

## Cooling rate effects on the thermoluminescence glow curves of Arkansas quartz

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Samples of quartz annealed at high temperatures are known to exhibit thermoluminescence (TL) properties which depend on the rate of cooling of the samples to room temperature. Powder samples of Arkansas quartz were annealed in air at temperatures between 500 and 900 °C and were cooled to room temperature at different cooling rates. The TL of both slowly and fast cooled samples was measured at various doses of beta radiation; a fast cooling rate leads to significant enhancements of the TL intensity for the “110 °C” TL peak, as well as a change in the ratio of the relative intensities of the main TL peaks. The well-known  $T_m - T_{\text{stop}}$  method of analysis resulted in several well-defined plateaus at different temperatures for the fast cool and slow cool samples, while the thermal quenching parameters  $C$  and  $W$  and kinetic parameters of the TL peaks were found to be independent of the cooling rate. This new result provides further evidence for the cooling rate effects being due to slow ionic processes, rather than the much faster electronic processes involved in thermal quenching.

### 1 Introduction

The thermoluminescence (TL) properties of quartz have been studied extensively in both natural and synthetic samples because of its importance in dating and retrospective dosimetry [1]. Samples of quartz annealed at high temperatures are known to exhibit thermoluminescence properties that depend on the rate of cooling of the samples to room temperature [2, 3]. Rendell et al. [2] investigated the spectral changes occurring in the TL of quartz of various origins due to thermal treatments. These authors compared the emission spectra from hydrothermal quartz, synthetic quartz and samples of volcanic origin. The heat treatments affected both the relative intensities of the TL peaks, as well as the relative intensities of the various emission bands.

Recently Lima et al. [3] studied the effect of various thermal treatments on the TL glow curves and emission spectra of a natural quartz crystal. They found that annealing at high temperatures produced both new trapping states at low temperatures, as well as a new luminescence center around 370 nm. These authors attributed the presence of new TL peaks at low temperatures and the changes taking place in the relative TL peak heights, to the possible formation of clusters during the cooling down process.

While these researchers have reported this cooling rate effect in qualitative terms before, there has been no detailed quantitative study of the effect of the cooling rate on the TL properties and kinetic parameters of quartz. The purpose of the present investigation is to elucidate and quantify several aspects of these cooling rate effects, namely:

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- (i) to investigate the effect of the cooling rate on the kinetic parameters and TL dose response of the “110 °C” TL peak,
- (ii) to quantify the changes taking place in the relative TL peak heights, and
- (iii) to test for any changes occurring in the thermal quenching parameters of quartz under different cooling rates.

The experiments consist of a detailed study of the cooling rate effects on the TL glow curve of clear white Arkansas quartz annealed in air, at temperatures between 500 and 900 °C. Some samples were quenched rapidly to room temperature while other samples were left to cool in the annealing oven over the period of several hours. The TL of both types of samples was measured at various doses of beta radiation ranging from 0.1 to 20 Gy, and was found to obey first order kinetics. The well-known  $T_m - T_{\text{stop}}$  method of analysis was applied to the TL glow curves and resulted in several well-defined plateaus.

The results show that a fast cooling rate leads to significant enhancements of the TL intensity for the “110 °C” TL peak, as well as a change in the ratio of the relative intensities of the main TL peaks. On the other hand, the results of the initial rise method show that the  $E$  values for the fast cool and slow cool samples are identical in the temperature range 300–450 K.

The values of the thermal quenching parameters  $C$  and  $W$  were evaluated by studying the total TL area as a function of the heating rate, and were found to be in excellent agreement with previously published results. These quenching parameters are used to correct the  $E$  values obtained from applying the initial rise method.

The results of this study show that both fast cool and slow cool samples exhibit thermal quenching described by the same parameters  $C$  and  $W$ . This is a new experimental result which provides further evidence that cooling rate effects in quartz are due to slow ionic processes taking place in the crystal, instead of the much faster electronic processes involved in the thermal quenching effects in quartz.

## 2 Experimental

Samples of commercially available clear hydrothermal quartz (termed Arkansas quartz, from Carolina Scientific Co.) were crushed, ground and sieved and the 60–90  $\mu\text{m}$  grains were selected. These samples were annealed in air at temperatures between 500 and 900 °C. Some samples (termed fast cool or FC samples in the rest of the paper) were quenched rapidly to room temperature by placing them on a large copper slab, while other samples (termed slow cool or SC samples) were left to cool in the annealing oven at a much slower rate over the period of several hours. This high temperature annealing results in a well-known increase of the sensitivity to radiation by approximately three orders of magnitude [4], and hence the statistics of the experiment are greatly improved. Previous experimental and theoretical work has shown that the annealing process increases the magnitude of the TL signal by increasing the number of available recombination centers, while at the same time leaving the trapping parameters unaffected [4–6].

The samples were irradiated on-plate using a 100 mCi Sr-90 beta source with a nominal dose rate of 2 Gy/min, at various doses of beta radiation ranging from 0.1 to 20 Gy. Prior to irradiation the zero-dose TL was measured and was found to be of the order of the background. The TL glow curves were recorded with a conventional Daybreak TL equipment and a 9635QB photomultiplier tube using photon counting and with a Corning-60 blue filter. All TL glow curves were recorded with a linear heating rate of 4 °C s<sup>-1</sup> under nitrogen flow. The black body radiation was digitally subtracted from the TL glow curves and a HA-3 infrared rejecting filter was used to reduce thermal noise.

The  $T_m - T_{\text{stop}}$  method [7] is used to determine the number of overlapping TL peaks within the glow curve. During this method, an irradiated sample is heated to a temperature  $T_{\text{stop}}$ , then it is cooled rapidly to room temperature and reheated in order to measure the remaining glow curve. The process is then repeated with a new irradiation and heating to a slightly higher temperature  $T_{\text{stop}}$ . A total of 45 partial TL glow curves were produced in this manner for both FC and SC samples.

During the thermal quenching studies a slightly different experimental procedure was employed as follows. After irradiation, the powder samples of 2.5 mg weight were spread on the heating strip in an area of 1 cm<sup>2</sup> using a non-luminescent silicon oil. This procedure drastically decreases the temperature

lag between the sample and the heating element. The time interval between the end of irradiation and the readout was always less than 1 min. The thermal quenching TL measurements were performed with a 711-Littlemore analyzer and light emission was detected by an EMI 9635 QA photomultiplier tube. The heating strip was nichrome of thickness 0.8 mm. A constant beta dose of 2 Gy was employed throughout the thermal quenching studies.

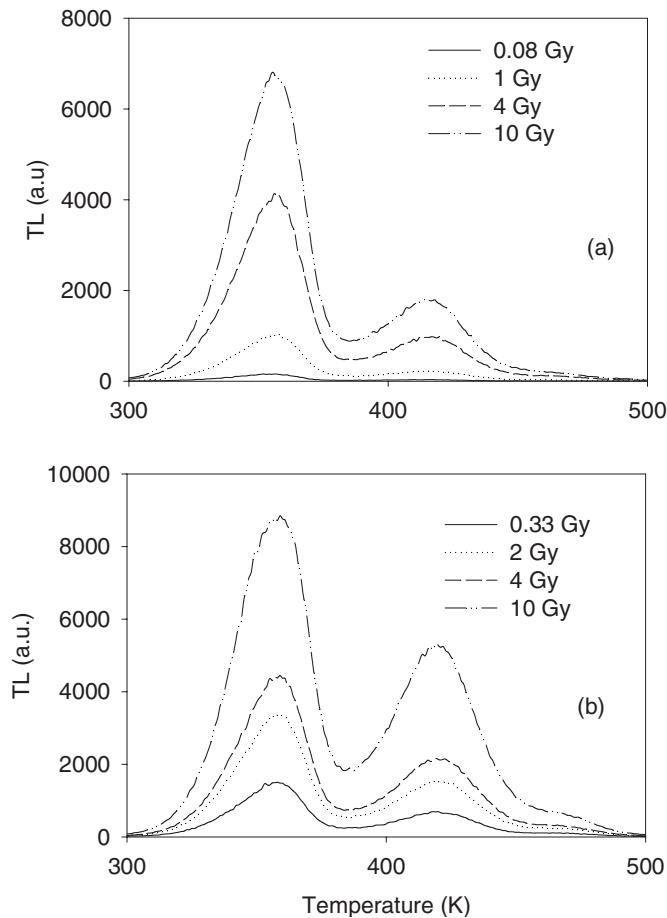
### 3 Experimental results

#### 3.1 The TL versus dose growth curves

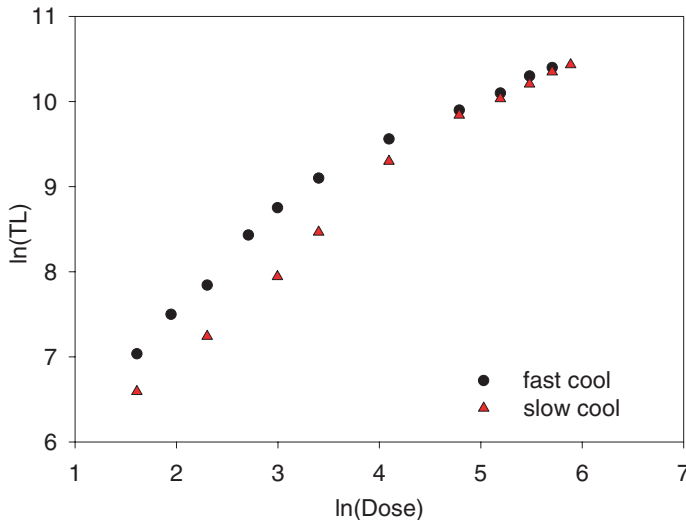
Figure 1 shows the evolution of the TL glow curves for both the fast cool and slow cool samples as a function of the beta dose. The lowest dose where a TL signal is detected is around 0.1 Gy and saturation occurs at a dose of 20 Gy. The TL glow curves for both the FC and SC samples consist of the low temperature glow peak at 370 K and secondary TL peaks around 420 and 470 K, as measured with a heating rate of  $4\text{ }^{\circ}\text{C s}^{-1}$ .

The data in Fig. 1 also show that the temperature of maximum TL intensity  $T_{\text{max}}$  changes very little within the dose range studied, a very strong indicator of first order kinetics [8].

Figure 2 shows the TL dose response for both FC and SC samples. For doses between 0.1 Gy and 10 Gy the TL response is seen to be linear. For doses above 10 Gy the TL response approaches saturation. The results of Fig. 2 show that apart from a sensitization or scaling factor, the TL dose response of both samples are identical.



**Fig. 1** TL at various doses for a) slow cool samples and b) fast cool samples.



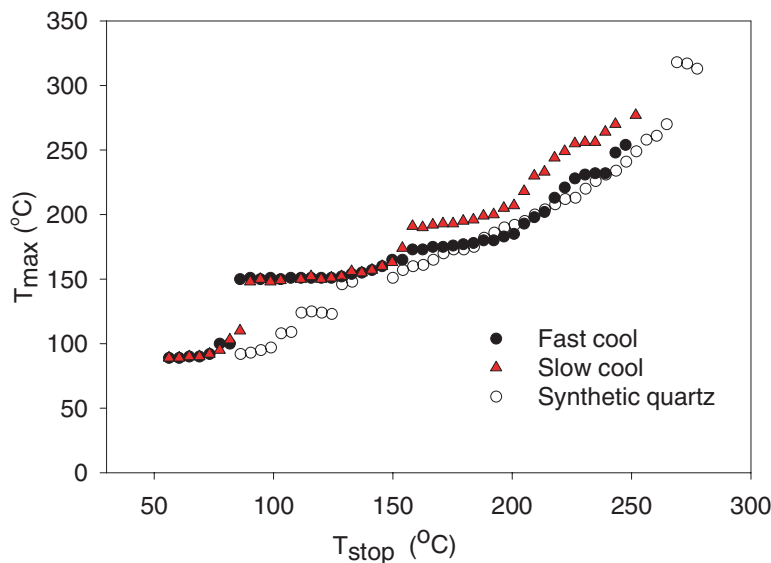
**Fig. 2** (online colour at: [www.interscience.wiley.com](http://www.interscience.wiley.com)) TL vs. dose response curves of the “110 °C” TL peak, for slow cool and fast cool samples.

### 3.2 The $T_m - T_{stop}$ method

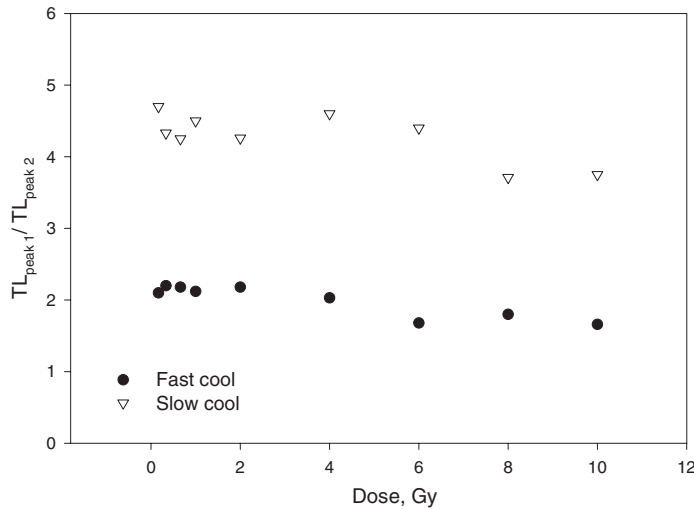
Figure 3 shows the results of applying the well-known  $T_m - T_{stop}$  method to both fast cool and slow cool samples annealed at 900 °C. Recently published  $T_m - T_{stop}$  data for synthetic quartz are also shown for comparison purposes [9]. The  $T_m - T_{stop}$  graph for synthetic quartz has been previously interpreted as consisting of a quasi-continuous distribution of 13 trapping levels [9]. In contrast, the Arkansas quartz data in Fig. 3 indicate the presence of only a few well-defined plateaus with  $T_{max}$  values located at about 90, 150, 170, 230, and 250 °C for the FC samples, and at 90, 150, 190, and 260 °C for the SC samples.

Close examination of Figs. 3 and 1 shows some significant differences between the fast cool and slow cool  $T_m - T_{stop}$  curves as follows:

- The FC signal is always higher than the SC signal (when they both received the same dose). This is true at all  $T_{stop}$  temperatures and all annealing temperatures studied.
- The  $T_m - T_{stop}$  data for FC and SC samples in Fig. 3 are identical up to a  $T_{stop}$  temperature of approximately 160 °C. For higher temperatures, the  $T_{max}$  values are systematically higher for the SC sam-



**Fig. 3** (online colour at: [www.interscience.wiley.com](http://www.interscience.wiley.com))  $T_m - T_{stop}$  graphs for Arkansas fast cool samples, Arkansas slow cool samples, and synthetic quartz.



**Fig. 4** Variation of the ratio of the TL peak at 110 °C to the TL peak at 150 °C as a function of the beta dose for slow cool and fast cool samples.

ples, indicating that the slow cooling process most probably creates additional TL traps at higher temperatures of 190 and 260 °C.

– The ratio of the major TL peaks at 90 °C and at 150 °C is different for the FC and SC samples. This is shown in Fig. 4 where the ratio of the intensity of the main TL peak at 110 °C to the TL peak at 150 °C is plotted as a function of the dose received by the sample. As seen in Fig. 4, this ratio is approximately equal to 2 for FC samples and equal to 4 for SC samples. These ratios are slow varying functions of the dose received by the sample.

The above general conclusions were found to be also true at lower annealing temperatures of 500 °C and 800 °C.

### 3.4 Initial rise analysis and thermal quenching effects

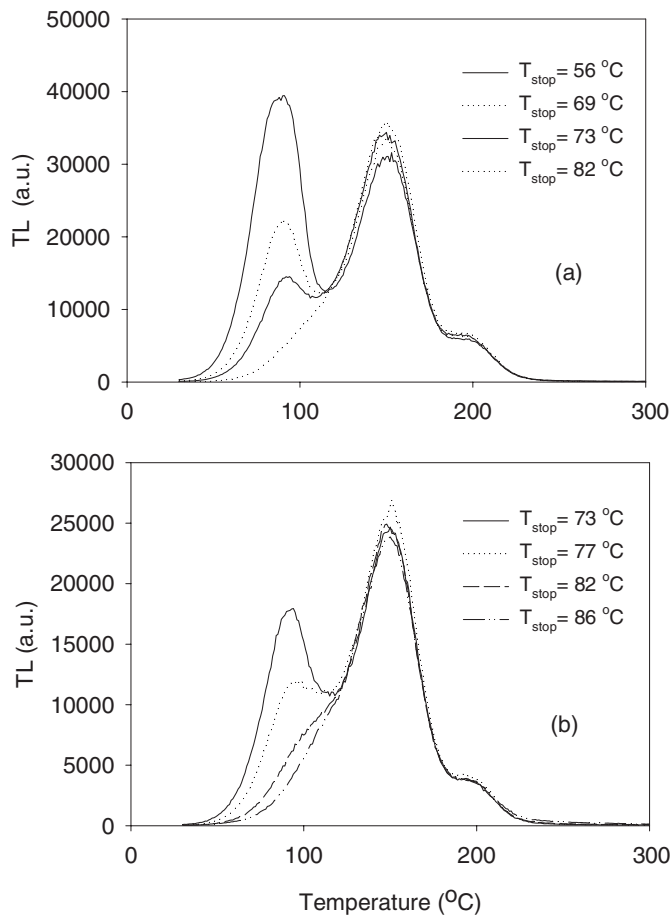
The initial rise (IR) method is one of the most reliable methods for evaluating the activation energy  $E$  [8]. However this method gives erroneous values of the activation energy  $E$  in cases where the thermal quenching effect is present. During thermal quenching, the luminescence efficiency decreases as the temperature increases. This was first pointed out by Wintle [10], who also pointed out the influence of the thermal quenching effect on the trapping parameters evaluated by the initial rise method.

Each of the  $T_m - T_{stop}$  measurements described above produces also a partial TL glow curve. Figure 5 shows some of these partial TL glow curves for both FC and SC samples. Figure 8 shows the results of applying the IR method of analysis to the 45 partial TL glow curves obtained using the  $T_m - T_{stop}$  procedure for the FC samples. In all data shown, the empirical “5%” rule of analysis is applied [8]. According to this rule, during initial rise analysis, one must only use data corresponding to the lower 5% of the TL maximum intensity. One notable feature of Fig. 8 is the sudden decrease in the  $E$  values for temperatures above 410 K. This sudden drop in the  $E$  values indicates that thermal quenching effects may be present. The rest of this section is dedicated to a detailed analysis of thermal quenching effects and in determining the thermal quenching parameters for both FC and SC samples.

The effect of thermal quenching is described mathematically by the thermal quenching efficiency  $\eta(T)$  given by [10]

$$\eta(T) = \frac{1}{1 + C \exp\left(-\frac{W}{kT}\right)}, \quad (1)$$

where  $W$  is the thermal activation energy for thermal quenching (in eV),  $C$  is a dimensionless constant,  $k$  is the Boltzmann constant, and  $T$  represents the temperature (in K). Wintle [10] measured the thermal



**Fig. 5** Some of the partial TL glow curves obtained for fast cool and slow cool samples, at different  $T_{\text{stop}}$  temperatures. A total of 45 such curves were measured for both fast and slow cool samples.

quenching parameters of annealed natural quartz using radioluminescence and a filter centered at 465 nm, and obtained  $C = 2.8 \times 10^7$  and  $W = 0.64$  eV. Wintle [10] also indicated that the quenching properties were independent of the wavelength of the observed luminescence, except at 495 nm. McKeever et al. [11] obtained  $C = 7.9 \times 10^6$  and  $W = 0.60$  eV by measuring the OSL intensity as a function of the sample temperature. Petrov and Bailiff [12] evaluated the quenching parameters for synthetic quartz and obtained  $W = 0.78$  eV and  $C = 3.1 \times 10^{10}$ .

The presence of the thermal quenching effect can be detected either by radioluminescence measurements or, in some cases, by a study of the TL intensity as a function of the heating rate. In the absence of thermal quenching the total area under the TL glow curve is expected to be independent of the heating rate used in measuring the TL glow curves. When thermal quenching is present, one expects that the total area under the TL glow curve will decrease with increasing heating rate. This effect has been used previously by Spooner [13] who studied thermal quenching effects of quartz in the UV region, as well as by Spooner and Franklin [14] who studied this phenomenon in the red wavelength region (600 nm) for sedimentary quartz. It is noted that the measured area in the TL experiments is that of an intensity–time curve, instead of an intensity–temperature curve. The time values on the  $x$ -axis are changed into temperature values by multiplying with the constant heating rate  $\beta$ .

Recently Nanjundaswamy et al. [15] studied the thermal quenching in several natural quartz samples, by measuring the TL signal as the heating rate was varied over several orders of magnitude. These authors were able to monitor the quenching parameters at two different emission wavelengths in the UV and in the blue region. They found a value of the activation energy of 0.60 eV for the UV region, and a

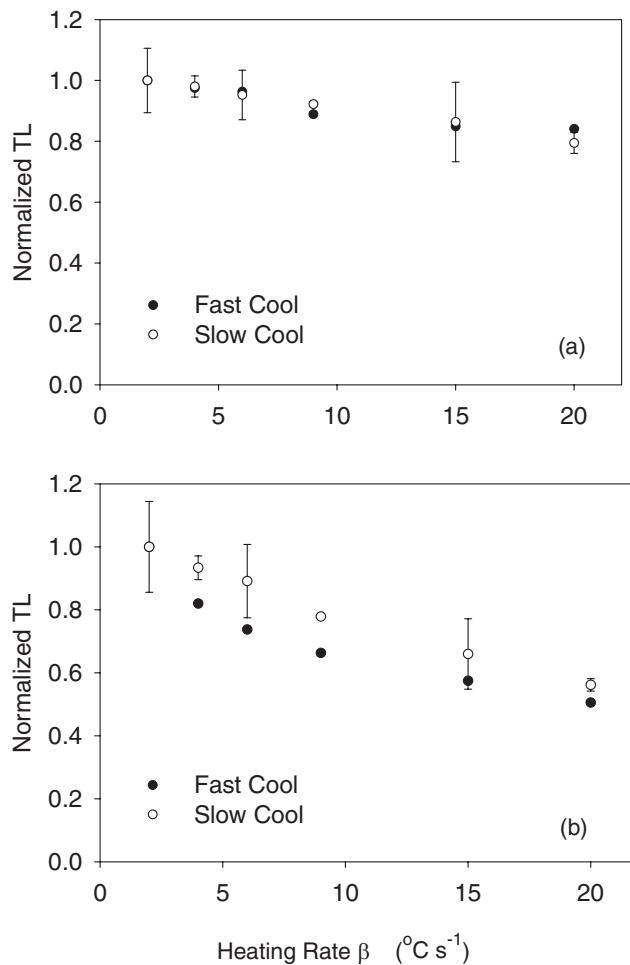
value of  $E = 0.90$  eV for the blue emission. In addition, their results provided confirmation for a Mott-Seitz mechanism of thermal quenching.

In the present experiment, the TL sensitivity is measured in terms of the glow peak integral. The behavior of the integral of the main TL peak at “110 °C” as a function of the heating rate  $\beta$  is shown in Fig. 6a. The data in this figure are normalized to the integral at the lowest available heating rate of  $2\text{ °C s}^{-1}$  is shown in Fig. 6a. The open circles correspond to the SC samples and the solid circles to the FC samples. In both cases the TL integral is reduced by almost 10% for heating rates between 2 and  $20\text{ °C s}^{-1}$ . The data in Fig. 6a shows that this low temperature glow peak suffers to a small degree from thermal quenching.

Figure 6b shows the behavior of the integral of the secondary TL peaks between 380 and 500 K, normalized to the integral at the lowest available heating rate of  $2\text{ °C s}^{-1}$ . The open circles correspond to the SC samples and the solid circles to the FC samples. In both cases the TL integral is reduced by almost 55% between the heating rates of 2 and  $20\text{ °C s}^{-1}$ . The thermal quenching effect is clearly dominant in this higher temperature region.

The following procedure is used to normalize the experimental data to a curve deduced numerically from Eq. (1):

Step 1: The TL-area versus heating rate  $\beta$  data are normalized to the lowest available heating rate of  $2\text{ °C s}^{-1}$ .



**Fig. 6** Results of thermal quenching analysis for a) low temperature TL integral and b) high temperature TL integral, as a function of the heating rate  $\beta$ .

Step 2: A TL efficiency curve is produced numerically using Eq. (1) with trial values of  $C$  and  $W$ .

Step 3: The value of the above efficiency curve is calculated at a temperature equal to the  $T_{\max}$  of the lowest heating rate.

Step 4: The normalized response found in step 1 is then multiplied by the value of the efficiency curve found in step 3. The values obtained in this manner can now be positioned on the efficiency curve of step 2 in order to see if the experimental data fits the efficiency curve.

Step 5: The process is then repeated for the TL-integral in the higher temperature region.

Figure 7 shows the results of applying the above normalization procedure to the experimental data of Figs. 6a, b. The experimental data gives an excellent fit to the calculated efficiency curve from Eq. (1), for both fast and slow cool samples. The best fit values of the quenching parameters obtained from Fig. 7 are  $C = 3.63 \times 10^7$  and  $W = 0.642$  eV. In conclusion, the present analysis of thermal quenching gives values of  $C$  and  $W$  in excellent agreement with previously published values of  $C$  and  $W$  [10, 11].

Moreover, the results also show that the cooling rate does not effect the values of the quenching parameters. This is consistent with the conclusions of Petrov and Bailiff [12] who attributed the cooling rate effects to slow ionic processes, rather than to the much faster electronic processes involved in thermal quenching.

It must be noted that a basic assumption in the above calculation is that the same  $C$  and  $W$  values describe the efficiency of both low temperature and high temperature glow peaks of the quartz samples studied.

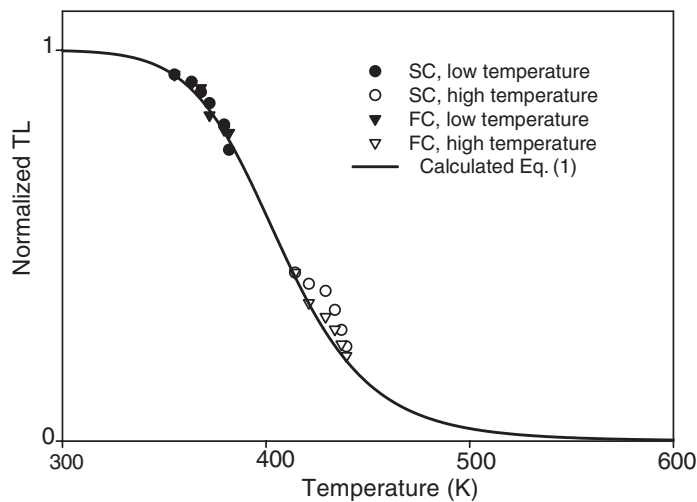
### 3.5 Initial rise $E$ -corrections

Petrov and Bailiff [16] proposed the following correction formula for the  $E$  values obtained by initial rise measurements:

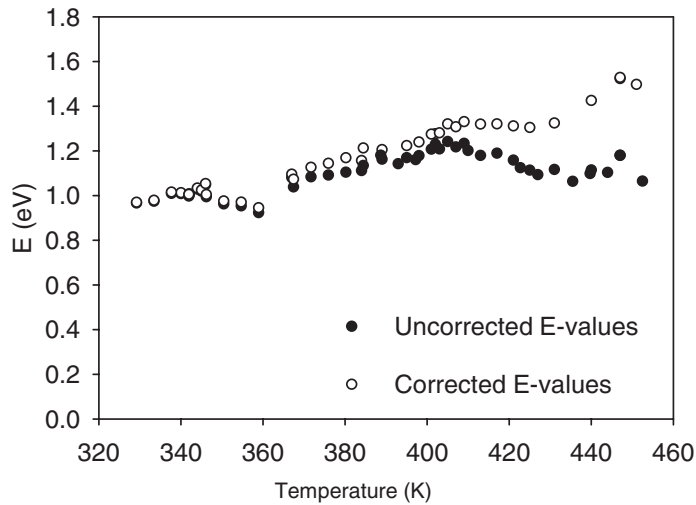
$$\Delta E = \frac{W}{1 + \left[ C \exp\left(-\frac{W}{kT}\right) \right]^{-1}}. \quad (2)$$

Recently Kitis [17] verified the applicability of this formula in the case of  $\text{Al}_2\text{O}_3$ , a material that exhibits strong thermal quenching effects. The correct value of the activation energy is obtained by adding the correction  $\Delta E$  to the value of  $E$  obtained from the initial rise method ( $E_{\text{IR}}$ ),

$$E_{\text{real}} = E_{\text{IR}} + \Delta E. \quad (3)$$



**Fig. 7** Results of fitting the results of Fig. 6 to Eq. (1).



**Fig. 8**  $E - T_{\text{stop}}$  data obtained from the partial glow curves in Fig. 6 for fast cool samples. The corrected  $E - T_{\text{stop}}$  data obtained using Eqs. (2) and (3) are also shown. Similar results were obtained for the slow cool samples.

Figure 8 shows the results of applying the Petrov–Bailey correction from Eqs. (2) and (3) to the energy values obtained by the initial rise technique for the fast cool samples. The same results were obtained for the slow cool samples, well within the accuracy of the present measurements. It can be seen that by correcting the initial rise  $E$  values by using Eqs. (2) and (3), a continuously increasing range of  $E$  values between 1.3 and 1.5 eV is obtained. This is in close agreement with the  $E$  values obtained by Petrov and Bailiff [12] for annealed synthetic quartz for temperatures between 420 and 520 K (see their Table 2, with values of  $E = 1.32\text{--}1.55$  eV).

#### 4 Discussion and conclusions

Petrov and Bailiff [12] argued that the TL changes observed during high temperature annealing treatments of quartz may be attributed mostly to slow ionic processes which are controlled by diffusion mechanisms and can result in the creation of both new traps and new luminescence centers. This proposed mechanism is also consistent with the dependence of the emission spectra on the cooling rate after thermal annealing, as observed by both Rendell et al. [2] and Lima et al. [3].

The fact that the quenching parameters found in this paper are independent of the cooling rate, provides further evidence for the cooling rate effects being due to slow ionic processes, rather than to the much faster electronic processes involved in thermal quenching.

The quantitative experimental results presented in this paper also show that a fast cooling rate leads to significant enhancements of the TL intensity for the “110 °C” TL peak, as well as a change in the ratio of the relative intensities of the main TL peaks. On the other hand, the shape of the TL dose response for the “110 °C” TL peak remained unchanged for different cooling rates apart from a sensitization factor, indicating that the different cooling rates most probably alter the number of recombination centers but leave the kinetic parameters unchanged. This is further substantiated from the results of the initial rise method, which showed that the  $E$  values for the fast cool and slow cool samples are identical in the temperature range 300–450 K, within the accuracy of the experiments.

The results of the  $T_m - T_{\text{stop}}$  method show that the slow cooling process most probably creates additional TL traps at higher temperatures of 190 and 260 °C. These results are in agreement with the recent results of Lima et al. [3] who also showed that slow cooling rates seem to create additional TL peaks/traps, as well as produce changes in the relative TL peak heights.

The analysis of the initial rise  $E$  values presented in this paper shows that it is possible to obtain correct results using the initial rise method in combination with the  $T_m - T_{\text{stop}}$  method, even in the presence of strong quenching effects. This type of analysis should prove useful for analyzing complex TL glow curves in the presence of thermal quenching.

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