

## DETAILED KINETIC STUDY OF THE THERMOLUMINESCENCE GLOW CURVE OF SYNTHETIC QUARTZ

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**Abstract** — A detailed kinetic analysis has been performed of the thermoluminescence (TL) glow curve of high purity synthetic quartz. The kinetic parameters of the glow peak at 110°C were evaluated for doses ranging from 0.1 Gy to 100 Gy using glow curve deconvolution (GCD), initial rise, variable heating rate and phosphorescence decay methods. All the methods gave results that agree within the experimental errors.

### INTRODUCTION

The 110°C thermoluminescence (TL) peak of quartz has been studied extensively in both natural and synthetic samples because of its importance in dating (Bailey<sup>(1)</sup> and references therein). It is generally assumed that this TL peak follows first order kinetics. There have been few detailed studies of the kinetics of the complete TL glow curve of quartz and of the 110°C peak in particular. Recently Spooner and Questiaux<sup>(2)</sup> used the technique of isothermal decay by stepped isothermals as well as several other standard techniques of TL analysis to measure the kinetic parameters of the prominent TL glow peaks of sedimentary quartz. A detailed GCD analysis of the complete TL glow curve for natural quartz was published recently by Kitis<sup>(3)</sup>.

In this paper a detailed analysis is presented of the kinetic parameters of the glow peak at 110°C for doses ranging from 0.1 Gy to 100 Gy. The standard techniques of glow curve deconvolution (GCD), initial rise, variable heating rate and phosphorescence decay are employed. To the best of our knowledge, no other studies have employed all these different methods in quartz.

### EXPERIMENTAL

Samples of high purity synthetic quartz of the premium Q-type (manufactured by Sawyer Research Products) were crushed, ground and sieved and the 60–90 mm grains were selected. Prior to measurement the zero-dose TL was measured and was found to be of the order of the background. In order to maximise the TL signal from the powder aliquots, they were annealed in air for 1 h at an oven temperature of 900°C. It has been shown previously<sup>(4,6)</sup> that the annealing process increases the magnitude of the TL signal by increasing

the number of available recombination centres, while at the same time leaving the trapping parameters unaffected.

The TL glow curves were recorded with a conventional Daybreak TL equipment and a 9635QB photomultiplier tube using photon counting. All TL glow

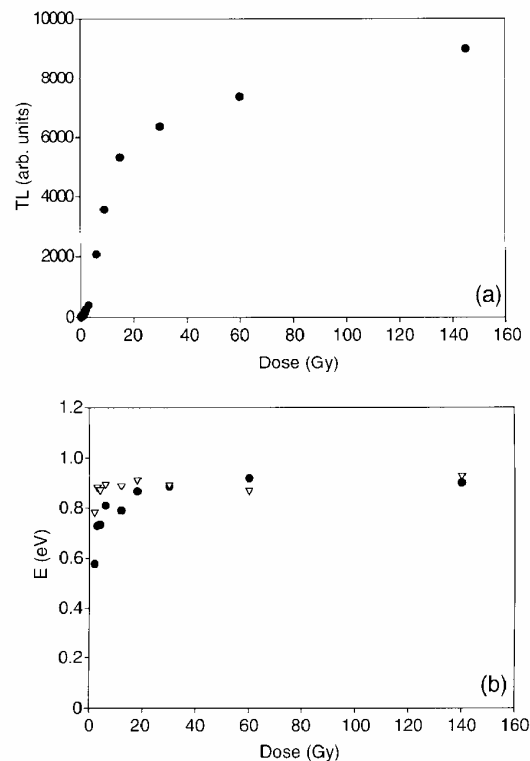


Figure 1. (a) TL vs. dose for the 110°C TL peak in synthetic quartz. (b) Variation of the activation energy ( $E_{GCD}$ ) with dose as obtained using GCD analysis ( $\nabla$ ). The  $E$  values from the initial rise method are also shown ( $E_{IR}$ )( $\bullet$ ).

curves were recorded with a linear heating rate of  $4^{\circ}\text{C}\cdot\text{s}^{-1}$  under nitrogen flow. The powder samples are irradiated on-plate using a 100 mCi  $^{90}\text{Sr}$  source with a dose rate of  $2\text{ Gy}\cdot\text{min}^{-1}$ . The black body radiation was digitally subtracted from the TL glow curves.

The glow curves were recorded using narrow band interference filters (from Oriel Corporation), with peak transmissions located at intervals of 20 nm in the 400–560 nm region. The transmission coefficient of the filters is typically between 20 and 35%, with a very narrow transmission band with a FWHM of  $\pm 5\text{ nm}$ . In addition to the narrow interference filters, a HA-3 infra-

red rejecting filter is used to reduce thermal noise. The narrow band filters are used to ensure detection of essentially monochromatic light from the samples, an important consideration during kinetic analysis of TL glow curves.

The  $T_m$ - $T_{\text{stop}}$  method<sup>(7)</sup> is used to determine the number of overlapping TL peaks within the glow curve. This procedure produces a total of 43 distinct data points shown in Figure 2(b) below, 24 of which have been fitted for GCD analysis. The reason for fitting only 24 of the 43 glow curves is that there are very small changes occurring between successive  $T_{\text{stop}}$  values.

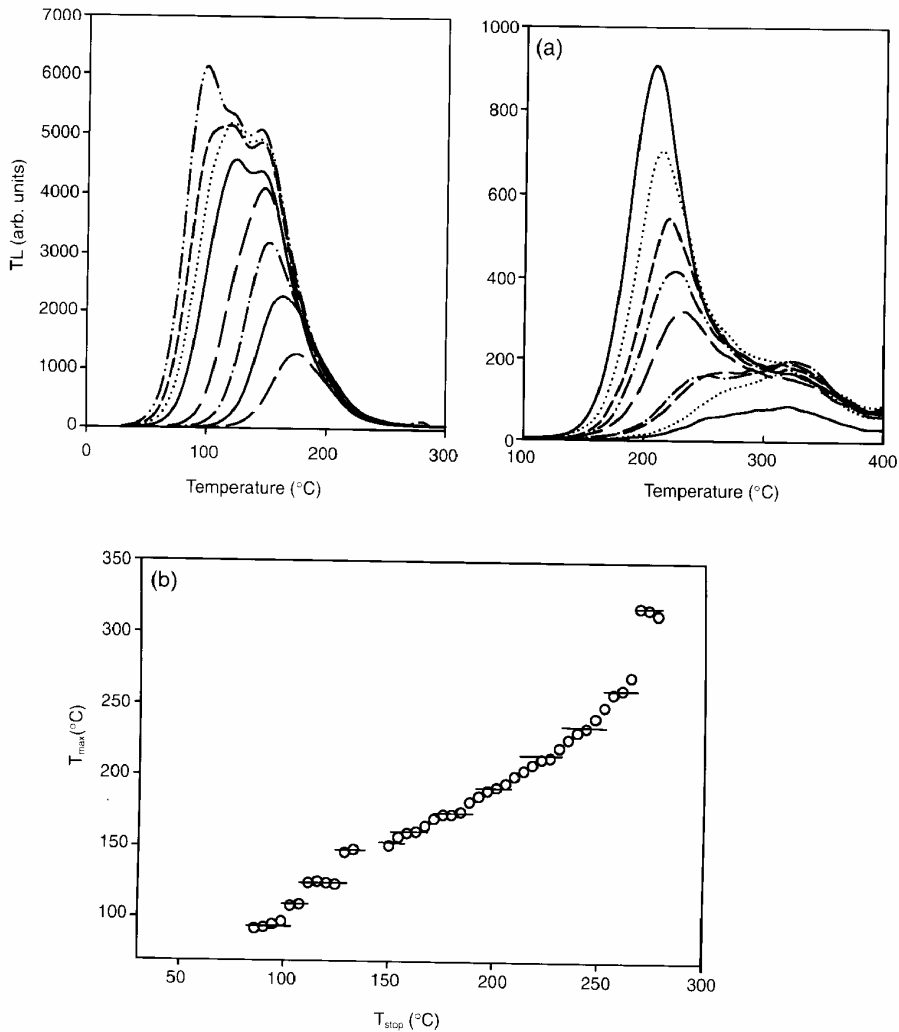


Figure 2. (a) The  $T_m$ - $T_{\text{stop}}$  method yields 24 different glow curves, 17 of which are shown here. (b) The  $T_m$ - $T_{\text{stop}}$  method indicates the presence of 13 distinct TL peaks.

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## EXPERIMENTAL RESULTS

## The TL vs dose growth curves

The lowest dose where a TL signal is detected is around 0.1 Gy and saturation occurs at a dose of 120 Gy. The results of Figure 1(a) were obtained using a 400 nm narrow band filter and show two distinct regions of superlinearity, for low doses (<10 Gy) and high doses (>10 Gy). The properties of these two regions as a function of the annealing temperature have been previously studied in detail by Charitides *et al.*<sup>(4)</sup>.

## GCD analysis of the 110°C TL peak at various doses

Figure 1(b) shows the results of performing a GCD analysis of the 110°C TL peak for various doses. The data in Figure 1(b) show that the energy of the 110°C TL peak shows a very small variation over the dose region of 0.1–120 Gy, with an average value of  $E = 0.87 \pm 0.04$  eV. The E values obtained using the initial

rise method are also shown in Figure 1(b), and their average is  $E = 0.79 \pm 0.11$  eV, within the statistical limits of the E values obtained from the GCD analysis. Wintle<sup>(8)</sup> studied the effect of thermal quenching on the 325°C peak in quartz. Our data show that the 110°C peak also suffers from thermal quenching. However, this effect becomes important only for very high heating rates. It is estimated that the E-values shown in Figure 1(b) are not affected significantly by thermal quenching at the heating rate employed in the present experiment.

## Phosphorescence results

Quartz aliquots were irradiated at a constant irradiation temperature with a dose of 40 Gy and the phosphorescence was measured immediately after the end of the irradiation. As expected, the phosphorescence of a first order TL peak obeys an exponential decay law. The experiment was repeated at different temperatures between 19 and 45°C and the logarithm of the decay constant is plotted as a function of the inverse irradiation temperature  $1/kT$ . The slope of this line gives the activation energy  $E = 0.82 \pm 0.04$  eV for the 110°C TL peak.

## Heating rate method

The well-known heating rate method<sup>(9)</sup> was applied for heating rates between 0.5 and 4°C.s<sup>-1</sup>. The slope of the graph  $\ln(T_m^2/\beta)$  against  $1/kT$  gives the activation energy  $E = 0.79 \pm 0.12$  eV, in agreement with the previous methods. At higher and lower heating rates deviations were observed from the straight line, in agreement with the measurements of Spooner and Questiaux<sup>(2)</sup>.

## GCD analysis of the whole TL glow curves

Figure 2(a) shows the results of applying the  $T_m$ - $T_{stop}$  method. A total of 43 different TL glow curves were obtained as discussed above, 24 of which were analysed using GCD analysis. The results of using the  $T_m$ - $T_{stop}$  method are shown in Figure 2(b) and they indicate the presence of at least 13 distinct TL peaks in the glow curves. It is noted that the distribution of E values in Figure 2(b) can be considered as a quasi-continuous distribution which can be approximated by these 13 peaks<sup>(7)</sup>.

The E and s values corresponding to these 13 peaks were obtained using GCD analysis and are shown in Table 1. All 24 TL glow curves were fitted using the same kinetic parameters E and s shown in Table 1, but different relative peak heights. An example of successful GCD analysis is shown in Figure 3(a). Very good fits were obtained for all 24 TL glow curves, with FOM values between 0.04 and 0.09.

The GCD analysis was performed using the MINUIT program<sup>(10)</sup>. Special attention was given to selecting

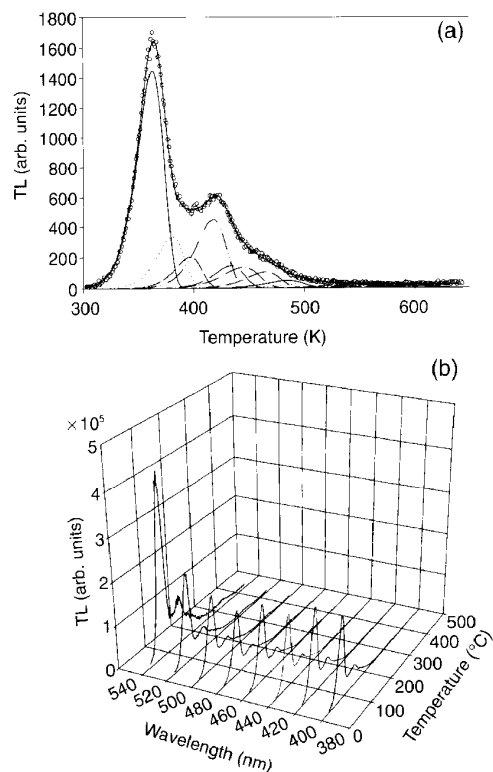


Figure 3. (a) Results of GCD analysis, showing a fit with FOM=0.040. A total of 24 such TL glow curves were fitted successfully. (b) The TL glow curves in the 400–560 nm region.

between the many possible solutions of the GCD analysis using some recently published acceptance criteria for the E and s values. Kitis<sup>(3)</sup> has shown that for first order peaks the quantity  $C_b = \exp(2kT_m/E-1)$  varies within a very narrow range between 0.38 and 0.40, and can be used as a criterion for accepting or rejecting the results of GCD analysis. The values of the coefficient  $C_b$  for the 13 peaks considered here are also shown in Table 1, and they are well within the acceptance limits.

#### Emission spectra in the region 400–560 nm

Figure 3(b) shows the results of measuring the TL glow curves using narrow band filters in the region 400–560 nm. The quartz samples received a small dose of 2 Gy. By comparing the TL glow curves at various wavelengths it is found that the shapes of the TL glow

curves and therefore the kinetic parameters of the TL peaks remain the same in the region 400–560 nm, at least within the accuracy of the experiment and for the low dose employed here. The data shown in Figure 3(b) have been corrected for the efficiency of the photomultiplier tube and the transmission of the filters, as provided by their manufacturers.

#### DISCUSSION AND CONCLUSIONS

Spooner and Questiaux<sup>(2)</sup> measured the kinetic parameters for prominent TL peaks at 110, 160, 180, 220, 280, 325 and 380°C (as measured with a heating rate of  $5^\circ\text{C}\cdot\text{s}^{-1}$ ). Their E values are shown in Table 1 and are higher than the E values obtained in the present study, a fact that could be due to the different types of quartz involved in the two studies.

Table 1. Results of the GCD analysis of 24 glow curves.

Peak	E (eV)	$T_{\max}$ (°C) ( $\beta=4^\circ\text{C}\cdot\text{s}^{-1}$ )	s ( $\text{s}^{-1}$ )	$C_b$	From Ref. 2, $\beta=5^\circ\text{C}\cdot\text{s}^{-1}$	
					E (eV)	$T_{\max}$ (°C)
1	0.85	90	$1.9 \times 10^{11}$	0.396		
2	1.00	108	$5.4 \times 10^{12}$	0.393	0.91	110
3	1.10	124	$3.0 \times 10^{13}$	0.391		
4	1.10	148	$4.2 \times 10^{12}$	0.393		
5	1.20	161	$2.5 \times 10^{13}$	0.392	1.08	160
6	1.22	172	$1.9 \times 10^{13}$	0.392	1.16	180
7	1.20	192	$2.6 \times 10^{12}$	0.393		
8	1.20	212	$7.0 \times 10^{11}$	0.394	1.38	220
9	1.20	231	$2.1 \times 10^{11}$	0.395		
10	1.25	257	$1.6 \times 10^{11}$	0.396		
11	1.30	288	$9.1 \times 10^{10}$	0.396	1.50	280
12	1.33	322	$3.2 \times 10^{11}$	0.397	1.65	325
13	1.40	360	$2.3 \times 10^{10}$	0.398	2.07	380

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