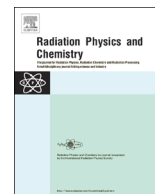




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Thermoluminescent kinetics for negligible retrapping: Its application to the analysis of the glow curve of $Y_2O_3:Eu^{+3}$



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HIGHLIGHTS

- A kinetics has been derived without resorting to the quasi-equilibrium approximation (QE).
- The expression for the glow curve does not contain derivatives.
- Analysis of the main glow peak of the $Y_2O_3:Eu$ shows that the QE approximation does not always hold.

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ABSTRACT

In this article a novel algorithm for analysing glow peaks resulting from traps having negligible retrapping is reported. The algorithm features two advantages: (1) an expression for the light intensity has been derived without resorting to the quasi-equilibrium approximation, and (2) no differential equation has to be integrated. The algorithm has been employed for analysing the main glow peak of $Y_2O_3:Eu^{+3}$.

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1. Introduction

Glow curve deconvolution is a frequently employed procedure for investigating the kinetics involved in the thermoluminescence of compounds. Basically deconvolutions are employed for finding parameters characterising the luminescent mechanisms, such as trapping probabilities of electrons (or holes) by traps and recombination centres, activation energies and frequencies factors (Chen and McKeever, 1997). The last two are related to the escape probability of an electron (or hole) from a trap centre. The first step for performing a deconvolution consists in adopting a model based on the experimental findings at hand. A simple model, known as OTOR (one trap-one recombination centre) is shown in Fig. 1.

The first step in deconvolutions is to find a theoretical expression for the glow curve, which contains the trap parameters, i.e., $I_{th}(T, \alpha)$, where α stands for the set of parameters. The parameters are given different guess values until a satisfactory fit is achieved. Instead of changing randomly the parameters, an algorithm, such

as the Levenberg–Marquardt algorithm (L–M algorithm), is usually employed to find the parameters that yield the best fit between the theoretical and the experimental glow curve (Horowitz et al., 1995). The goodness of the fit is evaluated by means of the factor of merit (FOM) given by

$$FOM = \frac{\sum_{j=1}^N |I_{th}(t_j, \alpha) - I_{exp}(t_j)|}{\sum_{j=1}^N |I_{exp}(t_j)|} \times 100\% \quad (1)$$

where $I_{exp}(T)$ stands for the recorded glow curve.

A set of parameters is acceptable if the FOM is less than 5% (Horowitz et al., 1995).

Given a model of traps and recombination centres the kinetics is described by a set of coupled differential equations. From the set of differential equations it is necessary to obtain $I_{th}(T, \alpha)$ in order to employ the L–M algorithm. As pointed out by Lewandowski and McKeever in practice the system of coupled differential equation describing correctly the thermoluminescent kinetics usually become intractable, so that exact analytical solutions are unobtainable for even the simplest of systems (Lewandowski et al., 1991). For the OTOR model a closed expression for $I_{th}(T, \alpha)$ can be obtained when retrapping is negligible against recombination, and by resorting to

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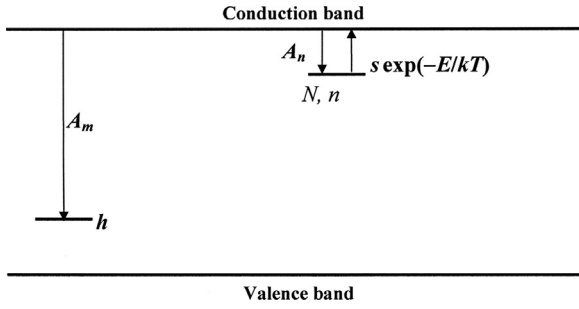


Fig. 1. OTO model. A_m is the recombination probability, h is the concentration of holes in the recombination centre, A_n is the retrapping probability, N is the concentration of traps, n is the concentration of trapped electrons, s is the frequency factor, E the activation energy and k is the Boltzmann constant.

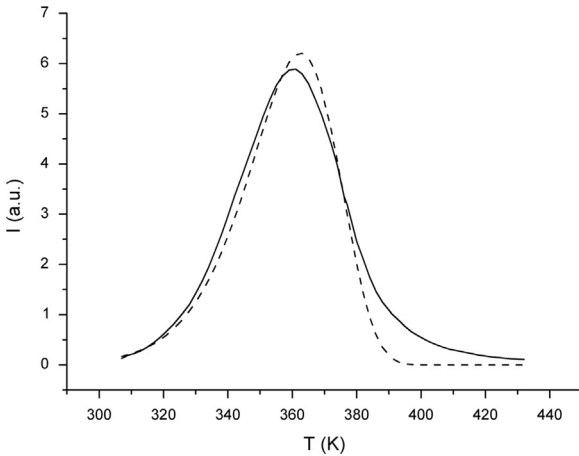


Fig. 2. Glow curve obtained with $\beta=1$ K/s (solid line) and the peak resulting employing FO kinetics (dash line). FOM=15.4%.

the quasi-equilibrium approximation (QE) (Chen and Mckeever, 1997):

$$I_{th}(T, s, E, n_0) = n_0 s \exp\left(-\frac{E}{kT}\right) \exp\left\{-\frac{s}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{ku}\right) du\right\} \quad (2)$$

where β stands for the heating rate. The QE approximation assumes that $dn_c/dt \cong 0$ and $n_c \ll n$, where n_c stands for the concentration of electrons in the conduction band. The kinetics described by Eq. (2) is known as first order (FO) kinetics.

Ato et al. (1968) investigated the thermoluminescence characteristics of rare-earth activated Y_2O_3 compounds. From the dependence of γ -dose intensity on the γ -irradiation rate they concluded that the main peak of $Y_2O_3: Eu^{+3}$ at 348 K follows the FO kinetics. Therefore we employed Eq. (2) for analysing the main glow peak shown in Fig. 2, which was obtained with a heating rate $\beta=1$ K/s. The figure also shows the peak that best fit the experimental one employing the FO kinetics. The parameters are: $s=10^9$ s $^{-1}$, and $E=0.78$ eV.

As can be seen the fit is bad, which is reflected in the FOM of 14%. An attempt has been made to fit the glow curve with two traps (see Fig. 3). The frequency factors and energies of the traps are: $s_1=3.0 \times 10^{10}$ s $^{-1}$, $E_1=0.83$ eV, $s_2=2.5 \times 10^{10}$ s $^{-1}$, and $E_2=0.87$ eV. The FOM amounts to 4.8. Even though the FOM is acceptable, the fit between 380 and 400 K is bad. The high temperature part of the peak is difficult to fit with FO kinetics because this kinetics yields peaks having an abrupt descent at the high temperature side.

Since Eq. (2) has been derived by resorting to the QE approximation we investigated the kinetics resulting from a trap with negligible retrapping but without the QE approximation.

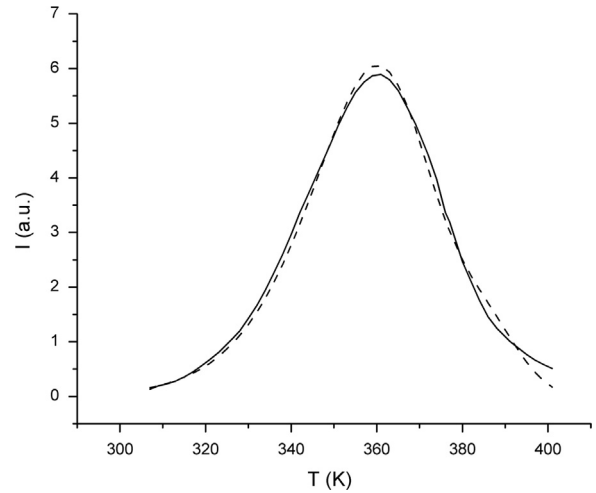


Fig. 3. Glow curve obtained with $\beta=1$ K/s (solid line) and the peak resulting employing FO kinetics (dash line). FOM=4.8%.

2. Algorithm

The set of equations describing the model shown in Fig. 1 are:

$$\frac{dn(T)}{dT} = -\frac{s}{\beta} n(T) \exp\left(-\frac{E}{kT}\right) + A_n(N - n(T))n_c(T) \quad (3)$$

$$\frac{dh(T)}{dT} = -\frac{A_m}{\beta} n_c(T)h(T) \quad (4)$$

$$h(T) = n(T) + n_c(T) + M \quad (5)$$

In Eq. (5) we introduce the concentration M of deep thermally disconnected traps, i.e., traps that retain the trapped electrons (or holes) for the temperatures a sample is subjected to. The thermally disconnected traps are supposed to be fully occupied. $M > 0$ if the deep traps are electron traps, and $M < 0$ if they are hole traps. Eq. (5) describes the charge neutrality.

If retrapping is negligible against the release of electrons from the trap, the term $A_n(N - n(T))n_c(T)$ can be dropped in Eq. (3). Thus the equations read:

$$\frac{dn(T)}{dT} = -\frac{s}{\beta} n(T) \exp\left(-\frac{E}{kT}\right) \quad (6)$$

$$\frac{dh(T)}{dT} = -\frac{A_m}{\beta} n_c(T)h(T) \quad (7)$$

$$h(T) = n(T) + n_c(T) + M \quad (8)$$

Eq. (6) can be integrated immediately resulting:

$$n(T) = n_0 \exp\left\{-\frac{s}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{ku}\right) du\right\} \quad (9)$$

From Eqs. (7) and (8) it can be obtained:

$$\frac{dh(T)}{dT} = -\frac{A_m}{\beta} (h(T) - n(T) - M)h(T) \quad (10)$$

The light intensity is given by

$$I(T) = -\beta \frac{dh(T)}{dT} \quad (11)$$

From the integration of this equation it results:

$$h(T) = CTE - \frac{1}{\beta} \int_{T_0}^T I(u) du \quad (12)$$

The constant CTE can be found by resorting to Eq. (8) for $T=T_0$, namely, $h(T_0) = n_0 + M$. Thus

$$h(T) = n_0 + M - \frac{1}{\beta} \int_{T_0}^T I(u) du \quad (13)$$

We define $F(T) = \int_{T_0}^T I(u) du$, so that

$$h(T) = n_0 + M - \frac{1}{\beta} F(T) \quad (14)$$

From Eqs. (10), (11) and (14) it results:

$$I(T) = A_m \left(n_0 - n_0 \exp \left\{ -\frac{s}{\beta} \int_{T_0}^T \exp \left(-\frac{E}{ku} \right) du \right\} - \frac{F(T)}{\beta} \right) \left(n_0 + M - \frac{F(T)}{\beta} \right) \quad (15)$$

This equation is a self-consistent equation since $F(T)$ is computed from the experimental glow peak. The introduction of $F(T)$ allows to avoid the integration of the differential equations, a calculation that on occasions required a large number of steps in order to prevent the differential equations from becoming stiff.

3. Deconvolution

As it is well known, when analysing a glow curve several sets of parameters having acceptable FOM's are obtained. Therefore it is necessary to resort to criteria in order to choose the set, which is in accordance to experimental findings at hand. The criteria we employed are: (1) the sets of parameters obtained for two different doses should agree, and (2) the parameters should be in accordance with the observed fading of the TL signal.

The samples were irradiated with a 10mCi ophthalmic 90-Sr beta-source rendering a dose rate of 1.44 Gy/h at the sample position.

Two glow curves, corresponding to irradiation times of 1 and 21 h, have been recorded.

Fig. 4 shows the glow peak and that resulting from the fitting employing Eq. (15) for the sample which has been irradiated 1 h. Fig. 5 corresponds to the irradiation time of 21 h.

Some remarks should be made with respect to the values of n_0 and M indicated in Table 1. Since n_0 should be proportional to the area A of the glow curve, namely, to $F(T_{max})$, where T_{max} is the highest temperature of the interval, the glow curve has been recorded, n_0 may be written as $n_0 = CF(T_{max})$. Choosing $C = 1$, n_0 is measured as the area of the peak. Thus M in Eq. (15) may be also given relative to the area of the glow curve. The quotient of the trapped electrons at the beginning of the recording of the glow curves for both doses is nearly 10. Since the relationship between the irradiation times amounts to 21, it is clear that the fading of the thermoluminescence is high.

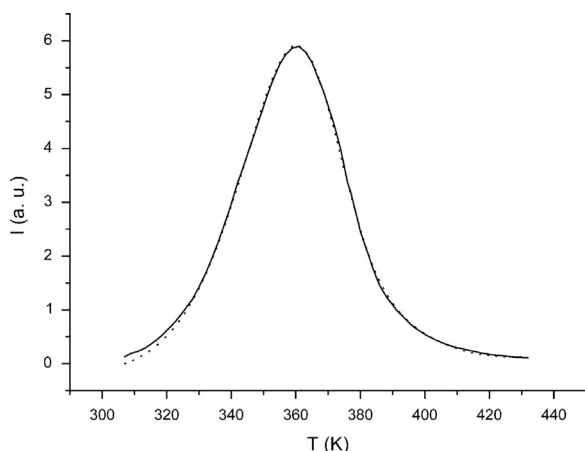


Fig. 4. Glow peak (solid line) and peak resulting employing the new algorithm (dash line) for the sample irradiated for 1 h.

As can be seen in Fig. 4 the fit is excellent, which indicates that the concentration of electrons in the conduction band and its changes with temperature cannot be ignore. Fig. 6 shows the concentration of trapped electrons and the concentration of electrons in the conduction band for the sample irradiated for 1 h.

The activation energy computed by employing the Initial Rise method is 0.91 eV. It differs by 13.7% from the value obtained from the deconvolution. This difference is due to the fact that the quasi-equilibrium approximation does not hold. According to the thermoluminescence models frequently employed nowadays, which are derived employing the quasi-equilibrium approximation, or the heuristic General Order kinetics, the emitted light intensity may be written:

$$I(T) = se^{-E/kT} f(T, \alpha) \quad (16)$$

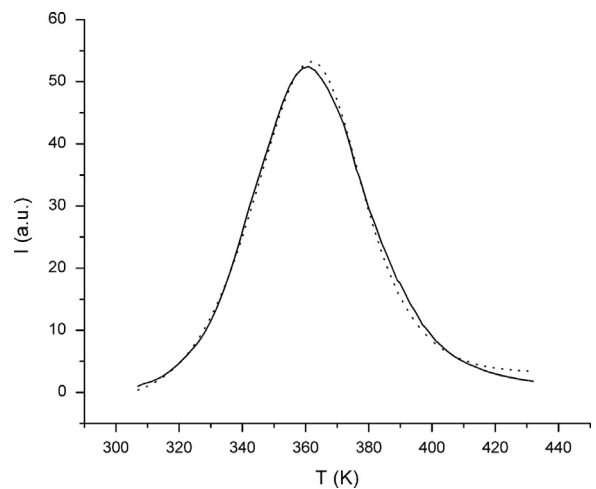


Fig. 5. Glow peak (solid line) and peak resulting employing the new algorithm (dash line) for the sample irradiated for 21 h.

Table 1.

Parameters obtained by deconvolution employing Eq. (15) for the two irradiation times.

	n_0	s (s^{-1})	E (eV)	M	FOM (%)
1 h irradiation	252	11×10^9	0.79	1158	3.4
21 h irradiation	2553	6.6×10^9	0.78	1291	4.1

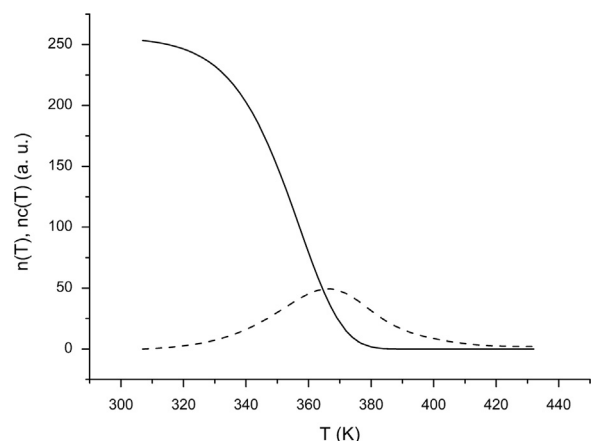


Fig. 6. Concentration of trapped electrons (solid line), and electrons in the conduction band (dash line).

where $f(T, \alpha)$ is a function of the temperature and the set of parameters of the model. This set is indicated again with α .

A temperature $T1$ is defined such as $T1 < TM$, where TM is the temperature of the peak maximum, and $I(T1)/I(TM) = 0.1$. For the interval of temperatures up to $T1$ is $f(T, \alpha)$ nearly constant. Thus by plotting $\ln(I(T))$ vs. $-1/kT$ a straight line is obtained, whose slope is the activation energy. The following example illustrates that the activation energy computed by means of the Initial Rise method may differ from the true value.

By defining $x(T) = n(T)/N$, $h'(T) = H(T)/N$, $MM = M/N$, and $AM = A_m N$, Eqs. (6)–(8) become:

$$\frac{dx(t)}{dT} = -\frac{s}{\beta} x(T) \exp\left(-\frac{E}{kT}\right) \quad (17)$$

$$\frac{dh'(t)}{dT} = -\frac{A_m}{\beta} h'(T)(h'(T) - x(T) - MM) \quad (18)$$

These set of differential equations have been integrated in order to obtain a glow curve for the following set of parameters: $\beta = 1 \text{ K/s}$, $x_0 = 0.001$, $MM = 10$, $h_0' = x_0 + MM = 10.001$, $s = 10^{10} \text{ s}^{-1}$, $E = 0.79 \text{ eV}$, and $AM = 1 \text{ s}^{-1}$. The glow curve is shown in Fig. 7.

The Initial Rise calculation gives activation energy of 0.96 eV , namely, a value about 21% higher than the value employed for generating the glow curve. As can be seen in Fig. 8 the quasi-equilibrium approximation does not hold.

Finally we investigated the fading of the thermoluminescence at 16°C . If retrapping is negligible the area A of the glow curve should

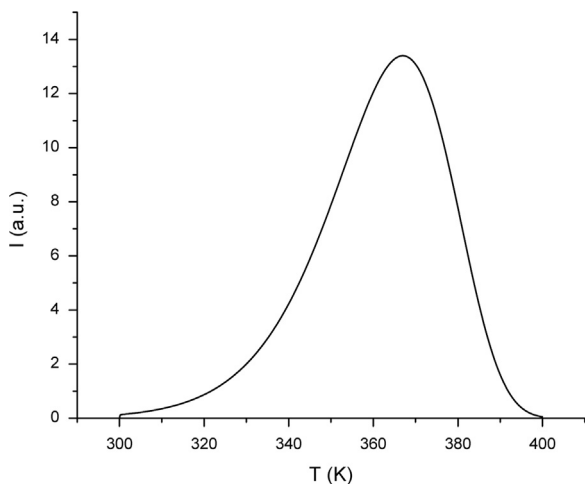


Fig. 7. Synthetic glow curve generated with the parameters given in the text.

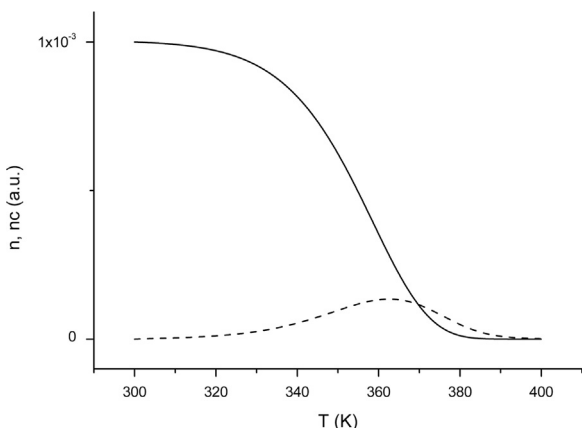


Fig. 8. Comparison of the concentration of electrons in the conduction band (dash line) and the concentration of trapped electrons (solid line).

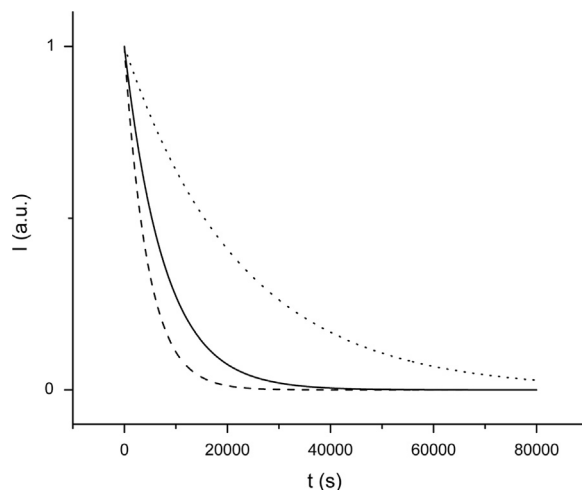


Fig. 9. Experimental fading (solid line), fading according to the kinetics without the QE approximation (dash line), and fading employing the FO kinetics and two traps.

decrease according to $A(t)/A(t=0) = \exp(-s \exp(-E/kT)t)$. With t we indicate the elapsed time between irradiation and recording of a glow curve. Thus $A(t)/A(t=0) = \exp(-1.1 \times 10^{10} \text{ s}^{-1} \exp(-0.79 \text{ eV}/k \times 289 \text{ K})t)$, i. e., according to $A(t)/A(t=0) = \exp(-t/4545 \text{ s}^{-1})$. Experimentally we found that the area of the glow curves decreases as $A(t)/A(t=0) = \exp(-t/7813 \text{ s}^{-1})$. Fig. 9 shows the experimental fading, along with the fading obtained with the kinetics without the QE approximation. The figure depicts also the fading corresponding to the model of two traps having FO kinetics. As can be seen, the kinetics without the QE approximation is a better approach to the experimental fading. This result along with the better FOM obtained with the kinetics put forward in this article indicates that the QE approximation does not hold in the case of the $\text{Y}_2\text{O}_3: \text{Eu}^{+3}$ compounds.

4. Conclusions

From the results reported the following conclusions can be drawn:

1. The quasi-equilibrium approximation can lead to an incorrect analysis of glow curves.
2. In cases where the quasi-equilibrium approximation does not hold the Initial Rise method might not be valid.
3. Eq. (15) will yield reliable parameters because it was derived without resorting to the quasi-equilibrium approximation.

Finally it should be remarked that the analysis of glow curves with Eq. (15) avoids the integration of the set of differential equations, which overcomes the possibility of the differential equations becoming stiff, and reduces computational times. It is worth mentioning also that Eq. (15) can be extended to a model of several traps, the only limitation being one recombination centre.

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