission is gathered from the exit port. The baffle prevents light emitted from the sample from reaching the exit port directly. The effect of the sphere is to integrate the light emission from the sample over all possible emission angles.

The sample is positioned at an angle of around 10^{o} (non-critical) to the incident beam so that reflected incident light strikes the wall of the sphere rather than being reflected back out the entrance port.

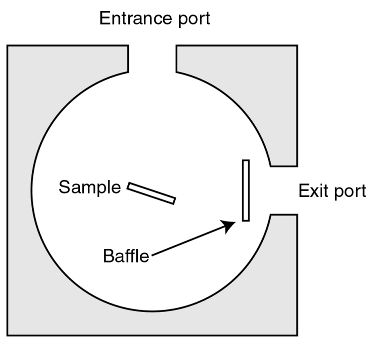

Fig. 3: Integrating sphere and sample

For our measurements, a 4" sphere made from Spectralon was used in the Fluoromax 3 spectrofluorimeter.

To reduce the effects of self-absorption on the measured quantum yield, weakly-doped samples were studied. Dye concentrations were typically around 20-30ppm by weight, giving an absorbance of around 0.1. Both higher and lower concentrations were tried, however higher concentrations gave erroneous readings due to self-absorption and lower concentrations were not reliable because too little of the incident light was absorbed to measure accurately.

The spectrum of the excitation light is recorded both with the sample in the sphere and out of the sphere. The difference in areas is proportional to the amount of light absorbed. The area of the spectrum of the fluorescence from the sample is proportional to the amount of light emitted. The FQY can be calculated from these areas.

Results for the five dyes (in weak concentrations) are shown in Table 1. Also shown are the FQY as measured by BASF.

Table 1. FQY of Lumogen F dyes

Dye	FQY (measured)	FQY (BASF)
Violett 570	97%	94%
Gelb 083	95%	99%
Gelb 170	97%	94%
Orange 240	100%	100%
Rot 305	99%	98%

Performance of a LSC module

A small (10x10cm) LSC module was constructed and its efficiency measured. The LSC sheet (cast by Lucite) used a mixture of four of the Lumogen dyes (Violett 570, Gelb 083, Orange 240, Rot 305) to achieve an optical density of at least 2 over the range

350-580nm. The sheet was 3mm thick. Four laser-grooved buried-contact solar cells (NaREC) were glued to each edge of the sheet and connected in parallel.

The absorption spectrum of the sheet is shown in Fig. 4 below.

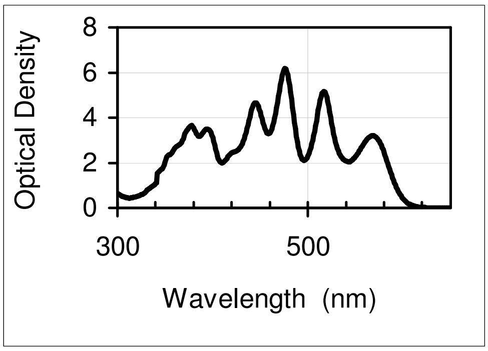

Fig. 4: Absorption spectrum of mixed-dye sheet

The efficiency was measured under one-sun illumination with an AM1.5 spectrum using NaREC's solar simulator.

Measurements were initially taken with all of the cells connected. However, the LSC sheet heated up under exposure to the simulator and three of the cells either cracked internally or detached from the LSC. One remaining cell remained attached and functioning and measurements were taken from it. The overall module output was assumed to be four times the output of the single edge cell which was measured.

Initially, an overall module efficiency of 2.1% was measured. However, when a diffusely reflecting sheet of white paper was placed behind the LSC sheet, the efficiency increased to 2.4%. The sheet of paper will reflect escaped fluorescence emission back into the sheet, giving it more change of being re-absorbed and emitted towards the solar cell.

Several factors probably led to a reduction in efficiency. For example, there were air gaps between the solar cell and the sheet at various points, reducing illumination of the cell. The surface of the sheet was not perfectly smooth, increasing the loss of fluorescence from the sheet. The finger spacing of the cells was not optimised for the edge emission from the sheet. Finally, electrical connection was only made at one point on the solar cell's busbar – the series resistance of the busbar will reduce the current draw and the efficiency.

Ray-tracing simulations

A Monte-Carlo ray-tracing simulator is currently under development[6]. The software calculates random incident rays on the LSC and follows their path through the device, including reflection from surfaces, absorption by dyes, absorption by the host matrix and absorption by the cells.

Simulations have been done using a mixture of four dyes, corresponding to the actual LSC module which was constructed. The predicted maximum efficiency is 3.9%. Considering the factors which probably reduce the efficiency in the constructed module, an efficiency of 2.4% is extremely promising.

Conclusions

The Lumogen F fluorescent dyes appear to be ideally suited to LSC use because of their high quantum efficiency and wide range of absorption when combined.

An LSC module using four of the dyes was constructed and its efficiency measured as 2.4%. Theoretical simulations suggest a maximum efficiency of 3.9%.

Further work will study the i) the photostability of the dyes in PMMA to determine their suitability for outdoor use and ii) FQY measurements of mixed dyes in one sheet.

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