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Numerical analysis of the irradiation and heating processes of thermoluminescent materials

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ABSTRACT

The deconvolution of thermoluminescence (TL) glow curves into a sum of individual peaks described by First Order Kinetic (FOK) equations, implies that retrapping probability should be negligible compared with recombination during the readout (to avoid non-linearity) but not during irradiation (to allow the filling of the traps with the produced electron-hole pairs). In this contribution, some examples of TL glow curves simulated using a general model are discussed to show that FOK shape and deconvolution into individual glow peaks fitted by FOK equations is compatible with a non-negligible traps filling process during irradiation with the appropriate choice of kinetic parameters and probability factors.

1. Introduction

The emission of thermoluminescence (TL) can be theoretically modelled as the result of transitions of electron and holes between the conduction and valence bands in a material with localized states acting either as trapping or recombination centres (McKeever, 1988; Chen and McKeever, 1997; Chen and Pagonis, 2014). During irradiation, the created electron-holes pairs are trapped in these metastable states and then, during the heating of the material, they are released and recombined or retrapped, depending on the kinetics parameters and transition probabilities.

The models range from the simplest situation of one trapping state and one recombination centre (OTOR) to complex energy-levels with several trapping states and allowed transitions (radiative and non-radiative). In most of the cases, the set of differential equations governing the processes does not have an analytic solution. Nevertheless, assuming the quasi equilibrium condition for the simplest OTOR model, the first order kinetics (FOK) equation (McKeever, 1988; Chen and McKeever, 1997) is obtained for the case of no retrapping, as well as the mixed order kinetics in case of high retrapping-recombination ratios (Gómez-Ros et al., 2006).

Despite of the complexity of the possible TL models, the experimental glow curves actually measured in many TL synthetic materials commonly used in dosimetry (e.g. LiF: Ti,Mg LiF:Mg,Cu,P) can be fitted by a sum of first order kinetic glow peaks (Horowitz and Yossian, 1995; Muñiz et al., 1995; Delgado and Gómez-Ros, 2001). This may seem contradictory for two reasons: i) FOK equation is derived assuming that probability of retrapping is negligible compared with the probability of recombination but recombination is required to fill the trapping centres during irradiation; and ii) glow curve deconvolution with two or more peaks (two or more traps) assume that the TL glow curve is the (linear) sum of the individual glow peak but the differential equations system describing the TL emission is not linear.

The main purpose of this work is to present some examples of TL glow curves simulated using a general model, to show that FOK shape and deconvolution into individual peaks fitted by FOK equations is compatible with a non-negligible traps filling process during irradiation (i.e. a non-zero retrapping probability). Therefore, there is no restriction for the traffic of electrons during process, irradiation and readout, thus allowing them to be trapped and released according to the corresponding probability factors and kinetic parameters.

2. Materials and methods

The general model has been considered, consisting of several trapping states for electrons and two competing recombination centres, one radiative and one non-radiative (McKeever, 1988; Chen and McKeever, 1997). The allowed transitions are schematically shown in Fig. 1 and they are: electron trapping and releasing from traps to the conduction band, capture and releasing from of holes from centres to the valence band and both radiative and non-radiative recombination of electrons with holes in the recombination centres. The set of equations describing the processes are:

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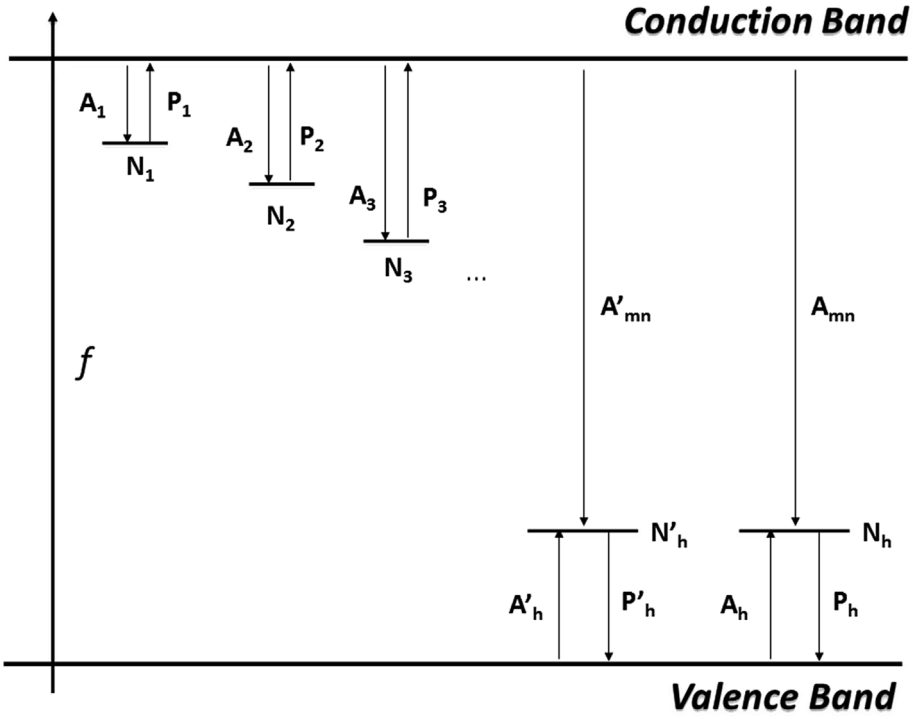

Fig. 1. Energy levels and allowed transitions scheme for the considered model.

$$\begin{aligned}
\dot{n}_c &= f + \sum_i p_i n_i - n_c\left[\sum_i A_i(N_i - n_i) + A'_{mn} m' + A_{mn} m\right] \\
\dot{n}_i &= -p_i n_i + A_i(N_i - n_i) n_c \\
\dot{m}' &= A'_h(M' - m') n_h - A'_{mn} m' n_c - p'_h m' \\
\dot{m} &= A_h(M - m) n_h - A_{mn} m\, n_c - p_h m \\
\dot{n}_h &= f - A'_h(M' - m') n_h + p'_h m' - A_h(M - m) n_h + p_h m
\end{aligned} \tag{1}$$

where the meaning of the symbols is:

n_c; electron concentration in the conduction band (cm^{-3})
n_i; electron concentration in the trapping centres i (cm^{-3})
m'; hole concentration in the non-radiative recombination centres (cm^{-3})
m; hole concentration in the radiative recombination centres (cm^{-3})
n_h; hole concentration in the valence band (cm^{-3})
N_i; total density of electron trapping centres i (cm^{-3})
M'; total density of non-radiative recombination centres (cm^{-3})
M; total density of radiative recombination centres (cm^{-3})
f; rate of production of electron-hole pairs during irradiation ($cm^{-3}s^{-1}$)
A_i; probability factor for the electron trapping centres i (cm^3s^{-1})
A'_h; probability factor for the non-radiative recombination centres (cm^3s^{-1})
A_h; probability factor for the radiative recombination centres (cm^3s^{-1})
A'_{mn}; non-radiative recombination probability (cm^3s^{-1})
A_{mn}; radiative recombination probability (cm^3s^{-1})
s_i, E_i; frequency factor (s^{-1}), activation energy (eV) for electron trapping centres i, $p_i = s_i\, exp(-E_i/kT)$
s'_h, E'_h; frequency factor (s^{-1}), activation energy (eV) for the non-radiative recombination centres, $p'_h = s'_h\, exp(-E'_h/kT)$
s_h, E_h; frequency factor (s^{-1}), activation energy (eV) for the radiative recombination centres, $p_h = s_h\, exp(-E_h/kT)$
T; temperature (K)
K; Boltzman's constant (8.617×10^{-5} eV/K)

The differential equations system (1) has been numerically solved using the Runge-Kutta-Fehlberg Method (RKF45) (Cheney and Kincaid, 2002). To simulate the irradiation of the material, production of electron-hole pairs at a rate f while keeping a constant temperature has been assumed. For the simulation of the TL glow curve, the system (1) has been solved with f = 0 (no irradiation) and a linear heating $T(t) = T_0 + \beta t$. In this case, the TL intensity of the thermoluminescence is proportional to the rate of radiative recombination of electrons and holes, i.e.:

$$I_{TL}(t) = -\dot{m} = -\frac{1}{\beta}\frac{dm}{dT} \tag{2}$$

Deconvolution analysis of the TL glow curves have been performed assuming a linear combination of First Order Kinetic (FOK) glow peaks to obtain their corresponding kinetic parameters (E, T_m, I_m, s) (Muñiz et al., 1995; Delgado and Gómez-Ros, 2001).

3. Results and discussion

Two cases of the general model described by equation (1) and illustrated in Fig. 1 are especially relevant in order to show how glow peaks due to combined retrapping/recombination processes can be however fitted by FOK equations.

3.1. Two traps model

The model consists of two traps and one radiative recombination centre with a negligible probability of thermal release of trapped hole ($p_h = 0$) that it is described by a simplified version of equations system (1) as follows:

$$\begin{aligned}
\dot{n}_c &= f + \sum_{i=1}^{2} p_i n_i - \sum_{i=1}^{2} A_i(N_i - n_i) n_c - A_{mn} m\, n_c \\
\dot{n}_1 &= -p_1 n_1 + A_1(N_1 - n_1) n_c \\
\dot{n}_2 &= -p_2 n_2 + A_2(N_2 - n_2) n_c \\
\dot{m} &= A_h(M - m)\, n_h - A_{mn} m\, n_c \\
\dot{n}_h &= f - A_h(M - m)\, n_h
\end{aligned} \tag{3}$$

Table 1
Kinetic parameters for the two traps model.

parameters		trap 1	trap 2
trapping centres	E_i (eV)	1.44	3.63
	s_i (s^{-1})	10^{15}	10^{15}
	A_i (cm^3s^{-1})	10^{-7}	10^{-7}
	N_i (cm^3)	10^{10}	10^{10}
radiative recombination centre	A_{mn} (cm^3s^{-1})	10^{-7}	
	A_h (cm^3s^{-1})	10^{-6}	
	M (cm^3)	10^{11}	

To simulate the irradiation of the material, equation (3) have been solved using the kinetics parameters listed in Table 1 for a constant temperature T = 273 K and a rate of production of electron-hole pairs $f = 7.4 \times 10^6$ $cm^{-3}s^{-1}$, thus obtaining the concentration of trapped electrons and holes, respectively $n_1(t)$, $n_2(t)$, m(t), as a function of irradiation time. Then, using these concentrations after increasing irradiation times as initial conditions, the system has been solved again assuming f = 0 and a linear heating from T_0 = 273 K at a heating rate β = 2 K/s to obtain the corresponding TL glow curves. The *f* value has been chosen to obtain a density of produced electron-hole pairs high enough to fill the trapping centres but not so high to produce saturation effects for the longest irradiation time later considered.

With the chosen values for the kinetic parameters, thermal release of trapped electrons is almost negligible at 273 K so both trapping centres were filled homogeneously during irradiation ($A_1 = A_2$, $N_1 = N_2$). Afterwards, the temperatures range during the heating cycle does not permit that the trapped electrons in the trap 2 can be released into the conduction band because:

$$p_2 = s_2 \exp(-E_2/kT) \approx 0 \rightarrow \dot{n}_2 \approx A_2(N_2 - n_2)n_c > 0 \quad (4)$$

Thus, $n_2(t)$ always increases. By the contrary, the competition between the trapping and release processes in trap 1 gives:

$$p_1 = s_1 \exp(-E_1/kT) > A_1(N_1 - n_1) \quad \rightarrow \quad \dot{n}_1 < 0 \quad (5)$$

Fig. 2 shows the glow curve obtained after a simulated irradiation during t = 0.1 s (dots) together with the evolution of trapped electron concentration, n_1 (dotted line) and n_2 (dashed line) as a function of the temperature. Both n_1 and n_2 remain constant up to 400 K approximately. When temperature is high enough, trapped electrons in traps 1 start to be released into the conduction band and, because the probability to be trapped by trap 2 or to recombine is higher than to be retrapped by trap 1, the obtained glow peak is very well fitted by a first order kinetic equation (solid line) (E_1 = 1.42, $s_1 = 3.4 \times 10^{14}$ s^{-1}, FOM = 0.4%), although the fitted value for the frequency factor is underestimated. As it was expected from equations (4)-(5), n_1 and n_2 respectively decreases and increases monotonically. These results agree with those reported by Basun et al., (2003).

Good fitting results (FOM = 0.4–1.18%) are obtained simulating longer irradiation times (0.1–2s) but the fitted values for E_1 and s_1 are increasingly underestimated. Fig. 3 shows the fitted E_1 values as a function of irradiation time, together with the corresponding values of $A_2(N_2\text{-}n_2)$. Both values are correlated because the concentration of trapped electrons in trap 2, n_2, increases with irradiation time thus decreasing the value of $A_2(N_2\text{-}n_2)$. According to equation (3), the lower the $A_2(N_2\text{-}n_2)$ value is, the higher the contributions of recombination and retrapping by trap 1 are. Then, a wider glow peak is obtained and the fitted E_1 value is lower.

3.2. TLD-100 type model

A more complex model has been analysed using the kinetics parameters shown in Tables 2 and 3. In this case, the model is the general one described in section 2, consisting of six electron trapping centres, one radiative and one non-radiative recombination centres. The E and s values of the traps 1–5 have been chosen looking to reproduce the shape of a LiF:Ti,Mg (TLD-100) glow curve (Bos et al., 1994). The sixth trap has been included to obtain the same effect described in section 3.1, i.e.: the prevalence of recombination processes during the TL readout, even though non-zero retrapping probability factor has been considered. To achieve that, the values of the probability factors have been chosen in accordance with the E and s values to permit that the released electrons into the conduction band have more probability to be trapped by the other traps with higher E values than to be retrapped.

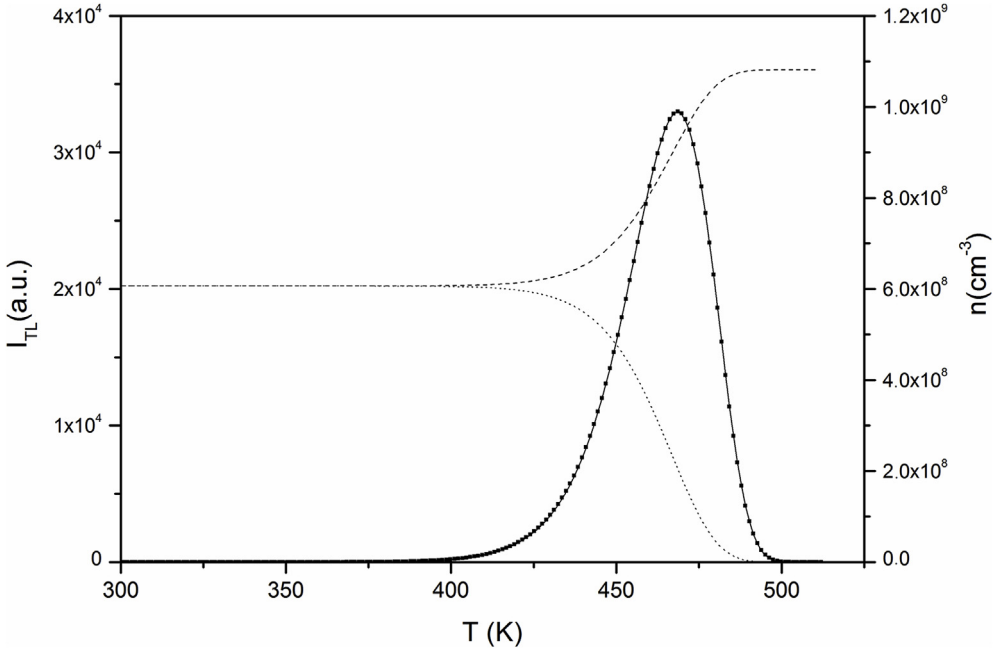

Fig. 2. Results of the simulation for the two traps model (see the text for the chosen parameters) showing: simulated glow curve (dots, left axis), fitted glow curve (continuous line, left axis), electron concentration in the trapping centres (right axis), n_1 (dotted line) and n_2 (dashed line).

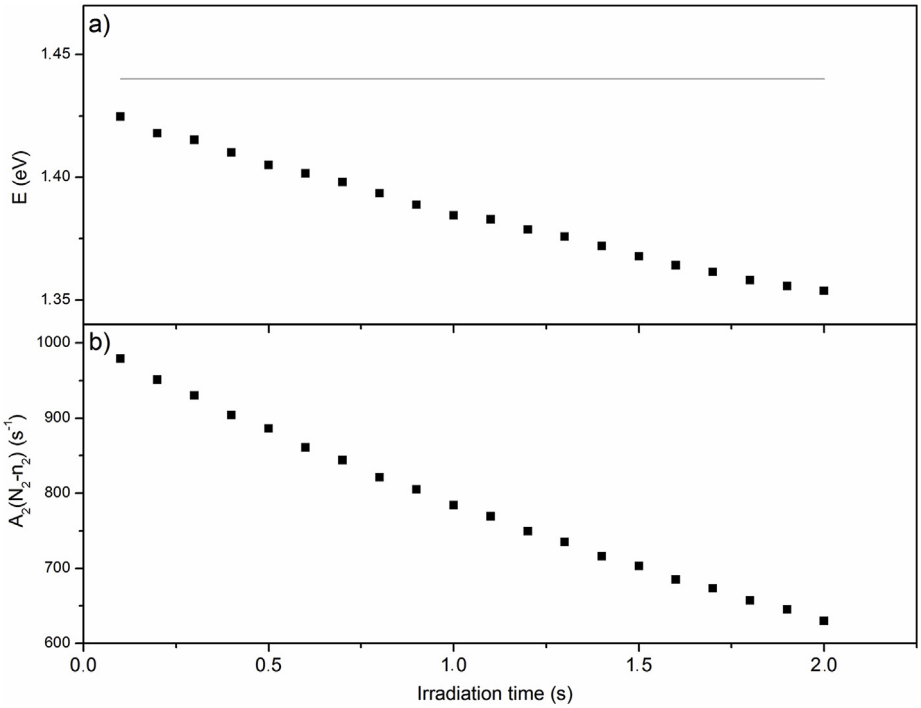

Fig. 3. Results of the simulations for the two trap model as a function of irradiation time (between 0.1 s and 2 s): a) fitted activation energy E_1 obtained using a first order kinetic equation compared with the reference 1.44 eV; b) value of $A_2(N_2-n_2)$ (see the text for the discussion).

The assumed rate of production of electron-hole pairs during irradiation has also been $f = 7.4 \times 10^6$ $cm^{-3}s^{-1}$.

Fig. 4 presents the glow curve (dots) obtained after a simulated irradiation during t = 120 s, together with the evolution of trapped electron concentrations n_1 - n_6 (dashed lines from left to right) as a function of the temperature. The glow curve have been simulated assuming the parameters shown in Tables 2 and 3 and a heating rate of 2 K/s. Analogously to the case discussed in the previous section 3.1, the glow curve can be fitted by a sum of five first order kinetic glow peaks (solid lines) because of the competing effect of trap 6 (with a very low release probability $p_6 = s_6\, exp(-E_6/kT)$) that works as an electrons sink, thus making retrapping in traps 1–5 negligible compared with recombination process during the heating cycle.

Table 4 shows the fitting results corresponding to four TL glow curves obtained with the same parameters and irradiation time but different heating rates (2, 4, 8, 12 K/s). The estimation of E and s values based on the various heating rates method (VHR) (Chen and McKeever, 1997) is also provided. As it can be seen, a good fitting is always obtained assuming FOK glow peaks shape, even when the probability factor for the electron trapping centres is not negligible. Nevertheless, the fitted Ei and si values differ from the actual values used to simulate the model and such a difference increases when faster heating rates are considered (up to 10% for the activation energy and very significantly in case of the frequency factor).

Moreover, a set of glow curves has been simulated for increasing irradiation times up to 5×10^4 s and the same heating rate ($\beta = 2$ K/s).

Table 3
Kinetic parameters for the recombination centres in the TLD-100 type model.

parameters	recombination centres	
	radiative	non-radiative
A_{mn} (cm^3s^{-1})	10^{-8}	10^{-8}
A_h (cm^3s^{-1})	10^{-5}	10^{-11}
M (cm^3)	10^6	10^9
E_h (eV)	3.2	3.2
s_h (s^{-1})	4.1×10^{10}	10^{10}

Fig. 5a displays the fitted E_i values compared with the true values used to simulate the glow curves and shown in Table 2. As it can be seen, E_5 tends to be underestimated because the corresponding peak appears when n_6 is rapidly increasing and it is the only trapping centre able to act as an electron sink.

In Fig. 5b, the area of fitted peaks 3 + 4 + 5 (identified in the figure) as TL_{area} is plotted versus the irradiation time. Assuming that the absorbed dose would be proportional to the irradiation time, the TL area exhibits an initial linear dependence on the irradiation time (absorbed dose), followed by a supra-linear region at higher doses due to the filling of the non-radiative recombination centre for long irradiation times.

Table 2
Kinetic parameters for the trapping centres in the TLD-100 type model.

parameters	trapping centres					
	trap 1	trap 2	trap 3	trap 4	trap 5	trap 6
E_i (eV)	0.95	1.28	1.42	1.51	2.00	6.02
s_i (s^{-1})	10^{15}	4.0×10^{16}	1.6×10^{16}	2.1×10^{16}	4.1×10^{20}	10^{12}
A_i (cm^3s^{-1})	10^{-8}	10^{-8}	10^{-8}	10^{-8}	10^{-8}	10^{-8}
N_i (cm^3)	10^{10}	10^{10}	10^{10}	10^{10}	10^{10}	10^{10}

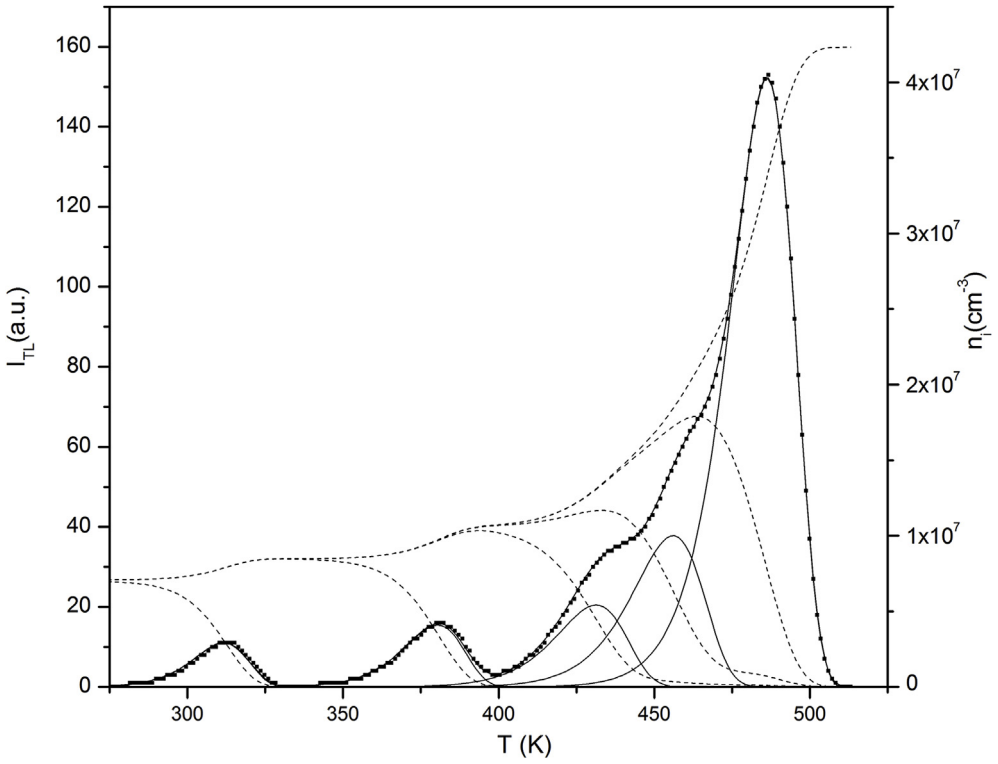

Fig. 4. Result of the simulation for the TLD-100 type simulated model (see the text for the chosen parameters) showing:: simulated glow curve (dots, left axis), fitted glow curve and individual glow peaks (continuous line, left axis), electron concentration in the trapping centres (dashed line right axis).

4. Conclusions

As it has been shown, the presence of retrapping processes, needed to explain the filling of trapping centres during irradiation, can be compatible with the fitting of the resulting TL glow curve by FOK individual peaks, for the adequate values of kinetic parameters and probability factors. This can be achieved both for a single peak glow curve and for a complex glow curve (5 peaks). Moreover, other phenomena like supralinearity can be also reproduced together with the FOK behaviour, assuming two competing radiative and non-radiative recombination centres.

CRediT authorship contribution statement

J.F. Benavente: Conceptualization, Methodology, Formal analysis, Software, Data curation, Writing - original draft. **J.M. Gómez-Ros:** Validation, Writing - review & editing, Supervision, Project administration, Funding acquisition. **A.M. Romero:** Visualization, Investigation.

Declaration of competing interest

X The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 4
Comparison between the fitted and the reference values for E and s in the TL glow curves simulated assuming the TLD-100 type model and 4 different heating rates.

parameter		peak 1	peak 2	peak 3	peak 4	peak 5	FOM
T_M (K)	2 K/s	311.8	380.4	431.3	456.0	486.2	0.40%
	4 K/s	317.4	386.5	438.3	463.1	492.6	0.55%
	8 K/s	323.2	393.1	446.1	470.3	499.5	0.64%
	12 K/s	327.1	397.2	451.0	475.2	503.9	0.58%
E (eV)	reference	0.95	1.28	1.42	1.52	2.00	
	VHR	0.98	1.32	1.45	1.67	2.05	
	2 K/s	0.93	1.27	1.40	1.54	1.95	0.40%
	4 K/s	0.91	1.24	1.38	1.55	1.90	0.55%
	8 K/s	0.91	1.24	1.38	1.58	1.85	0.64%
	12 K/s	0.92	1.23	1.36	1.61	1.84	0.58%
s (s^{-1})	reference	1.0×10^{15}	4.0×10^{16}	1.6×10^{16}	2.1×10^{16}	4.1×10^{20}	
	VHR	1.7×10^{15}	6.6×10^{16}	1.4×10^{16}	6.1×10^{17}	4.1×10^{20}	
	2 K/s	2.5×10^{14}	1.4×10^{16}	3.6×10^{15}	1.6×10^{16}	3.3×10^{19}	0.40%
	4 K/s	1.2×10^{14}	5.8×10^{15}	2.1×10^{15}	2.7×10^{16}	1.0×10^{19}	0.55%
	8 K/s	1.2×10^{14}	6.2×10^{15}	2.6×10^{15}	5.8×10^{16}	2.9×10^{18}	0.64%
	12 K/s	1.5×10^{14}	4.8×10^{15}	1.5×10^{15}	1.1×10^{17}	2.4×10^{18}	0.58%

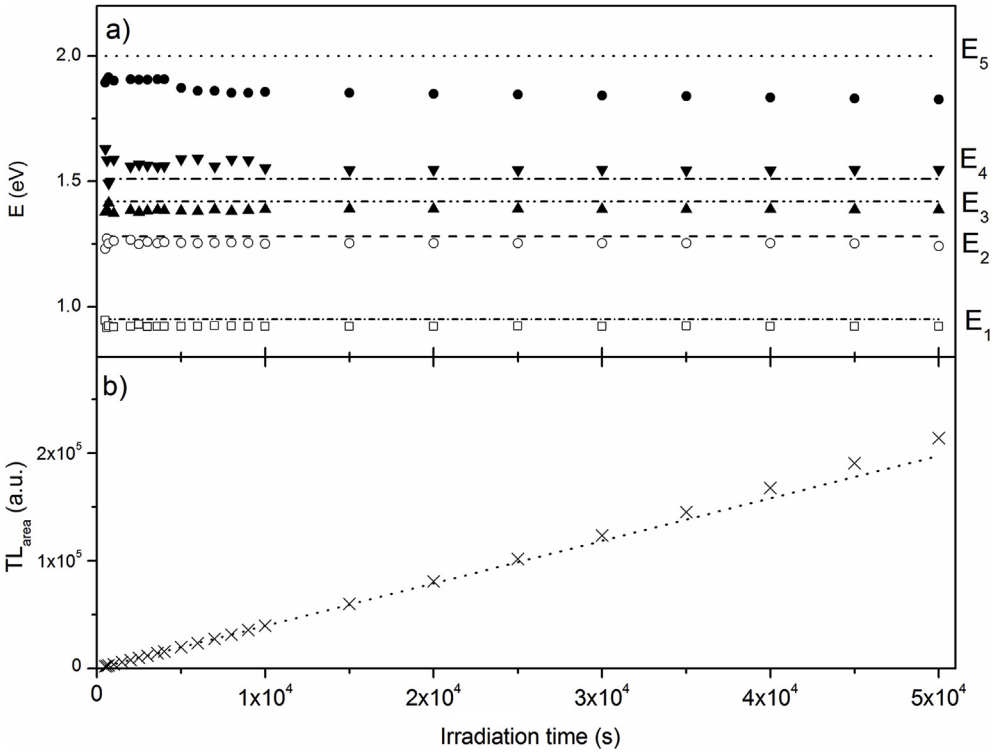

Fig. 5. Results of the simulation for the TLD-100 type simulated model as a function of irradiation time: a) fitted activation energy values for E_1 (open squares), E_2 (open circles), E_3 (close up triangles), E_4 (close down triangles) and E_5 (close circles), obtained using first order kinetic equations compared with the reference (Table 2); b) area of fitted peaks 3 + 4 + 5 (TL_{area}) as a function of simulated irradiation time.

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