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Properties of thermoluminescence glow curves from tunneling recombination processes in random distributions of defects

George Kitis [a], Vasilis Pagonis [b,*]

[a] Nuclear Physics Laboratory, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
[b] Physics Department, McDaniel College, Westminster, MD 21157, USA

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ABSTRACT

Localized electronic recombination processes in donor–acceptor pairs of luminescent materials have been recently modeled using a new kinetic model based on tunneling. Within this model, recombination is assumed to take place via the excited state of the donor, and nearest-neighbor recombinations take place within a random distribution of centers. An approximate semi-analytical version of the model has been shown to simulate successfully thermally and optically stimulated luminescence (TL and OSL), linearly modulated OSL (LM-OSL) and isothermal TL processes. This paper presents a detailed analysis of the geometrical properties of the TL glow curves obtained within three different published versions of the model. The dependence of the shape of the TL glow curves on the kinetic parameters of the model is examined by allowing simultaneous random variations of the parameters, within wide ranges of physically reasonable values covering several orders of magnitude. It is found that the TL glow curves can be characterized according to their shape factors μ_g, as commonly done in TL theory of delocalized transitions. The values of the shape factor are found to depend rather weakly on the activation energy E and the frequency factor s, but they have a strong dependence on the parameter ρ' which characterizes the concentration of acceptors in the model. It is also shown by simulation that both the variable heating rate and initial rise methods are applicable in this type of model and can yield the correct value of the activation energy E. However, the initial rise method of analysis for the semianalytical version of the model fails to yield the correct E value, since it underestimates the low temperature part of the TL glow curves. Two analytical expressions are given for the TL intensity, which can be used on an empirical basis for computerized glow curve deconvolution analysis (CGCD).

1. Introduction

Over the past twenty years there has been considerable experimental and modeling work trying to understand the nature and properties of luminescence signals from feldspars, especially in connection with the associated phenomenon of "anomalous fading" based on quantum mechanical tunneling ([1–15]).

Recently Jain et al. [14] presented a new general kinetic model which quantifies localized electronic recombination of donor–acceptor pairs in luminescent materials. Recombination is assumed to take place via the excited state of the donor, and to take place between nearest-neighbors within a random distribution of centers. Two versions of the model were presented by these authors, an exact model that evolves in both space and time, and an approximate semi-analytical model evolving only in time. Good agreement was found between the two versions of the model, and simulated successfully both thermally stimulated luminescence (TL) and optically stimulated luminescence (OSL). The model also demonstrated the power law behavior for OSL signals simulated within the model.

A third version of the model was published by Pagonis et al. [16], who examined the full model by Jain et al. [14] and obtained analytical expressions for the distribution of remaining donors at any time t during several experimental situations. These authors gave examples for the derived distributions of donors in each experimental case, and similarities and differences between the different experimental modes of stimulation were pointed out.

Kitis and Pagonis [17] showed that the initial system of simultaneous differential equations developed by Jain et al. [14] can be approximated to a very good precision by a single differential equation describing stimulated luminescence emission in this system. These authors were able to obtain analytical solutions of this single differential equation for several possible modes of stimulation, namely TL, OSL, linearly modulated OSL (LM-OSL) and isothermal TL (ITL). They also derived the exact analytical form for the power law behavior in this system, and demonstrated how typical experimental TL glow curves and infrared stimulated luminescence signals (IRSL) can be

* Corresponding author. Tel.: +1 410 857 2481; fax: +1 410 386 4624.
E-mail address: vpagonis@mcdaniel.edu (V. Pagonis).

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analyzed using the derived analytical equations, and what physical information that can be extracted from such experimental data.

The goals of the present paper are as follows.

(a) To carry out a detailed analysis of the geometrical properties of the TL glow curves obtained within the three published versions of the model by Jain et al. [14], for a wide range of the kinetic parameters.
(b) To investigate how the parameters in the model affect the geometrical shape factor μ_g and to develop empirical equations relating μ_g to the parameters in the model, similarly to what has been previously done in TL theory of delocalized transitions.
(c) To investigate by simulation whether the variable heating rate method and initial rise methods of TL analysis are applicable in the TL glow curves of this model.
(d) To develop different types of analytical expressions for the TL intensity, that can be used for computerized glow curve deconvolution analysis (CGCD).

2. Overview of the model by Jain et al. [14]

In this section we briefly review the three different versions of the model by Jain et al. [14] available in the literature, for the case of TL processes.

2.1. The original full model of Jain et al. [14]

The physical assumptions in the model of Jain et al. [14] are summarized in Table 1 of their paper. The main physical assumption in the model is the presence of a random distribution of hole traps in the luminescent volume, and an associated range of random nearest-neighbor recombination probabilities. Furthermore, stimulated recombination takes place only via the excited state of the electron trap, by either optical or thermal stimulation. The concentration of holes is assumed to be much larger than the concentration of electron traps, and an electron can tunnel only to its nearest hole. In the exact form of the model presented by Jain et al. [14], the differential equations for a TL process are as follows:

$$\frac{\partial n_g(r',t)}{\partial t} = -An_g(r',t)+Bn_e(r',t) \tag{1}$$

$$\frac{\partial n_e(r',t)}{\partial t} = An_g(r',t)-Bn_e(r',t)-\frac{n_e(r',t)}{\tau(r',t)} \tag{2}$$

$$L(t) = -\frac{dm}{dt} = \int_0^\infty \frac{n_e(r',t)}{\tau(r',t)}dr' = -\int_0^\infty \left(\frac{\partial n_g(r',t)}{\partial t}+\frac{\partial n_e(r',t)}{\partial t}\right)dr' \tag{3}$$

$$\frac{dT}{dt} = \beta \tag{4}$$

$$\tau = s^{-1}\exp\left(\frac{r'}{(\rho')^{1/3}}\right). \tag{5}$$

The following parameters and symbols are used in the model: $n_g(r',t)$and $n_e(r',t)$are the instantaneous concentrations of electrons in the ground state and in the excited state correspondingly. These concentrations depend on both time t and on the dimensionless separation distance parameter r' which is defined by $r'=(4\pi\rho/3)^{1/3}r$, where r represents the actual donor–acceptor separation distance. The dimensionless number density of acceptors parameter ρ' is defined by $\rho'=(4\pi\rho/3)\alpha^{-3}$, where ρ represents the actual number density of acceptors and α is the potential barrier penetration constant (Huntley, [5]). m is the instantaneous concentration of acceptors (holes), n is the instantaneous concentration of all the donors, and if N represents the instantaneous concentration of electrons in thermally disconnected states such that charge is conserved, then $m=n+N=(n_g+n_e)+N$. The parameter A represents the thermal excitation rate from the ground to the excited state, and is equal to $A=s\exp(-E/kT)$ where $E=$ thermal activation energy, s is the frequency factor, β is the linear heating rate, T is the temperature of the sample and τ is the tunneling lifetime. B is the relaxation rate from the excited into the ground state, and $L(t)$ is the instantaneous luminescence resulting from recombination taking place via the excited state. If the equivalence principle is assumed to be valid, one also has $B=s$.

In this full version of the model of Jain et al. [14] the TL intensity $L(t)$ is calculated from the numerical solution of the system of differential equations (1)–(5).

2.2. The approximate version of the model by Pagonis et al. [16]

Pagonis et al. [16] examined the full model by Jain et al. [14] and obtained partial analytical solutions of the system of differential equations (1)–(5). These authors obtained the following analytical expressions for the distribution of remaining donors at any time t:

$$n_g(r',t) = 3n_0(r')^2\exp[-(r')^3]\exp[-\exp(-(\rho')^{-1/3}r')\int_0^t Adt']. \tag{6}$$

This analytical equation describes the evolution of the distribution of electrons in the ground state as a function of the time t elapsed since the beginning of the optical or thermal stimulation. It is valid for several types of excitation used in typical TL or OSL experiments.

The TL luminescence intensity $L(t)$ is found from the expression

$$L(t) = \int_0^\infty A\exp(-(\rho')^{-1/3}r')n_g(r',0)\exp[-\exp(-(\rho')^{-1/3}r')\int_0^t Adt']dr'. \tag{7}$$

This integral expression allows a numerical calculation of the luminescence intensity L(t), by integrating numerically over the possible range of the dimensionless variable $r'=0$ to $r'=\infty$.

Although it is not possible to obtain a closed analytical form for the luminescence intensity as a function of time in this version of the model, $L(t)$ can be easily evaluated by numerically integrating Eq. (7) over the distance r'.

2.3. The analytical form of the semianalytical version of the model [17]

Jain et al. [14] presented a semianalytical version of their model, in which one uses a critical tunneling lifetime τ_c. Kitis and Pagonis [17] were able to obtain the following analytical expressions for the concentration of electrons in the ground state $n_g(t)$and for the luminescence intensity $L(t)$ at time t:

$$n_g(t) = n_o e^{-\rho'\left[\ln\left(1+z\int_0^t Adt'\right)\right]^3} = n_o e^{-\rho'[F(t)]^3} \tag{8}$$

$$L(t) = -\frac{dn_g}{dt} = 3n_o\rho' F(t)^2 zAe^{-F(t)}e^{-\rho'[F(t)]^3} \tag{9}$$

with the quantity $F(t)$ defined by

$$F(t) = \ln(1+z\int_0^t Adt'). \tag{10}$$

Eqs. (8)–(10) are very general, and are applicable for several different types of thermal and optical stimulation. In the special case of TL with a linear heating rate β, the temperature T varies with time t as $T=T_o+\beta t$ where T_o is the room temperature. The excitation probability for the TL process is given by $A=s\exp(-E/kT)$ and the integral in Eq. (10) can be approximated by its well-known series approximation (see for example the book