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Ray Trace Modelling of Multiple Dyes in a Luminescent Solar Concentrator

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MULTIPLE DYE LUMINESCENT SOLAR CONCENTRATORS AND COMPARISON WITH MONTE-CARLO RAY-TRACE PREDICTIONS

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ABSTRACT: A previously developed Monte-Carlo ray-trace model has been modified to incorporate multiple luminescent species. Liquid luminescent solar concentrators (LSCs) have been fabricated to verify the ray-trace predictions for LSCs containing multiple luminescent dyes. Single dye and multiple dye solutions of varying concentrations can be easily prepared and inserted into the experimental liquid LSC setup. In this way, experimental uncertainties, such as reduction in the luminescent quantum yield, can be reduced. Hence, the *spectral* effects of various single and multiple dyes can be analysed and compared more accurately with ray-trace predictions. Initial results from the liquid LSC characterisation and comparison with model predictions are presented here.

Keywords: Multiple dye solar luminescent concentrators, ray-tracing

1 INTRODUCTION

Luminescent solar concentrators (LSCs) are static, non-imaging concentrators which do not require expensive solar tracking and concentrate both direct and diffuse light. A standard LSC [1,2] consists of a flat transparent polymer plate doped with a luminescent dye. Incident insolation passing through the LSC device matrix is absorbed by the dye. Red-shifted light is subsequently emitted isotropically. As the refractive index of the plate is larger than that of the surrounding air, a large fraction of emitted light is guided by total internal reflection (TIR) to the plate edges, where PV cells are attached (Fig. 1). Liquid LSCs have been used here, due to their ease of fabrication, instead of solid polymer plates.

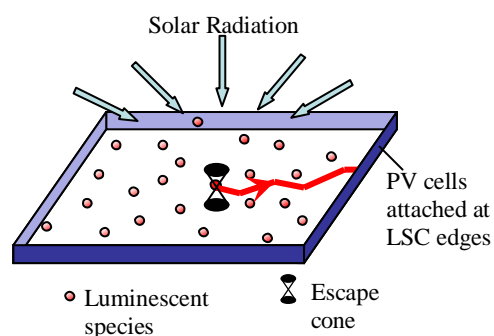


Fig.1 A standard luminescent solar concentrator consisting of a flat transparent polymer plate doped with a luminescent species. Light emitted by the luminescent species, outside the escape cone, is guided to plate edges where PV cells are attached.

The addition of multiple dyes in an LSC allows the absorption of the solar spectrum to be enhanced [3,4,5] compared to a single dye LSC. However, as there may be a large degree of overlap between different dyes' absorption and emission spectra, re-absorption losses may increase significantly in a multiple dye LSC. It is therefore even more important that re-absorption of emitted photons is modelled accurately in multiple dye LSCs. The objective in this study is to develop an apparatus which will allow easy measurement of electrical output from LSCs containing multiple dyes of varying concentrations, and hence, verify whether re-

absorption effects in multiple dye LSCs are being accurately calculated by the ray-trace model.

2 EXPERIMENTAL LIQUID LSC

Uncertainty, due to quantum yield losses and in the magnitude of matrix material attenuation and scattering, which can occur in solid LSC plates during the polymerisation process, is avoided by using the dyes in solution in a liquid LSC. With these experimental uncertainties reduced, *spectral effects* (absorption and re-absorption) can be analysed and compared more accurately with ray-trace predictions. Multiple dye mixes can be more easily and reproducibly prepared in solution than in a solid polymer, allowing many more combinations of dye concentrations to be tested.

A removable 10 x 4 x 0.5 cm quartz cuvette was used as a liquid LSC container (see Fig. 2). The spectrum of the metal halide incident light source is shown in Fig. 3(d). A 2.0 x 0.3 cm silicon photodiode was placed adjacent to one side of the cuvette at a right angle to the incident beam (see Fig. 2). The different dye solutions can then be placed, in turn, into the cuvette and the resulting photodiode short circuit current (J_{sc}) measured. Three Perylene dyes [6] (BASF Lumogen Yellow 170, Orange 240 and Red 305) of varying concentrations (given in Table 1) were prepared in chloroform solution. The dyes were shown to be stable in solution over the length of time required to take the electrical measurements. The absorption and emission spectra of each dye are shown in Fig. 3. The ray-trace model, described in 2.1, was used to predict which particular multiple dye mixes should attain significantly higher, similar, and significantly lower J_{sc} values than the best single dye. Based on the model predictions, four multiple dye mixes, given in Table 2, were prepared. The predicted and measured J_{sc} values for the single and multiple dye mixes are presented in section 3.

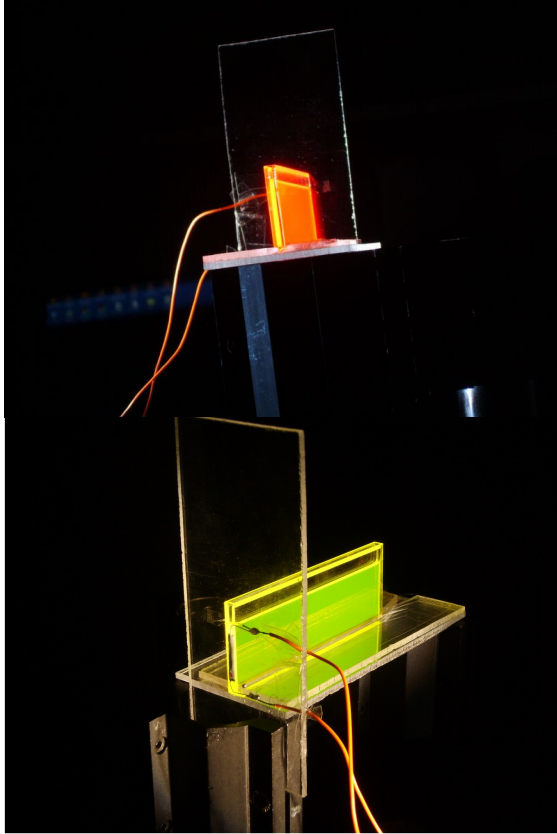


Fig. 2. A liquid LSC is pictured containing two different dye samples. A silicon photodiode is placed adjacent to one side of the liquid LSC, at right angles to the incident beam, to measure the intensity of light emerging at this side.

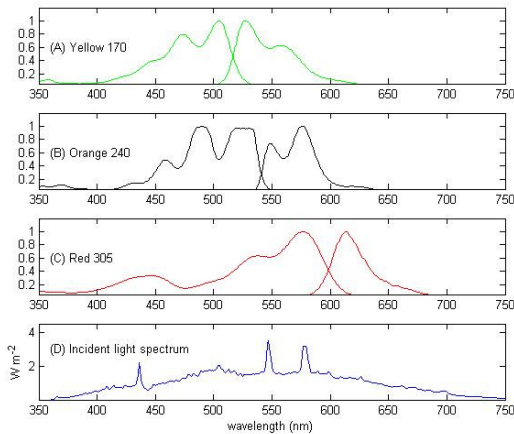


Fig 3. Normalised absorption and emission spectra of (A) Lumogen Yellow 170, (B) Lumogen Orange 240 and (C) Lumogen Red 305. The spectrum of the incident light is plotted in (D). The shorter wavelength emitting dye(s) overlap significantly with the longer wavelength absorbing dye(s), resulting in a large degree of re-absorption in the LSC containing all three dyes.

Dye	Abbreviation	Concentration (mg/ml)
Lumogen Yellow 170	Y1	0.03125
	Y2	0.0625
	Y3	0.125
	Y4	0.25
Lumogen Orange 240	O1	0.05
	O2	0.1
	O3	0.2
	O4	0.4
Lumogen Red 305	R1	0.025
	R2	0.05
	R3	0.1
	R4	0.2

Table 1. Luminescent dyes and varying concentrations used.

2.1 Ray-trace modelling of multiple dye LSCs

Monte-Carlo ray-trace modelling [7-11] is used to determine the LSC optical efficiency and edge emission spectrum. With the edge emission spectrum and the spectral response of the PV cell attached at the edge, the short circuit current can be calculated. In the model, a large number of rays, of a given initial angle and wavelength are traced through the LSC from a random starting point on the front surface until the ray is lost from the system (due to matrix material attenuation or non-unity quantum yield) or until the ray escapes through one of the LSC surfaces. As a ray travels between two surfaces inside the LSC, the total probability of an absorption event (P_{abs}) is calculated using the dye absorption coefficients, α , at the particular wavelength of the ray;

$$P_{abs} = 1 - e^{-(\alpha_1 + \alpha_2 + \dots + \alpha_n)(d)}$$

where, d is the pathlength between surface intersection points and n is the number of dyes. Assuming absorption occurs, the ratio of the relative individual dye absorption probabilities is then used to determine which dye has absorbed the ray;

$$1 - e^{-(\alpha_1 d)} : 1 - e^{-(\alpha_2 d)} : \dots : 1 - e^{-(\alpha_n d)}$$

The probability of an emission event is given by the luminescent quantum yield (QY) of each particular dye. The QY of the dyes in chloroform was obtained from the dye suppliers [6]. Randomly generated numbers are tested against the calculated probabilities, in each case, to determine whether the event occurs or not. The wavelength of a ray, following an emission event, is assigned at random from a weighted distribution corresponding to the emission spectrum of the absorbing dye. When an emitted ray intersects a surface boundary, the probability of reflection or transmission is determined from the Fresnel equations. A random number is again generated to determine whether reflection or transmission ensues.

3 RESULTS

3.1 Comparison of predicted and measured J_{sc} of liquid LSCs

The measured and predicted relative short circuit current (J_{sc}) for each concentration of the single dyes (see Table 1) are shown in Fig. 5. Of the single dye concentrations tested, R4 (0.2 mg/ml Lumogen red 305) obtained the highest J_{sc} . Measured and predicted J_{sc} values obtained for all other samples are shown relative to the J_{sc} values obtained for R4.

One surface (10 x 0.5 cm surface) of the quartz cell currently being used has a frosted surface which needs to be removed in order to allow efficient total internal reflection to occur at this surface. J_{sc} values predicted by the ray-trace model were higher than measured values and the side with the frosted surface may be one reason for this.

The model predictions do show the same trends of increasing J_{sc} with increasing concentration of each single dye. Predicted J_{sc} is highest for R4 and lowest for

Y1 and R1, in agreement with the measured values. The four particular dye mixes used are listed in Table 2. The measured and predicted J_{sc} for the dye mixes are shown in Fig. 5. Dye mixes 1 and 2 show a predicted increase compared to R4, mix 3 has almost the same predicted J_{sc} , while mix 4 shows a decrease, all matching the relative measured J_{sc} values within the experimental errors. This indicates that re-absorption in multiple dye LSCs, arising from the spectral overlap between different dyes, is accurately calculated in the ray-trace model.

Only the dye concentrations listed in Table 1 were used in the liquid LSC. Of interest would be to use the *optimum* concentration of each dye for comparing the optimum performance of single dye LSCs to multiple dye LSCs. However, the initial aim here is not to find dye concentrations to maximise the electrical output, but to validate the ray-trace model for multiple dyes. While initial results are presented here and reasonable agreement between measurements and predictions is shown, the experimental setup requires some refinement in order to reduce the experimental error and show that the *absolute* predicted J_{sc} values match measured values.

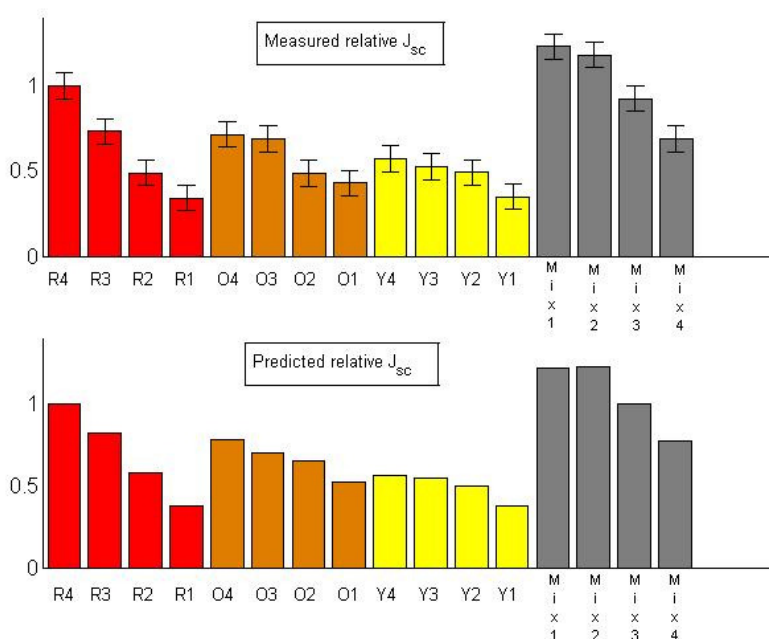


Fig. 5. Measured and predicted short circuit current (J_{sc}) values for the dye samples listed in tables 1 and 2. The model predictions show the same trends of increasing J_{sc} with increasing dye concentration. Dye mixes 1 and 2 show a predicted increase compared to R4, while mix 4 shows a predicted decrease, matching the trend of the measured J_{sc} values.

Sample	Measured relative J_{sc} ± 0.075	Predicted relative J_{sc}
Mix 1 (R4+O4)	1.23	1.22
Mix 2 (R4+O4+Y4)	1.18	1.23
Mix 3 (R2+O2+Y2)	0.92	0.99
Mix 4 (Y2+O2)	0.69	0.77

Table 2. Measured and predicted J_{sc} of multiple dye liquid LSCs (relative to R4). The J_{sc} values are also plotted in Fig.5.

CONCLUSION

The addition of multiple dyes in an LSC allows the absorption of the solar spectrum to be enhanced compared to a single dye LSC, with the disadvantage that re-absorption losses may increase significantly. It is important, therefore, that re-absorption of emitted photons is modelled accurately in multiple dye LSCs. A previously developed Monte-Carlo ray-trace model has been modified to incorporate multiple luminescent species. A liquid luminescent solar concentrator (LSC) has been fabricated to allow model predictions for multiple dye LSCs to be verified experimentally. The liquid LSC setup allows samples of single or multiple dyes, at varying concentrations, to be easily tested whilst

also avoiding uncertainties which may arise in the polymerisation process of solid LSC plates.

While the experimental setup requires some refinement, initial results have been presented. The model predictions match the measured trends of increasing short circuit current (J_{sc}) with increasing single dye concentrations. The predicted increase/decrease in J_{sc} for multiple dye mixes, relative to the best single dye used, also agree with measurements, indicating that re-absorption arising from spectral overlap between multiple dyes is accurately calculated in the ray-trace model.

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