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MATHEMATICAL STUDY OF THE THERMOLUMINESCENCE PROCESS IN $K_2YF_5:Tb^{3+}$

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This paper presents results of studying the simulated thermoluminescence (TL) glow curve in potassium–yttrium double fluoride doped with trivalent optically active Tb^{3+} ions ($K_2YF_5:Tb^{3+}$). Samples have been irradiated with different doses (0.24, 2.4 and 24 Gy) of beta particles. Four trapping states and one kind of recombination-centre model have been used in this simulation. The activation energy and order of kinetics are determined using the general-order kinetic model. The results obtained using the authors' proposed models were tested and compared with the experimental glow curve of $K_2YF_5:Tb^{3+}$. The comparison has shown that the proposed model can predict more accurately and easily the behaviour of the TL glow curve at three different doses.

INTRODUCTION

Thermoluminescence (TL) is a widespread phenomenon exhibited by solids of practically all forms and categories, i.e. single crystals, polycrystalline materials, amorphous materials, inorganic and organic materials; the most popular application of TL has now become personnel monitoring. It is to be noted that metals do not exhibit TL whereas all insulators and semiconductors are expected to exhibit TL. This is because of the presence of trapping levels within the band gap (E_g) of these materials. The majority of thermoluminescence dosemeters based on alkali fluorides and alkaline-earth fluorides, in particular, doped with rare earth ions, are extensively utilised for dosimetry of ionising radiation and, on the other hand, now there has been a revival of interest in developing new ultra-sensitive thermoluminescent dosimetric materials[(1)], thanks in large part to advances in environmental monitoring and radiotherapy. In the literature, many TL glow curves have been determined[(2)], and a variety of methods of analysis have been developed[(3)]. Several methods are applied to obtain the trap parameters of an isolated TL glow peak[(4–15)]. However, the main problem when estimating the trap parameters is the presence of several overlapping peaks within the TL glow curve. Very few methods exist, which allow for the separation of the TL glow curve into its individual components[(16–19)].

The complex alkali yttrium fluorides can provide an exceptional possibility for developing such TL phosphors. The TL properties of the novel crystalline materials, such as KYF_4, K_2YF_5 and $LiKYF_5$, can considerably change depending on the kind of optically active rare earth ions incorporated into such lattices and their concentration in the lattice[(20–25)]. In the present paper, the kinetics of TL glow curves of $K_2YF_5:Tb^{3+}$ irradiated with different beta particles have been simulated using the authors' proposed model.

EXPERIMENTAL

Figure 1 shows the TL response for the $K_2YF_5:Tb^{3+}$ irradiated at three different doses namely 0.24, 2.4 and 24Gy. Samples were irradiated by using a 10-mCi ophthalmic $^{90}Sr/^{90}Y$ beta-source rendering a dose rate of 0.024 Gy min^{-1} at the sample position. A Harshaw-Bicron 3500 TL reader was used for recording the TL emission of the investigated samples from 323 up to 648 K with a linear heating rate of 1 K s^{-1}. Single-channel detection was performed at room temperature by using a Hamamatsu H9319 photon-counting head having sensitivity between 300 and 850 nm. Annealing of the samples at 375°C for 1 min was performed immediately after recording the TL glow curve in order to empty completely the filled traps. The TL glow curves are made up of a low-intensity TL glow peak at 380 K and two main peaks at 410 and 503 K. Taking into account the width and the shape of the third glow peak, it could be made up of two overlapped peaks (at 484 and 519 K, respectively). The data in Figure 1 also show that the temperature of maximum TL glow peaks (T_m) is unchanged within the dose range studied.

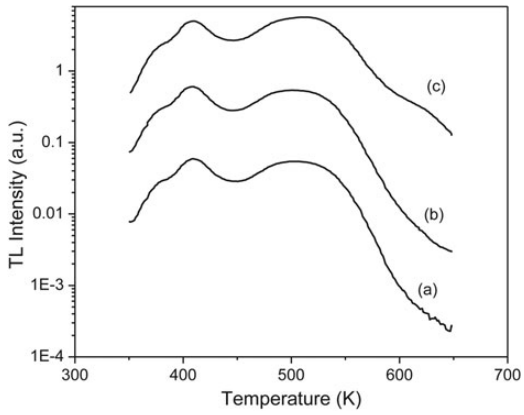

Figure 1. TL glow curve of $K_2YF_5:Tb^{3+}$ irradiated at RT with three different doses: (**a**) 0.24 Gy, (**b**) 2.4 Gy and (**c**) 2 4 Gy.

RESULTS

Kinetic parameter determination

At first place, the authors calculate the kinetic parameters that will be used later at the proposed model. In order to be able to understand the nature of the traps formed in $K_2YF_5:Tb^{3+}$ under irradiation, the authors have employed the analysis of Kitis *et al.*[26] who derived expressions for the TL glow curve deconvolution (GCD) for first, second and general orders of kinetics using the experimentally obtained maximum peak intensity (I_m) and the maximum peak temperature (T_m).

The free parameters to be determined through nonlinear curve fitting are then the activation energy (E) and the order of kinetics (b). In their analysis, the general order kinetics is generally given by:

$$I(T) = sn_0 \exp\left(-\frac{E}{kT}\right) \cdot \left[1 + (b-1)\frac{s}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) dT'\right]^{-b/(b-1)}, \quad (1)$$

which when solved approximately gives:

$$I(T) = I_m (b)^{b/(b-1)} \exp\left(\frac{E\,(T-T_m)}{kT\quad(T_m)}\right) \cdot \left[(b-1)(1-\Delta)\frac{T^2}{T_m^2}\exp\left(\frac{E\,(T-T_m)}{kT\quad(T_m)}\right) + Z_m\right]^{-b/(b-1)}, \quad (2)$$

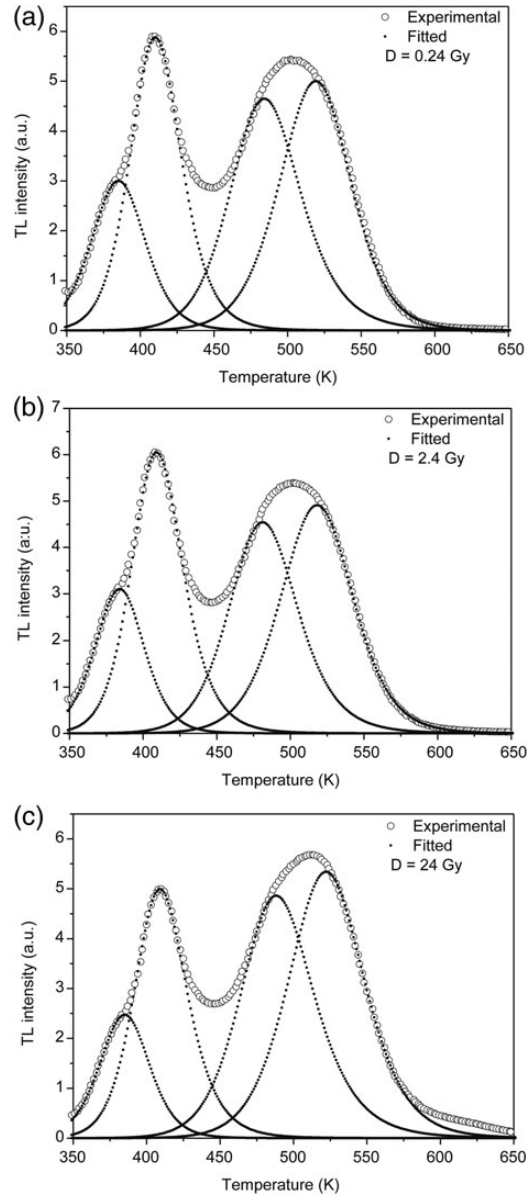

Figure 2. Typical theoretical curves fitting with experimental data for beta dose of (**a**) 0.24 Gy, (**b**) 2.4 Gy and (**c**) 24 Gy. The open circle represents the experimental curve.

where $\Delta = \frac{2kT}{E}$, $\Delta_m = \frac{2kT_m}{E}$, $Z_m = 1 + (b-1)\Delta_m$. The frequency factor s is therefore given by:

$$s = \frac{\beta E}{kT_m^2}\frac{1}{Z_m}\exp\left(\frac{E}{kT_m}\right). \quad (3)$$

Table 1. Kinetic parameters obtained by the GCD method assuming the GOK model.

Dose (Gy)	T_m (K)	β (K s^{-1})	μ_g	E (eV)	b	s (s^{-1})	Life time at RT τ (s)	Area (a.u)	FWHM (K)	I_m (a.u)
0.24	385	1	0.50	0.870	1.7	1.0×10^{10}	9.22×10^{4}	1.448	43	3.090
	410		0.52	1.155	1.9	8.0×10^{13}	9.21×10^{5}	2.720	40	5.898
	484		0.52	1.197	1.98	8.0×10^{11}	4.86×10^{8}	2.976	56	4.945
	519		0.49	1.295	1.65	1.35×10^{12}	1.39×10^{10}	3.183	57	5.077
2.4	384	1	0.50	0.870	1.7	1.0×10^{10}	9.22×10^{4}	13.743	39	3.159
	409		0.52	1.155	1.98	8.0×10^{13}	9.21×10^{5}	28.102	41	6.054
	481		0.52	1.197	1.9	8.0×10^{11}	4.86×10^{8}	27.988	55	4.805
	518		0.50	1.295	1.7	1.35×10^{12}	1.39×10^{10}	31.689	57	5.089
24	385	1	0.50	0.880	1.7	5.5×10^{9}	2.49×10^{5}	110.194	39	2.544
	409		0.52	1.155	2.0	9.0×10^{13}	8.18×10^{5}	237.284	42	5.000
	488		0.52	1.190	2.0	3.0×10^{11}	9.82×10^{9}	323.212	58	5.061
	522		0.49	1.280	1.8	6.0×10^{11}	1.73×10^{10}	361.959	60	5.485

Sample of K_2YF_5:Tb^{3+} was irradiated with 0.24, 2.4 and 24 Gy.

The goodness of the fit was measured with the figure of merit (FOM) given by[27]:

$$\mathrm{FOM} = \sum_{i=1}^{n} \frac{100|\Delta y_i|}{A}, \tag{4}$$

where n is the number of data points, Δy_i is the difference between the experimental and the fitted points and A is the integral of the fitted glow curve in the region of interest.

By fitting the experimental data with Equation (2), the authors obtained the kinetic parameters for each dose. Typical results of the fitting are shown in Figure 2a, b and c for the doses of 0.24, 2.4 and 24 Gy, respectively.

The well-defined nature of the glow curve at the range of doses cited above is manifested by the perfect fit of the theoretical curve with the experimental data. The kinetic parameters obtained through the fitting are presented in Table 1 where it can be seen that all the peaks manifest a general-order kinetic (GOK) of order 2 with I_m and area under peaks increases, which is an indication of increased number of defects. The near-constant value of the activation energy as a function of dose is an indication that the shift in the energy level induced by defect clustering manifests itself through a change in the peak temperature.

The lifetime (τ) of electron in traps can be estimated using the following equation:

$$\tau = s^{-1} \exp\left(\frac{E}{kT}\right), \tag{5}$$

where E is the trap depth (activation energy), τ is the lifetime, s is the pre-exponential factor and T is the storage temperature in absolute scale.

Modelling of TL process in K_2YF_5:Tb^{3+}

The model used is shown in Figure 3 and is rather similar to several models given in the literature by many authors[28–31]. Four trapping states are taken into consideration, four electron traps (ET) and one recombination centre (RC). For easy reference, Figure 3 shows in schematic form the transitions involved in the model.

The corresponding rate equations describing the traffic of electrons during excitation stage are (in this stage, the authors assumed that the transitions of the traps to the conduction band are not possible) as follows:

$$\frac{dn_i}{dt} = n_c(N_i - n_i)A_i, \tag{6}$$

for ($i = 1,\ldots,4$)

$$\frac{dm}{dt} = n_v(M - m)B - A_m m n_c, \tag{7}$$

$$\frac{dn_v}{dt} = X - B(M - m)n_v, \tag{8}$$

$$\frac{dn_c}{dt} = \frac{dm}{dt} + \frac{dn_v}{dt} - \sum_{i=1}^{4} \frac{dn_i}{dt}. \tag{9}$$

The governing equations for the heating stage are as follows:

$$\frac{dn_i}{dt} = n_c(N_i - n_i)A_i - n_i s_i \exp\left(-\frac{E_i}{k_B T}\right), \tag{10}$$

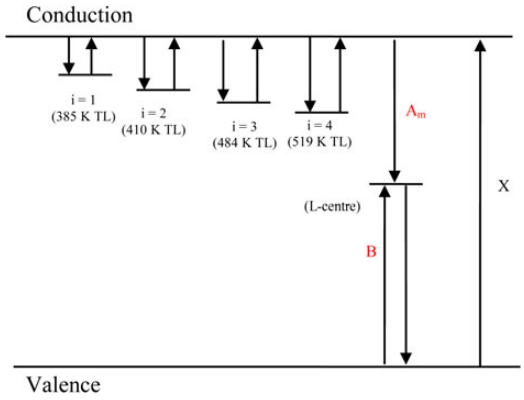

Figure 3. Energy level diagram of the four-trap and one-recombination-centre model. The arrows indicate the possible transitions.

for (i = 1,. . .,4)

$$\frac{dm}{dt} = -A_m m n_c, \tag{11}$$

$$\frac{dn_c}{dt} = \frac{dm}{dt} - \sum_{i=1}^{4} \frac{dn_i}{dt}. \tag{12}$$

The TL intensity is given by the following expression:

$$I(T) = n_c m.B. \tag{13}$$

where n_i (i = 1,. . .,4) represents the concentration of electrons in traps, N_i (i = 1,. . .,4) denotes the corresponding concentration of electrons in traps, M is the concentration of RCs, s_i (i = 1,. . .,4) is the corresponding frequency factor, E_i (i = 1,. . .,4) represents the activation energy of the traps, k_B is the Boltzmann constant, m is the concentration of holes in the RCs and n_c and n_v are the concentration of electrons and holes, respectively, in the conduction and valance bands. A_i (i = 1,. . .,4) are the retrapping probabilities, B(cm^3 s^{-1}) is the trapping coefficient of free holes in centres, A_m (cm^3 s^{-1}) is the recombination coefficient for free electrons with holes in centres and T is the temperature. In what follows, the authors will assume that $T = T_0 + \beta t$, where T_0 is the initial temperature for recording the TL glow curve, β is the constant heating rate and t is the time. X (cm^{-3} s^{-1}) is the rate of production of electron–hole pairs, which is proportional to the excitation dose rate. Thus, if the length of excitation is t_D (s), the total concentration of produced electron–hole pairs is $X.t_D$ (cm^{-3}), which is proportional to the imparted dose. The constant heating rate in this work was chosen to be 1 K s^{-1}. An important point to be mentioned with regard to the simulations reported here is that the authors always start the simulations with empty traps and centres. Besides, it is important to remark that was not taking into account the quasi-equilibrium approximation. The simulation starts by assuming some initial guess values for the free parameters A_i and B, which cannot be extracted directly from the

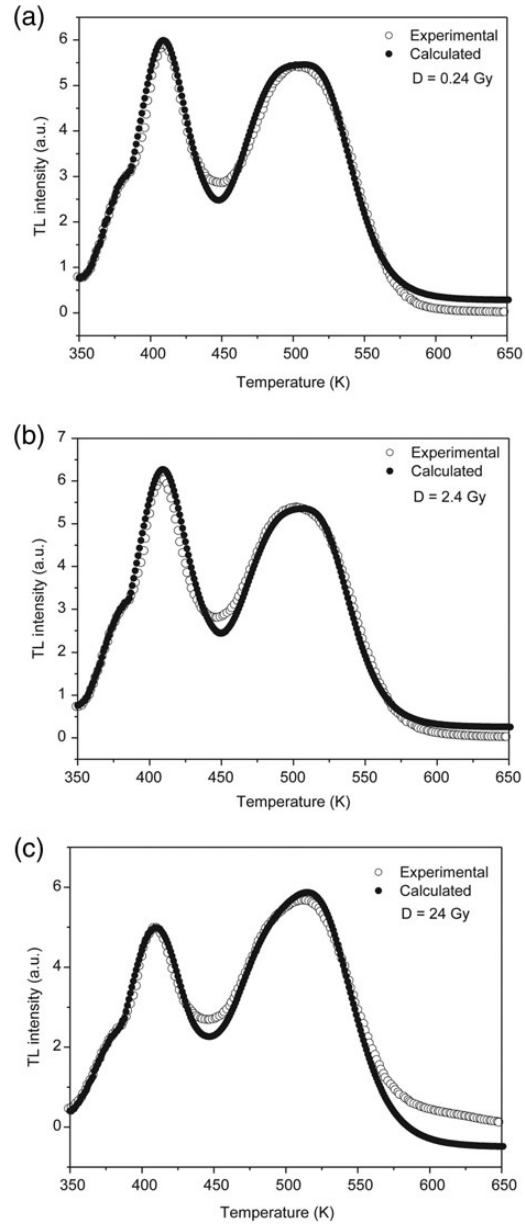

Figure 4. Comparison between the experimental (open circle) and the calculated (dot line). TL glow curves of K_2YF_5:Tb^{3+} sample. The set of parameters are reported in Table 2.

Table 2. Sets of kinetic parameters used in the simulation presented in this paper.

Dose (Gy)	Levels	Parameters				
		N_i (cm^{-3})	E_i (eV)	s_i (s^{-1})	A_i ($cm^3\ s^{-1}$)	B_i ($cm^3\ s^{-1}$)
0.24	1 (385 K)	3.0×10^7	0.870	1.0×10^{10}	5.0×10^{-7}	0
	2 (410 K)	3.0×10^7	1.155	8.0×10^{13}	2.0×10^{-7}	0
	3 (484 K)	2.2×10^8	1.197	8.0×10^{11}	1.7×10^{-8}	0
	4 (519 K)	1.25×10^9	1.295	1.35×10^{12}	6.1×10^{-9}	0
	L-centre	1.0×10^{10}	2.00	2.0×10^{10}	1.0×10^{-10}	1.0×10^{-8}
2.4	1 (384 K)	3.0×10^7	0.870	1.0×10^{10}	5.0×10^{-7}	0
	2 (409 K)	3.0×10^7	1.155	8.0×10^{13}	2.0×10^{-7}	0
	3 (481 K)	2.2×10^8	1.197	8.0×10^{11}	1.0×10^{-8}	0
	4 (518 K)	1.25×10^9	1.295	1.35×10^{12}	5.0×10^{-9}	0
	L-centre	1.0×10^{10}	2.00	2.0×10^{10}	1.0×10^{-10}	1.0×10^{-8}
24	1 (385 K)	3.0×10^7	0.880	5.5×10^9	8.0×10^{-7}	0
	2 (409 K)	3.0×10^7	1.155	9.0×10^{13}	1.0×10^{-6}	0
	3 (488 K)	2.2×10^8	1.190	3.0×10^{11}	1.1×10^{-7}	0
	4 (522 K)	1.25×10^9	1.280	6.0×10^{11}	1.0×10^{-8}	0
	L-centre	1.0×10^{10}	2.00	2.0×10^{10}	1.0×10^{-10}	1.0×10^{-8}

experimental TL curve. These guess values were set manually in such a way that the computed glow curve nearly matched the experimental one as much as possible.

Numerical results

In the present study, the Matlab odes23 solver was used to solve numerically the relevant sets of equations. The calculated TL glow curves (dot line) using the proposed model and the experimental TL glow curves (open circle) for the $K_2YF_5:Tb^{3+}$ sample for the doses of 0.24, 2.4 and 24 Gy are shown in Figure 4a, b and c, respectively. The simulated TL glow curves in these figures were obtained by solving the set of differential equations 6–13. The sets of parameters used in this simulation are given in Table 2. The values of FOM obtained are 2.92, 2.83 and 3.12 % for the doses 0.24, 2.4 and 24 Gy, respectively. FOM values are <5 %, indicating the good result of the deconvolution process.

CONCLUSION

In this paper, the GOK model has been used to evaluate the trap parameters of the individual TL glow peaks present in the $K_2YF_5:Tb^{3+}$ single crystal. The authors have studied the effect of the dose rate on the TL glow curves using the authors' proposed model; this last consists of four electron traps (ETs) and a single RC. The simulated curves obtained using the authors' proposed model were in good agreement with the experimental glow curves of $K_2YF_5:Tb^{3+}$ corresponding to three different doses, namely 0.24, 2.4 and 24 Gy.

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