An efficient algorithm for computerized deconvolution of thermoluminescent glow curves

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ABSTRACT

The models employed so far for deconvolving thermoluminescent glow curves are either derived by neglecting the interaction among traps and resorting to the quasi-equilibrium approximation, or are simply phenomenological. Several published articles have shown that the approximations are difficult to justify. Further it has never been shown that they are rigorously applicable to any known system. As to the phenomenological model it is no physically meaningful. An algorithm is reported which allows analyses of glow curves without the aforementioned approximations.

1. Introduction

The computerized deconvolution of a thermoluminescent glow curves (CDTGC) requires the integration of a set of coupled differential equations describing the thermoluminescent model adopted. The following set of equations corresponds to the model shown in Fig. 1:

$$\frac{dn_1(t)}{dt} = -s_1 \cdot n_1(t)\exp\left(-\frac{E_1}{kT}\right) + A_{n1}(N_1 - n_1(t))n_c(t), \tag{1}$$

$$\frac{dn_2(t)}{dt} = -s_2 \cdot n_2(t)\exp\left(-\frac{E_2}{kT}\right) + A_{n2}(N_2 - n_2(t))n_c(t), \tag{2}$$

$$\frac{dh(t)}{dt} = -A_m n_c(t) \cdot h(t), \tag{3}$$

$$h(t) = n_1(t) + n_2(t) + n_c(t) + M. \tag{4}$$

With N_i and n_i the concentration of trap #i and the concentration of trapped electrons in it are respectively indicated. s_i stands for the attempt-to-scape frequency, E_i for the activation energy of trap #i. $s_i\exp\left(-\frac{E_i}{kT}\right)$ is the probability a trapped electron being freed. $A_{n,i}$ and $A_{m,i}$ denote the retrapping and recombination probabilities respectively of trap #i. M is the concentration of thermally disconnected traps, i.e., traps that retain the trapped electrons for the temperatures a sample is subjected to, and k the Boltzmann constant. Thermally disconnected traps are supposed to be fully occupied. The temperature is the absolute one.

This system of coupled differential equations has to be integrated taking into account the initial values $n_{01} = n_1(t = 0)$, $n_{02} = n_2(t = 0)$, $n_{c0} = n_c(t = 0)$ and $h_0 = h(t = 0)$. This is an impractical task because of the huge computational time required by deconvolutions: first of all the fitting algorithms employed in deconvolutions, such as the Levenberg-Marquardt method (L-M method), require that the set of coupled differential equations be integrated a large number of times and secondarily because the solutions of the differential equations can be unstable unless the step size of integration is taken to be extremely small (stiffness), which in turn contributes to increase computational times. To overcome both problems some approximations are made in order to obtain analytical expressions for the light intensity. The main approximation is the quasi-equilibrium approximation (QE). It assumes that $(dn_c)/dt \cong 0$ and $n_c \ll n$. The QE approximation and other approximations related to the relative values of trapping and recombination probabilities are applied to models like that shown

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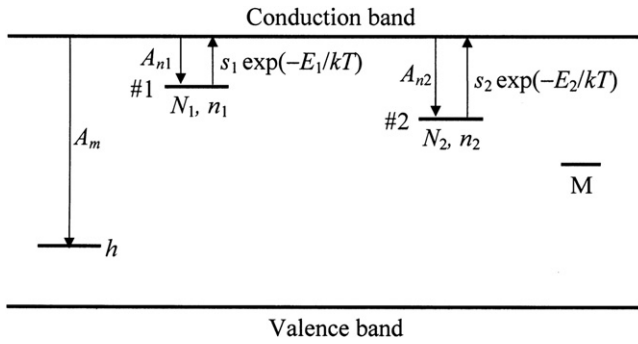E-mail address: ecaselli@exa.unicen.edu.ar (E. Caselli).

Fig. 1. model described by the set of coupled differential equations. n_c stands for the concentration of electrons in the conduction band and h for the concentration of holes in the recombination center.

in Fig. 1 but without trap #2. The resulting models are known as first, second and mixed order (FO, SO and MO respectively) (Chen and McKeever, 1997). Second and mixed orders are appropriate for glow curves having only one peak. Since most of the glow curves have two or more peaks, interaction between traps must be included, and no analytical expression for the light intensity can be obtained. For this reason an empirical model, dubbed general order (GO), has been put forward (May and Partridge, 1964). This model contains a parameter b which is not physically meaningful and is loosely related to retrapping. This model and FO are nowadays frequently used for glow curves having two or more peaks. The QE approximation is difficult to justify. Numerical studies have called into question the validity of the QE approximation (Lewandowski and McKeever, 1991; Marcazzo et al., 2007).

As stated above, since most glow curves are made up two or more peaks, interactions between traps must be included in the analysis of the kinetics (Sakurai, 2001; Sunta et al., 1999; Marcazzó et al., 2009). Thus when it comes to investigate the physics involved in the TL of a given compound the most frequently used models are not appropriate.

In the next section an algorithm is reported which allows the analysis of glow curves taking into account interaction among traps and without resorting to the QE approximation.

2. Algorithm

Glow curves are usually recorded by heating a sample at a constant heating rate, i.e. $T(t) = T_0 + \beta t$, where β stands for the heating rate. Thus equations (1)–(4) as functions of the temperature read:

$$\beta \frac{dn_1(T)}{dT} = -s_1 \cdot n_1(T) \exp\left(-\frac{E_1}{kT}\right) + A_{n1}(N_1 - n_1(T))n_c(T), \quad (1b)$$

$$\beta \frac{dn_2(T)}{dT} = -s_2 \cdot n_2(T) \exp\left(-\frac{E_2}{kT}\right) + A_{n2}(N_2 - n_2(T))n_c(T), \quad (2b)$$

$$\beta \frac{dh(T)}{dT} = -A_m n_c(T) \cdot h(T), \quad (3b)$$

$$h(T) = n_1(T) + n_2(T) + n_c(T) + M. \quad (4b)$$

Then the light intensity as a function of the temperature is given by:

$$I(T) = -\beta C \frac{dh(T)}{dT} = CA_m \cdot n_c(T) \cdot h(T). \quad (5)$$

C is a constant that takes into account the light collection by a phototube and its response. The following change of variable is made in Eqs. (1b) and (2b):

$$x_i(T) = \frac{n_i(T)}{N_i}, \quad i = 1, 2 \quad (6)$$

then

$$\beta \frac{dx_i(T)}{dT} = -s_i \cdot \exp\left(\frac{-E_i}{kT}\right) \cdot x_i(T) + A_{n1} \cdot (1 - x_i(T))n_c(T). \quad (7)$$

If $x0_i = x_i(T = T0) \leq 0.01$, Eq. (7) turns into:

$$\beta \frac{dx_i(T)}{dT} = -s_i \cdot \exp\left(\frac{-E_i}{kT}\right) \cdot x_i(T) + A_{ni} \cdot n_c(T). \quad (8)$$

Usually the doses for which Eq. (8) holds depend on the compound, but for most substances it holds for doses up to several tens of Gy. From Eq. (5),

$$n_c(T) = \frac{I(T)}{C.A_m \cdot h(T)}. \quad (9)$$

Here $I(T)$ is the experimental thermoluminescence curve.

Further, if $R_i = \frac{A_{ni}}{A_m}$, Eq. (7) can be written as:

$$\beta \frac{dx_i(T)}{dT} + s_i \cdot \exp\left(\frac{-E_i}{kT}\right) \cdot x_i(T) = \frac{R_i.I(T)}{C.h(T)}. \quad (10)$$

From Eq. (5) one has

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

By integration, Eq. (11) turns into:

$$h(t) = h_0 - \frac{\int_0^t I(u)du}{\beta \cdot C}, \quad (12)$$

where $h_0 = h(T = T_0)$.

$$\text{if} \quad F(T) = \int_{T_0}^T I(u)du \quad \text{then,} \quad (13)$$

$$h(T) = h_0 - \frac{F(T)}{\beta \cdot C}. \quad (14)$$

$F(T)$ can be found from the experimental thermoluminescence curve $I(T)$ by employing Eq. (13). Further, from Eq. (4) $h(\infty) = M$ since $n_1(\infty) = n_2(\infty) = n_c(\infty) = 0$ and from Eq. (14) $h(\infty) = h_0 - (F(\infty))/(\beta \cdot C)$. Thus

$$h(\infty) = M = h_0 - \frac{F(\infty)}{\beta \cdot C}, \quad (15)$$

from which

$$h_0 = M + \frac{F(\infty)}{\beta \cdot C}. \quad (15b)$$

Denoting by A the area of the thermoluminescence curve, i.e. $F(\infty)$, one gets:

$$C \cdot h(T) = M' + \frac{A}{\beta} - \frac{F(T)}{\beta}, \quad (16)$$

where $M' = C \cdot M$. Thus,

$$\beta \frac{dx_i(T)}{dT} + s_i \cdot \exp\left(\frac{-E_i}{kT}\right) \cdot x_i(T) = \frac{R_i \cdot I(T)}{M' + \frac{A}{\beta} - \frac{F(T)}{\beta}}. \qquad (17)$$

Multiplying both sides of Eq. (17) by $\exp\left(\frac{s_i}{\beta} \int_{T_0}^{T} \exp\left(-\frac{\epsilon_i \cdot T_0}{u}\right) du\right)$ and after some mathematical manipulations one obtains:

$$\frac{d}{dT}\left[\exp\left(s_i \int_{T_0}^{T} \exp\left(-\frac{\epsilon_i \cdot T_0}{u}\right) du\right) \cdot x_i(T)\right]$$

$$= \frac{R_i \cdot I(T) \cdot \exp\left(s_i \int_{T_0}^{T} \exp\left(-\frac{\epsilon_i \cdot T_0}{u}\right) du\right)}{M' + \frac{A}{\beta} - \frac{F(t)}{\beta}}. \qquad (18)$$

Where T_0 denotes the temperature at which the recording of a glow curve starts.

Integrating both sides of Eq. (18) between T_0 and T one obtains:

$$\beta \exp\left[s_i \int_{T_0}^{T} \exp\left(-\frac{\epsilon_i \cdot T_0}{u}\right) du\right] \cdot x_i(T) - \beta x_{0i}$$

$$= \int_{T0}^{T} \frac{R_i \cdot I(T) \cdot \exp\left(s_i \int_{T_0}^{T} \exp\left(-\frac{\epsilon_i \cdot T_0}{u}\right) du\right)}{M' + \frac{A}{\beta} - \frac{F(T)}{\beta}},$$

where $x_0 = x_i(T = T_0)$

Thus $x_i(T)$ can be written as

$$x_i(T) = x_0 \cdot \exp\left(-\frac{s_i}{\beta} \int_{T_0}^{T} \exp\left(-\frac{\epsilon_i \cdot T_0}{u}\right) du\right)$$

$$+ R_i \int_{T_0}^{T} \left[\frac{I(z)}{M' + \frac{A}{\beta} - \frac{F(z)}{\beta}} \cdot \exp\left(\frac{s_i}{\beta} \int_{z}^{x} \exp\left(-\frac{\epsilon_i \cdot T_0}{u}\right) du\right)\right] dz. \qquad (19)$$

From Eq. (4) one can get for $n_c(T)$:

$$n_c(T) = h(T) - n_1(T) - n_2(T) - M. \qquad (20)$$

Substituting $n_c(T)$ by the expression given by Eq. (9) one obtains:

$$\frac{I(T)}{C.A_m.h(T)} = h(T) - n_1(T) - n_2(T) - M, \qquad (21)$$

from which one gets

$$I(T) = C \cdot A_m \cdot h(T) \cdot [h(T) - n_1(T) - n_2(T) - M]$$

$$= \frac{A_m}{C} \cdot C \cdot h(T) \cdot [C \cdot h(T) - C \cdot n_1(T) - C \cdot n_2(T) - C \cdot M]. \qquad (22)$$

Calling, $R' = \frac{A_m}{C}$ and substituting $C \cdot h(T)$ by Eq. (16) one obtains:

$$I(T) = R' \cdot \left(M' + \frac{A}{\beta} - \frac{F(T)}{\beta}\right) \cdot \left(\frac{A}{\beta} - \frac{F(T)}{\beta} - C \cdot n_1(T) - C \cdot n_2(T)\right). \qquad (23)$$

Since $C \cdot n_i(T) = C \cdot N_i \cdot x_i \cdot (T)$,

$$I(T) = R' \cdot \left(M' + \frac{A}{\beta} - \frac{F(T)}{\beta}\right) \cdot \left(\frac{A}{\beta} - \frac{F(T)}{\beta} - N'_1 \cdot x_1(T) - N'_2 \cdot x_2(T)\right), \qquad (24)$$

where $N'_1 = C \cdot N_i$.

Equation (24), along with Eq. (19) for each trap center, can be used to fit the experimental glow curve. This is a kind of self-consistent calculation since experimental results are employed in the theoretical expression for $I(T)$, i.e., $I(T)$ itself and $F(T)$.

The procedure outlined is efficient when employing technical computing softwares, such as Matlab or Mathcad. Both softwares require the indication of the function which will be fitted to the experimental results. Thus the integration of the set of the differential equations must be indicated as a function. We employed Mathcad 8. The time required by the method we proposed takes 5 s to obtain $I(T)$, and the time required by the integration of the differential equations indicated as a function takes 15 s. It must be noted that deconvolution times depend not only on the time required for integrating the set of differential equations, but also on the speed with which the deconvolution algorithm converges to the solution. Thus if the deconvolution requires the integration of the differential equation 200 times, the use of the algorithm we proposed amounts to a reduction of the computing times of nearly 2000 s. This is why our algorithm is efficient.

The algorithm put forward in this article is robust because the problem of differential equations becoming stiff is overcome since it depends on simple mathematical operations and integrals.

In order to evaluate the algorithm put forward we employed it for deconvolving the dosimetric peak of the glow curve of BeO (Thermalox 995). In what follows we will refer to this model as the Interactive Trap Model (ITM).

3. Deconvolution of the main peak of BeO (Thermalox 995)

Samples of BeO were irradiated with electrons of a Sr-90 source having an activity of 10 mCi. Fig. 2 shows the glow curves for three different times of irradiation, namely, 672, 6720 and 67200 s. The doses correspond to nearly 0.2, 2 and 20 Gy respectively. The glow curves were recorded with a heating rate $\beta = 1\ K/s$.

A thorough analysis of the glow curve of BeO samples has been made by Bacci and Furetta (Bacci et al., 1989). They employed all the standard methods generally used to present. Later, Sakurai and Gartia perform the analysis by solving the system of coupled differential equations. They resorted to the Runge−Kutta−Gill method (Sakurai and K Gartia, 1996). The model they adopted has only one trap, namely, they did not take into account the high temperature peak. This approach can be used for glow curves showing the high temperature peak much smaller than the low temperature one, as the glow curve corresponding to 67200 s in Fig. 2. Since the high temperature peak changes a little with dose for doses resulting from irradiation times larger than 60000 s compared to the low temperature peak, it may be assumed that $(dn_2(t))/dt \approx 0$, i.e., the net traffic of electrons between the conduction band and the high temperature trap is negligible. In order to make tractable the numerical integration of the system of equations Sakurai and Gartia put forward a fitting procedure performed in two stages: first a set of parameters is allowed to vary $(E_1, s_1, A_{n1}$ and $M)$ and later the remaining one (A_m). Further they made the analysis assuming that $n_1 \approx N_1$ and $n_2 \ll N_1$, which is not a general situation.

In this article we report the analysis of the low temperature peak for doses far below saturation and higher than 20 Gy. For doses higher than 20 Gy the high temperature peak becomes much smaller than the low temperature peak and can be ignored. Thus
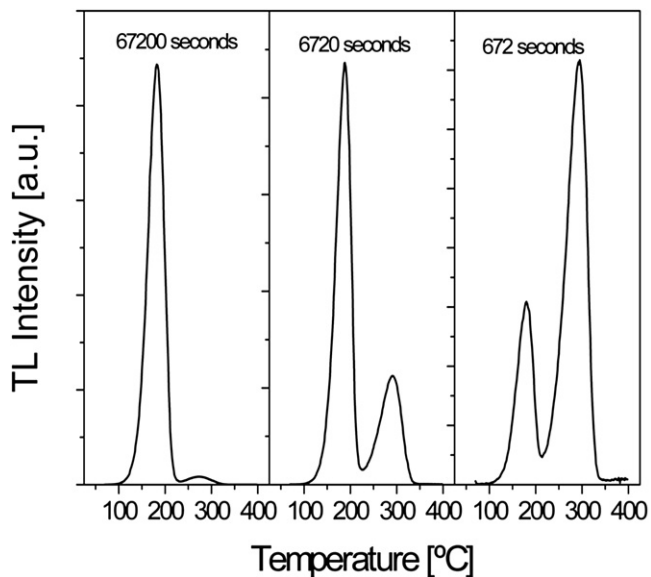
Fig. 2. Glow curves of BeO.

	Sakurai and Gartia	ITM
Heating rate (K s^{-1})	0.93	1.00
E (eV)	1.09	1.14
s (s^{-1})	4.58×10^{11}	3.02×10^{11}
$A_m N(s^{-1})$	0.26	
$A_m N(s^{-1})$	8.7×10^{-2}	
M/N	1.2	0.001
$R = A_n/A_m$	2.9	1.32×10^{-5}

position on dose. For instance, Sambhunath Singh et al. have analyzed the low temperature peak of BeO with the MO kinetics (Shambhunath Singh et al., 1998). The model contains a parameter α given by $\alpha = (N' \cdot x_0)/(N' \cdot x_0 + M')$. They obtained $\alpha = 0.85$, a value for which the peak maximum should shift to lower temperatures when the dose increases. Since a shift of the peak maximum is not observed by increasing the dose (see Fig. 2) the resulting parameters must be rejected.

The constancy of the peak position with dose is a characteristic of the FO kinetics. FO kinetics is obtained under the assumptions of negligible retrapping and the QE approximation. Since $R = 0.001$, the retrapping is negligible compared to the recombination. Fig. 3 depicts both the trap filling factor $x_1(T) = n_1/N$ (N = concentration of traps) and the normalized concentration of electron in the conduction band, n_c/N. As can be seen the QE approximation does not hold for temperatures above 420 K (see Fig. 4). It is worth noting that for temperatures above 470 K, when the trap is almost empty, there is a significant concentration of electrons in the conduction band which gives rise to a slower decrease of the peak than expected with FO kinetics. Thus the shape of the peak cannot be fitted with FO. A similar analysis applies to the deconvolution employing MO. As can be seen in figure 7 of the article by Shambhunath Singh et al. (1998), the curve resulting from MO kinetics lies below the experimental curve on the high temperature part of the peak because of the QE approximation.

It should be pointed that the position of a peak does not change with dose when the flux of electrons from the conduction band to a recombination center is much larger than the flux of electrons
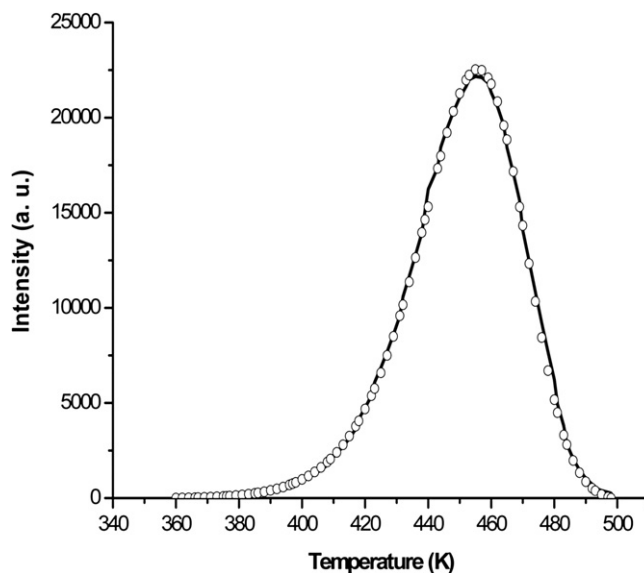
the net traffic of electrons between the conduction band and trap 2 is negligible compared to the traffic between the conduction band and trap1, i.e., $dn_2/dt \ll dn_1)/dt$. Thus equation (2) can be ignored. When a sample is irradiated the flow of electrons to a given trap is given by $A_{ni} \cdot (N_i - n_i)$. For doses up to 0.2 Gy $A_{n1} \cdot (N_1 - n_1) < A_{n2} \cdot (N_2 - n_2)$ since peak 2 is larger than peak 1. For higher doses $A_{m1} \cdot (N_1 - n_1) \gg A_{m2} \cdot (N_2 - n_2)$ as can be seen in Fig. 2. Assuming that the A_{n1}'s do not change with dose the findings can be explained by $N_2 - n_2 \approx 0$ for doses higher than 20 Gy and $N_1 \gg N_2$.

Under the aforementioned assumptions, the set of equations (1)–(4) reduces to:

$$\frac{dn_1(t)}{dt} = -s_1 \cdot n_1(t) \exp\left(-\frac{E_1}{kT}\right) + A_{n1}(N_1 - n_1(t))n_c(t), \quad (25)$$

$$\frac{dh(t)}{dt} = -A_m n_c(t) \cdot h(t), \quad (26)$$

$$h(t) = n_1(t) + n_c(t) + M. \quad (27)$$

For a constant heating rate, $T(t) = T_0 + \beta \cdot t$ and following the same steps leading to Eq. (24) we obtain:

$$I(T) = R' \cdot \left(M' + \frac{A}{\beta} - \frac{F(T)}{\beta}\right) \cdot \left(\frac{A}{\beta} - \frac{F(T)}{\beta} - N_1' \cdot x_1(T)\right). \quad (28)$$

Employing Eqs. (19) for $x_1(T)$ and (28) for $I(T)$, the resulting parameters from the fitting procedure are shown, along with the parameters reported by Sakurai and Gartia, in Table 1. Fig. 3 shows the low temperature peak and that obtained by fitting. The agreement between both values of the activation energy is quite good, as the agreement between both values of the attempt-to-scape frequency s. The values we found for both the normalized concentration of the thermally disconnected trap (M/N) and the ratio of the retrapping to recombination probability R differ significantly from those reported by Sakurai and Gartia. It is well known that by choosing different guess values several sets of parameters can be obtained having similar figure of merit (FOM) (Chen and McKeever, 1997). Thus criteria must be employed to discard those results which are not in accordance with experimental findings, such as, for instance, the dependence of the peak

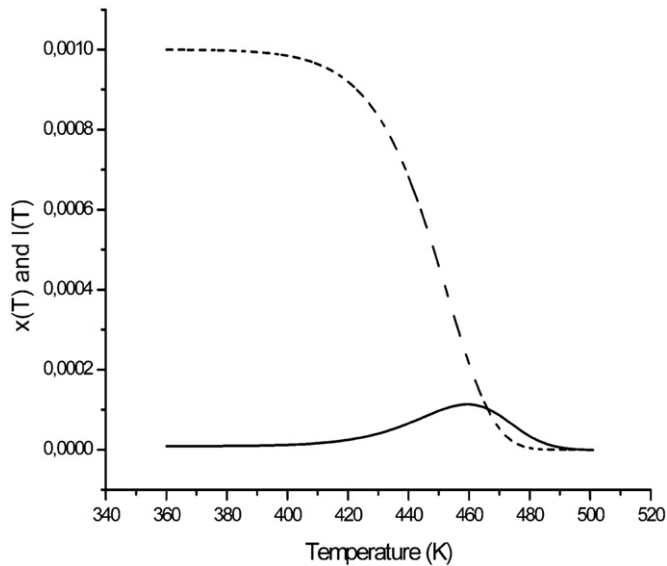**Fig. 3.** Experimental (solid line) and deconvoluted peak (circles).

Fig. 4. trap filling factor $x(T)$ (broken line) and filling factor of the conduction band $n_c(T)$ (solid line).

from the conduction band to the trapping center. This may happen in two situations: 1) the retrapping probability is low, i.e., $R \simeq 0$, as the result for R we have obtained ($R = 1.32 \times 10^{-5}$), or 2) there is a large concentration of fully occupied thermally disconnected traps M compared to the concentration of the trap N, as the result for $M > N$ obtained by Sakurai and Gartia, namely $M' = 1.2\ N'$ (see Table 1). We employed the parameters reported by them as guess

values and obtained a FOM of 5%. The FOM for the set of parameters we found is 1%. Thus, both sets of parameters are acceptable, and further investigation is necessary to establish which one is the correct one.

4. Conclusions

Both the model put forward in this article and the algorithm replacing the integration of the set of differential equations permit analyses of glow curves taking into account interactions among traps and without resorting to the QE approximation. The deconvolution of the glow curve of BeO (Thermalox 995) is an example of a compound whose glow curve cannot be analyzed with the kinetics employed so far.

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