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Analysis of the glow curve of KMgF3:Lu compounds without resorting to the quasi-equilibrium approximation

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HIGHLIGHTS

- Glow curves of KMgF3:Lu have been analysed without resorting to the QE approx.
- The glow curves have been analysed taking into account interactions among traps.
- The algorithm used will not become stiff.
- The kinetics parameters obtained do not depend on the dose.
- The agreement between the two sets of parameters obtained shows that the QE approximation does not hold.

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ABSTRACT

In this article we report an expression for the thermoluminescence light, which is derived from the set of differential equations by assuming negligible retrapping, but without resorting to the quasi-equilibrium approximation. The expression has been employed for analysing the glow curve of KMgF3:Lu fluoroperovskite compounds.

1. Introduction

A glow curve, for which its shape does not change significantly with dose, is usually analysed by employing first order kinetics (FO). This kinetics is derived from the equations describing the traffic of carriers (electrons and holes) among traps, recombination centres and bands, by assuming negligible retrapping, and by resorting to the quasi-equilibrium approximation (QE) (Chen and McKeever, 1997). The QE approximation states that the time derivative of the concentration of electrons in the conduction band (CB) is negligible against the time derivatives of the concentration of electrons in trap centres and the concentration of holes in recombination centres (Chen and McKeever, 1997). The validity of this approximation has been investigated. The investigations show that the QE approximation does not always hold (Chen and Pagonis, 2012; Marcazzó et al., 2007).

A heuristic kinetics, known as general order (GO), has been put forward by May and Partridge (May and Partridge, 1964). This kinetics contains a parameter indicated with b, which is loosely related to retrapping. If b is closed to 1, the kinetics is FO. Thus the analysis of a glow curve with the GO model should yield a value of b near to 1. The glow curve of the compound KMgF3:Lu has been analysed with the GO kinetics (González et al., 2004). The glow curves were analysed considering three intense peaks, and two weak ones. Two of the main peaks have $b = 2$. A peak having $b > 1$ should drift to lower temperatures as the dose increases. Measurements of the glow curves for different doses show that the positions of the main peaks do not change with dose, as shown in Fig. 1 for 5 and 50 Gy. A remark is worth to be highlighted: Sakurai and Gartia state that one of the defects of the GO kinetics arises

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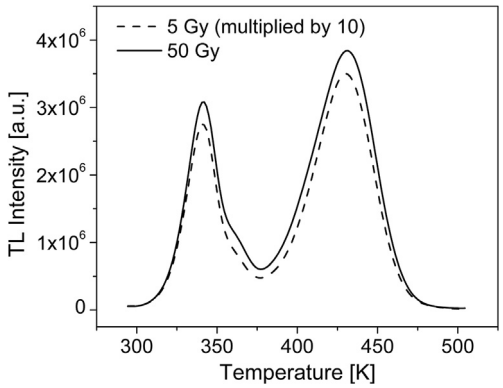

Fig. 1. Glow curves of $KMgF_3$:Lu.

from the fact that traffic of electrons and/or holes among traps is ignored (Sakurai and Gartia, 2003). Because of the aforementioned remarks we report the kinetics parameters of the KMgF3:Lu compounds obtained with a kinetics derived without resorting to the QE.

2. Model and algorithm

A simple model, known as OTOR (One Trap – One Recombination centre) is shown in Fig. 2.

Where $p = s.exp(-E/kT)$ is the probability that a trapped electron being freed from a trap and CB and VB indicate the conduction and valence band, respectively.

The rate equations describing the model shown in Fig. 2 are:

$$\frac{dn(T)}{dT} = -\frac{s}{\beta}\cdot n(T)\exp\left(-\frac{E}{kT}\right) + A_n[N - n(T)]n_c(T) \quad (1)$$

$$\frac{dh(T)}{dT} = -\frac{A_h}{\beta}n_c(T)\cdot h(T) \quad (2)$$

$$h(T) = n(T) + n_c(T) + M \quad (3)$$

where A_n and A_h stand for the retrapping and for the recombination probability respectively. h indicates the concentration of holes in the recombination centre (H), N is the concentration of traps, and n the concentration of trapped electrons, n_c is the concentration of electrons in the conduction band, s is the frequency factor, and E the activation energy of the trap. β is the heating rate and k is the Boltzmann constant. m stands for the concentration of trapped electrons in thermally disconnected traps and M is the concentration of thermally disconnected traps, which are supposed to be fully occupied.

If retrapping is negligible against the release of electrons from the trap, it is possible to eliminate the term $A_n[N - n(T)]n_c(T)$ in Equation (1). Then, the equations read:

$$\frac{dn(T)}{dT} = -\frac{s}{\beta}\cdot n(T)\exp\left(-\frac{E}{kT}\right) \quad (4)$$

$$\frac{dh(T)}{dT} = -\frac{A_h}{\beta}n_c(T)\cdot h(T) \quad (5)$$

$$h(T) = n(T) + n_c(T) + M \quad (6)$$

Integrating the Equation (4):

$$n(T) = n_0\exp\left\{-\frac{s}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{ku}\right)du\right\} \quad (7)$$

From Equations (5) and (6) it can be obtained:

$$\frac{dh(T)}{dT} = -\frac{A_h}{\beta}[h(T) - n(T) - M]\cdot h(T) \quad (8)$$

The light intensity is given by

$$I(T) = -\beta\frac{dh(T)}{dT} \quad (9)$$

and integrating this equation it results:

$$h(T) = C - \frac{1}{\beta}\int_{T_0}^{T} I(u)du \quad (10)$$

where C can be obtained by resorting to Equation (6) for $T = T_0$, namely, $h(T_0) = n_0 + M$. Then

$$h(T) = n_0 + M - \frac{1}{\beta}\int_{T_0}^{T} I(u)du \quad (11)$$

If $F(T) = \int_{T_0}^{T} I(u)du$ then

$$h(T) = n_0 + M - \frac{1}{\beta}F(T) \quad (12)$$

Finally, from Equations (8), (9) and (12) it can be obtained:

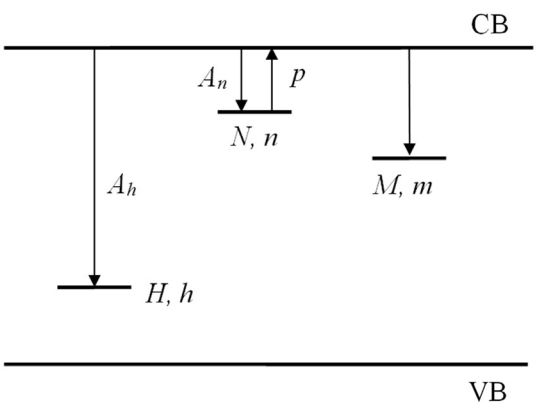

Fig. 2. The OTOR model.

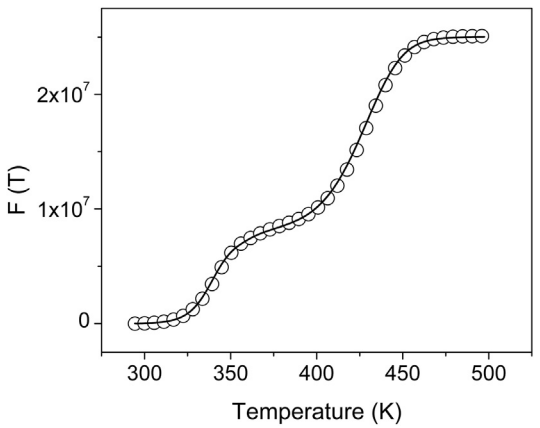

Fig. 3. Experimental (open circle) and theoretical (solid line) $F(T)$ function.

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Table 1
Frequency factors and energies of the three traps for two different doses.

Dose (Gy)	s_1 (10^{15} s^{-1})	E_1 (eV)	n_{01}	s_2 (10^{13} s^{-1})	E_2 (eV)	n_{02}	s_3 (10^{10} s^{-1})	E_3 (eV)	n_{03}	M	FOM (%)
5	1.0	1.07	3.86×10^6	6.4	1.08	3.68×10^5	1.5	0.96	2.08×10^7	6.01×10^{10}	3.9
50	1.0	1.07	4.48×10^7	3.0	1.06	5.85×10^6	1.5	0.96	2.38×10^8	5.89×10^{10}	4.9

$$I(T) = A_m\left(n_0 - n_0\exp\left\{-\frac{s}{\beta}\int_{T0}^{T}\exp\left(-\frac{E}{ku}\right)du\right\} - \frac{F(T)}{\beta}\right)\cdot\left(n_0 + M - \frac{F(T)}{\beta}\right) \tag{13}$$

This equation is a self-consistent equation since $F(T)$ is computed from the experimental glow peak. The introduction of $F(T)$, which must be given in an analytical form, 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. Fig. 3 shows the $F(T)$ as a function of temperature.

If more than one trap is present Equation (13) becomes:

$$I(T) = A_m\left(\sum_{i=1}^{q}\left[n_{0i} - n_{0i}\exp\left\{-\frac{s_i}{\beta}\int_{T0}^{T}\exp\left(-\frac{E_i}{ku}\right)du\right\}\right] - \frac{F(T)}{\beta}\right)\cdot\left(\sum_{i=1}^{q} n_{i,0} + M - \frac{F(T)}{\beta}\right) \tag{14}$$

where i is for identified each trap.

The goodness of the fit is evaluated by means of the factor of merit (*FOM*) given by

$$\mathrm{FOM} = \frac{\sum_{j=1}^{N}|I_{th}(t_j,\alpha) - I_{\exp}(t_j)|}{\sum_{j=1}^{N}|I_{\exp}(t_j)|}\cdot 100\% \tag{15}$$

where $I_{\exp}(T)$ stands for the recorded glow curve and α stands for the set of parameters of the traps. A set of parameters is acceptable if the *FOM* is less than 5% (Horowitz and Yossian, 1995).

3. Samples and glow curves

KMgF3:Lu monocrystal phosphor was made at the Physics Department of Rome University "La Sapienza" (González et al., 2004). Samples of perovskite have been obtained from the melt of KF and MgF_2 in the stoichiometric ratio by the Kyropoulos method. Doped crystals were obtained by adding a proper amount of the Lu impurity to the melt. Crystals of $KMgF_3$ with a concentration of 0.34 mol% of Lu and dimensions of 5 × 5 × 2 mm were obtained. The samples were irradiated a room temperature with a 3.7×10^8 Bq ophthalmic ^{90}Sr beta-source rendering a dose rate of 0.022 Gy min^{-1} at the sample position. TL glow curves were recorded in nitrogen atmosphere from 350 K up to 670 K with a constant heating rate of 2 K/s by using a Harshaw 4000 TL Reader. Aforementioned Fig. 1 shows glow curves of $KMgF_3$:Lu irradiated with two different doses, namely, 5 and 50 Gy.

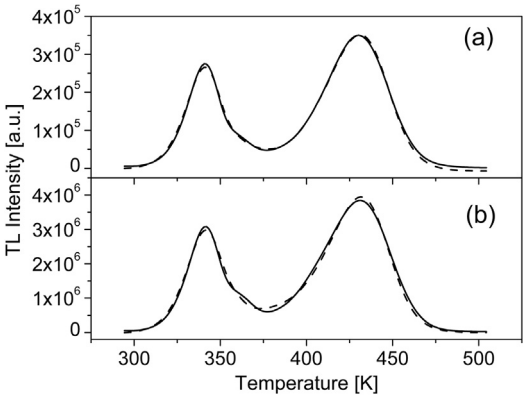

Fig. 4. Experimental (solid line) and theoretical (dash line) glow curves for 5 (a) and 50 (b) Gy, respectively.

4. Results

The Equation (14) has been employed for analysing the experimental glow curves of $KMgF_3$:Lu. From inspection of Fig. 1, glow curves have been analysed considering three traps. In table 1 the resulting parameters are shown.

Since the area of the glow curve is proportional to the initial concentration of trapped electrons, namely, $A = C(n_{01} + n_{02} + n_{03})$, then $n_{01} + n_{02} + n_{03} = A/C$. Thus taking $C = 1$ the concentration of electrons will be given in units of area, which is the unit employed in Table 1.

Fig. 4 shows the experimental and the theoretical glow curves for 5 and 50 Gy, respectively. It is evident from the figure that the agreement between two curves is excellent.

5. Conclusion

The glow curves of $KMgF_3$:Lu for two doses, 5 and 50 Gy, have been analysed considering three traps. FO kinetics yields FOM's much higher than 5%. Analysis of both glow curves with the General Order Kinetics yiels parameters for the two doses that do not agree, while by using Equation (14) proposed in this work, the FOM's for the two doses are lower than 5%. Comparison of the concentration of trapped electrons and the concentration of electrons in the conduction bands shows the QE assumption does not hold. This result suggests that it is advisable to employ the kinetics without the QE approximation since the FO kinetics is a special case.

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