Theoretical Study of Light Emission in Europium-Chelate-Doped Polymer Optical Fibres

B García-Ramiro¹, J Arrue¹, M A Illarramendi¹, F Jiménez¹ and J Zubia¹
¹ Faculty of Engineering in Bilbao. University of the Basque Country (UPV/EHU), E48013- Bilbao, Spain

E-mail: mariabegona.garciar@ehu.eus

Abstract. We analytically and computationally study the generation of light in poly (methyl methacrylate) polymer optical fibres (PMMA POFs) doped with a typical coordination complex, or chelate, of Eu³⁺. The system has been modelled by means of four rate equations that describe the temporal and spatial evolution of the generated power, the pump power, and the concentrations of excited ligands and europium ions. For this paper, the system has been solved in stationary state by using the fourth-order Runge-Kutta method. The results show the influence of several parameters of light sources based on europium-chelate-doped POFs both on the optimum fibre length and on the output power, including the effect of the attenuation of the emitted red light. Additionally, we have derived a simplified analytical expression that serves to model the evolution of the generated power as it propagates while the pump power is still non-negligible.

1. Introduction
POFs are very suitable for working in the visible region of the spectrum, with distinct advantages such as easiness of handling and of light coupling. Their performance has been steadily improving in recent decades. Furthermore, due to their lower manufacturing temperatures than those of their glass counterparts, it is feasible to dope POFs with organic dyes or rare-earth organic complexes. Hence, it is possible to take advantage of the absorption and emission properties of these types of dopants in the visible spectrum in order to achieve enhanced light sources based on amplified spontaneous emission, which has interest in various applications [1-3].

Whereas dye-doped POFs present the problem of photodegradation, this does not occur with lanthanides like europium, which emits in the red [1]. However, europium ions are impractical to be used as lone dopants, because europium is not directly soluble in PMMA. Furthermore, the absorption cross section of the isolated europium ions is too low to manufacture compact devices. Both difficulties are solved by making each ion part of a chelate containing various absorbing ligands together with the ion. This is the case of a typical europium chelate analysed here, which exhibits high red fluorescence (at 613 nm). This wavelength is close to the low-loss window of PMMA, so material absorption losses are reduced, thus facilitating light propagation.
2. Theoretical model

Figure 1 illustrates schematically the energy levels and transitions of a typical chelate that are relevant to the phenomena that will be studied in this paper, i.e. those affecting the behavior of light sources based on a POF doped with this type of dopant.

We have modelled the system by means of four rate equations. Two of them describe the evolution with time of the concentrations of excited ligands \( N_T \) and of excited europium ions \( N_D \) for any position along the optical fibre; and another two include the spatial and temporal changes of the generated power \( P \) and of the pump power \( P_p \), respectively. These equations can be written as follows:

\[
\frac{\partial N_T}{\partial t} = -\frac{N_T}{\tau_{T,S0}} \frac{\sigma^e}{h (c/\lambda_s)} A_{core} + (N - N_T) P_p - W_{ET} \frac{N - N_D}{N} N_T + \frac{W_{BT}}{N} \frac{N - N_T}{N} N_D
\]

(1)

\[
\frac{\partial N_D}{\partial t} = -\frac{N_D}{\tau_{D,F}} \frac{\sigma^e}{h (c/\lambda_s)} A_{core} + N_D P + W_{ET} \frac{N - N_D}{N} N_T + W_{ET} \frac{N - N_D}{N} N_T - \frac{W_{BT}}{N} \frac{N - N_T}{N} N_D
\]

(2)

\[
\frac{\partial P}{\partial z} = \frac{\sigma^e N_D P}{\tau_{D,F} (c/\lambda_s)} A_{core} - \frac{1}{v_z} \frac{\partial P}{\partial t} - \alpha P
\]

(3)

\[
\frac{\partial P_p}{\partial z} = \frac{\sigma^a (N - N_T) P_p}{v_z} - \frac{1}{v_z} \frac{\partial P_p}{\partial t}
\]

(4)

Here, \( \lambda_s \) and \( \lambda_p \) stand for the emission and pump wavelengths, \( N \) represents the dopant concentration per unit volume, \( \tau_{T,S0} \) and \( \tau_{D,F} \) are the decay lifetimes from \( T \) to \( S_0 \) and from \( D \) to \( ^{7}F_2 \), respectively, \( \sigma^e \) is the emission cross section of the dopant at \( \lambda_s \), \( \sigma^a \) is the absorption cross section of the dopant at \( \lambda_p \), \( A_{core} \) is the
area of the fibre cross section, $h$ is Planck’s constant, $c$ is the speed of light in vacuum, and $v_z$ is the speed of light in the fibre core. The parameter $\alpha$ is the attenuation coefficient of the doped fibre at $\lambda_s$, and $\beta$ represents the fraction of spontaneously generated photons that are emitted in guided directions towards the output end of the fibre with respect to the number of photons spontaneously emitted in all directions.

When the pump power is continuous, and after the stationary state has been reached, the partial derivatives with respect to time are zero. As a consequence, the first members of equations (1) and (2) are equal to 0, which allows us to isolate $N_T$ and $N_D$ in terms of $P$ and $P_p$. By substituting these expressions into (3) and (4), we obtain a set of two ordinary differential equations, which are then solved by using the fourth-order Runge-Kutta method. The boundary conditions are as follows: $P_p(z = 0)$ is constant, and $P(z = 0)$ is 0.

3. Theoretical results

One important design parameter is the optimum fibre length, i.e. the length travelled by the generated power $P$ until it just reaches its maximum value. Figure 2 shows the influence of the dopant concentration on the optimum fibre length for two different values of $\alpha$. In figure 2(a), $\alpha$ is the value that has been measured in our laboratory for a typical europium-chelate-doped POF (around 0.23 m$^{-1}$). As a consequence, the optimum fibre length decreases in a similar way in both figures (a and b) as $N$ is increased by threefold from a certain value: this length is approximately divided by three (or exactly, when $\alpha = 0$). This can be explained as follows: if we increase the concentration, the average distance between molecules is reduced, whereas the molecules can still be assumed to be independent from each other due to the shielding of each europium ion by the surrounding ligands. Therefore, the same output emission will be achieved in a shorter fibre length ($z$) but with a greater dopant concentration as long as it contains the same number of dopant molecules in total, because the europium ions will continue emitting independently, i.e. without energy transfers from ion to ion. However, only if the attenuation of the emission in the considered distance $z$ is 0, as happens in figure 2(b), is the rule of inverse proportionality between concentration and fibre length satisfied. In figure 2(a), even though the concentration is multiplied by three, the optimum distance is reduced to a longer value than one third of the original one, owing to the lower absorption in the red caused by the PMMA in a shorter distance $z$. Specifically, the optimum fibre length, which should have been reduced from 1.28 m to 0.42 m in theory in figure 2(a), has only been reduced to 0.46 m.

![Figure 2(a)](#)

**Figure 2(a).** Evolution of the generated power along the fibre for two different concentrations $N$ (molecules/m$^3$) of dopant, with $\alpha = 0.23$ m$^{-1}$.

![Figure 2(b)](#)

**Figure 2(b).** Evolution of the generated power along the fibre for different concentrations $N$ (molecules/m$^3$) of dopant, with $\alpha = 0$. 
As for the emission powers corresponding to the optimum lengths for both concentrations, these are considerably different from each other in figure 2(a), but they are exactly the same in figure 2(b). As a matter of fact, having a non-negligible $\alpha$ reduces the net gain along the pumped length of fibre, which explains the higher peak power when the travelled distance is shorter. In the absence of attenuation, the height of the peak of $P(z)$ is independent of the concentration, as shown in figure 2(b).

Let us now analyse the variation of the optimum fibre length with the pump energy in the case of employing a high pump power that produces amplified spontaneous emission (ASE). As can be observed in figure 3, this length increases almost linearly with the pump power in the range of distances in which the pump power penetrates into the fibre saturating $N_D$. The reason for this is that the population of europium ions is completely inverted in that range (i.e. all the ions are in the excited state). Therefore, if one employs a longer fibre whose length is the original one multiplied by a certain factor and all the ions are to be excited, the required pump energy is also multiplied by the same factor, because the number of ions is increased in the same proportion as the fibre length is.

The linearity obtained in the results of figure 3 can also be explained in an analytical way. For this purpose, we have derived a simplified mathematical formula for $P(z)$ from equation (3) in stationary state when $N_D$ is approximately constant. In such a case, the derivative of $P$ with respect to time is 0, so equation (3) can be expressed as follows:

$$\frac{dP}{dz} = \left( \sigma' N_D P - \alpha \right) P + \frac{N_D}{\tau_{D,F}} \frac{c}{\ell} \beta A_{ow}$$  \hspace{1cm} (5)

In the case in which $P(z) = 0$, the analytical solution can be written as follows:

$$P(z) = \frac{N_D (h c / \ell)}{\tau_{D,F} (\sigma' N_D - \alpha)} A_{ow} \beta \left[ \exp \left( (\sigma' N_D - \alpha) z \right) - 1 \right]$$  \hspace{1cm} (6)

As can be observed, $P(z)$ increases in an approximately exponential way when $N_D$ is approximately constant, reaching a value that depends on the product of $N_D$ and $z$ ($\alpha$ is negligible as compared to the gain $\sigma' N_D$), which analytically proves the physical explanation given before for figure 3.

In order to show the values of $N_D$ and of the analytically predicted $P(z)$ corresponding to the conditions of figure 3, we have plotted the spatial evolution of $N_D$ and of $P(z)$ in figure 4. Figure 4(b) confirms that the exact values of $P(z)$ tend to increase in an exponential way while $N_D$ remains saturated.
Conclusions
We have modelled the emission of a typical europium-chelate-doped polymer optical fibre working as a light source by means of four rate equations that have been solved numerically in steady state. An analytical expression has also been worked out to validate the results and facilitate their interpretation. We have proved that the optimum fibre length that maximizes the output power depends on the pump power and, more slightly, on the attenuation of the fibre at the emission wavelength. However, this attenuation affects the output power much more than the optimum length is affected. The model developed can also be used to characterise these fibres working as optical amplifiers.

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