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A new evaluation technique for analyzing the thermoluminescence glow curve and calculating the trap parameters

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Abstract

A step-fitting simulation technique was developed for the thermoluminescence (TL) glow-curve analysis and the kinetic trap parameters determination. These parameters include the order of kinetics b, the activation energy E (eV) and the pre-exponential factor S'' (s^{-1}). A general equation was developed to estimate the order of kinetics b. The characteristics point of this equation is that any set of three data points in a TL glow curve can yield the kinetics order. Using this characteristic, an improved procedure was suggested to separate a composite glow curve, which includes several overlapping peaks, into its individual components and to obtain the trap parameters of the glow peaks. The program was used to analyze the TL glow curve of the UV dosimetric material pure zirconium oxide (ZrO_2).

PACS: 78.60.Kn

Keywords: Thermoluminescence; Trapping parameters; Glow peaks; Zirconium oxide

1. Introduction

Most of insulating or semi-conducting materials exhibit a thermoluminescence (TL) glow curve with one or more peaks when the charge carriers are released. This glow curve is a graphical representation of TL emission as a function of time or temperature. This emission is due to heating of a substance after the absorption of energy from ionizing radiation. The glow curve is related to trap levels lie at different depths in the band gap, between the conduction and the valence bands of a solid. These trap levels are characterized by different trap parameters. Hence, several peaks are found to appear in the TL glow curve at characterized temperatures [1,2]. Therefore, the glow curve provides information about parameters corresponding to each peak. In order to obtain the physical parameters associated with the various TL bands, it is necessary to fit a theoretical equation containing these parameters to the entire glow curve [3].

The aim of this work is to present a procedure for separating the TL glow curve into its component of glow peaks. Also, this work aims to present a new technique for obtaining the trap parameters of the individual glow peaks in sequence by using a program based on the general-order of kinetics. These parameters include the order of kinetics b, the activation energy E (eV) and the pre-exponential factor S'' (s^{-1}). Also, the relative value of the initial concentration of trapped electrons n_o (cm^{-3}) can be obtained analytically. In this work, a general equation is developed to estimate the order of kinetics b. The applicability of this technique is demonstrated here by analyzing the TL glow curve of the ultraviolet new dosimetric material pure zirconium oxide (ZrO_2).

2. Thermoluminescence kinetics

For general-order kinetics, the behavior of TL intensity of a phosphor is governed by the following equation [4]:

$$I = -\frac{dn}{dt} = \frac{n^b}{N^{b-1}} S \exp\left(\frac{-E}{kT}\right) \quad (1)$$

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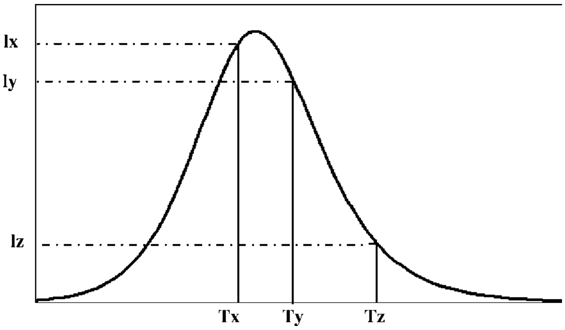

Fig. 1. An isolated TL glow peak. The parameters I_x, I_y, I_z, T_x, T_y and T_z are as defined in the text.

where I (in arbitrary units) is the TL intensity, n (cm^{-3}) the electron concentration trapped at time t (s), N (cm^{-3}) the traps concentration and k (eV/K) is the Boltzmann's constant. Eq. (1) is more general than the two equations describing the first- and second-order kinetics. The solution of Eq. (1) for $b \neq 1$ is given by [4]:

$$I = \frac{n_{\mathrm{o}} S'' \ \exp(-E/kT)}{\left[1 + [((b-1)S'')/\beta] \int_{T_{\mathrm{o}}}^{T} \exp(-E/kT')\, \mathrm{d}T'\right]^{b/(b-1)}} \tag{2}$$

where β ($\mathrm{K\,s^{-1}}$) is the linear heating rate and n_{o} (cm^{-3}) is the concentration of traps populated at the starting heating temperature T_{o} (K). The pre-exponential factor S'' (s^{-1}), which is defined as $S'' = S(n_{\mathrm{o}}/N)^{b-1}$ is constant for a given dose, but it varies with changing the absorbed dose, i.e., with n_{o} (cm^{-3}).

3. Determination of the trap parameters

Previously, several expressions have been suggested for obtaining b of a single glow peak [5–7]. These expressions assuming the concentration of populated traps at a temperature T_{i} during the TL run is proportional to the area A_{i}, where A_{i} is the area under the glow peak between the T_{i} and T_{f}, where T_{f} is the final temperature of the glow peak. As shown in Fig. 1, let us consider I_x is the TL intensity at a temperature T_x at any portion of the glow peak, Eq. (1), thus, becomes:

$$I_x = \frac{(A_x)^b}{N^{b-1}} S \exp\left(\frac{-E}{kT_x}\right), \tag{3}$$

where T_x (K) is the temperature corresponding to the intensity I_x, and A_x is the area under the glow peak between the T_x and T_{f}. Also, let us assume that $I_y = I_x/y$ and $I_z = I_x/z$ are the intensities at portions equal to $1/y$ and $1/z$ from the intensity I_x, respectively. Then, similar to Eq. (3), the following equations may be written:

$$I_y = \frac{I_x}{y} = \frac{(A_y)^b}{N^{b-1}} S \exp\left(\frac{-E}{kT_y}\right), \tag{4}$$

$$I_z = \frac{I_x}{z} = \frac{(A_z)^b}{N^{b-1}} S \exp\left(\frac{-E}{kT_z}\right), \tag{5}$$

where A_y and A_z indicate the areas under the glow peak from the temperatures T_y to T_{f} and T_z to T_{f}, respectively. As shown in Fig. 1, there are not any relations between the intensities at which T_x, T_y and T_z exist. Also, T_x can antecede T_y or vice versa and T_x may exist on the rising part whereas T_y can exist on the descending part of the glow peak.

From Eqs. (3) and (4) one obtains:

$$E = \{(\ln\, y) - b\, \ln[A_x/A_y]\} \left\{\frac{kT_xT_y}{T_x - T_y}\right\} \tag{6}$$

Also, from Eqs. (3) and (5) one obtains:

$$E = \{(\ln\, z) - b\, \ln[A_x/A_z]\} \left\{\frac{kT_xT_z}{T_x - T_z}\right\} \tag{7}$$

Now, by equating Eqs. (6) and (7), one can easily obtain:

$$b = \frac{T_y\,[T_x - T_z]\, \ln(y) - T_z\,[T_x - T_y]\, \ln(z)}{T_y\,[T_x - T_z]\, \ln\left[\frac{A_x}{A_y}\right] - T_z\,[T_x - T_y]\, \ln\left[\frac{A_x}{A_z}\right]}. \tag{8}$$

The order of kinetics b can be obtained after determining the parameters involved in Eq. (8).

Once the order of kinetics b is determined using Eq. (8), the activation energy E (eV) can be determined using Eqs. (6) or (7). Thereafter, the pre-exponential factor S'' (s^{-1}) in case of the general-order is obtained from Eq. (2). Thus [6,7]:

$$S'' = \frac{\beta E\ \exp(E/kT_{\mathrm{m}})}{\left[bkT_{\mathrm{m}}^2\right] - (b-1)\ E\phi \exp(E/kT_{\mathrm{m}})} \tag{9}$$

where T_{m} (K) is the temperature corresponding to the maximum intensity, I_{m}, of the glow peak and

$$\phi = \int_{T_{\mathrm{o}}}^{T_{\mathrm{m}}} \exp\left(\frac{-E}{kT'}\right) \mathrm{d}T'. \tag{10}$$

Therefore, once b and E are calculated and T_{m} is known, Eq. (9) can be used for obtaining S'' (s^{-1}), respectively. The last parameter to be obtained is the relative value of n_{o} (cm^{-3}). Usually n_{o} is not evaluated by using one of the analytical methods, but instead, n_{o} is taken either to be proportional to the height of the glow peak, I_{m}, at the peak temperature, T_{m}, or proportional to the area under the peak. However, instead of using the peak height or peak area, a simple analytical method has been developed to obtain the relative value of n_{o} in case of general-order glow peak, by inserting Eq. (9) into Eq. (2). In this case, an expression for the maximum intensity I_{m} can be found as [6]:

$$I_{\mathrm{m}} = \frac{n_{\mathrm{o}} S''\ \exp(-E/kT_{\mathrm{m}})}{((bkT_{\mathrm{m}}^2 S''/\beta\, E)\ \exp(-E/kT_{\mathrm{m}}))^{b/(b-1)}}. \tag{11}$$

Thus, n_{o} can be given as [6]:

$$n_{\mathrm{o}} = \frac{I_{\mathrm{m}}\ \exp(E/kT_{\mathrm{m}})}{S''} \left(\frac{bkT_{\mathrm{m}}^2 S''}{\beta E\ \exp(E/kT_{\mathrm{m}})}\right)^{b/(b-1)} \tag{12}$$

In Eq. (12), the parameters b, E, S'' and β are known, and the values of I_{m}, T_{m} can be obtained from the shape of the glow peak. Then, the relative value of n_{o} can be obtained.

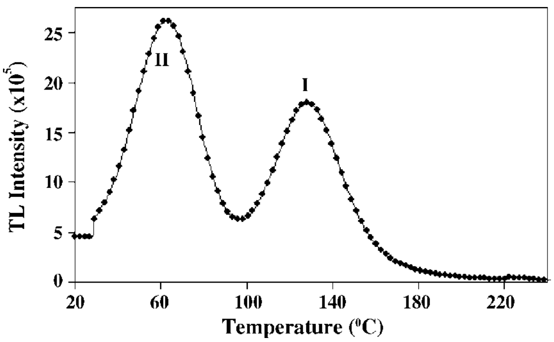

Fig. 2. TL spectrum of pure zirconium oxide samples under UV irradiation. The spectrum was measured with heating rate $\beta = 10\,^\circ\mathrm{C\,s^{-1}}$ [8].

4. Results

The above-mentioned technique will be used here to analyze and to obtain the trap parameters of the UV-irradiated pure zirconium oxide (ZrO_2) glow curve depicted in Fig. 2. The experimental details can be found elsewhere [8]. Recently, this material is used in the filed of UV dosimeter [8–12]. The glow curve as recorded with heating rate $\beta = 10\,^\circ\mathrm{C\,s^{-1}}$ shows two peaks: the higher one (peak I) at $T_\mathrm{m} = 129\,^\circ\mathrm{C}$ and the lower one (peak II) at $T_\mathrm{m} = 62\,^\circ\mathrm{C}$. Let us start with obtaining the trap parameters of the peak I. The value of b of this peak is calculated according to Eq. (8) at different intensities of the descending part starting from T_m. It is worth mentioning that, the rising part of this peak was not considered during the calculation due to apparent partial overlapping at this side with the lower temperature glow peaks of the glow curve. The values of b are obtained by fixing T_y and T_z with respect to T_x at intervals equal to 2.3 and 4.6 °C, respectively. The activation energy E is determined according to Eqs. (6) or (7), while the pre-exponential factor S'' ($\mathrm{s^{-1}}$) is estimated according to Eq. (9). Finally, the relative value of n_o is estimated according to Eq. (12). The values of E, S'' and n_o are determined for each calculated value of b. Fig. 3 shows the dependence of the parameters b, E, S'' and n_o on T_x. As shown in figure, the value of b starts to decrease quickly at the higher values of T_x, resulting in several orders of magnitudes reduction in the values of S''. Also, the values of the activation energy and n_o are affected with this fast decrease of b. Therefore, for this peak, the values of b is the result of calculations from the maximum intensity at temperature 129 up to 25% of the maximum intensity. The values of the parameters involved in this peak are listed in Table 1. Now using the average values of the parameters n_o, b, E, S'' and $\beta = 10\,^\circ\mathrm{C\,s^{-1}}$, the shape of higher temperature peak (I) is then fitted to Eq. (2). The theoretical peak, curve (b), with the average values of the trap parameters fits well to the experimental one, curve (a), as shown in Fig. 4. Using the previously determined theoretical shape of the higher temperature peak, curve (b), this peak is subtracted from the experimentally given glow curve, curve (a), to reveal the shape of the remaining part of the glow curve, curve (c) of Fig. 4.

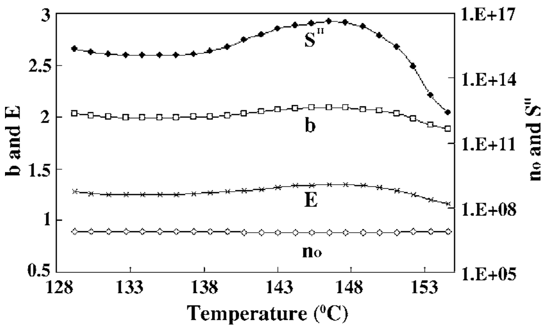

Fig. 3. The dependence of the trap parameters b, E, S'' and n_o of peak (I) on the temperature T_x.

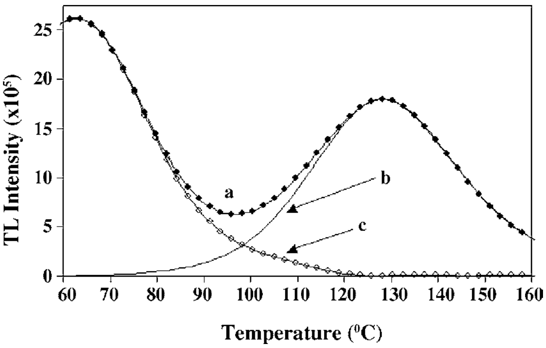

Fig. 4. Curve (a), a part from the experimental glow curve appearing in Fig. 2; curve (b), the theoretical glow peak (I) estimated according to Eq. (2) with $b = 2.02$, $E = 1.28$ eV, $S'' = 1.0 \times 10^{16}\ \mathrm{s^{-1}}$ and $n_\mathrm{o} = 7.5 \times 10^6$ (a.u.); curve (c), the remaining part of the experimental glow curve after of the subtraction of the theoretical peak (I) appearing in curve (b).

The above-mentioned procedures in case of peak (I) are then repeated to account for the peak (II) of the glow curve. Here, both the rising and the descending side of the peak have been used for obtaining b. The values of the trap parameters are listed in Table 1. Again, using the average values of the parameters n_o, b, E and S'', the shape of peak (II) is then fitted to Eq. (2). Again as shown in Fig. 5, the theoretical peak,

Table 1
Present method and CGCD data for the peaks I (129 °C), II (62 °C) and III (104 °C)

	Peak I (129 °C)		Peak II (62 °C)		Peak III (104 °C)	
	Present method	CGCD	Present method	CGCD	Present method	CGCD
b	2.02 ± 0.04	2.00	1.41 ± 0.04	1.4	1.00 ± 0.09	1.1
E (eV)	1.28 ± 0.04	1.29	0.71 ± 0.01	0.72	0.79 ± 0.06	0.82
S'' ($\mathrm{s^{-1}}$)	$(1.0 \pm 1.1) \times 10^{16}$	1.31×10^{16}	$(3.3 \pm 1.2) \times 10^{10}$	4.68×10^{10}	$(2.1 \pm 3.2) \times 10^{10}$	6.64×10^{10}
n_o (a.u.)	$(7.5 \pm 0.2) \times 10^6$	7.35×10^6	$(1.1 \pm .01) \times 10^7$	1.05×10^7	$(6.0 \pm 0.4) \times 10^5$	6.9×10^5

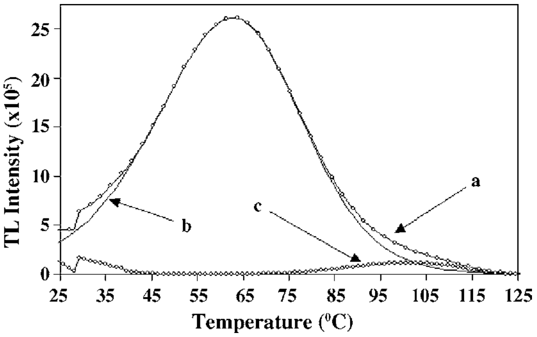

Fig. 5. Curve (a), typically the same as curve (c) in Fig. 4; curve (b), the theoretical glow peak (II) estimated according to Eq. (2) with $b = 1.41$, $E = 0.71$ eV, $S'' = 3.34 \times 10^{10}$ s^{-1} and $n_o = 1.1 \times 10^7$ (a.u.); curve (c), the remaining part of the glow curve after of the subtraction of the theoretical peak appearing in curve (b).

curve (b), with the average values of the trap parameters fits well to the remaining experimental one, curve (a). As shown in Fig. 5, curve (a) is equivalent with curve (c) of Fig. 4, i.e., the remaining part of the glow curve after of the subtraction of the theoretical peak (I). Using the previously determined theoretical shape of the lower temperature peak, curve (b) in Fig. 5, this peak is subtracted from the experimentally remaining glow curve, curve (a), to reveal the shape of the remaining part of the glow curve, curve (c). Now, we have a new overlapped small peak (III) between the main two peaks (I) and (II). The maximum intensity of this peak (III) appears at 104 °C.

Again, the above-mentioned processes in case of peaks (I) and (II) are then repeated to account for the peak (III) appearing at 104 °C. The average values of the trap parameters are listed in Table 1. Now using the average values of the parameters n_o, b, E and S'', the shape of peak (III) is then fitted to Eq. (2). The theoretical peak, curve (d), with the average values of the trap parameters fits well to the experimental one, curve (a), as shown in Fig. 6. Fig. 6 shows the deconvoluted glow curve estimated according to the average values of the trap parameters of the peaks appearing at 62, 104 and 129 °C, which fits well to the experimental one except a small shoulder at the rising part of the glow peak (II), as shown in Fig. 5, curve (c). We believe this shoulder is the lower part of the descending side of a fourth peak is not fadeout completely at this degree of temperatures. We did not try – by the present method – fitting of this shoulder for reasons of inconsistency.

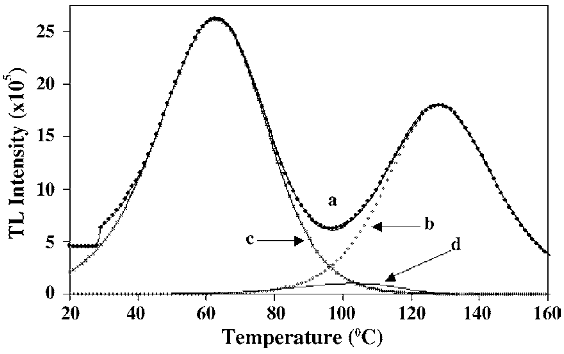

Fig. 6. Curve (a), a part from the experimental glow curve appearing in Fig. 2; curve (b), the theoretical glow peak (I); curve (c), the theoretical glow peak (II); curve (d), the theoretical glow peak (III) at 104 °C estimated according to Eq. (2) with $b = 1.00$, $E = 0.79$ eV, $S'' = 2.1 \times 10^{10}$ s^{-1} and $n_o = 6.0 \times 10^5$ (a.u.).

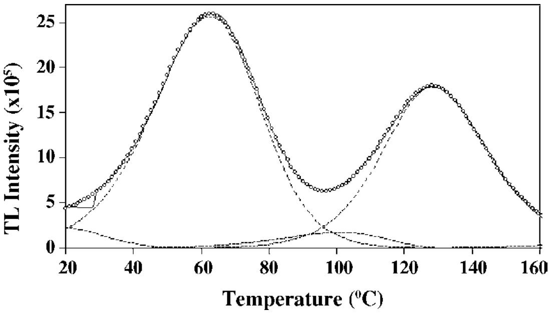

Fig. 7. The glow-curve deconvolution analysis of ZrO_2.

5. Discussion

Several methods are applied now to obtain the trap parameters of TL glow peak [13–18]. However, the main problem of measuring the trap parameters is the presence of several overlapping peaks within the TL glow curve. Very few methods exist, which allow for the separation of the TL glow curve into its individual components [7,19,20]. It is worthwhile mentioning that many scientists in the field of TL measurements use the least square method of non-linear function for computerized glow-curve deconvolution (CGCD). The application of CGCD technique for the decomposition of a composite thermoluminescence (TL) glow curve into its individual glow peaks is widely applied since 1980. The deconvolution method, applied to the TL glow curve allows getting the kinetics parameters. Many functions describing a single glow peak have been proposed, which are reviewed by Horowitz and Yossian [21]. In order to improve the value of the present work, the glow curve of ZrO_2 was analyzed also using the CGCD technique as described by Furetta et al. [22]. For this analysis, Eq. (2) was used for the deconvolution of a glow peak. The results of this deconvolution are shown in Fig. 7, and the trap parameters of the present method and the CGCD method are listed in Table 1. The results of the CGCD technique are very close to that obtained by the present method.

We applied in this paper to an improved technique for obtaining the trap parameters of overlapped TL glow peaks. The program begins with obtaining the trap parameters of the higher temperature glow peak by using the descending side of this peak. In all kinetic measurements on TL materials, methods or procedures must be chosen so as to eliminate or account for the effects of overlapping of the different glow peaks. We believe at this side of temperatures that the contribution due to the other peaks is negligible comparing with the peak under investigation. As it is above explained, this part of the peak is used successfully to obtain the trap parameters of the higher temperature peak of ZrO_2.

Another problem that must be mentioned here is actually related to the determination of the kinetics order b, where earlier authors have suggested several methods to obtain the trap parameters of TL glow peak. However, the difficulties arise due to the absence of previous knowledge regarding to the kinetics order b of the peak. The most important method for obtaining b is the symmetry factor μ_g. The difficulties with respect to the use of μ_g for obtaining b have been demonstrated elsewhere [5,6]. However, instead of using μ_g, several independent expressions have been derived which give the value of b in terms of its temperatures and areas at certain portions of the increasing and decreasing part of the glow peak [7]. In these expressions, a relative relation between the intensities must be existed for the selected portions of the peak. Here, Eq. (8) is a general expression of b, can be solved with respect to any three portions of the peak, where there are or there are not any systematic relation between these portions. Therefore, the old expressions of b may be considered as special cases of the general case obtained by using Eq. (8). Not only the above-mentioned merits of Eq. (8) but also it can be solved at any three portions rather than at the maximum intensity, I_m, of the glow peak.

Also, in this work, a complete system is presented to obtain the trap parameters involved in TL technique in sequence. These parameters include b, E (eV) and $S''(s^{-1})$. Consequently, one can obtain all of the above-mentioned trap parameters in one-run of TL glow peak and can fit the experimental results by using Eq. (2) for the general-order kinetics without extracting parameters with the assistance of other methods, such as initial rise methods, the peak shape methods or the isothermal decay method.

The above-mentioned technique has been used successfully to analyze the composite TL glow curve of the UV dosimetric material pure zirconium oxide (ZrO_2). According to this analysis, three peaks are detected at 62, 104 and 129 °C under UV irradiation. The trap parameters of the above-mentioned peaks are listed in Table 1. These values of parameters fit well the experimental curve of ZrO_2 as shown in Fig. 6. We believe the difficulty of applying the present technique to the highly complex TL glow curve. This may illustrate the limitations of the present technique.

6. Conclusion

In this paper, we apply to an improved technique of separating a complex TL glow curve includes several glow peaks into its components. The program begins with obtaining the trap parameters of the higher temperature glow peak by using the descending part of this peak. The shape of this peak is then fitted to the general-order kinetics. The theoretical peak with the average values of the trap parameters can fits well to the apparent parts of the experimental one. Subtraction of the higher temperature peak from the combined glow curve reveals the shape of the descending part of the pre-higher temperature peak. The above-mentioned process in case of the higher temperature glow peak is then repeated to account for the next peaks of the glow curve. The applicability of the present work are demonstrated by analyzing and fitting the composite TL glow curve of the UV dosimetric material pure zirconium oxide (ZrO_2).

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