

Influence of duration of annealing on thermoluminescence of natural quartz annealed at 1000 °C

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Abstract. The influence of duration of annealing on thermoluminescence of natural quartz annealed at 1000 °C is reported. The study looks at samples annealed for 10 and 60 min. A glow curve measured at 1 °Cs⁻¹ after beta irradiation to 50 Gy for the sample annealed for 10 min shows seven peaks at 68, 130, 176, 276, 300, 360, and 416 °C labelled I through VII. The sample annealed for 60 min has five peaks at 70, 128, 176, 234, and 308 °C labelled I-V respectively. A study of dosimetric features and kinetic analysis was carried out on the two prominent peaks, peak I and III for both samples. The electron trap responsible for peak I depletes faster at high duration of annealing between irradiation and measurement. In contrast, the electron trap for peak III was more stable for both samples. Kinetic analysis shows that peak I is a first-order peak and peak III a non-first-order peak. The activation energy obtained using the initial rise, whole glow peak, and curve fitting methods is ~0.95 eV for peak I and ~1.20 eV for peak III. In particular, the kinetic parameters obtained for both peaks decrease with annealing time. This suggests that the duration of annealing at 1000 °C has an effect on the trap parameters of natural quartz.

1. Introduction

Quartz is the second most abundant mineral after feldspar and is used widely in retrospective dosimetry and luminescence dating. Its use as a natural dosimeter in a variety of applications is well documented [1-10]. When quartz is heated at elevated temperatures, it undergoes phase transitions, namely at 573 °C and 870 °C [11, 12]. Several studies have shown that annealing improves the luminescence sensitivity of quartz. Bøtter-Jensen et al. [13] showed that annealing of quartz prior to irradiation can significantly increase its luminescence sensitivity. The significant increase, which occurs between the first two phase inversion temperatures, is attributed to alteration in the concentration of recombination centres [14]. Further work also shows that annealing affects the luminescence lifetimes [15, 16] and radioluminescence emission bands [17] of quartz.

There are for quartz, numerous studies on thermoluminescence (TL) reported in the literature. The so-called “110 °C peak” has been the peak of interest for most thermoluminescence investigations. The shape and kinetic parameters of this peak vary by a narrow range for all quartz samples even after extreme conditions of irradiation and heating [18]. Recent work (e.g. [2, 3]) has shown that annealing has little effect on the kinetic parameters of the “110 °C” peak of natural quartz at 800 °C. However, the influence of duration of annealing on thermoluminescence of natural quartz is yet to be investigated in

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greater detail. In his work, Chithambo [19] showed that lifetimes increase with annealing time for natural quartz annealed at 1000 °C in studies using time-resolved optical stimulation. This response of lifetimes to annealing is the motivation for the current investigation on the same quartz using thermoluminescence.

In this work, we investigated the influence of duration of annealing on thermoluminescence of natural quartz annealed at 1000 °C, that is beyond the second phase inversion temperature. Dosimetric features and kinetic analysis were carried out on the two prominent peaks of the samples annealed at 1000 °C for 10 and 60 min.

2. Experimental details

Natural sedimentary quartz of grain size 90 – 250 µm commercially available from BDH Ltd (UK) was used. The samples were annealed at 1000°C for 10 minutes and another for 1 hour. The quartz was annealed to remove any remanent signal and to improve its sensitivity to thermal stimulation. The same quartz annealed at 1000 °C has been used previously for thermoluminescence and luminescence lifetimes investigations [4, 19]. Experiments were performed using a RISØ TL/OSL DA-20 Luminescence Reader. The luminescence was detected by an EMI 9235QB photomultiplier tube through a 7 mm Hoya U-340 filter. Samples were irradiated at room temperature using a $^{90}\text{Sr}/^{90}\text{Y}$ β source at a rate of 0.10 Gy s^{-1} . All measurements were carried out at a heating rate of 1°C s^{-1} unless otherwise stated. The same sample mass of 30 mg was used throughout.

3. Results and discussion

3.1. General features of glowcurves

Figure 1 shows glow curves measured at 1°C s^{-1} from samples of natural quartz annealed at 1000 °C for 10 minutes (solid symbols) and 60 minutes (open symbols). The samples were irradiated to 50 Gy. The intensity of the sample annealed for 10 min is higher than that annealed for 60 min. For ease of reference, the samples annealed for 10 min and 60 min will be referred to as samples A and B respectively. The glow curves show four peaks for each sample as can also be seen in the inset. An intense peak (labelled I) was recorded at 68 and 70 °C for samples A and B respectively. Secondary peaks labelled II, III, and IV were recorded at 130, 176 and 276 °C respectively for sample A. In comparison, the peaks II, III, and IV are at 128, 176, and 308 °C respectively for sample B. The position of each of these peaks was verified using the thermal cleaning technique.

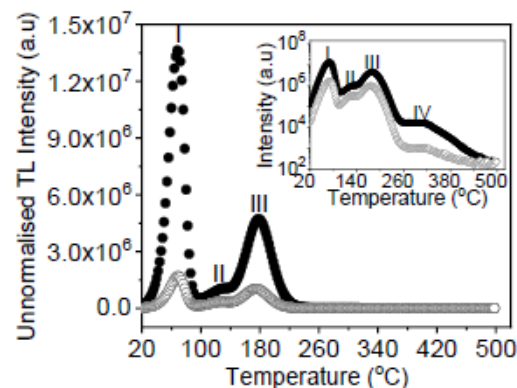


Figure 1. Thermoluminescence glow curves of natural quartz annealed at 1000 °C for 10 min (solid symbols) and 60 min (open symbols) measured at 1°C s^{-1} following irradiation to 50Gy. The inset shows the same curves on a semilogarithmic plot which reveals the presence of peak IV.

3.1.1. Resolution of peaks by thermal cleaning.

To determine the exact number of peaks in the glow curve and to obtain a clear rising edge of the individual peaks, the thermal cleaning technique [20] was used. In the method, an irradiated sample is heated to a temperature just beyond the final temperature of each peak that needs to be removed. In this

way, the electron traps responsible for such peak(s) are emptied. The sample is then cooled and reheated to a final temperature to record the whole glow curve. By adopting the procedure, sample A heated in turn to 100, 140, 250, 350, and 400 °C following irradiation to 50 Gy each time revealed the positions of peaks II, III, IV, V, VI, and VII as 130, 176, 276, 300, 360, and 416 °C respectively. Similarly, for sample B, the procedure revealed peaks II, III, IV, and V at 128, 176, 234, and 308 °C respectively following irradiation to 50 Gy each time and preheating to 95, 140, and 240 °C. In comparison, an unannealed sample of the same mass irradiated to the same dose showed six peaks at 72, 122, 174, 254, 280, and 416 °C [3]. The relevant plots for this method are available as *supplementary information*. Thus, the thermal cleaning technique revealed that thermoluminescence of sample A consists of seven peaks, whereas that of sample B consists of five peaks. The difference in the number of peaks for both samples can be ascribed to the influence of annealing.

3.2. Dosimetric features

For a material to be considered a good dosimeter, its luminescence signal should be properly reproducible, ideally not fade or if so only slowly. These dosimetric features were studied on peaks I and III, the two most prominent peaks of the annealed quartz. These peaks are well defined compared to other peaks in the glow curves.

3.2.1. Fading.

Fading of a TL signal occurs as a result of the escape of electrons from an electron trap between irradiation and measurement. This causes the TL intensity to decrease or fade between irradiation and measurement. For this study, the intensities of peaks I and III were monitored for different durations between irradiation and measurement up to 5 hours. Figure 2 shows the change of TL intensity with delay for peak I measured after a dose of 50 Gy. The intensity decreases with delay. The data were fitted with the function:

$$f(t) = I_0 \exp\left(-\frac{t}{\tau}\right), \quad (1)$$

from which the mean lifetime τ was evaluated as 7784 s (half-life = 5395s) and 4686 s (half-life = 3248 s) for samples A and B respectively. The result shows that lifetime decreases with duration of annealing. Galloway [15] has also reported that lifetimes in natural quartz decrease when the annealing temperature is increased beyond 600 °C. For peak III (graph omitted), the intensity was constant with delay between irradiation and measurements implying that the electron trap corresponding to peak III is stable. Thomas and Chithambo [5] have also reported a similar occurrence of stable intensity with delay for peak III for the same unannealed quartz irradiated to 10 Gy after a 20 h delay.

3.3. Assessing the order of kinetics

3.3.1. Influence of dose on peak position.

The order of kinetics of peaks I and III was assessed by studying the dependence of peak position T_m on dose. For a first-order peak, T_m is independent of dose, whereas T_m decreases with dose for a second-order peak [21]. Peak I was determined to be independent of irradiation between 10 and 300 Gy at 68.5 ± 0.6 °C for sample A and at 69.9 ± 0.3 °C for sample B. The results show that peak I for both samples follows first-order kinetics. This agrees with the findings for peak I for the same unannealed natural quartz reported by Folley and Chithambo [3]. Literature (e.g. [6-8]) shows that peak I generally referred to as the “110 °C peak” is a first-order peak for all quartz samples. Figure 3 shows the variation of position of peak III with dose for samples A (solid symbols) and B (open symbols). The position of peak III decreases with dose for both samples in a staircase manner, from which T_m is independent of dose at different levels of the decrease. That the position of peak III is independent of dose at different levels could imply that the peak for both samples is general order peak. In contrast, the position of peak III for an unannealed sample was reported to be independent of dose by Thomas and Chithambo [5] implying that annealing influences the change of its order of kinetics from first-order to non-first-order.

3.4. Kinetic analysis

In order to determine the kinetic parameters of peaks I and III, kinetic analysis was carried out using the initial rise, whole glow-peak, variable heating rate, and curve fitting methods. Several methods were

used in evaluating the kinetic parameters in order to corroborate the results. Kinetic analysis will only be reported for the annealed quartz. These results will be compared with the analysis of peak I reported by Folley and Chithambo [3] for the same unannealed quartz irradiated to 50 Gy and of peak III by Thomas and Chithambo [5] for a dose of 10 Gy. This is necessary for monitoring the influence of annealing on the kinetic parameters of the investigated peaks. For completeness, we also compare our values with ones from the literature.

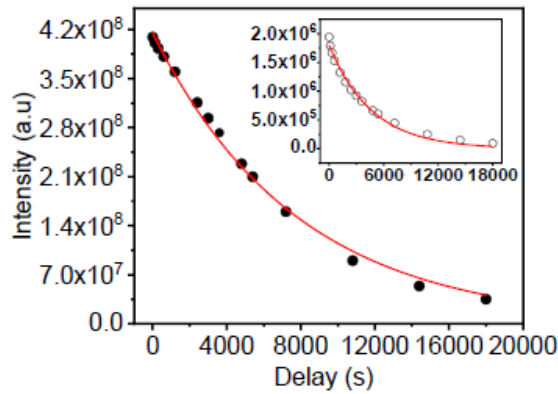


Figure 2. The variation of TL intensity with delay between irradiation and measurements for peak I. The inset shows data for sample B. The line passing through the data points is a fit of equation (1).

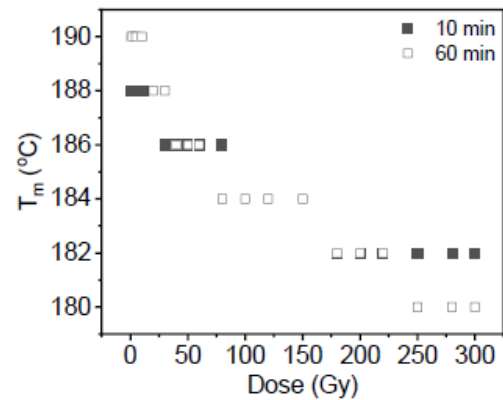


Figure 3. The influence of dose on the position of peak III for the samples annealed for 10 min (solid squares) and 60 min (open squares).

3.4.1. Initial rise method.

Peaks I and III were first analysed using the initial rise method, applicable to the clear rising edge of a glow peak whose intensity and temperature are related as:

$$I = C' \exp\left(-\frac{E}{kT}\right), \quad (2)$$

where E is the activation energy, k is Boltzmann's constant, and C' is a constant.

Plots of $\ln I$ against $1/kT$ for the initial rise portions of the peaks are shown in Figure 4. The activation energy of peak I for sample A (solid circles) was evaluated as 0.934 ± 0.004 eV. This value is consistent with 0.93 ± 0.03 eV for similar peak of an unannealed quartz reported by Folley and Chithambo [3] using the same method. The value of the activation energy is also in agreement with 0.92 eV reported by Mebhah et al. [9] for the same 110 °C peak of unannealed fired quartz irradiated to 10 Gy. In comparison, the activation energy for peak I for sample B (open circles) was evaluated as 0.904 ± 0.004 eV and agrees with 0.90 ± 0.01 eV reported by Yazici and Topaksu [10] for an unannealed quartz. This shows that annealing has minimal effect on the activation energy of peak I. Similarly, for peak III, the activation energy was determined to be 1.18 ± 0.01 eV and $E = 1.10 \pm 0.01$ eV for samples A (solid squares) and B (open squares) respectively. In comparison, the values of E for peaks I and III for sample B are slightly less than those obtained for sample A. An increase in the duration of annealing did not cause a significant increase in the activation energy.

3.4.2. Whole glow peak method.

The whole glow peak method was further used to determine the activation energy E , order of kinetics b , and frequency factor of peaks I and III. The method is best suited for a well-isolated glow peak whose area A under the glow peak is related to the order of kinetics b by:

$$\ln\left(\frac{I}{Ab}\right) = \ln\left(\frac{s'}{\beta}\right) - \left(\frac{E}{kT}\right), \quad (3)$$

where β is the heating rate, s' is the effective pre-exponential factor [20]. For first-order kinetics, s' becomes the frequency factor. Graphs of $\ln\left(\frac{I}{Ab}\right)$ against $\frac{1}{kT}$ for different values of b were plotted to determine the best choice for b . For peak I in sample A, this was determined as $b = 1.1$ ($R^2 = 0.99$) and as $b = 1.2$ ($R^2 = 0.999$) for peak I for sample B. For peak III, $b = 1.2$ and $b = 1.1$ for samples A

and B respectively. These values of b suggest that the peaks are of first-order kinetics. The activation energy for peak I for sample A was found as $E = 0.96 \pm 0.01$ eV. This is consistent with 0.95 ± 0.01 eV for the same quartz annealed for 60 minutes implying that the duration of annealing did not affect the activation energy of peak I. The values obtained for the activation energy for samples A and B as described are in good agreement with 0.98 ± 0.01 eV for unannealed quartz [3] implying that annealing has little effect on the activation energy. For peak III, $E = 1.09 \pm 0.01$ eV for sample A and $E = 1.02 \pm 0.01$ eV for sample B. The activation energy decreases with the duration of annealing. However, the value obtained for sample A compares favourably with 1.06 ± 0.01 eV [8] for peak III for the unannealed quartz, suggesting that annealing has little effect on the activation energy. The frequency factors obtained from the intercept of the plots for peak I are $1.5 \times 10^{13} \text{ s}^{-1}$ for sample A and $8.5 \times 10^{12} \text{ s}^{-1}$ for sample B. Similarly, for peak III, the frequency factor was evaluated as $1.1 \times 10^{11} \text{ s}^{-1}$ and $6.5 \times 10^{10} \text{ s}^{-1}$ for samples A and B respectively. The frequency factors for both peaks also decreases with the duration of annealing. The relevant plots for this method are available as *supplementary information*.

3.4.3. Curve fitting method.

Peaks I and III extracted from thermal cleaning were fitted using the expression:

$$I(T) = I_m b^{\frac{b}{b-1}} \exp\left(\frac{E(T-T_m)}{kTT_m}\right) \left[(b-1) \left(1 - \frac{2kT}{E}\right) \frac{T^2}{T_m^2} \exp\left(\frac{E(T-T_m)}{kTT_m}\right) + 1 + (b-1) \frac{2kT_m}{E} \right]^{-\frac{b}{b-1}}, \quad (4)$$

where I_m is the maximum peak intensity, and other parameters remain as defined previously [22].

The goodness of fit was tested by the so-called figure of merit (FOM) defined as:

$$FOM = \frac{\sum_p |y_{exp} - y_{fit}|}{\sum_p y_{fit}} \times 100\%, \quad (5)$$

where y_{exp} and y_{fit} represent the experimental intensity data and the values of the fitting function, respectively [23]. A fit is acceptable if $FOM \leq 3.5\%$ [23, 24].

The frequency factor was calculated by substituting the values of E and T_m into the expression:

$$s = \frac{\beta E}{kT_m^2} \exp\left(\frac{E}{kT_m}\right), \quad (6)$$

where all parameters maintain their meanings.

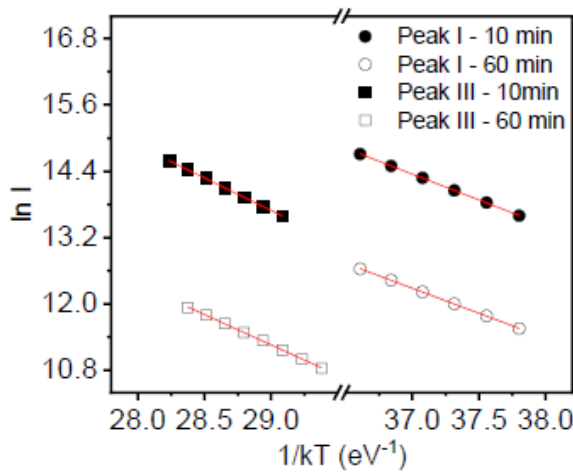


Figure 4. A plot of $\ln I$ against $1/kT$ for peak I and peak III using the initial rise method.

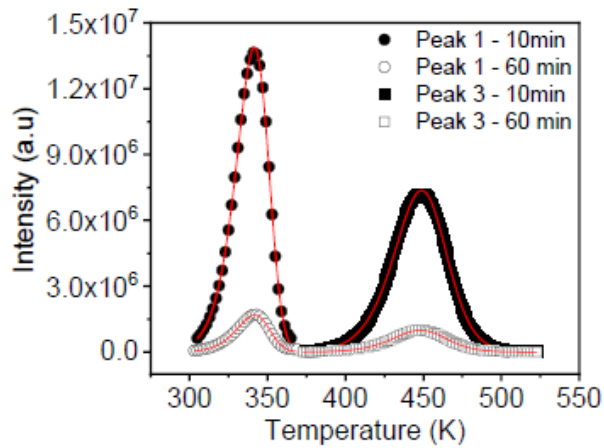


Figure 5. Curve fitting for peaks I and III. The solid lines through data points are the best fits of equation (4).

Figure 5 shows the best fit obtained for peaks I and III. The kinetic parameters determined for peak I are $E = 1.01 \pm 0.01$ eV and $b = 1.14 \pm 0.02$ with $FOM = 0.21\%$ for sample A whereas $E = 1.04 \pm 0.02$ eV and $b = 1.22 \pm 0.04$ with $FOM = 0.48\%$ for sample B. Here, the activation energy of sample A is only slightly lower than that of B implying that the duration of annealing has little effect on the activation energy of peak I. For peak III, $E = 1.23 \pm 0.01$ eV and $b = 1.46 \pm 0.01$ with $FOM = 0.36\%$ for sample A. These values are in good agreement with $E = 1.204 \pm 0.004$ eV and $b = 1.50 \pm$

0.01 with $FOM = 0.33\%$ for sample B. The E values obtained for peaks I and III for both annealed samples are consistent with literature values (e.g. $E = 1.01 \pm 0.01$ eV [3]), $E = 1.00$ eV [6], $E = 1.22$ eV [6], $E = 1.21 \pm 0.02$ eV [8]). The values of b suggest that peak I for both samples follow first-order kinetics whereas peak III is of general-order kinetics. This agrees with the findings from the dose dependence of peak position method. The FOM values show that the curve fits are reliable. The frequency factor for peak I was calculated as 7.7×10^{13} and 2.0×10^{14} s⁻¹ for samples A and B respectively. For peak III, $s = 4.5 \times 10^{12}$ s⁻¹ for sample A and $s = 2.0 \times 10^{12}$ s⁻¹ for sample B. These values are of the correct order of magnitude being consistent with the Debye vibration frequency.

4. Conclusion

The influence of annealing on thermoluminescence of natural quartz has been investigated through various methods of kinetic analysis. Peaks I and III, the two prominent peaks of the samples annealed for 10 and 60 min were analysed for kinetic parameters. We found that the thermoluminescence intensity decreases with the duration of annealing for both peaks. Lifetimes also decreases with annealing time. The activation energy and frequency factor obtained for both peaks using various methods decrease with the duration of annealing. This implies that the duration of annealing at 1000 °C has an effect on the trap parameters of natural quartz.

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