



An improved experimental procedure of separating a composite thermoluminescence glow curve into its components

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Abstract

We present an improved experimental procedure of separating a composite thermoluminescence glow curve into its components. Careful monitoring of the isothermal cleaning process using the initial rise method ensures the complete thermal removal of TL peaks. Digital subtraction of two experimental TL glow curves yields individual experimental TL glow peaks. Several standard methods (initial rise and whole glow curve) are used to obtain the energy values and frequency factors of the traps. The method has been used successfully to analyze the well-known composite TL glow curve of the dosimetric material LiF (TLD-100). The limitations of the method are illustrated by analyzing the highly complex TL glow curve of a UV irradiated synthetic calcite consisting of at least 6 TL peaks. Although the method works best for TL glow curves described by first order kinetics, it should also be applicable to more general kinetics. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

One of the important experimental problems in thermoluminescence (TL) is the presence of several overlapping peaks within the TL glow curve. Very few experimental methods exist which allow decomposition of the TL glow curve into its individual components.

The purpose of the present communication is to present an improved experimental procedure of separating a composite thermoluminescence glow curve into its component TL peaks. The method combines several well known techniques in a systematic manner which allows us to obtain the complete TL peaks *experimentally*. Once the data for the TL peak is obtained using the procedure, a number of techniques can be used to

obtain the kinetic parameters E , s and b of the TL peak.

The experimental protocol described here was used successfully for the well known dosimetric material TLD-100 which consists of five overlapping TL peaks. The limitations of the procedure are illustrated by applying it to the highly complex TL glow curve of a high purity synthetic calcite. Although considerable amount of digital data processing and experimental work is required for the present procedure, we obtained good results for the two materials studied. The limits of applicability of the method and the necessary conditions for its successful use are discussed.

2. Experimental

The LiF:Mg,Ti (TLD-100) powder used in this

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study was commercially obtained from Harshaw Chemical Co. The TLD-100 and calcite powders in this experiment are irradiated for 5 min using a UV source with an average wavelength of 350 nm. The TL glow curves are measured immediately after, with no post irradiation annealing employed. The calcite powder employed in this study is a high purity synthetic calcite powder (diameter 45–60 μm , 99.995% purity). Some of the TL characteristics of this calcite powder have been described previously (Pagonis and Michael, 1994; Pagonis et al., 1996).

The TL glow curves were recorded with a conventional Daybreak TL equipment and a 9635QB photomultiplier tube using photon counting. The data was collected with a microcomputer and the black body radiation was digitally subtracted. All TL glow curves were recorded using an Oriol Corporation narrow band interference filter with a peak transmission at 480 nm. The transmission coefficient of the filter is 30% with a narrow transmission band with a FWHM of ± 5 nm. In addition to the narrow interference filter, a HA-3 infrared rejecting filter is used to reduce ther-

mal noise. The narrow filter at 480 nm is used to ensure the detection of almost monochromatic radiation from the samples. All TL glow curves were measured under nitrogen flow with heating rates of 1°C/s for TLD-100 and 4°C/s for the calcite measurements. The error bars shown on the data curves represent the standard deviation of at least five runs performed with different aliquots of the powders.

3. Description of the experimental procedure

The main steps involved in our experimental procedure can be summarized as follows:

Step 1: As a first step, the well known $E-T_{\text{stop}}$ method or the T_m-T_{stop} method of analysis introduced by McKeever (1985) are used to determine the approximate number of peaks in the TL glow curve.

Step 2: After irradiation, the specimen are annealed isothermally at a temperature much lower than the maximum of the first TL peak. In our studies a temperature of about 20–30°C below the TL peak maximum was found to be adequate. Upon measurement of the TL glow curve, the first peak in the glow curve is found to be reduced in height while the height of the higher temperature peaks remains unaffected. An example of this step as applied to a glow curve consisting of peaks 3 and 4 of TLD-100 is shown in Fig. 1. Isothermal annealing reduces the height of peak 3 at 145°C, while peak 4 at 190°C remains unaffected.

Successful application of this step in the procedure is based on three assumptions, namely:

- (1) that successive peaks in the TL glow curve are sufficiently separated in energy E and frequency factor s for the method to be applicable. Furthermore, the traps are assumed to be thermally disconnected;
- (2) that good reproducibility of the TL signal is obtained in successive measurements of the TL glow curve; and
- (3) that there is a small amount of shifting or no shifting of the first TL peak in temperature for various annealing times.

Most dosimetric materials satisfy conditions (a) and (b), while condition (c) limits the applicability of the method to first order kinetics or at least to samples exhibiting small amount of retrapping. These limitations in the experimental procedure are further discussed in Section 5.

Step 3: The energy E of the first peak in the TL glow curve is determined using the initial rise portion of the TL glow curve. A plot of the natural logarithm of the TL signal as a function of the inverse temperature $1/T$ yields a line of slope $-E/k$ where k = Boltzmann constant. Accurate monitoring of the energy E

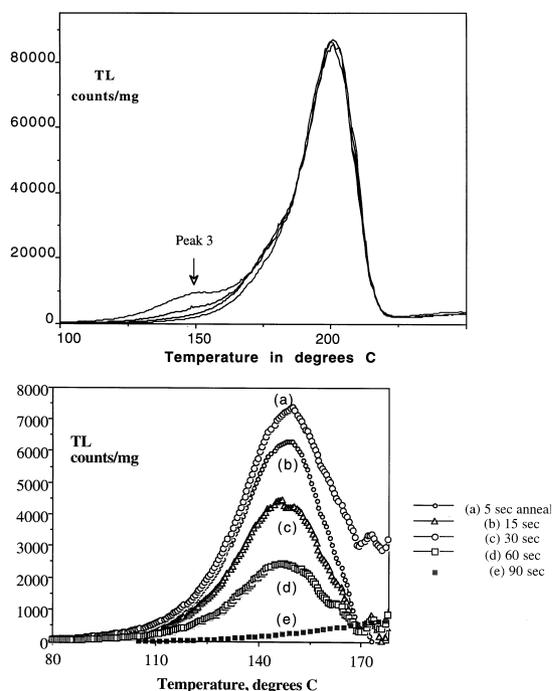


Fig. 1. (a) An example of the systematic thermal cleaning procedure as applied to a glow curve consisting of peaks 3 and 4 of TLD-100. Isothermal annealing at 120°C reduces the height of peak 3 at 145°C, while peak 4 at 190°C remains unaffected. (b) The same TL glow curves shown magnified in the low temperature area. Curve (e) corresponds to the complete thermal removal of peak 3 in TLD-100.

at this step is an essential part of the procedure. An abrupt change in the value of E will signify the complete removal of the first peak from the TL glow curve and the onset of the second TL peak.

Steps 2 and 3 are repeated several times for different annealing times until an abrupt change in the E values signifies the complete thermal removal of the first TL peak. The result of successive applications of steps 2 and 3 and the associated monitoring of the E values are shown in Fig. 2. It can be seen that curve (e) corresponds to the complete thermal removal of peak 3 at 145°C and the onset of peak 4 at 190°C.

Step 4: By digitally subtracting the TL glow curve

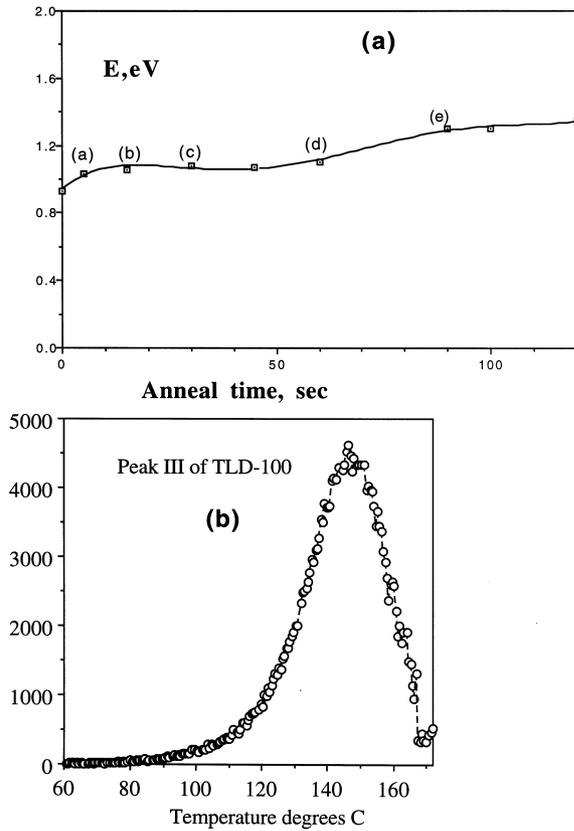


Fig. 2. (a) The energy E of peak 3 in the TL glow curve of TLD-100 is monitored using the initial rise portion of the TL glow curve. The E -values are obtained as usual from a plot of the natural logarithm of the TL signal as a function of the inverse temperature $1/T$. The abrupt change in the value of E signifies the complete removal of peak 3. The letters (a)–(e) correspond to the letters on Fig. 1(b). The curve is a guide to the eye. (b) By digitally subtracting curve (e) from the original TL glow curve we obtain experimentally the complete shape of peak 3.

obtained in steps 2 and 3 from the original TL glow curve we obtain the complete shape of the first TL peak *experimentally*. The result of subtracting curve (e) in Fig. 1 from the original TL glow curve is shown in Fig. 2(b).

Step 5: Having obtained the shape of the TL peak in the above manner, we can now apply the whole glow curve method of analysis to obtain the kinetic parameters E , s and b (McKeever, 1980, p. 85). The whole glow curve method is independent of the kinetics of

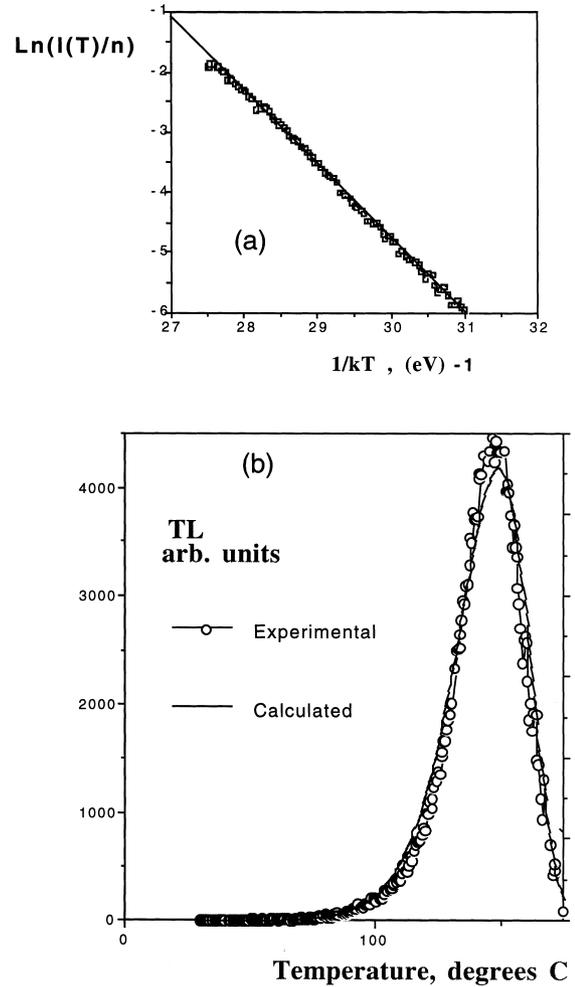


Fig. 3. (a) Application of the whole glow curve method of analysis to peak 3 of TLD-100. A plot of $\ln(TL/n)$ yields a straight line only for the correct value of the kinetic order $b = 1$. The slope and the intercept of the graph are used to find the energy $E = 1.05$ eV and the frequency factor $s = 2 \times 10^{11}$ Hz. Here TL is the intensity at temperature T and n represents the area under the TL peak beyond temperature T . (b) The calculated TL curve using the E , s and b values from (a) are compared with the experimental data.

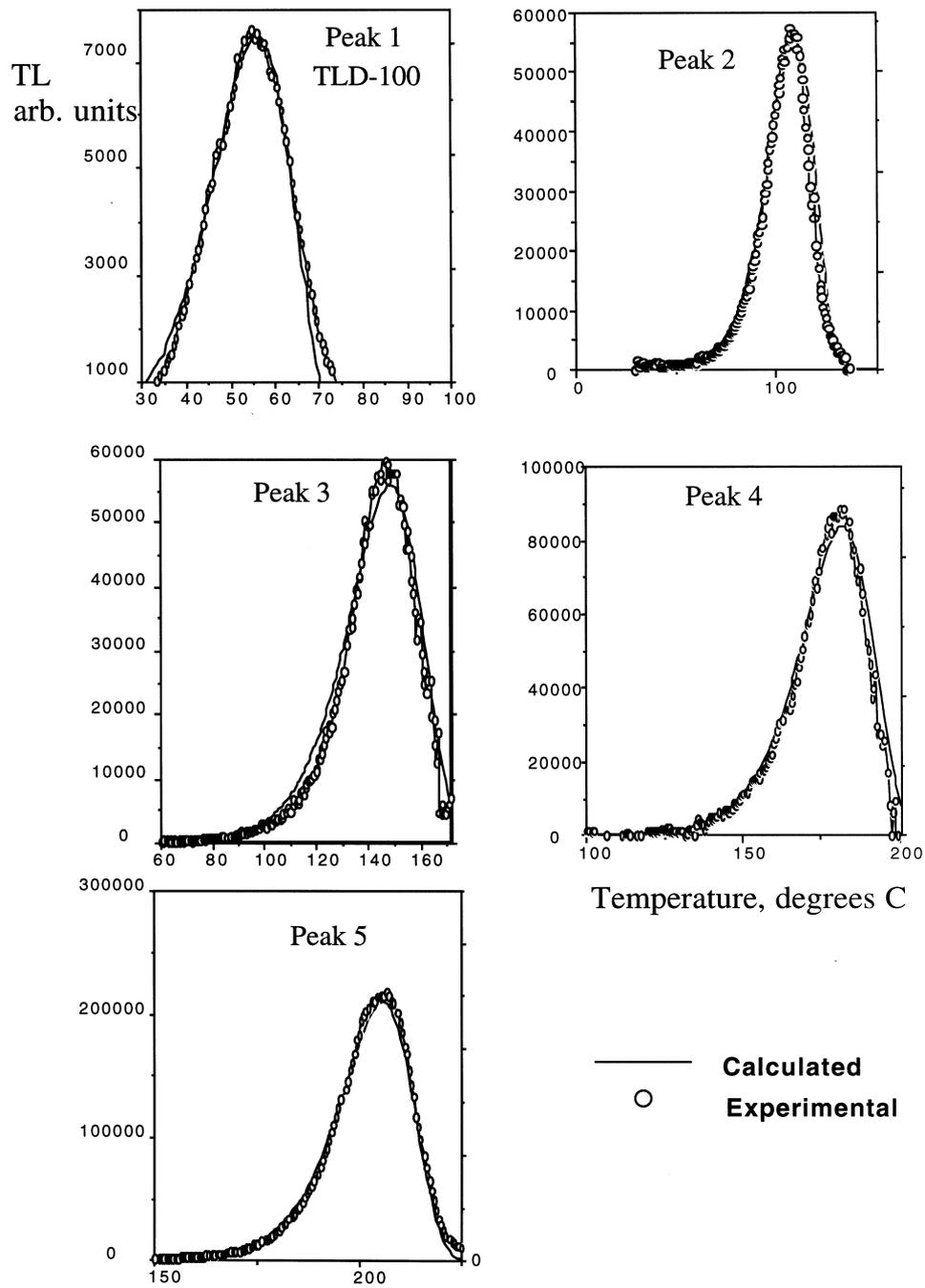


Fig. 4. Results of applying the procedure to the 5 peaks of TLD-100. The parameters E , s and b used in calculating the TL curves for TLD-100 are given in Table 1. The size of the circles corresponds to the standard deviation of 5 runs with different aliquots.

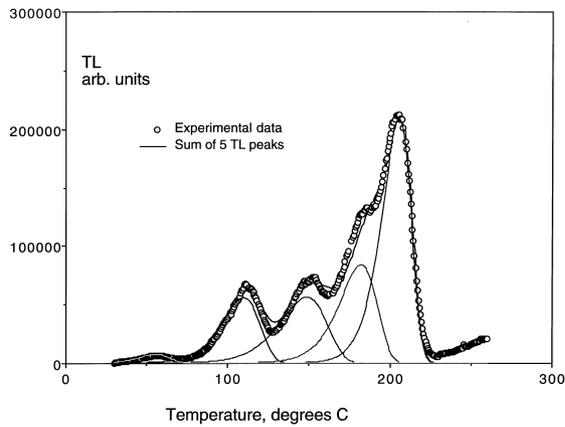


Fig. 5. Reconstruction of original TL glow curve for TLD-100. The size of the circles corresponds to the standard deviation of 5 runs with different aliquots. Calculation and experiment agree well within the experimental uncertainty.

the TL peak. A plot of the quantity $\ln(TL/n^b)$ vs the inverse temperature $1/T$ yields a straight line only for the correct value of the kinetic order b . Here TL is the intensity at temperature T and n represents the area under the TL peak beyond temperature T . The slope and the intercept of the graph are used to find the energy E and the frequency factor s .

Fig. 3 shows the application of this type of analysis to peak 3 of TLD-100; the graph in Fig. 3(a) yields a first order kinetics ($b = 1$) and the values $E = 1.05$ eV and $s = 2 \times 10^{11}$ Hz for the frequency factor. Fig. 3(b) shows a comparison of the calculated TL curve using these parameters E , s and b with the experimental data. At this point a least squares fit procedure can be used to optimize the values of E and s . As shown in Table 1, there is good agreement between the values of

E obtained using the initial rise and whole glow curve methods within the statistical uncertainty of the experiment.

Step 6: Steps 2–5 are now repeated for each successive TL peak in the glow curve. The result of applying our procedure to all 5 peaks in the TL glow curve of TLD-100 are shown in Fig. 4. Very good agreement between the experimental and calculated TL peaks is obtained. Table 1 compares the E , s , b values obtained in our study of TLD-100 with previous published values by Fairchild et al. (1982a,b).

Step 7: Reconstruction of the original TL glow curve — as a last step in the procedure, the five calculated TL peaks are summed in order to reconstruct the original TL glow curve. This step serves as a self-consistency test for successful application of the procedure. Any small satellite peaks which are not resolved by the procedure will show up as poor fitting to the original TL glow curve data. Examples of applying this step to TLD-100 and to the calcite sample are shown in Figs. 5 and 7 and are discussed in Section 4.

4. Experimental results

4.1. TLD-100

The TL glow curves for this material contain distinct TL peaks at 65, 105, 130, 145, 180 and 205°C when measured with a heating rate of 1°C/s. The values of E , s and b obtained in our study are summarized in Table 1 and are in close agreement with the 480 nm data of Fairchild et al. (1982a,b). Further comments on the E , s values for peak 5 are found in Section 5.

Table 1
Thermoluminescence kinetic parameters for TLD-100

| Fairchild et al. (1982a,b) | | | | Our data | | | | |
|----------------------------|---|----------|--------------------|--|---------------------------------------|----------|--------------------|-----|
| Peak No. | Peak temperature ($\beta = 0.17^\circ\text{C/s}$) | E (eV) | s (Hz) | Peak temperature ($\beta = 1^\circ\text{C/s}$) | E (eV) calculated from INITIAL RISE | E (eV) | s (Hz) | b |
| 1 | 62 | 1.04 | 10^{14} | 65 | 1.07 ± 0.02 | 1.00 | 2×10^{14} | 1 |
| 2 | 94 | 1.07 | 10^{13} | 105 | 1.04 ± 0.02 | 1.07 | 10^{13} | 1 |
| 3a | 112 | 0.99 | 10^{11} | 130 | — | — | — | — |
| 3 | 137 | 1.05 | 10^{11} | 145 | 1.15 ± 0.02 | 1.05 | 2×10^{11} | 1 |
| 4 | 170 | 1.54 | 4×10^{15} | 180 | 1.50 ± 0.02 | 1.54 | 10^{16} | 1 |
| 5 | 190 | 2.20 | 10^{22} | 205 | 2.20 ± 0.02 | 2.20 | 2×10^{22} | 1 |

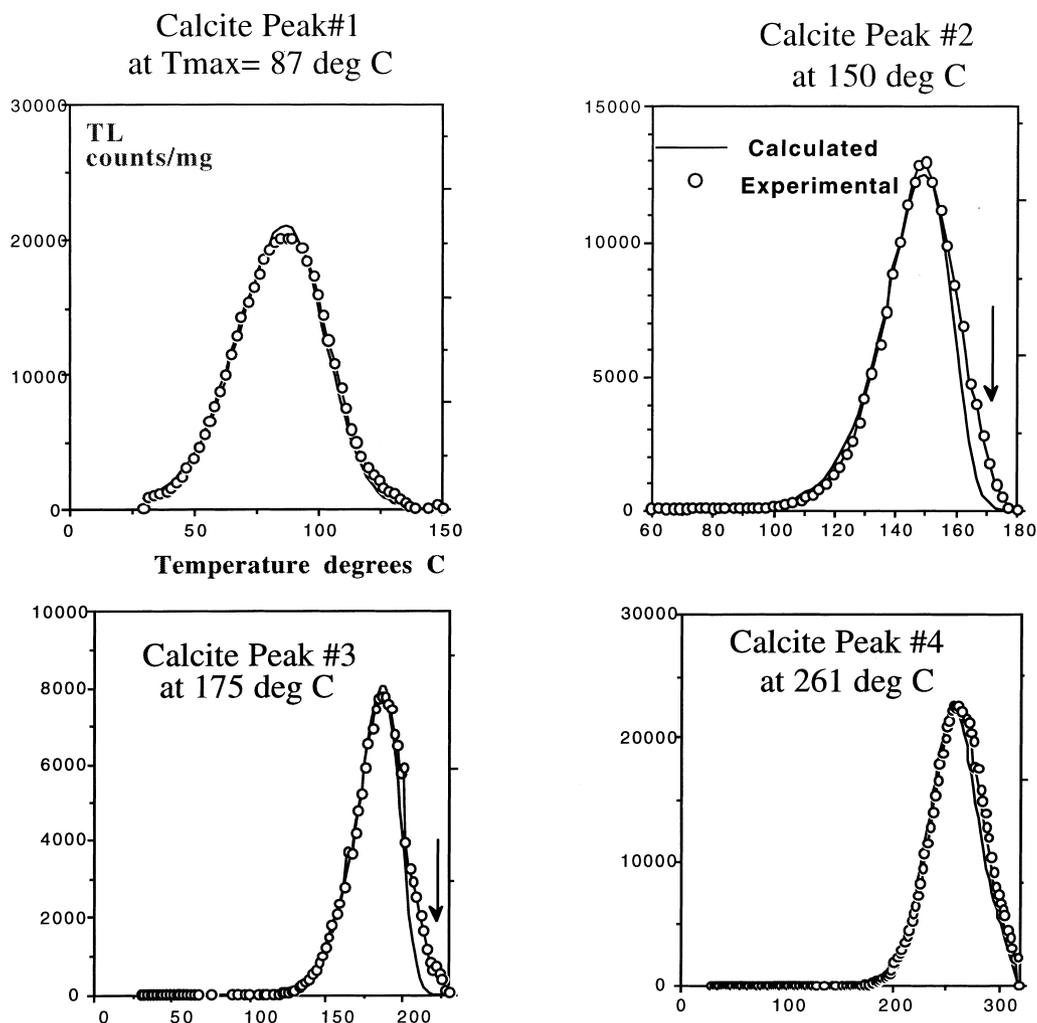


Fig. 6. The 4 overlapping TL peaks in the complex TL glow curve of calcite are analyzed using the procedure. The parameters E , s and b used in calculating the TL curves for calcite are given in Table 2. Disagreement between the calculated and experimentally determined TL peaks is due to two small satellite peaks shown by the arrows.

4.2. High purity synthetic calcite powder

As a second example of the applicability of our

procedure we used the highly complex TL glow curve of a synthetic calcite powder. The TL glow curves obtained after a 5 min UV irradiation of the

Table 2
Thermoluminescence kinetic parameters for UV-irradiated synthetic calcite

| Peak No. | Peak temperature ($\beta=4^{\circ}\text{C/s}$) | E (eV) calculated from INITIAL RISE | E (eV) Calculated from whole glow curve | s (Hz) | b |
|----------|--|---------------------------------------|--|--------------------|-----|
| 1 | 87 | 0.73 | 0.72 | 7×10^8 | 1 |
| 2 | 150 | 1.43 | 1.41 | 2×10^{16} | 1 |
| 3 | 175 | 1.50 | 1.32 | 5×10^{13} | 1 |
| 4 | 261 | 1.54 | 1.59 | 1×10^{15} | 2 |

synthetic calcite powder show overlapping TL peaks at 87, 150, 175, 261, 300 and 380°C. We note that the first TL peak at 90°C has been shown previously to correspond to a distribution of Energy values (Pagonis et al., 1996).

Fig. 6 shows the 5 TL peaks obtained when the procedure described in this paper is used. Application of the whole glow curve method yields the best straight lines when a value of $b = 1$ is used for the TL peaks at 87, 150 and 175°C and a value of $b = 2$ is used for the TL peak at 261°C. Fig. 6(b) and 6(c) show disagreements between the experimentally determined and the calculated TL peaks when the values of E , s from the whole glow curve are used, especially on the high temperature end of the data. The disagreement is due to two small satellite peaks which are shown by the arrows in Fig. 6.

Even though straight lines with correlation coefficients as high as 99.5% are obtained when applying the whole glow curve method, there is disagreement between calculation and experiment. We note that the applicability of the whole glow curve and peak shape methods have been questioned recently by Sunta et al. (1999) and will be discussed in the last section of the paper.

The two small satellite peaks are shown clearly when we attempt to reconstruct the original TL glow curve as in Fig. 7. These two peaks lie beyond the resolution limit of the procedure and show up at the location of the arrows.

5. Discussion and conclusion

The feasibility and usefulness of the systematic procedure described here were shown by applying it to TLD-100. Table 1 shows the E , s values for peaks 1–5 in good agreement with the 480 nm values of Fairchild et al. (1982a,b). Some comments are necessary concerning the unusual value of $s = 2 \times 10^{22}$ Hz for peak 5. The kinetic parameters of peak 5 of TLD-100 have been the subject of several studies and controversy. Different methods used by various authors have yielded a wide range of E , s values perhaps due to the underlying complexity of the kinetic process. For an extensive summary of this topic (see, for example, Chen and McKeever, 1997, p. 465).

The values of E , s reported here for peak 5 were obtained using an isothermal cleaning technique and whole glow curve analysis similar to the one introduced by Taylor and Lilley (1978). We also note that the combination of thermal cleaning and digital subtraction of TL glow curves in our procedure has several similarities to the method of Taylor and Lilley (1978) which was applied successfully in decomposing

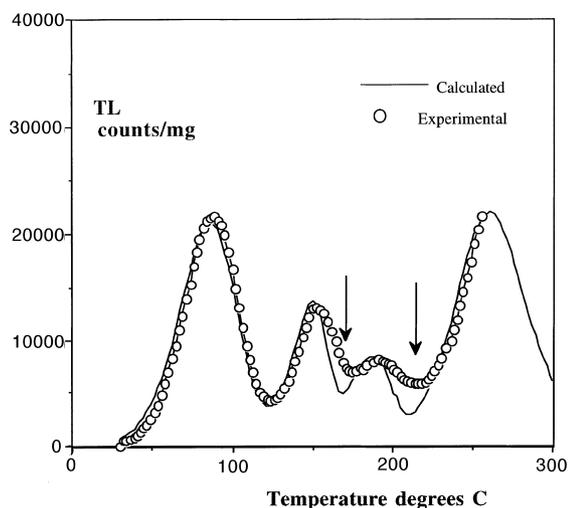


Fig. 7. Reconstruction of the original TL glow curve for calcite shows clearly the two small satellite peaks which lie beyond the resolution limit of the procedure.

the TL glow curve of LiF (TLD-100). Their method requires the presence of a high temperature TL peak with a “clean” descending part while the present procedure requires a clean ascending part of the TL peak. Not surprisingly, the method of Taylor and Lilley (1978) and the present procedure yield very similar values for peak 5.

Application of the procedure to the highly complex TL glow curve of synthetic calcite illustrates the limitations of the technique. The E , s values of the TL peaks must be reasonably separated from each other, an inherent problem for most experimental and computerized fitting techniques of this type. Most importantly, the method illustrates that the whole glow curve, initial rise and peak shape methods must be used carefully since they can lead to misleading values of E , s and b . Recently the limitation of the applicability of the initial rise and peak shape methods were discussed by Sunta et al. (1999) who found that these methods yield low values when the sample is irradiated near saturation and/or strong retrapping is present.

The strongest advantage of using the present experimental protocol is the ability to obtain the individual TL peaks *experimentally*. The procedure described here is most useful when first order kinetics or small retrapping is involved, because of the minimal shifting of TL peaks in temperature during the isothermal annealing. We believe that use of the present procedure in conjunction with computerized peak fitting methods can be a valuable tool of analysis.

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