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Simulation of the influence of thermal quenching on thermoluminescence glow-peaks

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The thermal quenching of luminescence efficiency is an effect which is present in many thermoluminescent (TL) materials. It causes a significant decrease of the luminescence signal and disturbs the shape of the glow-peaks. Therefore, in principle, the thermoluminescence kinetics theory cannot describe TL glow-peaks influenced by thermal quenching. In the present work a detailed simulation of the influence of the thermal quenching effect on thermoluminescence glow-peaks is presented. Specifically we study the shift of the quenched

glow-peak with heating rate and the effect on the various heating rate methods, the influence on the symmetry factor and the kinetic order of the glow-peak, and the effect of thermal quenching on the initial rise and peak shape methods for evaluating kinetic parameters. Furthermore, the evaluation of the thermal quenching parameters using the quenched glow-peak and the possibility of using the conventional expression describing a single glow-peak to fit the quenched glow peaks are also investigated.

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1 Introduction The thermal quenching effect is the reduction of the luminescence intensity of a thermoluminescent (TL) glow-peak as the sample temperature is raised. In the case of TL the effect appears when the signal is measured as a function of the heating rate. As the heating rate increases the glow-peak is shifted to higher temperatures and the integral of the glow-peak, which measures the luminescence efficiency, decreases. Among the TL materials which exhibit thermal quenching, the most widely known and investigated are Al₂O₃:C [1–3] and Quartz [4–9]. Al₂O₃:C is a very sensitive TL and optically stimulated luminescence (OSL) dosimeter, whereas quartz is the basic material in TL and OSL dating [10, 11] (and references therein). The effect has been also observed in OSL [9, 11, 12]. The model explaining thermal quenching in Al₂O₃:C and quartz is based on the Mott–Seitz mechanism [3]. The empirical expression for the thermal quenching luminescence efficiency derived from this model is given by [3]:

$$\eta = \frac{1}{1 + C e^{-W/kT}}, \quad (1)$$

where C is a dimensionless constant and W is the thermal quenching activation energy, T is the temperature of the sample, and k is the Boltzmann constant.

The thermal quenching parameters of Al₂O₃:C $W = 1.08$ eV and $C = 2.9 \times 10^{12}$ were measured by Akselrod et al. [3]. An important observation of Akselrod et al. [3], was that the W , C values obtained from the heating rate dependence of the TL glow-curve are independent on the sample type, the degree of trap filling, and the heating or cooling rate. In pioneer work by Wintle [4] the thermal quenching parameters for quartz $W = 0.64$ eV and $C = 2.8 \times 10^7$ were obtained. Parameter values very close to that of Wintle [4] were evaluated by McKeever et al. [5] and Kitis et al. [6] for TL, and Spooner [12] and Chitambo [9]. On the other hand Petrov and Bailiff [8] obtained a different set of parameter values, i.e., $W = 0.78$ eV and $C = 3.1 \times 10^{10}$. In the present work the thermal quenching parameters values of Wintle [4] will be considered as reference values.

The influence of thermal quenching is not restricted to the reduction of the TL intensity. It influences also the methods used to evaluate the trapping parameters of a TL glow-peak. Under the influence of thermal quenching the initial rise method [10] underestimates the values of the activation energy E [6–8, 13]. The activation energies evaluated by the peak shape methods [10] are also strongly underestimated [2]. On the other hand the various heating

rate methods [10], seem to be less influenced by thermal quenching [2].

The experimental glow-curve is thermally quenched, whereas the unquenched glow-curve is completely unknown. Therefore, any information extracted from the experimental, i.e., quenched glow-curve, through the application of the conventional kinetics expressions will be in principle erroneous. The aim of the present work is to attempt a detailed simulation of the influence of the thermal quenching effect on all parameters which can be evaluated from an experimental glow-curve. Specifically we investigate the influence of thermal quenching on the following experimental parameters. (i) the peak integral, (ii) the peak height, (iii) the peak maximum temperature, (iv) the methods used to evaluate the trapping parameters, and (v) the evaluation of thermally quenching parameters (W , C). Conclusions are drawn about the degree of reliability of information extracted from the experimental (quenched) glow-curves.

2 Simulation method

2.1 TL glow-peak theory The simplest model in thermoluminescence consists of two energy levels, one electron trap and one recombination center (OTOR).

The differential equations governing the traffic of electrons between the trap level, the recombination center, and the conduction band are:

$$\frac{dT}{dt} = \beta, \quad (2)$$

$$\frac{dn}{dt} = -ns e^{-E/kT} + n_c(N - n)A_n, \quad (3)$$

$$\frac{dn_c}{dt} = ns e^{-E/kT} - n_c(N - n)A_n - n_c(n + n_c)A_m, \quad (4)$$

$$\frac{dm}{dt} = -n_c(n + n_c)A_m. \quad (5)$$

The charge neutrality, which dictates that

$$m = n + n_c \quad (6)$$

is included in the above set of differential equations. Equation (2) accounts for the linear increase of temperature.

N (cm^{-3}) is the total concentration of the electron traps in the crystal, $n(T(t))$ (cm^{-3}) is the concentration of the filled electron traps in the crystal, $n_c(T(t))$ (cm^{-3}) is the concentration of the free carriers in the conduction band, $m(T(t))$ (cm^{-3}) is the concentration of the recombination centers in the crystal, A_n ($\text{cm}^3/\text{s}^{-1}$) is the capture probability of the traps, A_m ($\text{cm}^3/\text{s}^{-1}$) is the capture probability of the recombination center, E (eV) is the activation energy of the electron traps, s (s^{-1}) is the frequency factor of the electron trap, k (eV/K) is the Boltzmann constant, β is the constant heating rate, t the time (s), T (K) the temperature, and η the thermal quenching efficiency given by Eq. (1).

The instantaneous luminescence intensity is given by:

$$I(t) = -\frac{dm}{dt} = \eta n_c m A_m. \quad (7)$$

The rate equations (2)–(5) describing the traffic of electrons during the linear heating are coupled first order non-linear differential equations which unfortunately cannot be solved in a close form. The development of analytical expressions giving explicitly the relationship between the TL intensity and the temperature, requires some simplifying assumptions with the most important one being the quasi-equilibrium (QE) conditions. The QE assumption is:

$$\left| \frac{dn_c}{dt} \right| \ll \left| \frac{dn}{dt} \right|, \left| \frac{dm}{dt} \right|. \quad (8)$$

The QE assumption requires that the free electron concentration in the conduction band is quasi-stationary. In practice this means that the concentration $n_c(T(t))$ is always much less than the concentration of $n(T(t))$.

The inequalities of Eq. (8) allow a simplification of the rate equations (2)–(5). If combined with the additional dictate that $dn_c/dt \simeq 0$, the “general one trap” (GOT) equation for TL intensity is derived [10]. Assuming negligible re-trapping, i.e., $A_n \ll A_m$, then first order kinetics is obtained, whereas by assuming $A_n = A_m$ second order kinetics is derived. However, both first and second order kinetics are extreme cases of the OTOR model. The OTOR model predicts mainly glow-peaks with kinetics order between first and second. The analytical expression available to describe these glow-peaks is the empirical general order kinetics equation [14]:

$$I(T) = n_0 \left(\frac{n_0}{N} \right)^{b-1} e^{-(-E/kT)} \quad (9)$$

$$\times \left[1 + \frac{s(b-1)}{b} \left(\frac{n_0}{N} \right)^{b-1} \int_{T_0}^T e^{-(-E/kT)} dT \right]^{-(b/(b-1))},$$

where b is the kinetic order.

It must be noted that the mixed order kinetics expressions are also used during TL work. The mixed order kinetics results from simplifying assumptions of a model, which in addition to the one trap and one recombination center also has another thermally disconnected trapping level. This inactive trapping level contributes to the resulting glow-peak shape through the neutrality condition. However, the differences between general and mixed order kinetics glow-peak shape are negligible [15].

2.2 Selection of reference glow-peaks The selection of the appropriate glow-peaks for the simulation requires first the knowledge of the thermal quenching efficiency. It was decided to use values of the thermal quenching parameters which are widely used in literature; the parameters $W = 0.64$ eV and $C = 2.8 \times 10^7$ by Wintle [4] were selected. The schematic presentation of thermal quenching efficiency given by Eq. (1) is shown in Fig. 1

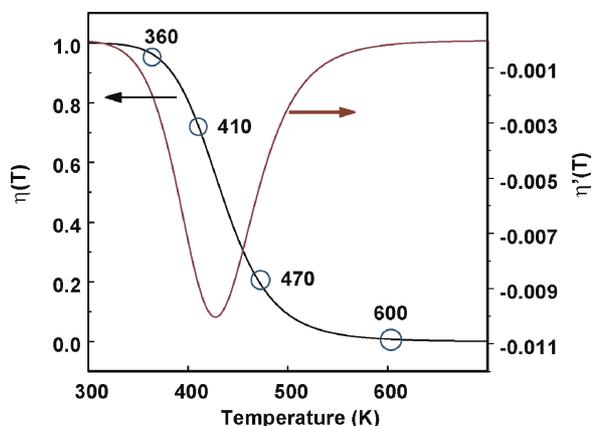


Figure 1 (online color at: www.pss-a.com) The thermal quenching efficiency and its first derivative. The open circles correspond to the positions of the peak maximum temperature, T_m at a heating rate $\beta = 1$ K/s, of the selected glow-peaks for the simulation.

along with its first derivative. By equating the second derivative of Eq. (1) to zero, it is found that the value of thermal quenching efficiency at its maximum variation rate (in absolute values) is given by:

$$\eta_m = 0.5 + \frac{2kT_{nm}}{W}, \quad (10)$$

where T_{nm} is the temperature of the maximum $|\eta_m|$. Since, usually it is $kT_{nm} \ll W$, it was found by Dallas et al. [16] that $n_m = 0.54 \pm 0.007$ for every W, C pair. This value of n_m is useful for selecting the simulated glow-peaks.

The linear heating rates used by the conventional TL readers range from 0.1 up to 30 K/s, whereas in practice heating rates are usually limited between 1 and 15 K/s. The peak shift caused by using this range of heating rates is always less than 100 K. Therefore, there is no single experimental TL glow-peak which can cover the complete range of $\eta(T)$ values shown in Fig. 1. For this reason four reference glow-peak maximum temperatures were selected, in order to cover the whole $\eta(T)$ range. These peak maximum temperatures T_m at a heating rate of 1 K/s are shown by the open circles in Fig. 1.

In the case of TL each T_m corresponds theoretically to an infinite combination of E, s values. Depending upon the E, s pair the glow-peak could be very narrow or very broad. This plays an important role in the influence of thermal quenching

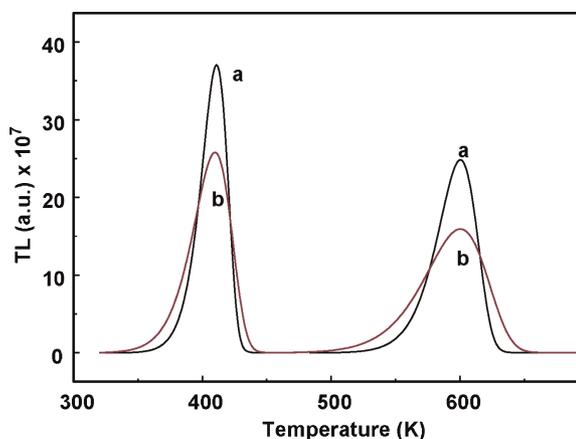


Figure 2 (online color at: www.pss-a.com) Characteristic examples of reference glow-peaks chosen for this study at 410 and 600 K corresponding to (a) narrow glow-peaks and to (b) broad glow-peaks.

since the range of $\eta(T)$ values for each glow-peak will be different. For this reason at each peak maximum position two pairs of E, s values were selected. Examples for the T_m at 410 and 600 K are shown in Fig. 2. For both glow-peaks, curve (a) is the narrow peak shape, whereas curve (b) is the broad peak shape.

Another parameter of importance for this study is the kinetic order b . Since thermal quenching varies strongly as a function of the temperature across the glow-peak, its influence on the high temperature part of the peak is very different for a first order kinetics peak with symmetry factor 0.42 and for a second order kinetics peak with a symmetry factor of 0.52. Therefore, for each reference glow-peak we studied both cases of first and second order kinetics.

2.3 Reference glow-peaks data The parameters used for the numerical solution of the system of differential equations governing the TL process are the following. Since the trap occupancy (case of $n_0 \ll N$) could affect the kinetic order and peak maximum of the glow-peak, we used the value $N = n_0 = 10^{10} \text{ cm}^{-3}$, i.e., the trap is in saturation. In this way one avoids influences on the peak shape other than thermal quenching effects. In the OTOR model the case of first order kinetics can be obtained when $A_n = 10^{-10} \text{ cm}^3/\text{s}$ and $A_m = 10^{-7} \text{ cm}^3/\text{s}$, and the case of second order of kinetics is obtained for the values $A_n = A_m = 10^{-7} \text{ cm}^3/\text{s}$. The kinetic parameters of the reference glow-peaks are listed

Table 1 Kinetic parameters of the reference glow-peak used in simulation.

| peak | 360 K | | 410 K | | 470 K | | 600 K | |
|--------|-------|------------------------|-------|-----------------------|-------|-----------------------|-------|-----------------------|
| | E | s | E | s | E | s | E | s |
| broad | 0.7 | 2.98×10^8 | 0.95 | 3.16×10^{10} | 1.15 | 1.26×10^{11} | 1.25 | 1.259×10^9 |
| narrow | 0.9 | 3.163×10^{11} | 1.4 | 2.82×10^{16} | 1.5 | 1×10^{15} | 2 | 3.98×10^{15} |

The kinetic order of both broad and narrow glow-peak was of first order for $A_n = 10^{-10} \text{ cm}^3/\text{s}$ and $A_m = 10^{-7} \text{ cm}^3/\text{s}$ and of second order of kinetics for $A_n = A_m = 10^{-7} \text{ cm}^3/\text{s}$. The activation energy E is in eV and the frequency factor s in s^{-1} .

in Table 1. Hereafter, each reference peak will be referred in the text with its peak maximum at a heating rate of 1 K/s. The temperature resolution used during simulation was 0.01 K.

2.4 Quantities evaluated from simulation During numerical solution of the differential equations a number of quantities were evaluated, which are necessary for this study. The following quantities were evaluated for both quenched and unquenched glow-peaks:

1. The total peak integral.
2. The peak maximum intensity I_m .
3. The peak maximum temperature T_m , as well as, the T_1 and T_2 , which are the temperatures at the half maximum intensity $I_m/2$ at the low and at the high temperature part of the glow-peak, respectively.
4. The full width at half maximum $\omega = T_2 - T_1$, and the half widths $\tau = T_m - T_1$ and $\delta = T_2 - T_m$.
5. The geometrical symmetry factor $\mu_g = \delta/\omega$ and the integral symmetry factor $\mu'_g = (\text{integral from } T_m \text{ to } T_\infty) / (\text{total peak integral})$.
6. The triangle assumption pseudo-constants C_ω , C_τ , and C_δ [15, 17], which give the degree by which a single TL glow-peak is approximated by a triangle. These constants are the basis for the peak shape methods for evaluating of the activation energy E .

Once the integral symmetry factor μ'_g and T_m of each glow-peak is evaluated, then the kinetics order b of the glow-peak can be evaluated using the following Equation given by Kitis and Pagonis [17] (Eq. (18)):

$$\mu'_g = \left[\frac{b}{1 + (b-1)2kT_m/E} \right]^{(1/(b-1))}. \quad (11)$$

Equation (11) relates a TL peak obtained from the numerical solution of Eqs. (2)–(5) having an integral symmetry factor μ'_g , with a TL peak calculated from Eq. (9) having the same integral symmetry factor. As it is seen from the parameters involved in Eq. (11), the integral symmetry factor, μ'_g is a pure kinetic parameter unlike the geometrical symmetry factor μ_g , which is a simple geometrical factor. However their values are very similar.

The evaluation of the kinetic order b is included in the simulation together with the symmetry factor μ_g , since TL community is very familiar with both parameters.

The activation energy is evaluated using the following Equation given by Kitis and Pagonis [17](Eq. (22)):

$$E_\omega = C_\omega b \left[\frac{b}{1 + (b-1)2kT_m/E} \right]^{(1/(b-1))} \frac{kT_m^2}{\omega}. \quad (12)$$

Expressions similar to that of Eq. (12) are also derived by Kitis and Pagonis [17] (Eqs. (28) and (30)) for E_δ and E_τ . Although they are evaluated during the simulation, these additional expressions are not given here, and only the results concerning E_ω will be presented.

Equation (12) can be used only within the simulation and not for experimental glow-peaks, because the quantities C_ω and b cannot be evaluated from the experimental glow-peak. Equation (12) does not contain any approximations, unlike the expressions used in peak shape methods which are given by Chen [10, 18, 19] and also by Kitis and Pagonis [17].

The activation energy of the numerically derived TL peaks was also evaluated by two additional widely used methods. The initial rise method [10] and the variable heating rate method [10]. In the present simulation the initial rise method was applied in the initial part of the glow-peak up to the temperature corresponding to a TL intensity equal to 0.1 I_m . In the variable heating rate method the activation energy E is the slope of the plot of $\ln(\beta/kT_m^2)$ versus $1/kT_m$.

All the above mentioned parameters were evaluated for both unquenched and quenched TL glow-peaks.

3 Results The system of the differential equations (2)–(5) were numerically solved using the Mathematica software package. All results that will be presented below concern the quenched glow-peaks, since these are experimentally measured. Before we proceed to the presentation of the simulation results, it is useful to present the expected behavior of the peak area and the peak maximum intensity I_m of an unquenched glow-peak as a function of the heating rate. This is shown in Fig. 3 for the case of the broad reference TL glow peak at 360 K. As the heating rate increases, the area under the unquenched TL peak remains constant, while the maximum intensity will decrease.

3.1 Shift of T_m due to thermal quenching

Thermal quenching causes a shift of the temperature of maximum intensity T_m of a TL glow-peak towards lower temperatures [3]. So the T_m of the quenched glow-peak is less shifted to higher temperatures than the shift of T_m of the unquenched peak as a function of the heating rate. The simulation can help us study this shift and the parameters on which it depends in a systematic fashion. T_m is the basic experimental parameter on which the various heating rate

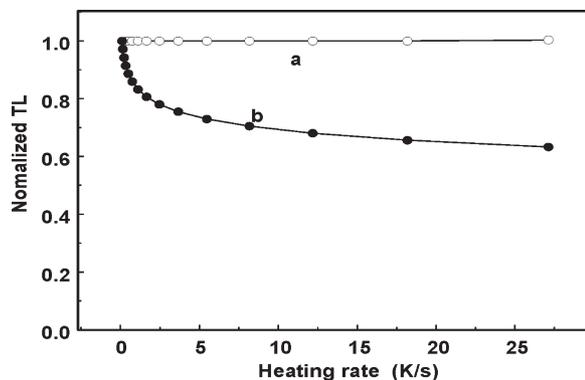


Figure 3 Example for the behavior of the peak area (a) and peak maximum intensity I_m (b), of unquenched glow-peak as a function of heating rate, for the case of reference broad TL glow-peak at 360 K.

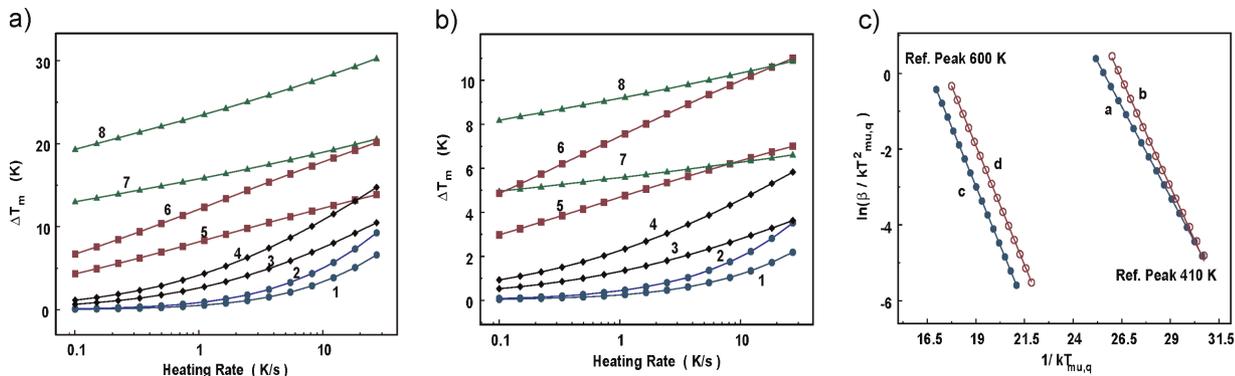


Figure 4 (online color at: www.pss-a.com) Curves (1) and (2) are for TL glow-peak 360 K and for first and second order kinetics, respectively. Similarly, curves (3) and (4) for peak 410 K, curves (5) and (6) for peak 470, and curves (7) and (8) for peak 600 K. The various heating rate method was applied with the data of curves (4) and (8) of broad second order kinetics TL peak at 410 and 600 K correspondingly. The curves (a) and (c) refer to unquenched TL glow-peak and curves (b) and (d) to quenched TL glow-peaks. (a) Case of broad reference peaks. (b) Case of narrow reference peaks. (c) Example plots of various heating rate method.

methods of calculating E are based. Therefore, the simulation can show how reliable this method is when applied to thermally quenched TL glow-peaks.

The shift of the quenched TL glow-peak will be expressed as the difference $\Delta T_m = T_{mu} - T_{mq}$, where T_{mu} and T_{mq} are the peak maximum temperatures of unquenched and quenched glow-peaks correspondingly. The results are shown in Fig. 4a–c. For both narrow and broad TL glow-peaks curves (1) and (2) stands for first and second order kinetics, respectively, for the TL peak at 360 K. Similarly, curves (3) and (4) for peak at 410 K, curves (5) and (6) for peak 470 K, and curves (7) and (8) for peak at 600 K.

In the VHR method the activation energy is the slope of the $\ln(\beta/kT_m^2)$ versus $1/kT_m$ plot [10]. Examples of various heating rate plots are given in Fig. 4 for the data of curves (4) and (8), which correspond to the broad second order kinetics TL peaks at 410 and 600 K. The results of the VHR method for all reference glow-peaks are shown in Fig. 5. The general observation is that the VHR method overestimates the value of the activation energy. The most serious overestimation can be seen for the broad second order reference TL glow-peaks and for a temperature region for which $\eta(T) < 0.5$ (see Fig. 1). In general, however, it can be concluded that the VHR when applied to thermally quenched narrow first order TL peaks gives reliable results. Another reason for possible failure of the VHR method is the temperature lag effect, which causes a significant temperature difference between the heating element and the temperature of the sample [20].

The conclusions from the above simulation results can be summarized as follows:

1. The shift of T_m due to thermal quenching is higher for the case of second order kinetics than for TL peaks following first order kinetics.
2. The shift of T_m due to thermal quenching is higher for the case of broad TL glow-peaks.
3. The shift increases as a function of the position T_m of each peak on the $\eta(T)$ curve shown in Fig. 1.

4. When thermal quenching takes place for $\eta(T) > 0.54$, as is the case for both broad and narrow peaks at 360 K, the temperature shift is low. Extrapolating to the experimental case, this shift is within the experimental error, so that the experimental parameter T_m can be considered a reliable parameter.
5. The situation is different in the temperature region where $\eta(T)$ values are less than 0.54 because the shift becomes large. Extrapolating to experimental cases, this shift is much higher than the experimental error and therefore the experimental parameter T_m cannot be considered a reliable parameter in these cases.
6. When the VHR method is applied to thermally quenched experimental glow-peaks, it gives reliable results only for narrow TL peaks and for $\eta(T)$ values much larger than 0.5.

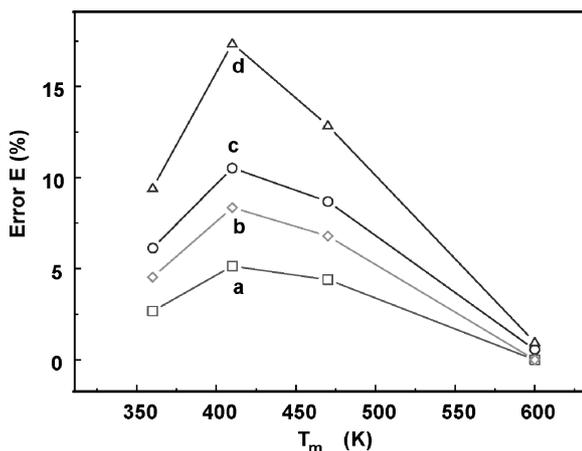


Figure 5 (online color at: www.pss-a.com) Error in the activation energy evaluation by the various heating rate method as a function of the peak maximum temperature of the reference TL glow-peaks. (a) Narrow first order, (b) narrow second order, (c) broad first order, and (d) broad second order.

3.2 Influence on the peak shape parameters In numerically generated TL glow-peaks the basic parameters which are related with its shape are the geometrical and integral symmetry factors. Since the values and behaviors of these factors are very similar, only the results for the more familiar geometrical symmetry factor will be presented. However, since the kinetic order b is a more familiar parameter, it was also included in the simulation using Eq. (11) and the relevant results will be presented as well.

The results on the influence of thermal quenching on the symmetry factor and on the kinetic order of all reference TL glow-peaks are shown in Fig. 6. Figure 6a shows the results for the broad reference TL glow-peaks. The curves (1a), (2a), (3a), and (4a) correspond to first order reference TL glow-peaks at 360, 410, 470, and 600 K correspondingly, whereas curves (1b), (2b), (3b) and (4b) correspond to the second order kinetics of the same reference TL glow-peaks. Figure 6c and d shows the same results for the narrow reference TL glow-peaks.

The qualitative behavior of the symmetry factor is similar for both broad (Fig. 6a) and narrow (Fig. 6c) reference TL peaks. There is a clear differentiation between TL peaks in the region of $\eta(T) > 0.54$ (peaks 360 and 410 K), and TL peaks in the region of $\eta(T) < 0.54$ (see Fig. 1) (peaks 470 K and 600 K).

In the case of first order kinetics the peaks at 360 K (curve (1a)) and 410 K (curve (2a)) the symmetry factor stays the same. However, in the case the peak 470 K (curve (3a)) the symmetry factor decreases from the value of 0.42 to a value of 0.39. In the case of the 600 K peak (curve (4a)) the symmetry factor remains the same at all heating rates with a value of 0.39. The corresponding behavior of the kinetic order shown in Fig. 6b in curves (1a), (2a), (3a), and (4a) is that the kinetics order is always 1, since there is no kinetic order $b < 1$ corresponding to symmetry factors less than 0.42. Therefore, thermal quenching does not seem to influence the apparent kinetic order of first order TL peaks.

In the case of second order kinetics TL peaks represented by curves (1b), (2b), (3b), and (4b) of Fig. 6a and c, the symmetry factor decreases as the heating rate increases and the TL peak shifts to higher temperatures. The corresponding behavior of the kinetics order is shown in Fig. 6b and d and curves (1b), (2b), (3b), and (4b). It is obvious that under the influence of thermal quenching a second order kinetics TL peak will appear as an intermediate kinetics order TL peak, with a kinetic order that varies with the heating rate. The case of the TL peak at 600 K (curves (4b)) is of interest, because it shows that when the thermal quenching is very strong both symmetry factor and kinetic order remain constant for all heating rates, giving the impression of a stable behavior.

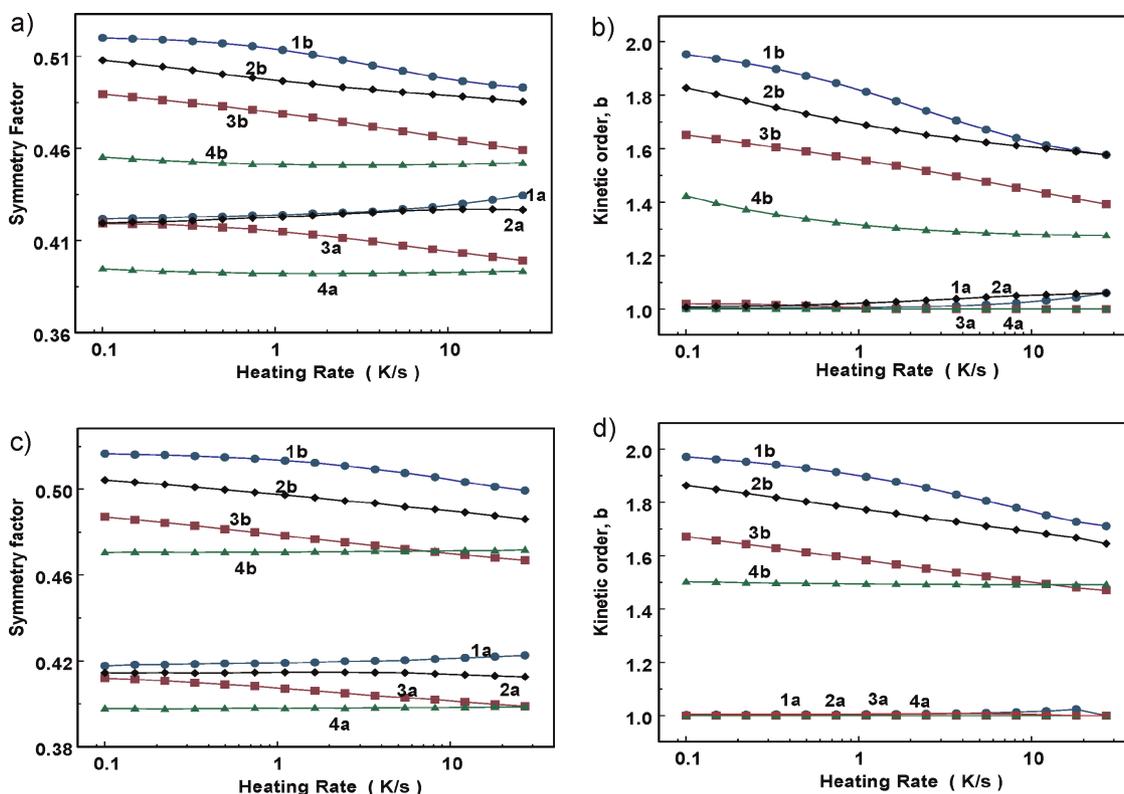


Figure 6 (online color at: www.pss-a.com) Influence of thermal quenching on the symmetry factor and on the kinetics order. Curves (1a), (2a), (3a), and (4a) represent first order kinetics and curves (1b), (2b), (3b), and (4b) represent second order kinetics for the reference TL glow-peaks at 360, 410, 470, and 600 K correspondingly. (a) Case of broad reference peaks-symmetry factor. (b) Case of broad reference peaks-kinetic order. (c) Case of narrow reference peaks-symmetry factor. (d) Case of narrow reference peaks-kinetic order.

The conclusions from the above simulation results can be summarized as follows:

1. Thermal quenching clearly influences the symmetry properties of both first and second order TL glow-peaks.
2. The symmetry factor and apparent kinetic order of quenched second order TL peaks decrease as the peak shifts to higher temperatures.
3. Thermal quenching influences TL peaks of any order, and not just those with first and second order kinetics.
4. For TL peaks in the temperature region where $\eta(T)$ is very small, the thermal quenching has a large effect even at the lower heating rates, and the effect remains the same independently of the heating rate.
5. Thermally quenched TL peaks with second order kinetics will appear to have a shape corresponding to an intermediate kinetic order b .

3.3 Influence of thermal quenching on the activation energy The application of peak shape methods and of the initial rise method to evaluate the activation energy of an experimental glow-peak is one of the major tasks in TL research. It is therefore important to

investigate the influence of thermal quenching on these methods of analysis.

The results of this investigation are shown in Fig. 7a–d. The first observation is that the success or failure of these methods depends strongly on the position of each reference TL glow-peak on the $\eta(T)$ plot shown in Fig. 1.

Figure 7a shows the results for the reference peak at 360 K. As can be seen, both the peak shape methods and initial rise method evaluate E with satisfactory accuracy relative to the input E value represented by the dash line. It is of interest to extrapolate the results of this peak to the experimental situation concerning the low temperature glow-peak of quartz known as the “110 °C” glow-peak. The thermal quenching parameters used in this study are those of Wintle [4], and the activation energy and peak maximum position correspond to those of this TL peak (see Table 1). The results of Fig. 7a explain the universality of the activation energy values for this peak reported in the literature over the years. From the lower heating rate of 0.1 K/s up to the highest rate of 27 K/s, the TL peak shifts from 332 to 421 K. The corresponding values of thermal quenching efficiency are $\eta(332 \text{ K}) = 0.99$ and $\eta(421 \text{ K}) = 0.69$. Since the results are exactly similar for

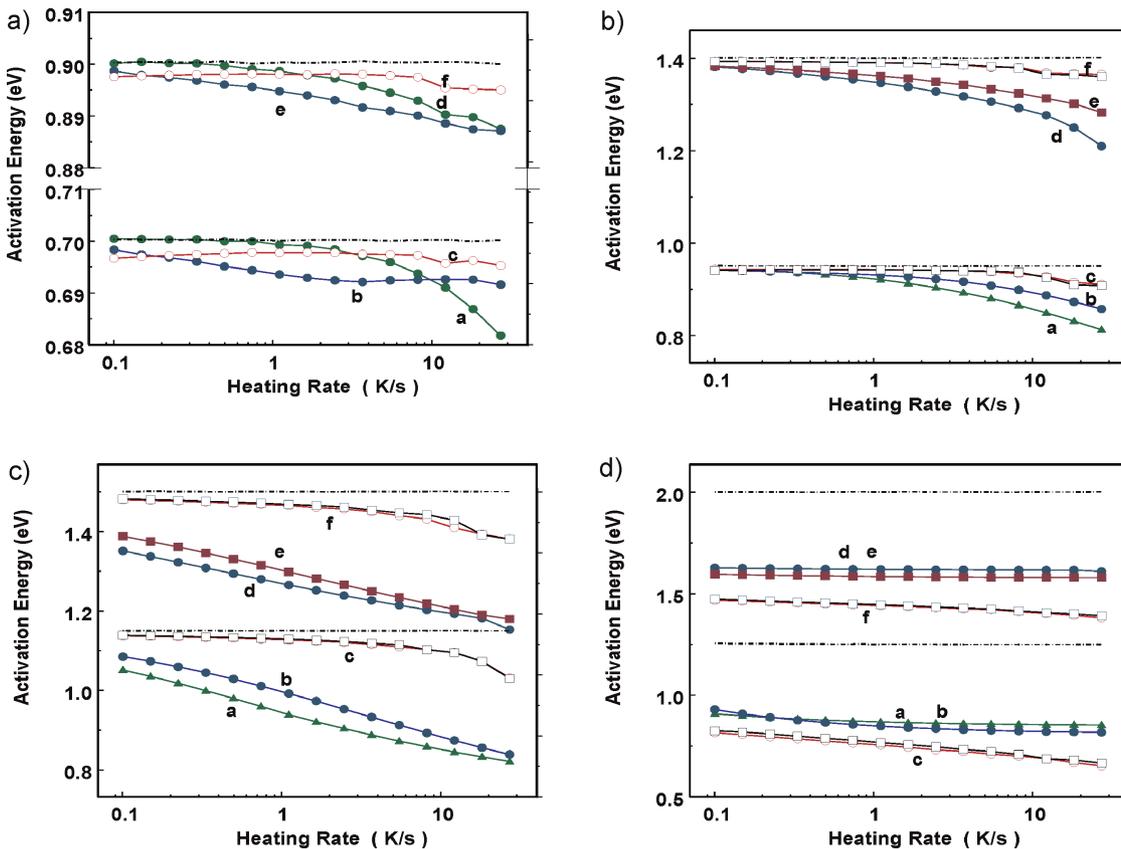


Figure 7 (online color at: www.pss-a.com) Influence of thermal quenching on the activation energy evaluated by peak shape methods and initial rise method. Curves (a) and (b) represent first and second order kinetics correspondingly and curve (c) the initial rise method for broad reference TL peaks, whereas curves (d) and (e) represent first and second order kinetics correspondingly and curve (f) the initial rise method for narrow reference TL peaks. The horizontal dash lines represent the input E values (see Table 1). (a) Reference peak at 360 K. (b) Reference peak at 410 K. (c) Reference peak at 470 K. (d) Reference peak at 600 K.

both broad and narrow reference TL peaks, it is possible to generalize and to argue that the influence of thermal quenching on the peak shape methods and initial rise method is negligible when $\eta(T)$ varies between 1 and 0.7. Therefore, the experimentally evaluated values of activation energy should be reliable.

Figure 7b shows the results for the reference peak at 410 K. From the lower heating rate of 0.1 K/s up to the highest one of 27 K/s the peak shifts from 379 to 461 K. The corresponding values of thermal quenching efficiency are $\eta(379\text{ K}) = 0.93$ and $\eta(461\text{ K}) = 0.38$ and in addition at the peak maximum the value of $\eta(410\text{ K}) = 0.76$. The peak shape methods reproduce the input values of E marked by the dash lines up to about 1 K/s which corresponds to $\eta(410\text{ K}) = 0.76$. On the other hand the initial rise method reproduces satisfactorily the input E values. Since the results are exactly similar for both broad and narrow reference TL peaks, one can conclude that the initial rise method gives reliable results for values of $\eta(T)$ values larger than 0.4.

Figure 7c shows the results for the reference peak at 470 K. From the lower heating rate of 0.1 K/s up to the highest one of 27 K/s the peak shifts from 436.5 to 526 K. The corresponding values of thermal quenching efficiency are $\eta(436) = 0.53$ and $\eta(526\text{ K}) = 0.08$ and in addition at the peak maximum the value of $\eta(470\text{ K}) = 0.27$. The peak shape methods fail to reproduce the input values of E marked by the dash lines even from the lower heating rate. As the heating rate and therefore the peak shift increases, the failure becomes more pronounced continuing the trends already seen for the reference peak at 410 K. Furthermore, the failure is higher for the first order kinetics peaks. On the other hand the initial rise method seems to underestimate slightly the input E values up to a heating rate of 5 K/s, for which $T_m \simeq 495\text{ K}$ and $\eta(495) \simeq 0.16$. The underestimation becomes significant for values of $\eta < 0.16$.

Figure 7d shows the results the reference peak at 600 K. For the lower heating rate of 0.1 K/s up to the highest one of 27 K/s the peak shifts from 550 to 684 K. The corresponding values of thermal quenching efficiency are $\eta(550\text{ K}) = 0.04$ and $\eta(684\text{ K}) = 0.003$ and in addition at the peak maximum the value of $\eta(600\text{ K}) = 0.013$. It is obvious that both methods fail to reproduce the input E values marked by the dash lines. Furthermore, the failure is greater for the initial rise method. It is also very interesting to notice that in this range of $\eta(T) < 0.1$ the underestimation of input E values starts at the lowest heating rates and remains the same as the peak shifts to higher temperatures, and stays independent of the $\eta(T)$ values. The underestimation of the energy is also the same for both first and second order reference TL peaks.

It is of interest, as in the case of TL peak at “110 °C” above, to extrapolate the results from this peak at 600 K to the experimental situation concerning the glow-peak of quartz known as the “325 °C” glow-peak. The stability of this TL peak over long periods of time is the cornerstone of thermoluminescence and OSL dating. The reference peak

at 600 K covers all possible cases of experimental peaks at these temperatures. According to the present results only the various heating rate method can give reliable results in some cases for narrow TL peaks, provided of course that the temperature lag effect is taken into account [20]. The curve fitting method, peak shape methods, and initial rise method will give seriously underestimated values of E . The real E value will be much higher than the estimate obtained from these methods of analysis, and therefore the real half life of the trapping level responsible for this peak should be much higher.

The conclusions from the above results can be summarized as follows:

1. The influence of thermal quenching on the peak shape methods and on the initial rise method depends exclusively on the thermal quenching efficiency values $\eta(T)$ in the temperature region of every TL peak.
2. For $\eta(T)$ values in the range 1–0.7, both peak shape methods and the initial rise method reproduce accurately the input E values.
3. For $\eta(T)$ values in the range 0.7–0.4, the peak shape methods start to underestimate the E values, whereas the initial rise method can reproduce the input E values up to $\eta = 0.38$.
4. For $\eta(T)$ values in the range 0.4–0.1, both peak shape methods and the initial rise method progressively underestimate the input E values as the $\eta(T)$ decreases.
5. For $\eta(T)$ values lower than 0.1, both methods underestimate drastically the input E values. The underestimation starts at the lowest heating rates and is independent of the $\eta(T)$ values.

By extrapolating the simulation results to the experimental case we can draw the following conclusions:

1. Taking into account the peak position and the thermal quenching parameters given by Wintle [4], the evaluation of the trapping parameters of the “110 °C” TL peak of quartz by any of the existing methods should give reliable results.
2. In the case of “325 °C” TL peak of quartz the simulation results from the reference TL peaks show that the evaluation of its trapping parameters with any method except perhaps the various heating rates method will give drastically erroneous values.

3.4 Evaluation of W , C parameters from the quenched glow-peaks

An important problem in luminescence research is the evaluation of the thermal quenching parameters W and C from the experimental TL data. The method used in Refs. [2, 3] is as follows. The thermally quenched experimental TL intensity as a function of temperature is:

$$I_q(T) = I_u(T)\eta(T) \quad (13)$$

where $I_q(T)$ and $I_u(T)$ are the quenched and unquenched TL intensities correspondingly. Equation (13) can be written as:

$$\frac{I_q(T)}{I_u(T)} = \eta(T). \quad (14)$$

In experimental work the TL intensity is expressed either by the total area of the glow-peak A , or by its peak maximum intensity I_m at temperature T_m . If the area A of a TL peak is measured between the temperature T_a up to a temperature T_b , then it is affected by all the values of η from $\eta(T_a)$ up to $\eta(T_b)$, and not by a unique value of η . On the other hand if the TL is measured with the peak height (I_m) then to each I_m value will correspond to a unique value of $\eta(T_m)$. Therefore, according to Eq. (14) one can evaluate the quantity:

$$\frac{I_{mq}(T_{mq})}{I_{mu}(T_{mu})} = \eta(T_{mq}) \quad (15)$$

where I_{mu} , T_{mu} and I_{mq} , T_{mq} are the peak maximum intensities and temperatures of unquenched and quenched reference TL peaks. Theoretically, if the quantity given by Eq. (15) is evaluated for various heating rates and then fitted with Eq. (1), one can obtain the thermal quenching parameters W and C . In practice, however, this method meets the following difficulties. The parameter I_{mu} corresponds to the unquenched TL peak and therefore it is unknown. Furthermore, contrary to what holds for the TL peak area A which is always constant, the maximum TL intensity I_m is not constant even for heating rates for which $\eta(T_m) = 1$ as is seen in Fig. 3. Therefore, there is no reference value that can be used to evaluate the quantity given by Eq. (15). Additionally, there are also experimental difficulties to obtain I_m correctly for various heating rates.

A potential solution is to consider the following quantity instead that of Eq. (15):

$$\frac{A_q}{A_u} = \eta(T_{mq}) \quad (16)$$

where A_u and A_q are the total peak areas of unquenched and quenched TL peaks. In principle this choice is rather arbitrary, because a unique value of η is attributed to a wide temperature region (T_a to T_b) covered by the complete TL peak. However, in practice it turns out that Eq. (16) is a good approximation of Eq. (15). The degree by which Eq. (16) approximates Eq. (15) can be estimated by the simulation.

The results of the simulation for all TL peaks examined in this study (narrow, broad, first, and second order) are shown in Fig. 8. Figure 8a shows the $\eta(T_{mq})$ values evaluated from Eq. (15), which is expected to coincide with the values from Eq. (1) plotted as a solid line, and they are not distinguishable in the figure.

Figure 8b shows the $\eta(T_{mq})$ values evaluated from Eq. (16), which has to be tested about how well it approximates Eq. (15). The solid line corresponding to Eq. (1) is also plotted. As it is seen the values $\eta(T_{mq}) = A_q/A_u$ almost coincide and follow systematically the $\eta(T)$ values of

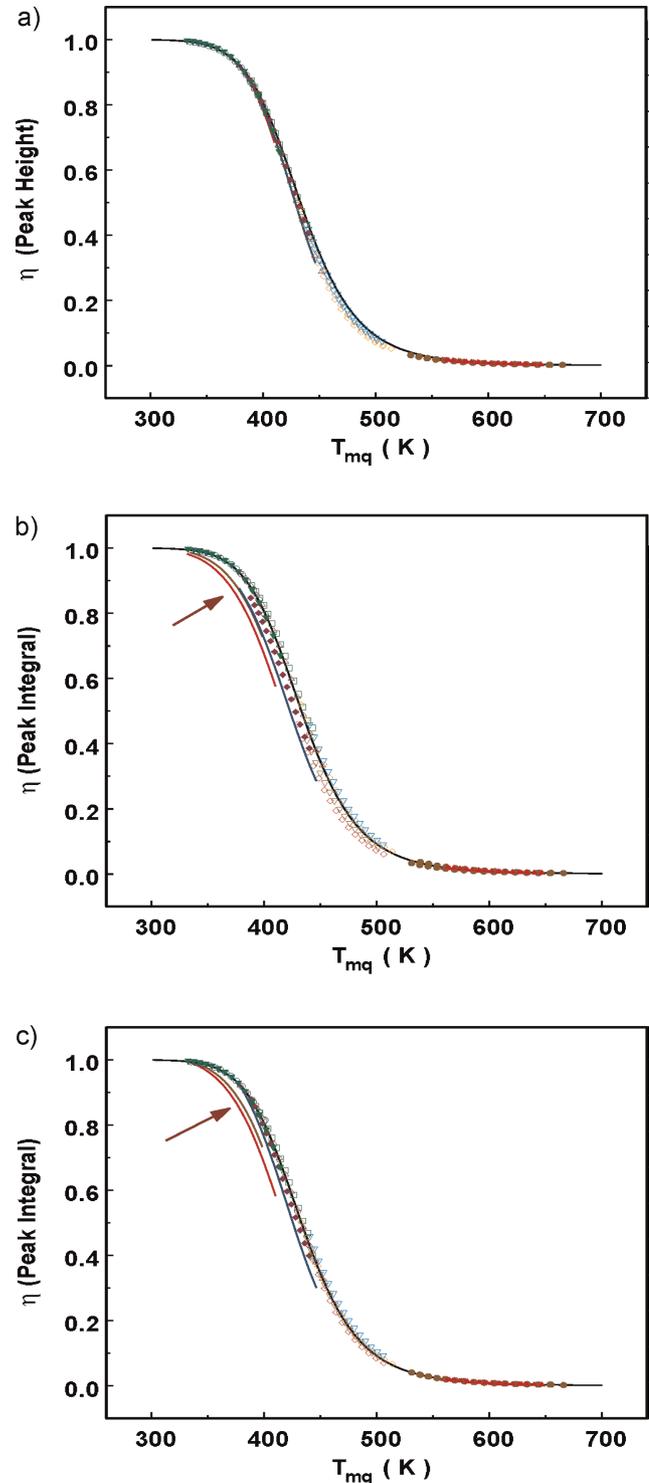


Figure 8 (online color at: www.pss-a.com) $\eta(T) = I_{mq}/I_{mu}$ and $\eta(T) = A_q/A_u$ as a function of the peak maximum temperature of quenched TL peak, T_{mq} . The solid line across the whole temperature region represents the values obtained from Eq. (1). (a) With $\eta(T)$ evaluated from I_m . (b) With $\eta(T)$ evaluated from peak area A . (c) With $\eta(T)$ evaluated from normalization.

Eq. (1). The only exceptions are two cases corresponding to the second order kinetics of broad and narrow reference TL glow-peaks at 360 K. These two cases are plotted as solid lines and are indicated by the arrow.

Another way to examine the approximation between Eq. (15) and Eq. (16) is to evaluate the W , C parameters using Eq. (15). From Eq. (1) and taking into account Eq. (16) one can obtain after some algebra:

$$\ln\left(\frac{A_u}{A_q} - 1\right) = \ln(C) - \frac{W}{kT_{mq}}. \quad (17)$$

Equation (17) represents a straight line with slope W and intercept $\ln(C)$. The resulting mean values from all reference TL peaks except the second order kinetics of broad and narrow reference peaks at 360 K (indicated by the arrow in Fig. 8b) were, $W = 0.641 \pm 0.013$ eV and $\ln(C) = 17.16 \pm 0.25$. The corresponding values for the second order kinetics of broad and narrow reference peaks at 360 K were $W = 0.546$ eV, $\ln(C) = 15.1$ and $W = 0.58$ eV, $\ln(C) = 15.95$ correspondingly.

Figure 8c represents a case found often in experiments, in which the unquenched area A_u is completely unknown but the thermal quenching parameters W and C are known. An example is the TL peaks of $\text{Al}_2\text{O}_3\text{:C}$ and all the TL peaks except the “110 °C” TL peak of quartz. The method that can be used to examine if the thermal quenching of such an experimental TL peak corresponds to known values of W and C was described by Kitis et al. [6]. The procedure is as follows:

1. From the TL glow-peak corresponding to the lowest experimental heating rate β_1 evaluate the T_{mq} , and then using the known W , C parameters evaluate the thermal quenching efficiency η , i.e., the $\eta(T_{mq}, \beta_1)$.
2. Assign the $\eta(T_{mq}, \beta_1)$ value to the TL peak area $A_q(\beta_1)$ obtained from the lowest heating rate.
3. Evaluate the $\eta(T_{mq}, \beta)$ values for all heating rates used, by the relation:

$$\eta(T_{mq}, \beta) = \frac{A_q}{A_q(\beta_1)} \eta(T_{mq}, \beta_1). \quad (18)$$

The above procedure is very useful in quartz studies during TL/OSL dating. The case of quartz is unique, because in the case of the “110 °C” TL peak there are experimental heating rates for which the unquenched values of peak area A_u can be obtained. This makes the evaluation of the thermal quenching parameters W , C an easy task. However, since thermal quenching take place at luminescence centers and quartz has several TL peaks at higher temperatures than the “110 °C” TL peak, one has to examine if all the other high temperature TL peaks are also thermally quenched with the same W , C parameters.

The tests of the above procedure are shown in Fig. 8c. It is interesting to note that the agreement with Fig. 8a is better

than, the agreement with Fig. 8b. The reason is that the normalization value of $\eta(T_{mq}, \beta_1)$ is evaluated directly from Eq. (1). The cases indicated by the arrow are the same as those of Fig. 8b.

The conclusions from the above simulated results can be summarized as follows:

1. The quantities I_{mq} and T_{mq} and peak area A_u from thermally quenched TL peaks can be safely used to evaluate the thermal quenching efficiency parameters W , C .
2. When I_{mq} cannot be evaluated accurately, the total peak area A_u can be used successfully instead.
3. When the unquenched values of I_{mu} and A_u are unknown, the evaluation of W , C becomes difficult.
4. When the unquenched values of I_{mu} and A_u are unknown but the thermal quenching parameters W , C are known, then the above method can be used to test the agreement of the experimental data with the known W , C values.

3.5 Reliability of the curve fitting method to thermally quenched TL peaks

The curve fitting techniques are among the basic tools of analyzing experimental TL data. There is a conceptual problem when the usual TL analytical expressions of first, second, and general order kinetics are used to fit thermally quenched TL glow-peaks and to analyze complex TL glow-curves. The reason is that a thermally quenched glow-peak is described by the equation $I_q(T) = I_u(T)\eta(T)$ (see Eq. (13)) and not by the unquenched form. A direct curve fitting using Eq. (13) is not practical and is limited only to single TL peaks, provided that in the temperature region of the TL glow-peak the $\eta(T)$ values are not too low [16]. It is, therefore, useful to examine how well the analytical expression $I(T)$ can fit a thermally quenched glow-peak.

The reference TL peak chosen (see Table 1) were: narrow second order TL peak at 470 K, narrow first order and narrow second order TL peak at 600 K. The TL peak at 470 K was chosen because its shape parameters vary with heating rate, and the peak at 600 K was chosen because thermal quenching has the strongest influence (see Figs. 6 and 7).

All selected reference TL peaks were fitted using the analytical expressions given by Eq. (9). The goodness of fit was tested by the figure of merit (FOM) [16].

In the case of the reference TL peak at 470 K the FOM values of the fitting was 0.2% at the heating rate of 0.5 K/s. As the heating rate increases the FOM value increases (becomes worst) up to 1.1% at a heating rate of 25 K/s. The activation energies E obtained are exactly similar to those from the peak shape methods shown in Fig. 7. This is not surprising since peak shape methods and curve fitting methods are equivalent in obtaining trapping parameters. On the other hand the fitting gave exact values for T_m , I_m , and the peak area A .

In the cases of a narrow second order reference peak at 600 K the FOM values of the fitting were from 1% at 0.5 K/s up to 1.8% at 27 K/s, whereas for the cases of narrow first

order reference peak at 600 K the FOM values of the fitting were from 2% at 0.5 K/s up to 3.5% at 27 K/s.

The conclusions from the above results can be summarized as follows:

1. The analytical TL expression describing an unquenched TL peak can be applied successfully to a quenched TL peak.
2. The worst FOM values (although acceptable) are obtained for first order peaks. The reason is that in the case of first order peaks the thermal quenching can reduce the symmetry factor μ_g to values lower than 0.42, as it is seen in Fig. 6b and c and curves (1a), (2a), (3a), and (4a).
3. One has to keep in mind that from the fitting of a quenched TL peak with an analytical expression describing an unquenched TL peak, the only reliable results are those for T_m , I_m , and the peak area A .
4. The trapping parameters (E , s , and b) approach reliable values only when in the temperature region of the TL glow-peak the thermal quenching efficiency η is larger than 0.7.

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