

NON-MONOTONIC DOSE DEPENDENCE OF THERMOLUMINESCENCE

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The thermoluminescence (TL) intensity in different materials is usually a monotonic increasing function of the dose, which quite often reaches a saturation value. In several materials, however, non-monotonic dose dependence has been observed. The TL intensity reached a maximum at a certain dose and decreased at higher ones. Some authors refer to this effect as ‘radiation damage’. In the present work, we show that the non-monotonic dependence can easily be demonstrated to result from competition between transitions model with two trapping states and two kinds of recombination centres. Two kinds of competition are considered. One in which competition during excitation dominates, the filling of the active luminescence centre is non-monotonic, and the resulting TL is non-monotonic. In the other, the filling of traps and centres is monotonically increasing, but the competition during heating causes TL intensity to reach a maximum and decline at higher doses.

INTRODUCTION

The dose-dependence function of thermoluminescence (TL) is normally an increasing function, which, ideally, starts linearly and then goes sublinear when the TL maximum intensity approaches a saturation value. In several materials, superlinear dose dependence was reported⁽¹⁾. At high doses of excitation, the dose-dependence behaviour is usually of approaching saturation. This is explained to be the result of trapping states and/or recombination centres being filled to capacity so that further irradiation does not contribute anymore to an increase in the emitted TL.

It has been reported in the literature that in several materials, the intensity of TL peaks reached a maximum as a function of the excitation dose and decreased at higher doses. Some authors consider this decrease as an unimportant fluctuation and still term it ‘saturation’. In other cases, however, it is clearly seen that the intensity goes down quite significantly after having reached a maximum.

The effect was reported as early as 1963 by Charlesby and Partridge⁽²⁾. They describe a decline of the maximum TL intensity in gamma-irradiated polyethylene as of 10^4 Gy and postulate that the cause of the effect is radiation damage in the material. Halperin and Chen⁽³⁾ reported on the UV excited TL in semiconducting diamonds. The secondary peak at ~ 150 K increased linearly with the dose at low doses with UV excitation, reached a maximum at a certain dose and decreased at higher doses. It is quite obvious that in diamonds, 3–5.5 eV photons cannot cause radiation damage. Cameron *et al.*⁽⁴⁾

described the non-monotonic dose dependence in LiF:Mg,Ti as a function of ^{60}Co gamma-rays excitation dose. In this material, which has been serving for many years as the main dosimetric material, they report on a rather broad range of linear dependence followed by a superlinear range after which a maximum value and a slight decline are seen. Jain *et al.*⁽⁵⁾ describe a significant decrease of the TL output of peak V in LiF, by a factor of ~ 2.5 from the maximum, and ascribe it to radiation damage. Their graphs show that at very high doses, the dose-dependence curves tend to level off following a range of significant decrease in the TL intensity. The effect of non-monotonic dose dependence has also been seen in quartz, the main material used for archaeological and geological TL dating. Ichikawa⁽⁶⁾ found that in gamma-irradiated natural quartz, the peak at $\sim 200^\circ\text{C}$ reached a maximum at $\sim 6 \times 10^4$ Gy and decreased at higher doses by a factor of ~ 2.5 . David *et al.*⁽⁷⁾ showed the dose dependence of some TL peaks in gamma-irradiated pink quartz, which revealed a decline following a maximum at 10^3 – 10^4 Gy.

A number of authors reported on the non-monotonic effect in the important dosimetric material $\text{Al}_2\text{O}_3:\text{C}$. For example, Yukihiro *et al.*⁽⁸⁾ described a somewhat superlinear dependence up to ~ 30 Gy of beta irradiation in the 450 K peak in some of the samples. The peak reached a maximum value and declined at higher doses. These authors explain the observed effects in $\text{Al}_2\text{O}_3:\text{C}$ using a model based on the occurrence of F/F^+ centres as well as on the other trapping states and centres.

In the present work, we suggest a rather general model, which does not assume a radiation damage of destruction of trapping states and/or

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recombination centres. We assume the existence of two trapping states and two kinds of recombination centres. These appear to occur in practically any dosimetric material. The competition over charge carriers during both excitation and heating is considered using both numerical simulation and intuitive considerations. Here, we assume a homogeneous excitation of the sample, which is a good approximation to the situation occurring with UV and X-ray exposure, as well as beta excitation and perhaps to a lesser extent, for gamma exposure.

THE MODEL

The model includes two electron trapping states, N_1 and N_2 and two kinds of hole recombination centres, M_1 and M_2 as shown in Figure 1. The trapping level N_1 is considered to be active in the sense that it releases electrons thermally into the conduction band with the relevant parameters E_1 , the activation energy, and s_1 , the frequency factor. The instantaneous occupancy of N_1 is denoted by n_1 . N_2 is considered to be disconnected; practically no electrons are released from N_2 into the conduction band, and, thus, this trapping state serves only as a competitor both during the excitation and the heating stages. The instantaneous occupancy of this level is denoted by n_2 . The retrapping probability coefficients are denoted by A_{n1} and A_{n2} . The instantaneous concentrations of electrons and holes in the conduction and valence bands are n_c and n_v , respectively. The rate of production of electrons and holes by the irradiation per unit volume per second is denoted by x , which is proportional to the dose rate. If the radiation is imparted at a constant rate for a period of time t_D , the total concentration of electrons and holes produced by the irradiation is $x \cdot t_D$, which is proportional to the dose D . The concentration of the radiative centres is denoted by M_1 and

that of the competitor, non-radiative centre by M_2 . The instantaneous occupancies of these centres are m_1 and m_2 , respectively. The trapping coefficients of free holes into M_1 and M_2 during the excitation are B_1 and B_2 , respectively. The recombination coefficients of free electrons with trapped holes in M_1 and M_2 , both during excitation and heating, are denoted by A_{m1} and A_{m2} . The rate of recombination into M_1 during heating is associated with the TL emission.

The set of coupled differential equations governing the process during the excitation is

$$-\frac{dm_1}{dt} = A_{m1}n_c m_1 - B_1 n_v (M_1 - m_1), \quad (1)$$

$$-\frac{dm_2}{dt} = A_{m2}n_c m_2 - B_2 n_v (M_2 - m_2), \quad (2)$$

$$\frac{dn_1}{dt} = A_{n1}n_c (N_1 - n_1) - s_1 \exp(-E_1/kT)n_1, \quad (3)$$

$$\frac{dn_2}{dt} = A_{n2}n_c (N_2 - n_2), \quad (4)$$

$$\frac{dn_v}{dt} = x - B_1 n_v (M_1 - m_1) - B_2 n_v (M_2 - m_2), \quad (5)$$

$$\frac{dm_1}{dt} + \frac{dm_2}{dt} + \frac{dn_v}{dt} = \frac{dn_1}{dt} + \frac{dn_2}{dt} + \frac{dn_c}{dt}. \quad (6)$$

It should be noted that usually, the last term in Equation 3 can be ignored since the irradiation is performed at a low enough temperature so that practically no electrons are thermally released during the excitation. Obviously, a similar term has been omitted from Equation 4 since the s_2 and E_2 values are such that no electrons are thermally released. During the excitation, electrons and holes reside in the conduction and valence bands, respectively. Since the materials in question are insulators, it is rather obvious that the concentration of the free carriers in the bands should be significantly smaller than those of electrons and holes in traps and centres.

In order to get conclusions from the model, a set of physically significant parameters should be chosen, and the set of simultaneous equations should be solved numerically. To follow the experimental procedure, a period of relaxation time is considered. This is done by taking the final values of all the occupancy functions as initial values for the relaxation stage, setting $x = 0$ in Equation 5 and solving numerically the coupled equations for a further period of time until n_c and n_v are negligibly small. In the final stage, the following set of simultaneous differential equations is to be numerically solved (see the dashed-line transitions in Figure 1), with the final values at the relaxation stage serving as initial values to the heating stage.

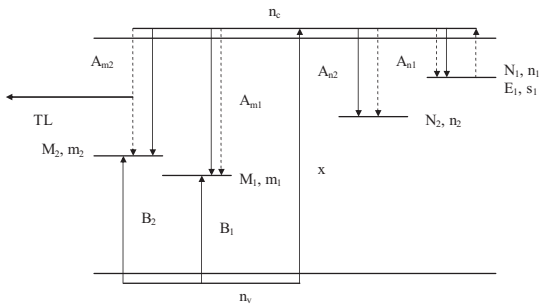


Figure 1. The energy level scheme of two trapping levels and two kinds of recombination centres. Transitions occurring during the excitation are given by solid lines and transitions taking place during the heating by dashed lines.

$$\frac{dn_1}{dt} = -s_1 n_1 \exp(-E_1/kT) + A_{n1}(N_1 - n_1)n_c, \quad (7)$$

$$\frac{dn_2}{dt} = A_{n2}(N_2 - n_2)n_c, \quad (8)$$

$$\frac{dm_1}{dt} = -A_{m1}m_1n_c, \quad (9)$$

$$\frac{dm_2}{dt} = -A_{m2}m_2n_c, \quad (10)$$

$$\frac{dn_1}{dt} + \frac{dn_2}{dt} + \frac{dn_c}{dt} = \frac{dm_1}{dt} + \frac{dm_2}{dt}. \quad (11)$$

Obviously, we have to specify the heating function, which we conventionally choose to be linear, $T = T_0 + \beta t$, where β is the (constant) heating rate. The TL emission is associated with the recombination into m_2 , therefore the intensity $I(T)$ is

$$I(T) = A_{m2}m_2n_c. \quad (12)$$

NUMERICAL RESULTS

In order to get the numerical results, sets of trapping parameters have been chosen, and the simultaneous sets of equations were solved. The Matlab ode23s solver has been used. Equations 1–6 are first solved for a certain value of the dose rate x , and then with $x = 0$ for a further period of relaxation time. Finally, the coupled set of Equations 7–11 is solved with the appropriate heating rate, using the same Matlab solver, the values of $I(T)$ are determined from Equation 12, and the maximum value is recorded.

It is quite obvious that the measured TL following excitation for a given set of trapping parameters within the present model depends on the competition processes during both the excitation and the heating of the sample. However, one can identify situations where the effects of competition during excitation are dominating and others where competition during heating is more important as explained below. Figures 2 and 3 show the simulated results of the maximum TL as a function of the dose. Note that the dose is given on a logarithmic scale.

The parameters chosen for Figure 2 are as follows: $M_1 = 3 \times 10^{21} \text{m}^{-3}$; $M_2 = 1 \times 10^{18} \text{m}^{-3}$; $A_{n1} = 3 \times 10^{-17} \text{m}^3 \text{s}^{-1}$; $A_{n2} = 3 \times 10^{-17} \text{m}^3 \text{s}^{-1}$; $E_1 = 1.0 \text{ eV}$; $s_1 = 1 \times 10^{12} \text{s}^{-1}$; $A_{m1} = 1 \times 10^{-17} \text{m}^3 \text{s}^{-1}$; $A_{m2} = 1 \times 10^{-16} \text{m}^3 \text{s}^{-1}$; $N_1 = 1 \times 10^{19} \text{m}^{-3}$; $N_2 = 1 \times 10^{21} \text{m}^{-3}$; $B_1 = 1.5 \times 10^{-17} \text{m}^3 \text{s}^{-1}$; $B_2 = 1 \times 10^{-17} \text{m}^3 \text{s}^{-1}$. The heating rate taken for all the simulated glow curves was $\beta = 1^\circ \text{C s}^{-1}$. The results show an increase of the TL maximum (solid line) with the dose up to a maximum at a ‘dose’ of $\sim 7 \times 10^{20} \text{m}^{-3}$, followed by a decrease of $\sim 35\%$

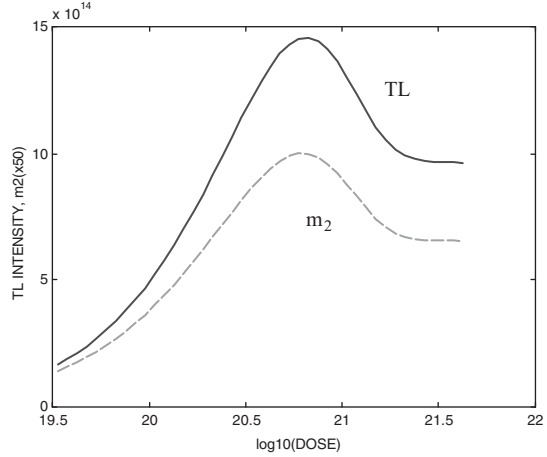


Figure 2. Simulated dose dependence of the maximum TL (solid line), and the radiative centre concentration at the end of irradiation, m_2 (dashed line), when competition during excitation dominates. The relevant set of parameters is given in the text.

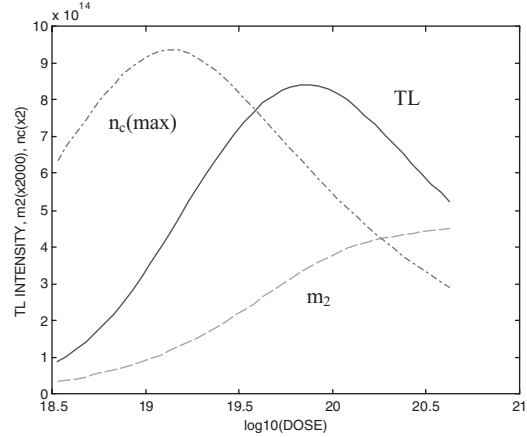


Figure 3. Simulated dose dependence of the maximum TL (solid line), the radiative centre concentration at the end of irradiation, m_2 (dashed line), and the values of $n_c(\text{max})$ (dashed-dotted line) when competition during heating dominates. The relevant set of parameters is given in the text.

after which the maximum TL intensity tends to level off at higher doses. This behaviour is very similar to experimental results reported in some materials⁽⁵⁾. A similar behaviour is seen in the plot of m_2 (at the end of the relaxation period) as a function of the dose (dashed line), and the levelling off at higher doses is also similar.

The parameters chosen for Figure 3 are as follows: $M_1 = 3 \times 10^{21} \text{m}^{-3}$; $M_2 = 1 \times 10^{18} \text{m}^{-3}$; $A_{n1} = 3 \times 10^{-17} \text{m}^3 \text{s}^{-1}$; $A_{n2} = 3 \times 10^{-20} \text{m}^3 \text{s}^{-1}$; $E_1 = 1.0 \text{ eV}$;

$s_1 = 1 \times 10^{12} \text{s}^{-1}$; $A_{m1} = 1 \times 10^{-17} \text{m}^3 \text{s}^{-1}$; $A_{m2} = 1 \times 10^{-18} \text{m}^3 \text{s}^{-1}$; $N_1 = 1 \times 10^{21} \text{m}^{-3}$; $N_2 = 1 \times 10^{19} \text{m}^{-3}$; $B_1 = 1.5 \times 10^{-19} \text{m}^3 \text{s}^{-1}$; $B_2 = 1 \times 10^{-17} \text{m}^3 \text{s}^{-1}$. The results show an increase of the maximum TL intensity (solid line) up to a simulated dose of about $7.5 \times 10^{19} \text{m}^{-3}$, and a decline from there on; this time no levelling off at high doses is observed. This resembles at least qualitatively the experimental results in quartz by Ichikawa⁽⁶⁾. The dashed line shows the dependence of m_2 as a function of the dose, which is an increasing function. Checking the dependence of the concentrations of the two trapping states and the recombination centre on the dose (not shown here), shows that all of them are increasing functions of the dose all along, including the dose at which the TL peak is maximal as a function of the dose. It is quite obvious that here, the competition during excitation does not have the main role in producing the non-monotonic dose dependence.

DISCUSSION

In this work, a model is offered to explain the rather common effect of non-monotonic dose dependence of TL. Competition during both the excitation stage and the heating stage is considered. The three phases of the experiment, namely, the irradiation, relaxation and heating are numerically simulated for different excitation doses, which yield the TL intensity vs. dose curves.

Two examples of the non-monotonic dose dependence are shown. In the case shown in Figure 2, the maximum of the TL vs. dose is reached at practically the same dose as that of the maximum occupancy of the radiation centre, m_2 . Such a comparison between the intensity and the relevant traps and centres occupancies cannot, of course, be made in the measured TL but can be done with the results of the simulations. This obviously is associated mainly with competition during the excitation. The interplay between the concentration functions (n_1, n_2, m_1, m_2) depends, in fact, on all the relevant parameters and, therefore, it is rather hard to describe qualitatively the dose dependence. The main point, however, is that the simulation shows that m_2 reaches a maximum and then goes down, and the TL maximum intensity follows a similar behaviour. Also, at higher doses, m_2 reaches nearly a plateau, and the TL intensity behaves similarly.

The situation is quite different with regard to Figure 3. Here, none of the occupancy functions reaches a maximum where TL maximises, but, rather, they are all still increasing. A close look at the output of the different concentrations reveals that although n_1, n_2, m_1, m_2 , are increasing, the mutual action between them results in a strong decrease in the value of the concentration of free

electrons, n_c , at the TL maximum as a function of the dose in this range. The product of increasing m_2 and decreasing n_c (Equation 12), which yields the emitted TL, reaches a maximum at a certain dose as seen in Figure 3 and decreases at higher doses owing to the fast decrease of n_c . For an alternative semi-intuitive explanation, we recorded m_2/m_1 at the end of the excitation, as a function of the dose (not shown here) for the set of parameters used for Figure 3. Although, as pointed out above, both m_1 and m_2 are increasing with the dose, m_1 is growing faster than m_2 from a certain dose D_m up, and, therefore, m_2/m_1 reaches a maximum at D_m and decreases at higher doses. The TL intensity follows roughly a similar behaviour, showing a maximum rather close to D_m , and then decreases. Obviously, the decrease of the TL signal can be associated with the stronger competition with the non-radiative centre m_1 at higher doses.

We consider, the success of the present work in demonstrating that the non-monotonic dose-dependence effect is not necessarily a result of a destruction of trapping states or recombination centres.

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