

Thermoluminescence characteristics of synthetic quartz

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Abstract

Quartz is one of the most abundant natural minerals in the crust of the earth. Due to its dosimetric luminescence properties, it is employed in retrospective dosimetry, archaeological and geological dating. The intensity and the structure of the TL glow curves of quartz are strongly dependent upon the origin, impurity content, formation condition and pre-irradiation heat treatment. The aim of this project is to study the mechanisms of thermoluminescence (TL), Phototransferred thermoluminescence (PTTL) and radioluminescence (RL) in synthetic quartz and to discuss the results in terms of physical characteristics of point defects involved. Thermoluminescence measurements were made on a sample of synthetic quartz in its as-received state (unannealed) synthetic quartz annealed at 500°C for 10 minutes. The unannealed sample shows six TL glow peaks located at 94, 116, 176, 212, 280 and 348°C at a heating rate of 5°Cs⁻¹. The annealed sample shows seven TL peaks at 115, 148, 214, 246, 300, 348 and 412°C at a heating rate of 5°Cs⁻¹. The intensity of peak I, at 94 and 115°C for the unannealed and annealed samples respectively, increases with irradiation. Peak I has an activation energy of approximately 0.90 eV and a frequency factor of the order of 10¹¹ s⁻¹. The order of kinetics is between 0.9 and 1.2. The unannealed synthetic quartz shows phototransferred thermoluminescence (PTTL) at the position of peak I after removal of the first three peaks followed by illumination. The PTTL intensities show peak shaped behaviour when plotted against illumination time. The PTTL showed a quadratic increase with dose. The material exhibits fading of PTTL intensity with delay time. Radioluminescence was measured on synthetic quartz unannealed and annealed at 500, 600, 700, 800, 900 and 1000°C for 10 to 60 min. The emission spectra of synthetic quartz show seven emission bands. The effect of irradiation on the RL spectra is to increase the intensity of all emission bands for samples annealed at temperatures less than or equal to 700°C. The effect of annealing time is to increase the RL amplitude for the samples annealed at temperatures greater than 700°C. The annealing temperature increases the RL amplitude of all emission bands of the spectrum for all samples.

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Chapter 1

Introduction

1.1 Luminescence

Luminescence is the emission of light from previously irradiated solids, typically insulators or semiconductors. The luminescent materials are also known as phosphors. Luminescence can also be defined as the release of the energy stored inside the phosphor during the process of excitation. During luminescence phenomenon, some energy source moves a valence electron of an atom from its ground state (lowest energy) into an excited state (higher energy) by supplying extra energy. Since this excited state is not stable, the electron moves back to its ground state by giving out this excess energy in form of light. In the process of luminescence, when radiation is incident on a material, some of its energy may be absorbed and re-emitted as light of long wavelength. The phenomenon is called luminescence. This phenomenon should be differentiated from incandescence which occurs when the material is heated at high temperature (black-body radiation etc). In luminescence, the wavelength of the emitted light is characteristic of the luminescent material not of the incident radiation. Here the role of the incident radiation is the excitation of electrons from the ground to the excited state or disturbance of the system from its equilibrium state [1, 2, 3]

1.1.1 Types of luminescence

The type of absorbed energy characterizes the luminescence. The luminescence is classified as photoluminescence when the emission is excited by non-ionizing photons. When the material is excited by ionizing radiation (X -rays, β -rays, γ -rays, α -particles) the luminescence is known as radioluminescence. The signal is called cathodoluminescence if the excitation is done by an electron beam. In addition to excitation by radiation, luminescence can be generated by chemical energy to produce chemiluminescence, mechanical energy for triboluminescence, electrical energy for electroluminescence, biochemical energy for bioluminescence and sound waves for sonoluminescence.

1.1.1.1 Fluorescence and Phosphorescence

In terms of the value of lifetime τ i.e., the time delay between the absorption of radiation and the emission of light, luminescence can be classified into two sub-classes, fluorescence or phosphorescence. Fluorescence is luminescence phenomenon where the light is emitted at a time τ less than 10^{-8} seconds after the absorption of radiation. Fluorescence emission is seen to be instantaneous as it has short lifetime. Fluorescence emission is seen to occur simultaneously with absorption of radiation and stops immediately when the radiation ceases. It is essentially temperature independent. Figure 1.1 illustrates the case of fluorescence in which the absorption of energy causes electrons to move from the ground state g to the excited state e (transition (i)). The inverse path (transition (ii)), that happens in short time intervals of less than 10^{-8} seconds, is the allowed luminescence transition.

In phosphorescence, the light is emitted at a time τ greater than 10^{-8} seconds after excitation and the decay of phosphorescence exhibits strong temperature dependence. Phosphorescence is characterized by delay between radiation absorption and light emission. This delay is due to the situation when an electron is excited (e.g. by ion-

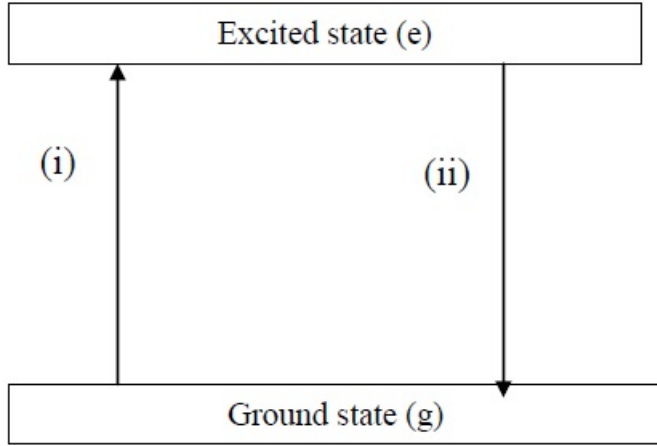


Figure 1.1: Excited state e and ground state g energy levels showing excitation and emission of fluorescence [3].

izing radiation) from a ground state g to a metastable state m (electron trap). An electron in the m -state can return to the ground state only by passing through the excited state e and this transition requires the energy E , termed activation energy which can be supplied by heating the sample. The m - e transition is followed by e - g transition, which occurs with emission of light.

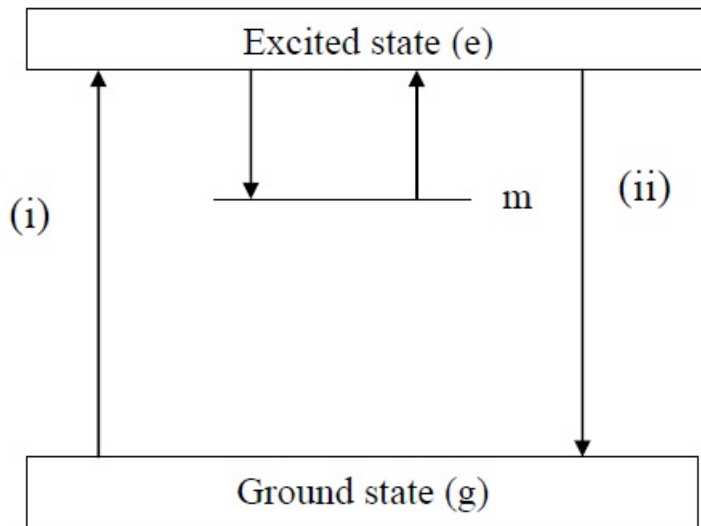


Figure 1.2: Schematic diagram illustrating the process of phosphorescence [3].

Phosphorescence is also classified into two sub-classes; short period phosphorescence where τ is less than or equal to 10^{-4} seconds and long period phosphorescence where

τ is greater than 10^{-4} seconds. It is in this long subclass that thermoluminescence is included. For phosphorescence phenomenon to be properly described and analyzed, the involvement of the metastable state energy level m is critical [1, 2]. We consider the phosphorescence process in the situation illustrated in figure 1.2 where g is the ground state, e is the excited state and m is the metastable state or electron trap. The probability p per unit time that a trapped electron will escape from a trap is given by the equation

$$p = s \exp \left(-\frac{E}{kT} \right). \quad (1.1)$$

The lifetime of the charge carrier in the metastable state at temperature T is given by $\tau = p^{-1}$. If n is the number of trapped electrons and if the temperature is kept constant, n decreases with time according to the following expression.

$$\frac{dn}{dt} = -pn. \quad (1.2)$$

Substituting the expression of p in equation 1.2 we get the following expression

$$\frac{dn}{dt} = -ns \exp \left(-\frac{E}{kT} \right). \quad (1.3)$$

Rearranging equation 1.3 leads to

$$\frac{dn}{n} = -s \exp \left(-\frac{E}{kT} \right) dt. \quad (1.4)$$

By integrating both sides of equation 1.4 we have

$$n = n_0 \exp \left(-st \exp \left(\frac{E}{kT} \right) \right). \quad (1.5)$$

where n_0 is the number of trapped electrons at time $t = 0$. The intensity of phosphorescence $I(t)$ is proportional to rate of recombination ($e \rightarrow g$) transitions and depends

on probability p of escape of an electron from the trap,

$$I(t) = Cnp = n_0s \exp\left(-\frac{E}{kT}\right) \exp\left[-st \exp\left(-\frac{E}{kT}\right)\right], \quad (1.6)$$

where C is the constant.

Equation 1.6 indicates that the phosphorescence decay is a simple exponential decay function of time when one trap is considered for measurement at a constant temperature.

1.1.2 Theory of thermoluminescence

Thermally stimulated luminescence (TSL) or thermoluminescence (TL) is defined as the emission of light from semiconductors or insulators which have been previously exposed to ionizing radiation [4, 5]. The graph of the thermoluminescence intensity as a function of temperature is known as a glow curve.

The band theory of solids is normally used to explain thermoluminescence. In insulators or semiconductors, there are two energy bands; an almost completely filled valence band and an almost empty conduction band. The energy bands are separated by a forbidden gap. This means that between these bands there are no electronic levels. Transitions between the valence band and the conduction band are allowed and produce "free" electrons in the conduction band and "free" holes in the valence band.

Imperfections in the crystal, associated with impurities or lattice defects, may create localized energy levels in the forbidden band gap. The position of energy levels depends on the nature of imperfections or defects and the lattice. Some of the defects are able to trap an electron or a hole. The defects where electrons or holes are trapped are called electrons traps or hole centres respectively. Ionizing radiation ionizes electrons from the valence band to the conduction band, leading to the presence of a significant concentration of free electrons in the conduction band and free holes

in the valence band [6]. The electrons are free to travel through the conduction band. Most recombine rapidly, but certain percentage of charge carriers is trapped; electrons are trapped in electron traps ("traps") and holes in hole traps("recombination centres").

Due to the heating of the material, trapped electrons at delocalized state get enough energy to escape from traps into the conduction band. They may either be retrapped at defects or recombine radiatively by emitting photons or non-radiatively with holes by emitting phonons. The light emitted by this process is known as thermoluminescence.

1.1.2.1 Models of thermoluminescence

The basic model assumes that the irradiation produces free electrons and holes and that some of them are trapped in a delocalized energy levels within the forbidden band. TL can be understood by considering a simple model consisting of two delocalized levels, an isolated electron trap (T) and a recombination center (RC). This model is commonly referred to as one-trap-one-recombination center model (OTOR). Figure 1.3 illustrates the OTOR model [2]. Parameters in the model are defined as follows: N and M are the concentration of electron traps and recombination centres respectively; n and m (cm^{-3}) are the concentration of trapped electrons and trapped holes respectively; n_c and n_v (cm^{-3}) are the concentration of electrons in conduction band and holes in valence band respectively. A_n and A_m (cm^3s^{-1}) are the retrapping and recombination probability respectively, B is the trapping probability coefficient of hole centers. X is proportional to the dose rate of excitation; it actually denotes the rate of production of electron-hole pairs by excitation per unit volume per second.

In order to describe the transfer of charge carriers during heating, a set of three differential equations was used [6]. With assumption that the TL emitted is associated with the recombination of free electrons with holes in recombination centres, the first

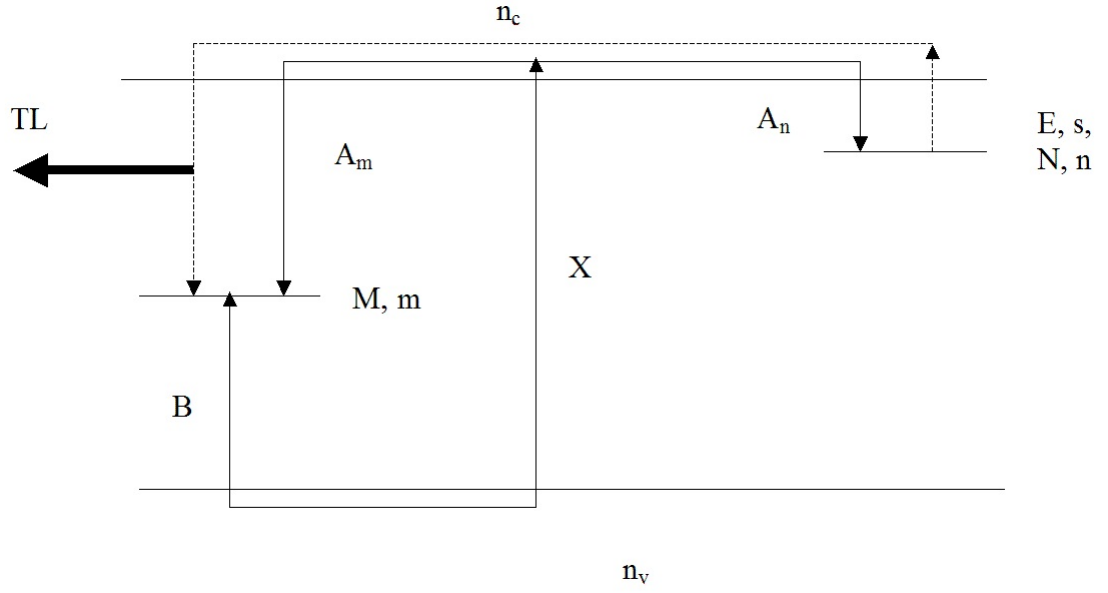


Figure 1.3: Energy band diagram describing thermoluminescence for simple model i.e. one-trap-one-recombination centre (OTOR). Transitions occurring during excitation are shown by solid lines and during heating by dashed lines. The thick arrow denotes the emitted TL.

equation states that the intensity is equal to the rate of recombination,

$$I(T) = -\frac{dm}{dt} = A_m m n_c. \quad (1.7)$$

The second equation deals with the population variation in trap n and possible retrapping,

$$\frac{dn}{dt} = n_c (N - n) A_n - n s \exp\left(-\frac{E}{kT}\right). \quad (1.8)$$

Equation 1.8 indicates that the rate of change of n is equal to the difference between the rate of retrapping and the rate of thermal release. The third equation relates the charge neutrality condition this means that electrons and holes are produced in pairs during irradiation,

$$\frac{dn_c}{dt} = \frac{dm}{dt} - \frac{dn}{dt}. \quad (1.9)$$

By replacing the right hand side of equation 1.9 with expressions in equation 1.7 and 1.8 we get

$$\frac{dn_c}{dt} = ns \exp\left(-\frac{E}{kT}\right) - n_c mA_m - n_c (N - n) A_n. \quad (1.10)$$

Two assumptions can be made for solving the previous set of equations: $n_c \ll n$ i.e. $dn_c/dt \ll dn/dt$ and $dn_c/dt = 0$ which means that the concentration of carriers in the conduction band does not change.

Now equation 1.10 becomes

$$ns \exp\left(-\frac{E}{kT}\right) - n_c mA_m - n_c (N - n) A_n = 0. \quad (1.11)$$

Rearranging equation 1.11 we get

$$ns \exp\left(-\frac{E}{kT}\right) = n_c [mA_m + (N - n) A_n]. \quad (1.12)$$

$$n_c = \frac{ns \exp\left(-\frac{E}{kT}\right)}{mA_m + (N - n) A_n}. \quad (1.13)$$

From equation 1.7, we recall that thermoluminescence intensity is given by:

$$I(T) = n_c mA_m. \quad (1.14)$$

Substituting n_c in equation 1.13 into equation 1.14, we get the following expression

$$I = -\frac{dm}{dt} = ns \exp\left(-\frac{E}{kT}\right) \frac{mA_m}{mA_m + (N - n) A_n}. \quad (1.15)$$

The term $ns \exp\left(-\frac{E}{kT}\right)$ in the right hand side of equation 1.15 is the number of electrons thermally released to the conduction band per unit time. The term $[mA_m/(mA_m + (N - n) A_n)]$ is the probability of non-retrapping of thermally released electrons [1, 2, 3, 4, 5, 6].

1.1.3 First order kinetics

For first order kinetics, equation 1.15 was solved analytically by making the assumptions that recombination dominates [4]. With $m A_m \gg (N - n) A_n$, equation 1.15 then becomes:

$$I = -\frac{dm}{dt} = n s \exp\left(-\frac{E}{kT}\right). \quad (1.16)$$

Also by combining the assumptions made that $dn_c = 0$ one can find, $dm/dt = dn/dt$. This means that the trapped electrons and holes are produced in pairs during irradiation. We can therefore write equation 1.16 as

$$I = -\frac{dn}{dt} = n s \exp\left(-\frac{E}{kT}\right). \quad (1.17)$$

Equation 1.17 is the equation of first order kinetics. By considering a constant heating rate $\beta = dT/dt$, equation 1.17 becomes

$$\frac{dn}{dT} = -\left(\frac{1}{\beta}\right) n s \exp\left(-\frac{E}{kT}\right). \quad (1.18)$$

Integration of equation 1.18 gives

$$I(T) = n_0 s \exp\left\{\frac{-E}{kT}\right\} \exp\left\{\frac{-s}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{kT}\right) dT\right\}. \quad (1.19)$$

The glow curve resulting from this equation has a characteristics of an asymmetric shape being wider on the low temperature side [2].

1.1.4 Second order kinetics

In this case, the same model (OTOR) and assumptions that retrapping of released charges dominates are used, i.e. $A_m m \ll (N - n) A_n$; pair production of electrons and holes ($m = n$) occurs and that the trap is far from saturation, $N \gg n$ were

used. Under these assumptions, the following equation is obtained [1] :

$$I = -\frac{dm}{dt} = \frac{mA_m n s \exp\left(-\frac{E}{kT}\right)}{NA_n}. \quad (1.20)$$

From the assumption that $m = n$, we obtain

$$I = \frac{A_m}{NA_n} n^2 s \exp\left(\frac{E}{kT}\right). \quad (1.21)$$

By setting $s' = sA_m/NA_n$ the equation becomes

$$I = n^2 s' \exp\left(-\frac{E}{kT}\right). \quad (1.22)$$

The solution of equation 1.22 gives the TL intensity for second order kinetics as

$$I(T) = n_0^2 s' \exp\left\{\frac{-E}{kT}\right\} \left\{1 + \frac{n_0 s'}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{kT}\right) dT\right\}^{-2}. \quad (1.23)$$

The glow curve characterized by this equation is approximately symmetric.

1.1.5 General order kinetics

When the simplifying assumptions used in the first- and second-order kinetics are not satisfied, the empirical formula for general order kinetics is given by the following equation [4, 6],

$$I(t) = -\frac{dn}{dt} = n^b s' \exp\left(-\frac{E}{kT}\right). \quad (1.24)$$

where s' has a dimension of $m^{3(b-1)}s^{-1}$ and b is defined as the general order parameter.

The integration of the equation for $b \neq 1$ gives,

$$I(T) = s'' n_0 \exp\left\{\frac{-E}{kT}\right\} \left\{1 + (b-1) \frac{s''}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{kT}\right) dT\right\}^{\frac{-b}{(b-1)}}. \quad (1.25)$$

where $s'' = s' n_0^{b-1}$ with unit s^{-1} . The equation includes the second order equation when $b = 2$ and can be transformed to first order when $b \rightarrow 1$.

Chapter 2

Kinetic analysis theory

Thermoluminescence properties of materials are characterized by parameters called kinetic parameters. Such parameters include the activation energy (E), frequency factor (s) and order of kinetics (b). These parameters provide useful information for better understanding of mechanisms involved in the emission of luminescence. Kinetic analysis deals with methods of establishment of kinetic parameters [7]. According to the way glow curve data are handled, methods of kinetics analysis are classified as initial rise, whole curve, peak position, peak shape, glow curve deconvolution and isothermal analysis [1, 2, 3]. The following sections provide a brief description of each method.

2.1 Initial rise method

This method of analysis is based on use of the low temperature tail of the glow peak. The initial rise method is based on the assumption that in the initial rise part of a glow peak, the thermoluminescence intensity is exponentially dependent on temperature. From equation 1.19 of first order kinetics, in the initial rise region of the peak the second exponential tends to unity, that is,

$$\lim_{T \rightarrow T_0} \exp \left[\int_{T_0}^T \frac{s}{\beta} \exp(-E/kT) dT \right] \sim 1$$

The second assumption is that the amount of trapped electrons n in the low temperature tail of TL peak is approximately constant. This assumption is considered valid for a temperature corresponding to an intensity less than 15 % of the maximum thermoluminescence intensity [3]. With these assumptions, equation 1.19 becomes

$$I(T) = C \times \exp\left(\frac{-E}{kT}\right). \quad (2.1)$$

where $I(T)$ is thermoluminescence intensity, E is the activation energy (eV), k is Boltzmann's constant and T is temperature in K [8]. Equation 2.1 can be transformed by taking natural logarithm on both sides to get:

$$\ln(I(T)) = C - \frac{E}{kT}. \quad (2.2)$$

A plot of $\ln(I)$ versus $1/kT$ will give a straight line with a slope $-E$ and from that the activation energy can be found.

In this method, the TL peak should be well defined, clearly separated from other peaks and not subject to thermal quenching. In case of overlapping or superposed peaks, McKeever [3] describes two methods of peak separation. The first method is called "thermal cleaning". This method consists of heating the sample to a temperature above the maximum temperature of the peak that needs to be cleaned in order to empty the trap responsible for that peak. After cooling down, the next step is to reheat the sample to record the whole glow curve. After this stage, the next glow peak should have a clear initial rise part.

The second method of peak separation is called " T_m - T_{stop} ". This method can be used to identify the peak temperature of closely overlapping peaks. The method consists of heating the previously irradiated sample to a given temperature T_{stop} at a linear heating rate from the low temperature part of the first peak of the glow curve. After cooling down, the sample is reheated at the same heating rate to measure the whole glow curve. The process is repeated by changing T_{stop} in small steps (2 or 3°C). After

each T_{stop} , the whole glow curve is recorded and the maximum temperature T_m is noted [8].

A plot of T_m versus T_{stop} from the glow curve containing overlapping peaks shows a staircase shaped structure. Each flat region of the plot corresponds to an individual peak. A related method is the evaluation of the activation energy (E) corresponding to each T_{stop} and this is called $E-T_{stop}$. The activation energies are plotted against T_{stop} and staircase curve results if the peak is composed of more than one overlapping peaks. Again each flat region indicates the presence of an individual peak [3].

2.2 Whole curve method

This method is also known by the name " area method" . It consists of transformation of a whole glow peak into a straight line. The area $n(T)$ under the glow peak is determined by summing all data points of thermoluminescence intensities I_i beyond temperature T_0 in the initial rise region up to a final temperature T_f at the end of the glow peak. The sum is multiplied by the temperature interval ΔT and divided by the heating rate β [8]:

$$Area = n(T) = \sum_{i=T_0}^{T_f} I_i \frac{\Delta T}{\beta}. \quad (2.3)$$

where $\Delta T = T_f - T_0$

For a glow peak which follows first order kinetics, $\ln(I/n(T))$ is a linear function of $1/kT$ with slope $-E$ where E is the activation energy. From the intercept $\ln(s/\beta)$, the frequency s can be found.

In the general order case, the method is based on the equation of general order kinetics [1]. By considering the linear heating rate $\beta = \frac{dT}{dt}$, equation of general order

kinetics shown by equation 1.24 becomes

$$I(T) = -\frac{dn}{dT} = \left(\frac{1}{\beta}\right) n^b s' \exp\left(-\frac{E}{kT}\right). \quad (2.4)$$

By taking the natural logarithm of both side of equation 2.4 we get

$$\ln\left(\frac{I}{n^b}\right) = \ln \frac{s'}{\beta} - \frac{E}{kT}. \quad (2.5)$$

The method is to plot $\ln(I/(n(T))^b)$ versus $1/kT$, where b is the order of kinetics. The value of b is changed to find one which gives the best fit. This is the order of kinetics. From that best fit, the activation energy E is found from the slope ($-E$) and the frequency factor is again found from the intercept $\ln(s'/\beta)$. This method can be applied to a clean and well defined glow peak.

2.3 Various heating rate method

Taking the logarithmic derivative of equation 1.19 with respect to temperature, equating the result to zero and setting the condition that $T = T_m$, gives the following expression [1].

$$\left[\frac{d(I(T))}{dT}\right]_{T=T_m} = \frac{E}{kT_m^2} - \frac{s}{\beta} \exp\left(-\frac{E}{kT_m}\right) = 0. \quad (2.6)$$

By rearranging equation 2.6 we get

$$\frac{\beta E}{kT_m^2} = s \exp\left(-\frac{E}{kT_m}\right). \quad (2.7)$$

By using the assumption that the frequency factor s and the activation energy E in equation 2.7 are constants, the change of peak maximum T_m is only caused by the heating rate. The increase in heating rate results in shift of the peak to higher

temperature [7]. Rearrangement of equation 2.7 gives

$$\ln \left(\frac{T_m^2}{\beta} \right) = \left(\frac{E}{k} \right) \frac{1}{T_m} + \ln \left(\frac{E}{sk} \right). \quad (2.8)$$

From equation 2.8, trapping parameters are found using Hoogenstraaten's method [2, 3, 8]. This method consists of plotting $\ln (T_m^2/\beta)$ versus $1/kT_m$. The activation energy E is found from the slope and the frequency factor from the intercept $\ln (E/sk)$. Once E is found, the frequency factor s can also be found from equation 2.7 as

$$s = \frac{\beta E}{kT_m^2} \exp \left(\frac{E}{kT_m} \right). \quad (2.9)$$

The change of the heating rate β with which the glow curve is taken causes the shift in the peak position. By changing heating rate β and recording the temperature T_m that correspond to the maximum intensity I_m , another method of determination of activation energy was proposed. The method considers two different heating rates and corresponding maximum temperatures [1, 6, 8]. From elimination of s in equation 2.7 using two different heating rates, the activation energy is determined using the resultant equation below

$$E = k \frac{T_{m1}T_{m2}}{T_{m1} - T_{m2}} \ln \left[\frac{\beta_1}{\beta_2} \left(\frac{T_{m1}}{T_{m2}} \right)^2 \right]. \quad (2.10)$$

During the analysis, the effect of satellite peaks is eliminated because the only maximum points namely maximum TL intensity and corresponding maximum temperature are recorded. This is one advantage of the various heating rate method.

2.4 Peak shape methods

In this method, Chen [2] proposed a method of evaluation of kinetic parameters based on the shape of a glow peak. He used three equations relating the activation energy

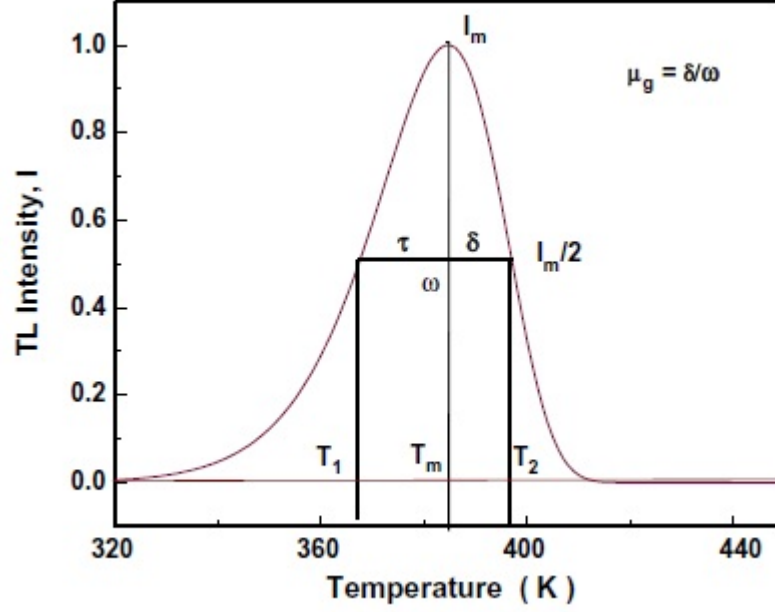


Figure 2.1: An example of a glow peak showing the associated geometric shape quantities [9].

with geometric shape quantities. These parameters are the full width of the peak at half maximum ω , low temperature half width τ and high temperature half width δ where $\omega = T_2 - T_1$, $\tau = T_m - T_1$ and $\delta = T_2 - T_m$ as shown in figure 2.1. Here T_1 , T_2 and T_m are low-temperature half-height, high-temperature half-height and the maximum temperature of the peak respectively. The geometric factor $\mu = \delta/\omega$ is used to determine the order of kinetics b . If the value of $\mu = 0.42$, the peak follows first order kinetics. When $\mu = 0.52$, the peak follows second order kinetics. The method uses a general equation to find the value of activation energy E , that is

$$E = C_\gamma \left(\frac{kT_m^2}{\gamma} \right) - b_\gamma (2kT_m), \quad (2.11)$$

where γ stands for ω , τ or δ . The constants C_γ and b_γ differ for first, second and general order and are given in table 2.1.

Table 2.1: Values of C_γ and b_γ used in calculation of the activation energy using equation (2.11) for general order kinetics [3].

	ω	τ	δ
C_γ	$2.52+10.2(\mu-0.42)$	$1.51+3(\mu-0.42)$	$0.976+7.3(\mu-0.42)$
b_γ	1	$1.58+4.2(\mu-0.42)$	0

2.5 Isothermal analysis method

Isothermal luminescence measurement consists of recording the luminescence intensity with respect to time at a constant temperature. The graph of TL intensity versus time is called an isothermal decay curve. Isothermal decay curves are used in the determination of trapping parameters and this method is called isothermal analysis [8].

2.5.1 First order kinetics

The solution of first order kinetics equation given in equation 1.17 with respect to time by keeping temperature constant is equal to equation 1.6 [10]

$$I(t) = n_0 s \exp\left(-\frac{E}{kT}\right) \exp\left[-st \exp\left(-\frac{E}{kT}\right)\right]. \quad (2.12)$$

The simple form of phosphorescence decay is therefore an exponential decay given by

$$I(t) = I_0 \exp(-pt), \quad (2.13)$$

where $I_0 = n_0 s \exp\left(-\frac{E}{kT}\right)$.

The decay constant p is given in equation 2.13 as

$$p = s \exp\left(-\frac{E}{kT}\right). \quad (2.14)$$

Using equation 2.13, the order of kinetics of the glow peak under study can be determined. If equation 2.13 gives the best fit for an isothermal decay curve, the

peak under study is expected to be of first order kinetics [2, 7]. From equation 2.13, the plot of $\ln(I(t))$ versus time gives a straight line of slope p . Using isothermal decay curves measured at various temperatures, values of p are found from each decay curve. A plot of $\ln(p)$ versus $1/kT$ yields a straight line of slope $-E$ from which the activation energy is found. The frequency factor s is determined from the intercept ($\ln s$).

2.5.2 General order kinetics

Solving the general order kinetics equation 1.24 with respect to time again by keeping temperature constant will give the thermoluminescence intensity as

$$I(t) = I_0 \left[1 + s' n_0^{b-1} (b-1) t \exp\left(-\frac{E}{kT}\right) \right]^{\frac{b}{1-b}}, \quad (2.15)$$

where $I(t)$ is the intensity a time t , I_0 is the intensity at $t = 0$. By rearranging equation 2.15, we get [8]

$$\left(\frac{I(t)}{I_0} \right)^{\frac{1-b}{b}} = \left[1 + s' n^{b-1} (b-1) t \left(-\frac{E}{kT} \right) \right]. \quad (2.16)$$

Plotting $\left[\frac{I(t)}{I_0} \right]^{\frac{1-b}{b}}$ against time will give a straight line of slope p' . In this method, the value of p' is found by changing the value of b at a particular measurement temperature till a straight line is found. The slope of that straight line is

$$p' = s' n^{b-1} (b-1) \exp\left(-\frac{E}{kT}\right). \quad (2.17)$$

By plotting $\ln(p')$ versus $1/kT$, the activation energy E is found from the slope $-E$.

2.5.3 Monotonic peak to glow curve transformation

An isothermal decay curve can be transformed into a TL-resembling glow peak that can be used in evaluation of kinetic parameters [2, 7]. The process consists of plotting a graph of $I \times t$ against $\ln t$. From the resulting glow peak at each measurement temperature, the time peaks t_{max1} , t_{max2} and the corresponding measurement temperatures T_1 and T_2 are collected. By increasing the measurement temperature, a shift of the peak is expected and the shift is given by equation [2].

$$\Delta \ln t_{max} = \ln t_{max2} - \ln t_{max1} = \frac{E}{k} \left(\frac{1}{T_2} - \frac{1}{T_1} \right). \quad (2.18)$$

From the equation, the activation energy E can be determined.

Chapter 3

Phototransferred thermoluminescence

Phototransferred thermoluminescence (PTTL) is a widely observed phenomenon in many thermoluminescent materials and is basically the thermoluminescence (TL) induced by charge transfer from deeper traps to shallower traps upon optical stimulation [11, 12]. The procedure for generating PTTL consists of the following steps. The first step is the ionization of charge carriers by irradiating the material and thereby creating free charges i.e., electrons and holes. Some of these charges get trapped at various localized trapping states within the sample. Trapped charges are removed from shallow traps by heating the material to a temperature high enough to empty shallow traps but leaving the deeper ones populated. The next step is the illumination of the sample at a lower temperature (usually at room temperature) with light of sufficient energy to stimulate charges from deeper traps. This illumination transfers the charges from deep traps to delocalized bands, from where a portion has the probability of being trapped in shallow traps, while others recombine. The last step is heating the sample to obtain the whole glow curve. TL from shallow traps is the phototransferred thermoluminescence [13].

Phototransferred thermoluminescence has been studied in a wide variety of materials and results suggest that it can be used as a tool for dosimetry and dating applications [12, 14]. The phototransferred charges are generally considered to be electrons.

3.1 PTTL models

For PTTL to be observed from a given material, the sample must have at least two electron traps. One deep trap which will serve as source of electrons during optical excitation (illumination) and one shallow trap into which the charges are transferred. The sample must also have at least one recombination centre which will allow radiative recombination to produce PTTL.

3.1.1 Description of PTTL

In description of PTTL, notation to be used in equations which describe the flow of charges in each of the PTTL steps is defined next: N_i , M_i will represent the concentration of any trap and recombination centre where the index i indicates the trap and recombination centre number respectively. n_i and m_i will be the concentration of electrons and holes in trap and recombination centre i respectively. A_i , A_h and A_m are the electron trapping, hole trapping and recombination probabilities respectively.

3.1.1.1 Simple model

The simple model to describe phototransferred thermoluminescence consists of one shallow trap and one deep trap each of concentration N_1 and N_2 respectively. The shallow trap has electron populations of n_1 and the deep trap has an electron populations of n_2 . The model also consists of one hole trap whose concentration is M ; the hole population is m . The hole trap acts as a recombination centre as shown in figure 3.1. At the beginning of the process all electron traps and recombination centre are free of charges. The irradiation of the sample causes the accumulation of charge carriers in the electron traps and recombination centres. The following equations describe the flow of charge during this irradiation process [14].

$$\frac{dn_c}{dt} = X - A_1 (N_1 - n_1) n_c - A_2 (N_2 - n_2) n_c - A_m m n_c + \gamma_1 n_1 + \gamma_2 n_2. \quad (3.1)$$

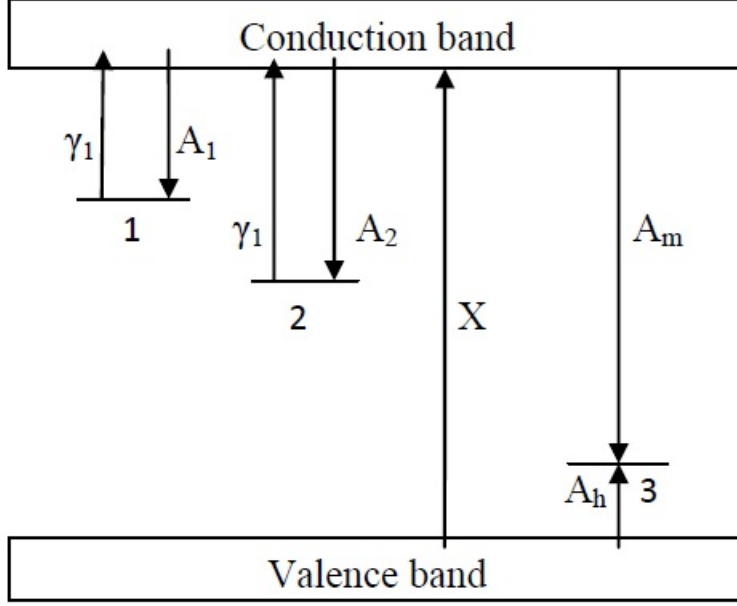


Figure 3.1: A simple model of PTTT composed of one shallow trap (level 1) and one deep trap (level 2) and one radiative recombination centre (level 3) [2] .

$$\frac{dn_1}{dt} = A_1 (N_1 - n_1) - \gamma_1 n_1. \quad (3.2)$$

$$\frac{dn_2}{dt} = A_2 (N_2 - n_2) - \gamma_2 n_2. \quad (3.3)$$

$$\frac{dm}{dt} = A_h (M - m) n_v - A_m m n_c. \quad (3.4)$$

$$\frac{dn_v}{dt} = X - A_h (M - m) n_v. \quad (3.5)$$

Here n_c and n_v are concentration of electrons in the conduction band and concentration of holes in the valence band respectively. X is the rate of electron-hole pair generation, and $\gamma_i = s_i \exp(-E_i/kT)$ is the rate of thermal excitation from trap i . The irradiation process is presumed to occur at the temperature at which the rate of thermal eviction from either trap is insignificant on the timescale of irradiation,

thus $\gamma_1 = \gamma_2 = 0$ (usually at room temperature). After irradiation, all traps are populated by electrons and recombination centres by holes. The next step is the depletion of electrons from shallow traps. This can be done by leaving the sample at room temperature for a time that is significant relative to the rate of thermal eviction of charges from shallow traps or by heating the sample to a temperature sufficient to empty the shallow trap. This process is called pre-heating. After pre-heating, there are no electrons in the shallow trap. The sample is now illuminated with photons of sufficient energy to evict charges from deep traps, so that they may be transferred to shallow traps.

The initial population at time $t = 0$ (after irradiation and removal of trapped electrons in the shallow trap and before illumination) are $n_{10} = 0$ and $n_{20} = m_0$. The rate equations which describes the traffic of charges from deep traps into shallow traps during illumination are:

$$\frac{dn_1}{dt} = n_c (N_1 - n_1) A_1 - n_1 s_1 \exp\left(-\frac{E_1}{kT}\right) - n_1 f_1, \quad (3.6)$$

$$\frac{dn_2}{dt} = n_c (N_2 - n_2) A_2 - n_2 f_2, \quad (3.7)$$

$$\frac{dm}{dt} = -n_c m A_m = \frac{m}{\tau}, \quad (3.8)$$

where A_1, A_2 and A_m are the trapping and recombination constants of shallow, deep and recombination centres respectively; f_1 and f_2 are optical excitation rates out of the shallow and deep traps respectively (s^{-1}) and $s_1 \exp(-E_1/kT)$ is the rate of thermal excitation (s^{-1}) out of the shallow trap [11, 14].

The term $n_1 s_1 \exp(-E_1/kT)$ in equation 3.6 can be ignored where optical stimulation is performed at a temperature at which thermal eviction of electrons from shallow traps is insignificant during the phototransfer process. The same assumption

is applied to the optical excitation term (i.e $n_1 f_1$). Thus, $s_1 \exp(-E_1/kT) = f_1 = 0$. If f_1 is considered significant, the electrons in shallow traps n_1 will be completely removed for long illumination times and the PTTL will go to zero. For the purpose of obtaining a steady state PTTL level after very long illumination time, f_1 must equal or approximately equal zero [14].

In addition to the assumption of quasi-equilibrium ($dn_c/dt = 0$) and that retrapping into the source traps is insignificant ($n_2 f_2 \gg n_c(N_2 - n_2)A_2$), then the solution of the above equations 3.6, 3.7 and 3.8 are [2, 14]

$$n_1(t) = N_1[1 - \exp(-Bt)], \quad (3.9)$$

$$n_2(t) = n_{20} \exp(-tf), \quad (3.10)$$

and

$$m(t) = m_0 \exp\left(-\frac{t}{\tau}\right), \quad (3.11)$$

where $\tau = (n_c A_m)^{-1}$ is the recombination lifetime and $B = n_c A_1$. Here B and τ are considered approximately constant only if the quasiequilibrium approximation ($dn_c/dt = 0$) is true [11]. These equations describe how population of charge carriers in each trap change with optical excitation time and hence the distribution of charges at the end of phototransfer process.

In order to measure PTTL signals the sample is heated. During heating, the electrons will be released from shallow traps and may either recombine at a radiative recombination centre to produce PTTL or be retrapped in deep traps. The flow of charge during heating is described by the following equations [15]:

$$\frac{dn_1}{dt} = A_1 (N_1 - n_1) n_c - \gamma_1 n_1, \quad (3.12)$$

$$\frac{dn_2}{dt} = A_2 (N_2 - n_2) n_c, \quad (3.13)$$

$$\frac{dm}{dt} = -A_m m n_c, \quad (3.14)$$

$$\frac{dm}{dt} = \frac{dn_c}{dt} + \frac{dn_1}{dt} + \frac{dn_2}{dt}. \quad (3.15)$$

The expression for n_c can be found from equation 3.13 and 3.14 and is given as [2, 16]

$$n_c = \frac{1}{A_2} \frac{d}{dt} [\ln (N_2 - n_2)] = \frac{1}{A_m} \frac{d}{dt} [\ln (m)]. \quad (3.16)$$

The integration of equation 3.16 gives

$$N_2 - n_2 = (N_2 - n_{20}) (m/m_0)^{\frac{A_2}{A_m}}. \quad (3.17)$$

With quasi-equilibrium condition, equation 3.15 can be written as

$$\frac{dm}{dt} = \frac{dn_1}{dt} + \frac{dn_2}{dt}. \quad (3.18)$$

Substitution of equations 3.12, 3.13 and 3.14 in equation 3.18 will give the value of n_c as:

$$n_c = \frac{\gamma n_1}{[A_1 (N_1 - n_1) + A_2 (N_2 - n_2) + A_m m]}. \quad (3.19)$$

Inserting the value of n_c in the equation 3.14 we find the value the TL intensity,

$$I(t) = -\frac{dm}{dt} = A_m \gamma n_1 m / [A_1 (N_1 - n_1) + A_2 (N_2 - n_2) + A_m m]. \quad (3.20)$$

From the assumption that the trapping probability into the deep trap is much greater than that of retrapping and recombination $A_2 (N_2 - n_1) \gg A_1 (N_1 - n_1) + A_m m$,

then for linear heating the equation 3.20 becomes

$$I(T) = -\beta \frac{A_m \gamma_1 n_1 m}{A_2 (N_2 - n_2)}. \quad (3.21)$$

Using equation 3.12 and the assumption that the probability of retrapping into the shallow trap is much smaller than the rate of release of trapped carriers, $\gamma_1 n_1 \gg A_1 (N_1 - n_1) n_c$, equation 3.12 will approximate be

$$\frac{dn_1}{dt} = -\gamma_1 n_1. \quad (3.22)$$

The substitution of the solution of the equation 3.22 and equation 3.17 in equation 3.21 the equation gives the value of n_{10} as:

$$n_{10} = (N_2 - n_{20}) \left[1 - (m_\infty / m_0)^{A_2 / A_m} \right]. \quad (3.23)$$

The algebraic transformation of equation 3.23 gives the the value of m_∞ as

$$m_\infty = m_0 \left[1 - (A_m / A_2) (n_{10} / (N_2 - n_{20})) \right]. \quad (3.24)$$

The area S_{PTTL} under the PTTL glow peak is found by integrating the the change in in the concentration of trapped holes (eqn 3.20) between the starting temperature T_0 up the final temperature T_f [2].

$$S_{PTTL} = \int_{T_0}^{T_f} I_{PTTL} dT = m_0 - m_\infty = \frac{A_m m_0 n_{10}}{N_2 - n_{20}}. \quad (3.25)$$

Equation 3.25 shows that the PTTL signal not only depends on the concentration of electrons in shallow traps at the end of illumination but also on the concentration holes in the recombination centre.

Using the values of concentration of charge carriers in traps at illumination time t given by equations 3.10, 3.9 and 3.11, the PTTL area measured following optical

stimulation for time t is given by the following equation [2].

$$S_{PTTL}(t) = \frac{Cm(t)n_1(t)}{N_2 - n_2(t)}. \quad (3.26)$$

The substitution of equation 3.10, 3.9 and 3.11 into equation 3.26 gives the equation below

$$S_{PTTL}(t) = \frac{C \exp(-t/\tau) N_1 (1 - \exp(-\beta t))}{(N_2/n_{20} - \exp(-tf))}. \quad (3.27)$$

Equation 3.27 is the description of the variation of PTTL peak area as function of illumination time. At long illumination time, $t \rightarrow \infty$, $n_2 \rightarrow 0$, $m \rightarrow n_1$, and the peak area start from zero at $t = 0$ and increases to a maximum area given by

$$S(\infty) = \frac{Cn_{1\infty}^2}{N_2}, \quad (3.28)$$

where $n_{1\infty} = m_{\infty}$ are the final concentration of electrons in shallow trap and holes at $t = \infty$ [2].

Alexander et al [14] used the charge neutrality condition to explain the behaviour of the PTTL behaviour as function of time.

$$n_c + n_1 + n_2 = m. \quad (3.29)$$

According to equation 3.29, this model assumes that n_1 is always less than or equal to m because of the charge neutrality condition. PTTL follows n_1 because there are enough holes available to accommodate the electrons produced during illumination and PTTL increases as n_1 increases. The model describes PTTL intensity as an increasing function of the illumination time when the optical excitation from equation 3.6 is negligible. If the optical excitation is not negligible at long illumination time the PTTL intensity will decay to zero.

Wintle and Murray [17] made some assumptions to determine the dependence of

PTTL signals as function of time. They showed that the PTTL signals follow

$$S_{PTTL}(t) = C \frac{f_2 n_{20}}{f_1 - f_2} [\exp(-f_2 t) - \exp(f_1 t)]. \quad (3.30)$$

If $f_1 = 0$, it means that the optical eviction of charges from shallow traps is negligible and equation 3.30 becomes

$$S_{PTTL}(t) = C n_{20} [1 - \exp(-f_2 t)]. \quad (3.31)$$

Alexander and McKeever [15] showed that equation 3.31 describes PTTL as the increasing function of illumination time up to a maximum level.

3.1.1.2 Complex model of PTTL

Experimental results from some materials showed that the PTTL intensity increases as a function of time to a maximum level and decreases to a steady state level at long illumination time. The simple model cannot explain the observed results [2, 14, 15]. In order to explain this behaviour of PTTL intensity against illumination time, an additional non-radiative recombination centre was introduced in the energy band diagram [14]. The band diagram is shown in figure 3.2 and is composed of one shallow trap (level 1) with electron populations n_1 , one optically active trap (level 2) with electron populations of n_2 and an optically inactive trap (level 3) with populations n_3 . The band diagram also has one radiative recombination centre (level 4) with hole population m_1 and non radiative recombination centre (level 5) with hole population m_2 . The charge neutrality equation for this model is given by the following equation

$$n_c + n_1 + n_2 + n_3 = m_1 + m_2. \quad (3.32)$$

From equation 3.32, n_1 may be less than or greater than m_1 . This means that n_1 may be increased and at long illumination time there are not enough holes in the

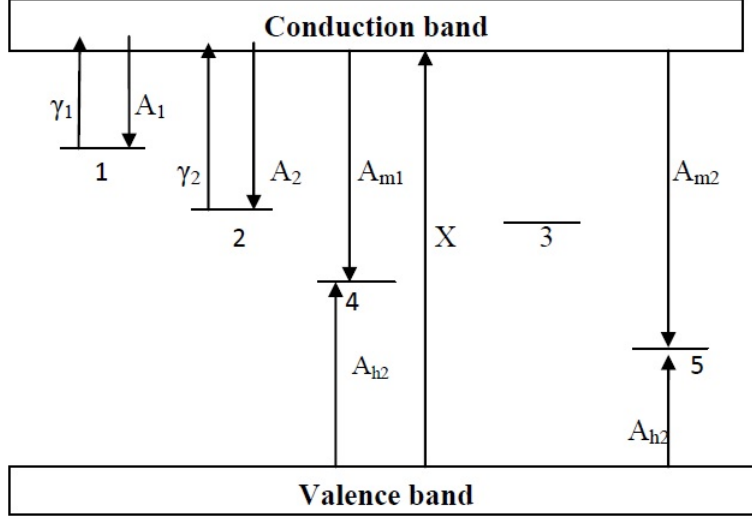


Figure 3.2: Energy band diagram used to explain PTTL against illumination time using complex model [2].

radiative recombination centre to recombine with these electrons. In summary, the structure of PTTL intensity versus illumination time is explained by the following equation.

$$I_{PTTL} = \min(n_1, m_1). \quad (3.33)$$

According to equation 3.33, PTTL will follow the minimum between the concentration of electrons in shallow trap and holes in radiative recombination centre [2, 14]. According to this model, at the start of illumination the number of electrons is less than the number of holes in the radiative recombination centre and increases with illumination time. The increase of n_1 with illumination will give the increase of PTTL signals. At longer illumination times, n_1 may become greater than m_1 . The decrease of holes in the radiative recombination centre is caused by recombination of electrons with holes. This recombination is the source of OSL signals obtained during the illumination process. At this time, the PTTL starts to follow m_1 and will decrease as m_1 decreases. According to this model, the non-zero steady state is obtained when there are no more electrons to be transferred from deep traps [2, 14].

Chapter 4

Quartz

4.1 Molecular structure of quartz

α -Quartz is the most stable and most common form of SiO_2 at standard temperature and pressure. The structure of quartz, shown in figure 4.1, consists of corner-sharing SiO_2 tetrahedra so that Si is bonded to four oxygen atoms and each oxygen is bonded to two silicon atoms. Quartz can thus be described as a network of interconnected SiO_2 tetrahedra and it is classified as a network silicate. The most common crystal morphology is hexagonal prism and rhombohedral forms inclined to the c -axis. It occurs in nature as α and β quartz. α -quartz is stable at temperatures less than 573°C . Above this temperature the form of quartz is β -quartz [18].

α -quartz has a rhombohedral structure and β -quartz has an hexagonal structure. The oxygen atoms are tetrahedrally shared between those of silicon, two of the Si-O bond in α -quartz, make an angle of 66° with optical (crystallographic) axis with bond length of $1.598 \text{ \AA}$, whilst two others make an angle of 44° with bond length of $1.616 \text{ \AA}$, thus the oxygen occurs as two equivalent pairs [3]. The Si-O bond is 40 % ionic and 60 % covalent. Due to its 60 % covalent bond, quartz has a rigid structure that prevents macroscopic diffusion of lattice atoms [3]

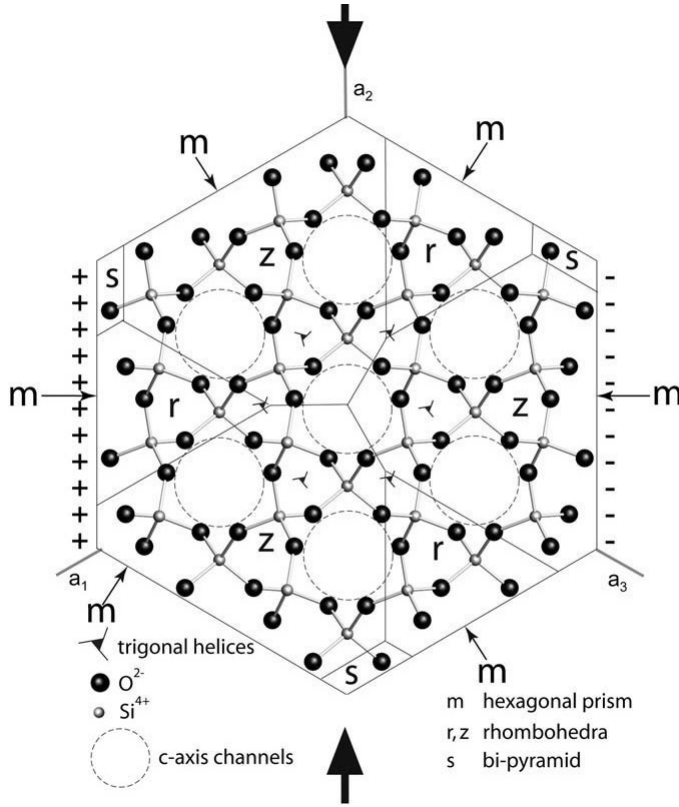


Figure 4.1: Molecular structure of α -quartz [18].

4.2 Chemical composition of quartz

Quartz is always nearly pure silicate with less than 0.2 percent of total impurities. Trace elements are present as substitutional and/or interstitial ions in the quartz lattice. The impurities appear by either replacing silicon or occupying sites in the large channels parallel to the c -axis. The principal substitutional ions are Al, Ti, Fe, Ge, P and Ga; interstitial are H, Li, Na and Fe [3, 18].

4.3 Defects in quartz

Quartz presents numerous defects in its crystal lattice as shown in figure 4.2. About 20 different types of defect centres have been observed in quartz. These can be grouped into two types. The first type are defects caused by foreign ions (foreign ions and interstitial defects), the second are centres associated with the oxygen vacancy

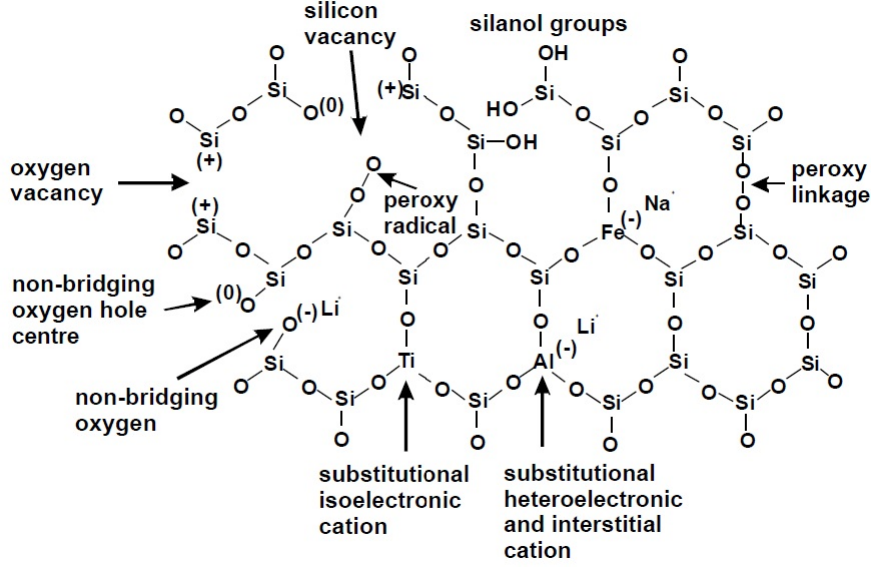


Figure 4.2: Schematic quartz structure showing the most common intrinsic and extrinsic lattice defects [19].

or silicon vacancy [19]. Silicon atom in the lattice can be replaced by Al^{3+} , Ga^{3+} , Fe^{3+} , Ge^{4+} , Ti^{4+} and P^{5+} .

4.3.1 Aluminium associated defects

Aluminium is a frequently occurring trace element in quartz. It substitutes silicon. Aluminium is trivalent and silicon is tetravalent. Compensation of charge neutrality is necessary. This charge compensation is provided by monovalent alkalis such as H^+ , Li^+ , Na^+ , K^+ , Cu^+ and Ag^+ . Because of strong attractive coulombic force between the interstitial ions (or holes) with the aluminium and due to their high mobility, the charge compensators are usually located adjacent to the substitutional Al ion. This gives rise to various aluminium associated centres such as $\text{Al} - \text{OH}^-$, $\text{Al} - \text{Li}^+$, $\text{Al} - \text{Na}^+$ or $\text{Al} - \text{h}^+$ [20]. The precursor state for this centre is the diamagnetic $[\text{AlO}_4/\text{M}^+]^0$ centre associated with an adjacent charge compensating cation $\text{M}^+(\text{Li}^+, \text{H}^+, \text{Na}^+ \text{ etc})$. Other common trace-element centres detected in quartz are $[\text{FeO}_4/\text{M}^+]^0$, $[\text{GeO}_4/\text{M}^+]^0$ and $[\text{TiO}_4/\text{M}^+]^0$ [18, 19].

4.3.2 Oxygen related defects

The oxygen related defect is attributed to the group of the E' centres which is associated with oxygen vacancies and oxygen excess centres O^- . Numerous types of E' centres exist. The simplest type is E'_1 defect which consists of an oxygen vacancy with an unpaired electron. The E'_2 centre also consists of an oxygen vacancy but with an unpaired proton. The third centre is E'_4 . It consists of an oxygen vacancy with a hydride ion (H^-) bonded to silicon atom.

A number of oxygen excess centres is present in quartz [18]. These oxygen excess centres include the non bridging oxygen hole centres (NBOHC). Its structure is denoted by $(\equiv Si-O\cdot)$; where $(\equiv)$ stands for bonds with three oxygen atoms and $(\cdot)$ indicates unpaired electron in an oxygen orbital [21, 22]. Oxygen excess centres also include peroxy radical which is denoted by $(\equiv Si-O-O\cdot)$, where the $(\cdot)$ stands for unpaired spin [18, 19, 23, 24]. Hydrogen can be incorporated in quartz, either as OH point defects or as molecular water in fluid inclusions. Incorporation of trace element in quartz as point defects is achieved by substitution of Si^{4+} by $4H^+$ referred as to $(4H)_{Si}$ or Hydrogarnet substitution. The defect is most characteristic of synthetic quartz [25].

4.4 Synthetic quartz

Synthetic quartz crystals are grown using the hydrothermal synthesis method. The crystal is very weakly soluble under normal temperature and pressure, but becomes soluble by hydrothermal reaction at high temperature and high pressure. Synthetic quartz is generally designed to have fewer defects than natural quartz, since these affect its electrical and optical characteristics. Those present relate mainly to traces of Al and alkalin metals, particularly to H in unannealed material, since the hydrothermal manufacturing process promotes formation of O-H related defects [25].

Chapter 5

Experimental details: Equipment

5.1 General remarks

In this work, synthetic quartz (Sawyer Research Products, Ohio, USA) was studied. The samples used were in powder form and mounted on stainless steel discs. Experiments were conducted using an automated RISø Luminescence Reader, model TL/OSL-DA-20. Firstly, the sample was heated at linear heating rate up to 500°C to erase all residual signals before irradiation. After removal of the background, the sample was irradiated using a $^{90}\text{Sr}/^{90}\text{Y}$ β irradiation source delivering about 0.1028 Gy/s to ionize the material and so create free charge carriers. The next step was to record the whole glow curve by heating the sample at linear heating rate up to 500°C. The TL readout was done in nitrogen atmosphere to avoid the spurious TL signals, to ensure good thermal contact between the sample and the heating planchet and to protect the heating system from oxidation at high temperatures.

5.2 RISø TL/OSL reader

Figure 5.1 shows the major units of the standard RISø thermoluminescence/optically stimulated luminescence reader (model TL/OSL-DA-20). The reader is composed

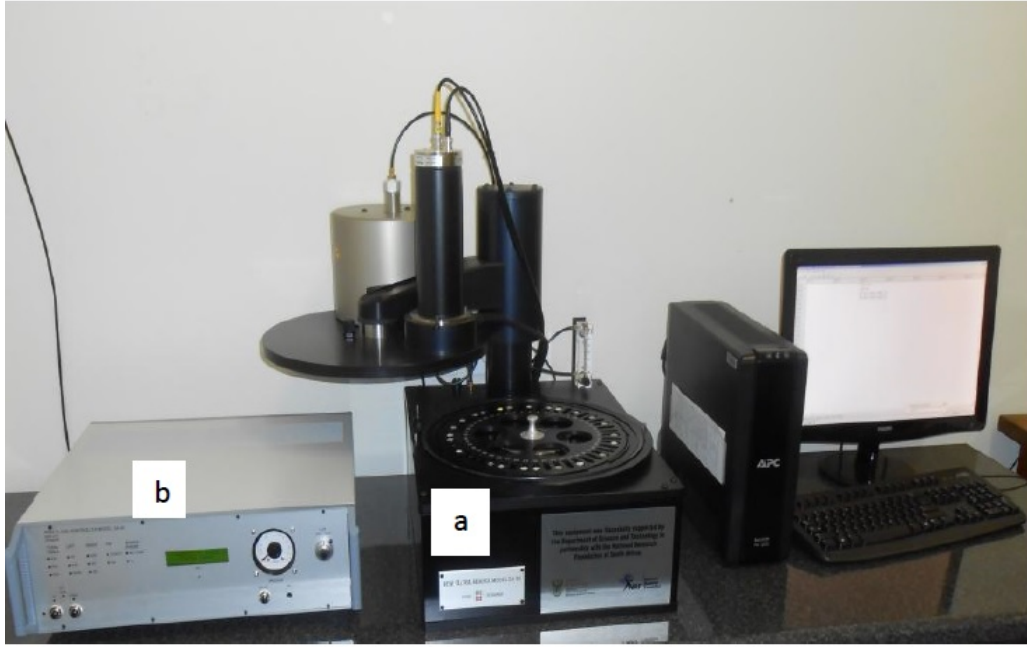


Figure 5.1: Thermoluminescence/Optically Stimulated Luminescence reader [26, 27].

mainly of two separate units. The hardware part called the Reader indicated by (a) and the controller indicated by (b) in the figure 5.1.

5.2.1 The Reader

The hardware is composed of three main components, the light detection system which detects the luminescence from the material, a luminescence stimulation system and an irradiation source. The material under study is mounted on a stainless steel disc using silicone oil for adhesion and loaded onto the sample carousel which has 48 positions meaning that it can accommodate up to 48 samples. In the measurement position, the sample can be stimulated either thermally by linearly increasing the temperature of the heating element or optically by light sources focused on the sample position. The emitted luminescence is detected by the light detection system [26].

5.2.1.1 The light detection system

The light detection system consists of two main components, a photomultiplier tube marked as (PMT) in figure 5.2 and detection filters [26, 28]. The role of the detection

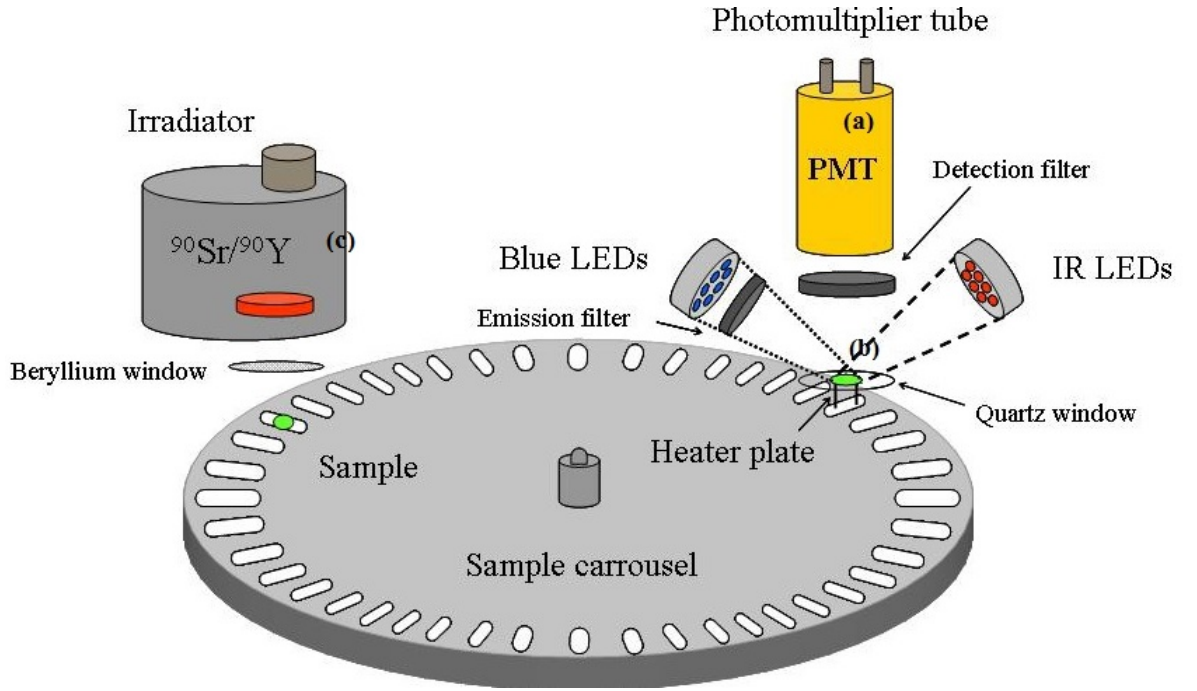


Figure 5.2: Schematic diagram illustrating the components of Risø TL /OSL reader [26].

filters is to protect the PMT from scattered light and to define the detection window. The luminescence emitted from the sample is detected by the photomultiplier tube using its sensitive component which is the photo-cathode. In RISø TL/OSL Reader, the standard PMT is the bialkali EMI 9235QB. It has its maximum quantum efficiency ranging between 200 and 400 nm, but extending to 700 nm and that characteristic makes it suitable for detection of luminescence signals from quartz and feldspar.

5.2.1.2 Luminescence stimulation system

The RISø reader model TL/OSL-DA-20 uses two systems of luminescence stimulation [26]. One is the heating system that can be used in TL measurements and the other is a light stimulation system that can be used in OSL measurements. The heating system plays a double role, one is to heat the sample and the second is to lift the sample to the measurement position. The Risø reader model TL/OSL-DA-20 heating system is the latest and most advanced and its heater is calibrated. Heating is done

by feeding a controlled current through the heating element. The heating system is able to heat up to 700°C at heating rates from 0.1 to 10 K/s. Heating rates above 5 K/s are not usually used in heating because they can cause thermal lag between the sample and the heating system. Heating must also be done in a nitrogen atmosphere in order to protect the heating system from oxidation at high temperature [26].

The RISø reader model TL/OSL-DA-20 uses also light emitting diodes (LEDs) as light stimulation sources. LEDs offer the possibility of stimulation at different intensities and varying the stimulation intensity as a function of time. Two types of LEDs are found in the RISø reader model TL/OSL-DA-20; 21 infrared LEDs (Vishay TSFF 5210) grouped in 3 clusters and 28 blue LEDs (NICHIA type NSPB-500AS) grouped in 4 clusters. Infrared LEDs have their peak emission at 870 nm (FWHM = 40 nm) and the power is approximately 145 mW/cm² at the sample position. Blue LEDs have a peak maximum at 470 nm (FWHM=20 nm). They have an emission angle of 15 degrees and power output of $\approx$ 4.8 Cd to 20mA.

5.2.2 Irradiation sources

The RISø reader model TL/OSL-DA-20 used in this study is equipped with a beta irradiation source. A beta irradiator is located above the sample carousel and it accommodates a $^{90}\text{Sr}/^{90}\text{Y}$ beta source which emits beta particles of maximum energy of 2.27 MeV. The irradiator has a nominal dose rate of 0.1028 Gy/s according to in-house calibration. The irradiation process is software controlled and only single sample irradiation is possible and the minimum irradiation time is 1 second.

5.3 The controller

All hardware components work under control of a 586 processor controller. The role of the controller is to maintain proper timing, sample positioning, data acquisition, error checking etc. The controller also has text display that shows the command which is

currently being executed, the display also reports the failure messages. The controller also operates under software control based on windows program for creating, editing and executing measurement sequences.

Radioluminescence (RL) is the luminescence emitted under exposure of a material to ionizing radiation [29]. In this work, the RL measurements were made on both unannealed and annealed synthetic quartz. For the latter, samples were annealed at 500, 600, 700, 800, 900 and 1000°C for 10, 30 and 60 minutes respectively. These experiments were conducted at the University of Milani Bicocca (UNIMIB). The RL signals were excited using X-rays through a Be window using a Philips 2274 X-ray tube with a tungsten target. The operating current and voltage were 20 mA and 20 kV respectively. For each sample, 40 consecutive spectra were measured and for each spectrum a dose of 10 ± 0.02 Gy was imparted to the sample. The RL signals were detected using an apparatus build in-house featuring a charge coupled device (Jobin-Yvon Spectrum One 3000) coupled to a spectrograph operating in the wavelength range 200 - 1100 nm [30, 31]. Using the deconvolution method, the RL spectrum measured from the sample annealed at 1000°C for 60 minutes was separated into seven Gaussian components using the commercial software Sigmaplot 2001 (Systat software, Inc.).

Chapter 6

Results and discussion

This chapter presents results of experiments on the study of thermoluminescence characteristics of Sawyer synthetic quartz in its as received (unannealed) state, and one annealed at 500°C for 10 minutes. The results are on dosimetric features, kinetic analysis and phototransferred thermoluminescence of the main TL peak. The radioluminescence characteristics of the unannealed and samples annealed at 500, 600, 700, 800, 900 and 1000°C for 10, 30 and 60 minutes each are also presented.

6.1 Thermoluminescence glow curve of synthetic quartz

This section presents general information concerning thermoluminescence glow curves measured from synthetic quartz. The glow curves were measured at linear heating rates after beta irradiation.

6.1.1 Thermoluminescence glow curve of unannealed synthetic quartz

In the investigation of the structure of the glow curve, the TL glow curve of the unannealed synthetic quartz was measured after a dose of 31 Gy by heating the sample to 500°C. Figure 6.1 shows the glow curve measured using a heating rate of 5°Cs⁻¹.

The sample was not heated before the irradiation. Figure 6.1 shows two peaks at around 100 and 400°C both with low TL intensity.

In the next measurement, the sample was heated to 500°C before irradiation. Figure 6.2 shows the TL glow curve from unannealed synthetic quartz heated to 500°C before irradiation. The resultant glow curve had a higher TL intensity compared to the one in figure 6.1. This implies that the sample was activated by heating to 500°C. Activation is defined as a slight increase in sensitivity due to heating the material to an activation temperature. This change of sensitivity is caused by combined effect of irradiating the sample and by heating the sample to a high activation temperature, typically around 500°C. Given that the sample had not been irradiated in this experiment, during natural irradiation holes accumulate in the hole reservoir. Heating the sample to 500°C leads to thermal activation of holes which are transferred from the reservoir to the luminescence centre. The increase of holes in luminescence centre results in the increase of TL sensitivity when a sample is irradiated with a small test dose [2, 32]. The peak at 122°C in figure 6.2 has higher intensity compared with the other peaks thus it is called the main peak. The inset is the same glow curve but with the y -axis transformed to a logarithmic scale. This transformation was done in order to estimate the number and the exact position of peaks. Due to peaks overlapping, the inset does not show clearly the position and number of all peaks in the glow curve.

In order to determine the number and position of peaks, the method of peak separation known as thermal cleaning was used. In thermal cleaning, the irradiated sample is heated to a temperature higher than the position of the glow peak to be cleaned. The heating process removes this peak. The next step is to reheat the sample without further irradiation to measure the whole glow curve. This produces the next peak with a clean rising edge[3]. During thermal cleaning, attention must be paid in the choice of the cleaning temperature in order to avoid the effect of the cleaning temperature on the position of the next peak.

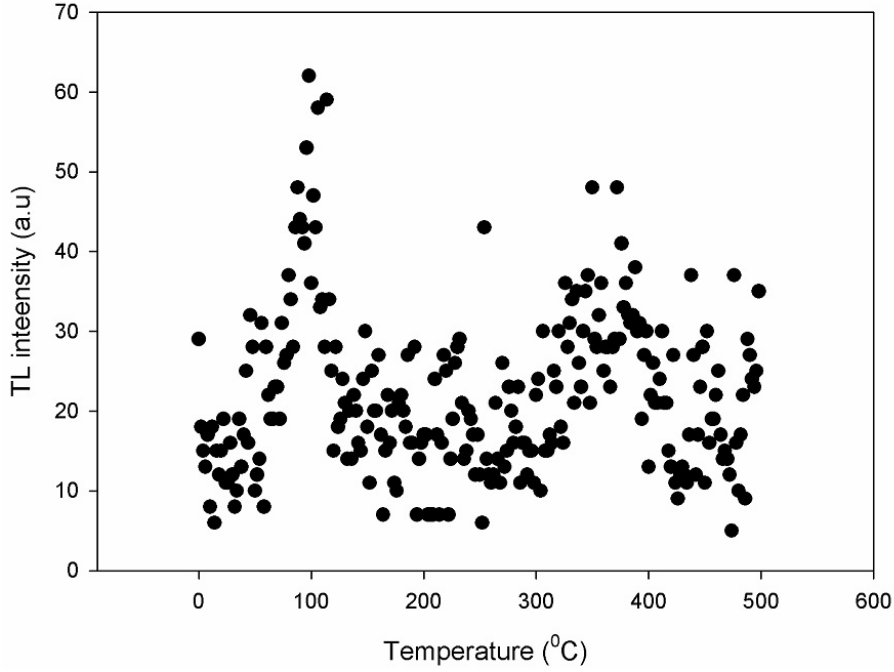


Figure 6.1: A glow curve from synthetic quartz measured at a linear heating rate of 5°Cs^{-1} after an irradiation dose of 31 Gy without preheat before dose.

In order to apply the thermal cleaning method, a new sample was prepared. Peak I (the main peak) was cleaned by heating to 100°C as it was located at 94°C . The glow curve measured after removal of peak I showed clearly the position of peak II at 116°C . In order to estimate the position of peak III, we cleaned the first two peaks by heating to 130°C . The glow curve measured after cleaning these two peaks showed the position of peak III at 176°C . In the next experiment, we cleaned peak III by heating to 185°C and the position of peak IV was approximated at 212°C . Peak IV was cleaned as well by heating to 240°C and peak V was found at 280°C . Peak VI was found at 348°C after cleaning the first five peaks by heating up to 310°C . Note that, the sample was irradiated once and then heated gradually to temperatures stated above. After peak separation, the peaks were scaled up to the intensity of peak I. Figure 6.3 shows the results of thermal cleaning and the combination of peaks after being separated and their intensity scaled up.

The glow curve of the unannealed synthetic quartz used in this study is a composite

of at least six peaks in addition to satellite peak. These peaks are located at 94, 116, 176, 212, 280 and 348°C when the sample is heated at a linear heating rate of 5°Cs^{-1} , figure 6.3. For the sample studied, the main peak has a satellite peak in its initial rise region.

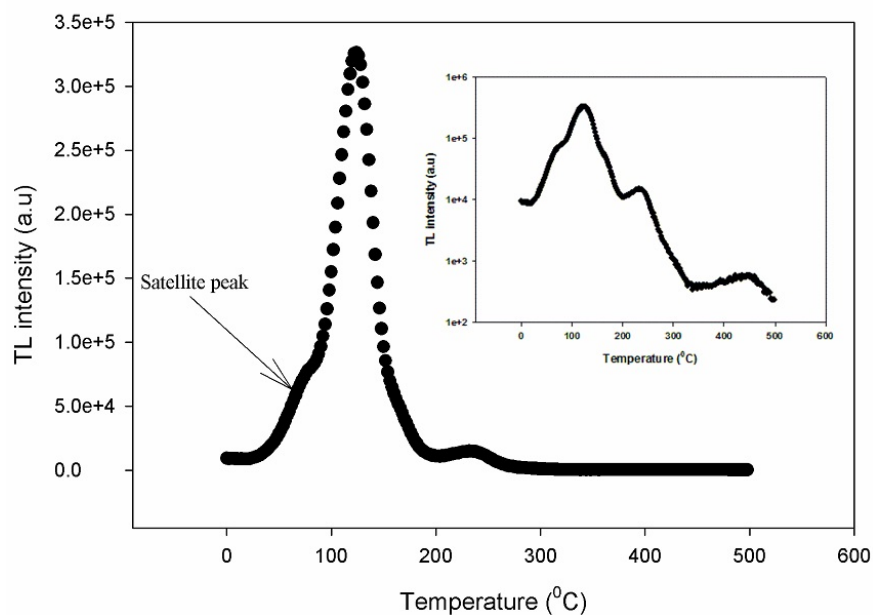


Figure 6.2: A glow curve from synthetic quartz measured at 5°Cs^{-1} after an irradiation dose of 31 Gy after preheat to 500°C . The arrow points to the satellite peak in the initial rise region of the main peak. The inset is the same glow curve with the TL axis transformed to a logarithmic scale to make peaks visible.

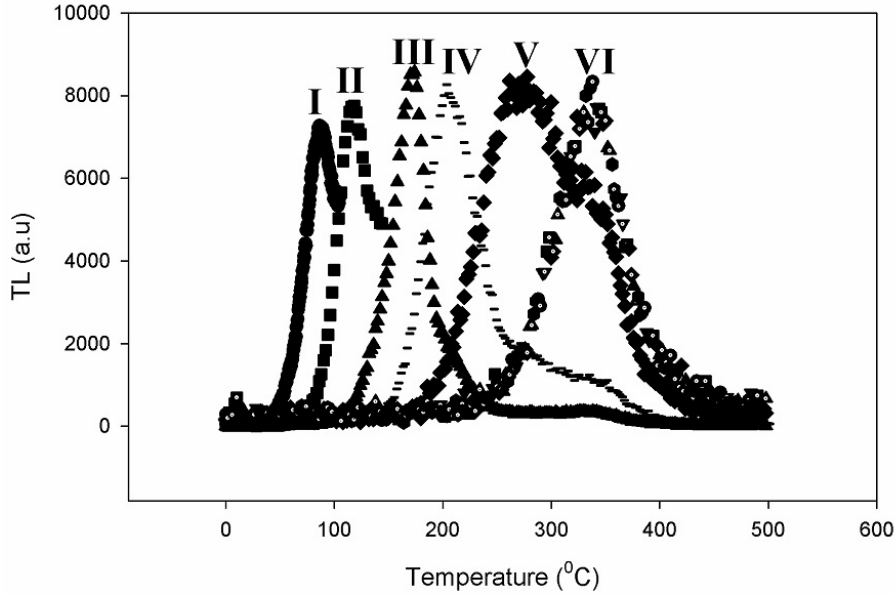


Figure 6.3: Thermoluminescence peaks of synthetic quartz after thermal cleaning. Glow curves were measured at 5°Cs^{-1} after a dose of 103 Gy.

6.1.2 Thermoluminescence glow curve of annealed synthetic quartz

The glow curve of unannealed synthetic quartz presents six glow peaks and peak I has a satellite peak in its initial rise part as shown in figures 6.2 and 6.3. In addition, good TL signals from the unannealed sample were obtained when it is preheated to 500°C before irradiation as shown in the previous section. In this section, a sample of synthetic quartz annealed at 500°C for 10 minutes was used to investigate the effect of annealing on the structure of the glow curve. In this study, a fresh sample was irradiated without preheat using a beta source to a dose of 31 Gy. The glow curve recorded after the irradiation by heating the sample at 5°Cs^{-1} to 500°C is presented in figure 6.4. Peak I of the glow curve of annealed sample has a satellite peak in its initial rise like unannealed sample. Unlike for the unannealed sample, heating the annealed sample up to 500°C after dose without preheat gave a glow curve with high TL signals. This is evidence that the annealing process played the role of activation.

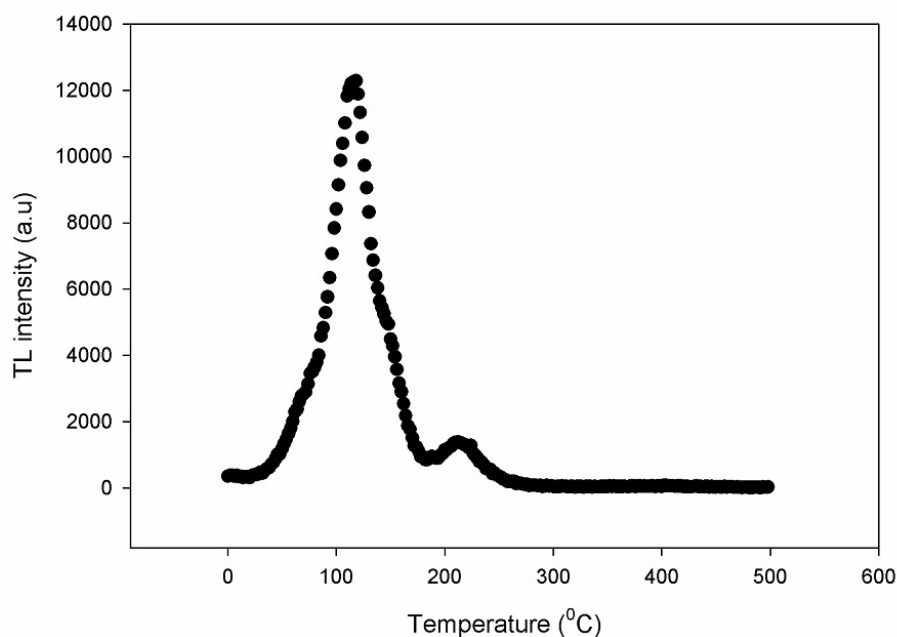


Figure 6.4: A glow curve of synthetic quartz annealed at 500°C for 10 minutes measured at 5°Cs⁻¹ after an irradiation dose of 31 Gy. The glow curve was measured after irradiation and without preheat to 500°C.

The results of thermal cleaning showed that the glow curve of the unannealed sample is a composite of at least 6 peak as shown in figure 6.3 and the position of each peak is given in section 6.1.1. Using thermal cleaning as was done in section 6.1.1 for unannealed sample, the effect of annealing on the number and position of peaks was investigated using synthetic quartz annealed at 500°C for 10 minutes. The results from thermal cleaning indicated that the glow curve of annealed synthetic quartz is a composite of at least seven glow peaks. There is also a satellite peak in the initial rise region of the main peak for the annealed sample. These peaks are located at 115, 148, 214, 246, 300, 348 and 412°C when the glow curve is measured at 5°Cs⁻¹. Figure 6.5 is the combination of peaks after being separated by thermal cleaning.

In this study, glow curves from the unannealed and annealed synthetic quartz showed the same general structure as shown in figure 6.2 and 6.4 respectively. The difference appeared in the temperature region between 300 and 500°C where the annealed sample showed the overlap of 3 peaks whereas the unannealed showed the overlap of

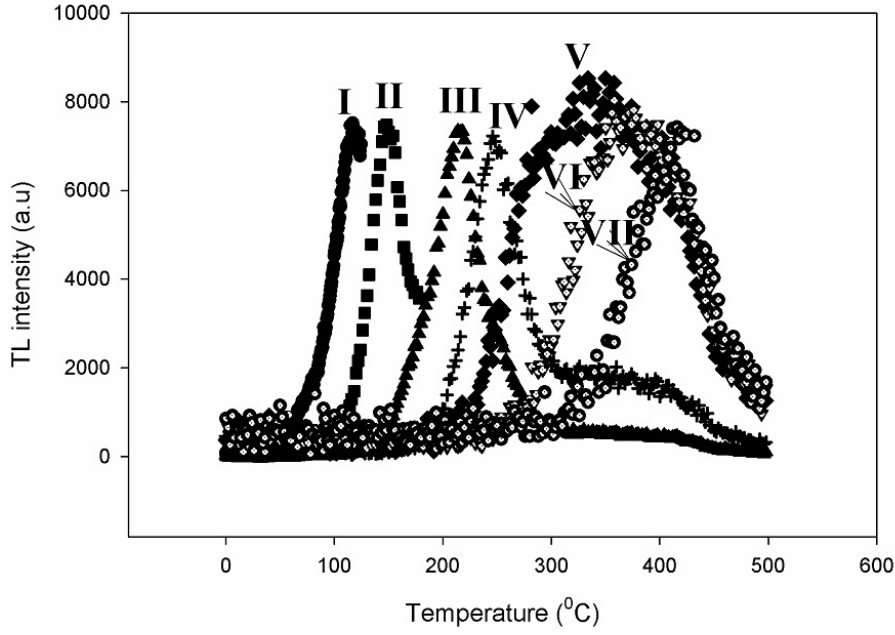


Figure 6.5: The combination of peaks of a TL glow curve of synthetic quartz annealed at 500°C for 10 minutes measured at 5°C s^{-1} after an irradiation dose of 31 Gy. The separate peaks were found using the thermal cleaning method. The arrows point to peaks VI and VII.

only two peaks.

6.2 Dosimetric features

This section presents the influence of sample treatment on TL properties of the main glow peak of synthetic quartz. The effect of repetitive measurement and heating rate on the position and maximum intensity of the main peak is presented. The influence of irradiation dose on maximum intensity and activation energy of peak I is also presented.

6.2.1 The effect of repetitive measurement on the position and the TL intensity of main peak

The influence of multiple measurements on the temperature and TL intensity of main peak was studied using two different samples of synthetic quartz. The samples were an unannealed synthetic quartz and a sample annealed at 500°C for 10 minutes.

6.2.1.1 The effect of repetitive measurement on the position of the main TL peak for unannealed synthetic quartz

Using a heating rate of 2°Cs^{-1} and an irradiation dose of 10 Gy, TL glow curves were measured from synthetic quartz by heating each sample up to 500°C. The temperature corresponding to the maximum TL intensity (T_m) of the main peak was noted. The process was repeated 9 times on the freshly re-irradiated sample and the peak temperature was noted at each cycle. The peak temperature plotted against the number of measurement is shown in figure 6.6. The graph indicates that the peak position is reproducible. From results of peak temperature reproducibility at fixed heating rate and dose, we expect the value of the activation energy of the trap responsible for that peak to also be reproducible.

6.2.1.2 The effect of repetitive measurement on the position of the main TL peak for annealed synthetic quartz

As in the case of the unannealed sample, synthetic quartz annealed at 500°C for 10 minutes was used to investigate the reproducibility of peak position. The aim of this experiment was to study the effect of annealing on the reproducibility of the peak position. After a dose of 31 Gy, the glow curves were recorded by heating the sample at 5°Cs^{-1} to 500°C. Figure 6.7 is the plot of peak temperatures recorded for 10 measurements. Like the unannealed sample, the position of the main peak of the annealed sample is reproducible. Results of figures 6.6 and 6.7 implies that

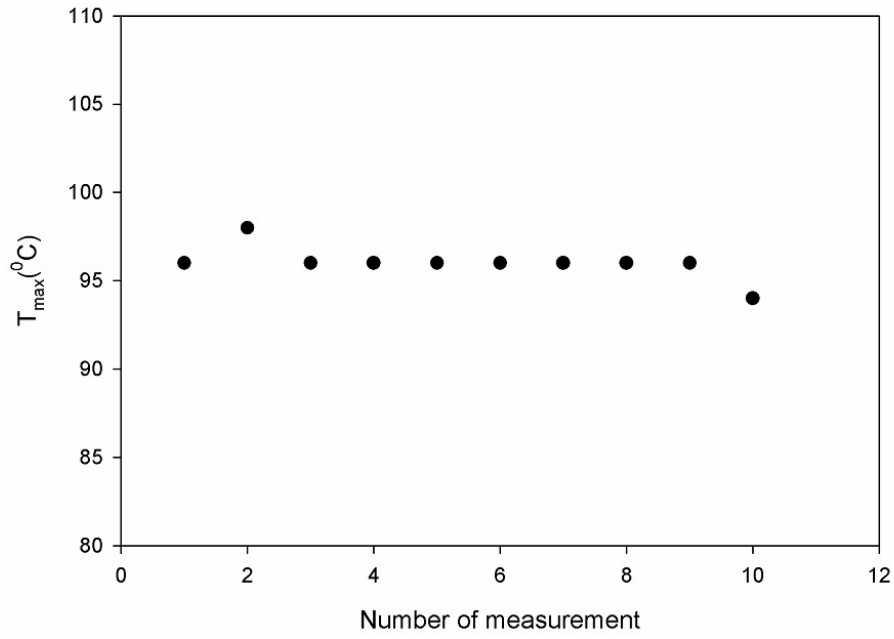


Figure 6.6: The effect of repetitive measurement on the peak position for the main peak in an unannealed synthetic quartz. Glow curves were measured at 2°Cs^{-1} after a dose of 10 Gy. T_{max} was measured once.

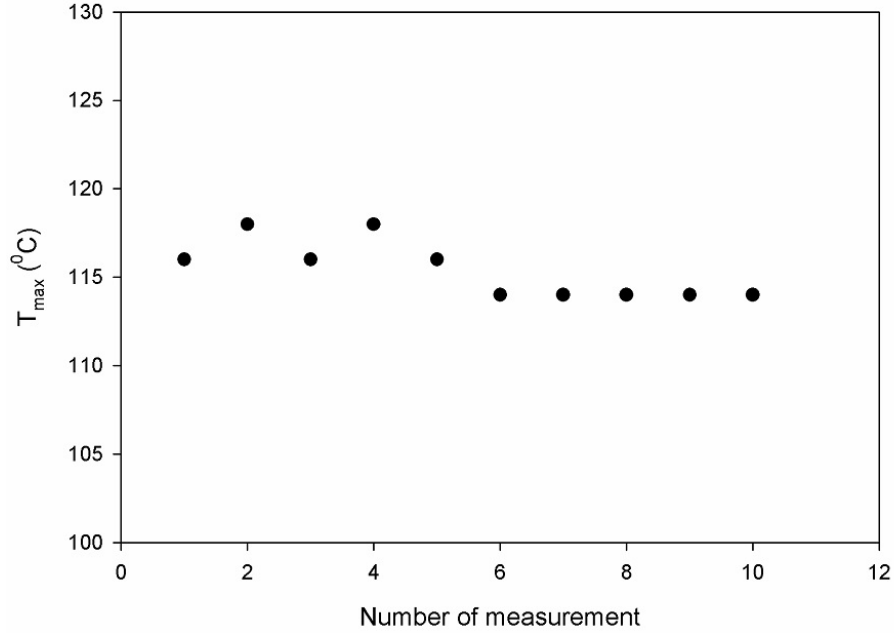


Figure 6.7: Effect of repetitive measurement on peak position for the main peak in annealed synthetic quartz. Glow curves were measured at 5°Cs^{-1} after a dose of 31 Gy. T_{max} was measured once.

reproducibility of position of the main peak of synthetic quartz was not affected by annealing.

6.2.1.3 The effect of repetitive measurement on the intensity of the main TL peak of unannealed synthetic quartz

The influence of multiple measurements on the maximum TL intensity of the main peak of the glow curve of unannealed synthetic quartz was studied. The TL intensity of the main peak of the glow curve measured at 5°Cs^{-1} after irradiation to 31 Gy was noted. The measurements were performed ten times. Figure 6.8 is the plot of maximum TL intensity of the main peak against number of measurement for the unannealed sample. The results indicate that the TL intensity decreases with repetition of irradiation and measurement.

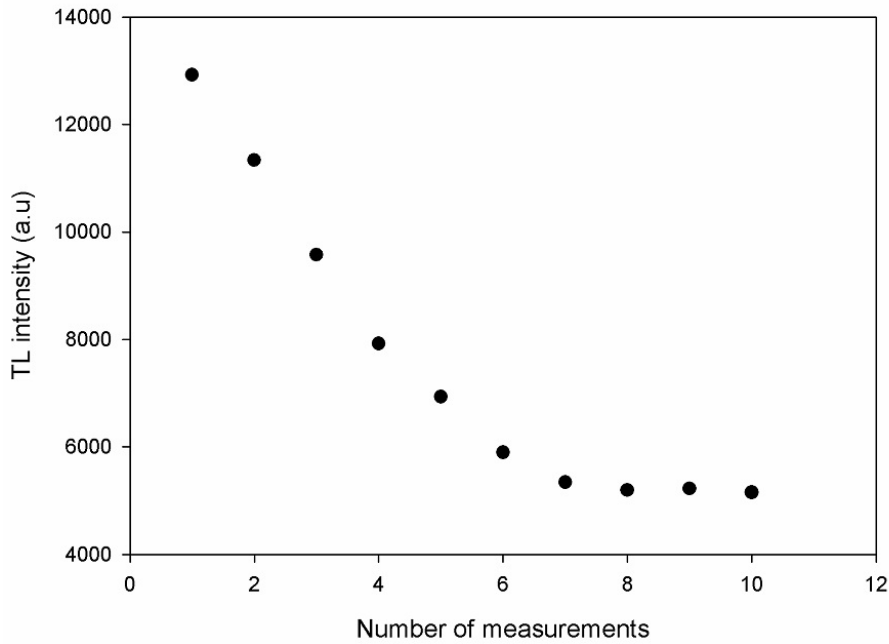


Figure 6.8: The effect of repetitive measurement on the maximum TL intensity of the main peak in unannealed synthetic quartz. Glow curves were measured at 5°Cs^{-1} after a dose of 31 Gy.

6.2.1.4 The effect of multiple measurements on the intensity of the main TL peak of annealed synthetic quartz

Decrease of TL intensity of peak I with repetitive measurements was found in an unannealed synthetic quartz as stated in the previous section. The objective of this experiment was to investigate the effect of annealing on the reproducibility of TL intensity upon multiple measurement. Figure 6.9 shows the change of the TL intensity of the main peak of synthetic quartz annealed at 500°C for 10 minutes as the measurements are repeated. As for the unannealed sample, the maximum TL intensity of the annealed sample decreases when the measurement is repeated.

The decrease in the TL intensity with repeated measurements may indicate the effect of de-sensitization. This decrease in TL intensity could be attributed to the competition experienced by centres responsible for the main peak during read out [2, 33, 34]. Alternatively, the change could be due to reduction in concentration of holes.

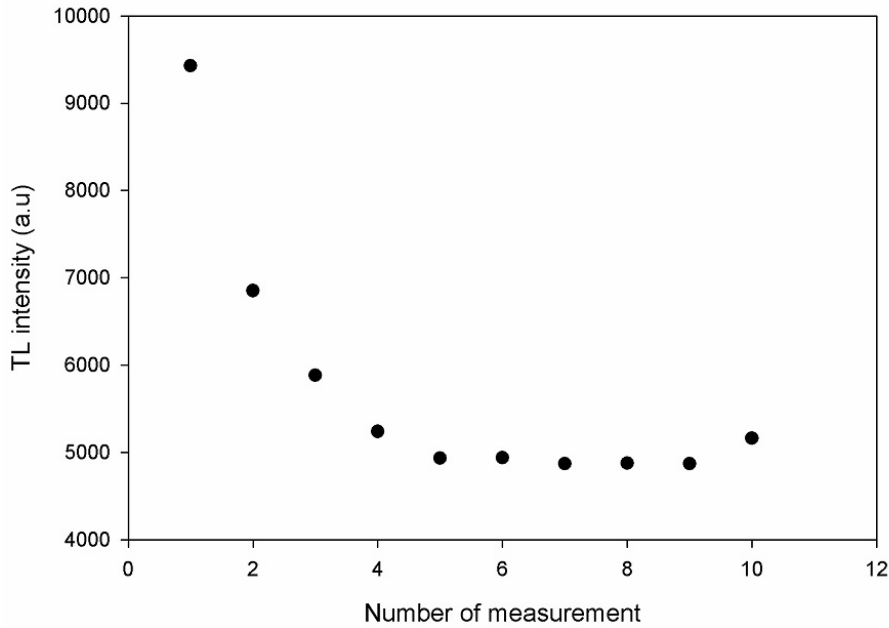


Figure 6.9: The TL intensity of the main peak plotted against number of measurement in annealed synthetic quartz. The intensities were noted from a peak measured at 5^{0}Cs^{-1} after a dose of 31 Gy.

6.2.2 Investigation of activation

The activation temperature of a TL material is the temperature at which its sensitivity starts to increase due to heating [2]. In order to estimate the temperature at which our sample was activated, an investigation was made to determine its thermal activation curve. For this study, we used 14 different samples of mass within 0.141 ± 0.002 g. Each sample was preheated at a specific temperature greater than 110°C before irradiation because the investigation was made on the main peak. The temperature was changed between 120 up to 500°C and each of the 14 samples was heated to a different temperature. After the preheat, the sample was given 21 Gy dose of irradiation and re-heated to the same temperature as the one we used before irradiation. At each temperature, the TL intensity of the main peak was noted. Figure 6.10 shows the change of the maximum intensity of the main TL peak as a

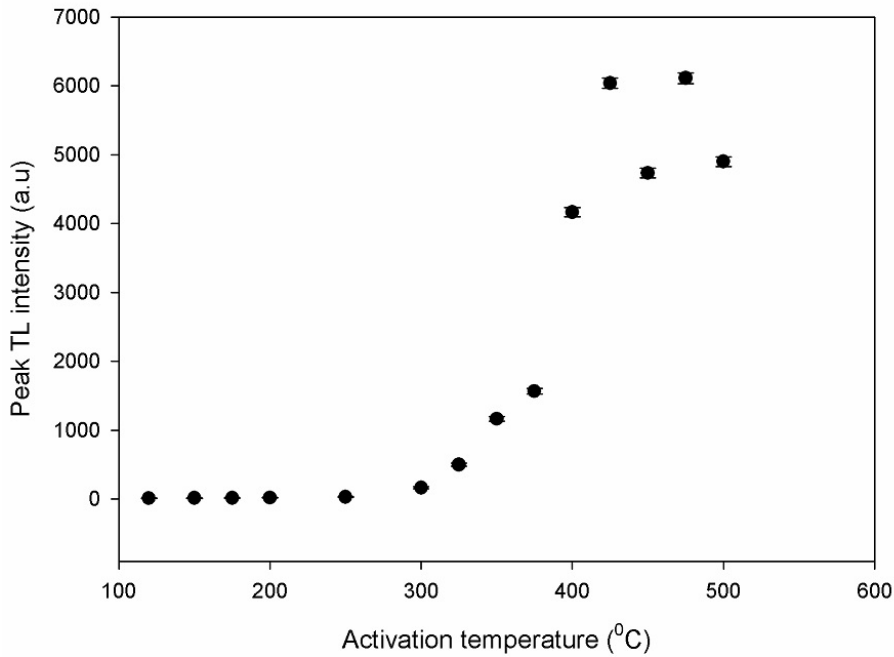


Figure 6.10: Graph of the TL intensity of the main peak of unannealed synthetic quartz plotted with respect to the activation temperature.

function of the preheating temperature. The error bars in the intensity data were each calculated using Poisson' statistics since the photon counts are random and the

error is given by the square root of peak intensity [35]. The graph shows that a significant increase of the TL intensity starts to appear approximately at 300°C. This result implies that the sample of synthetic quartz is thermally activated at a temperature around 300°C. Zimmerman's explanation for this effect is based on the band model consisting of one electron trapping state and two hole centres [2, 28, 34, 36]. One acts as a luminescence centre and the other as a reservoir and the probability of trapping holes is much larger for the reservoir than for the luminescence centre. According to the model, the irradiation accumulates holes in both centres but preferably to the reservoir and the electrons are accumulated in the trap. By heating the sample to the activation temperature, holes are transferred from the hole reservoir to the luminescence centre and the concentration of holes in the luminescence centre is increased. The increase of holes in luminescence centre is the cause of increase in sensitivity.

6.2.3 Study of sensitivity changes in unannealed synthetic quartz

This experiment was done for the purpose of investigating the causes of the increase of sensitivity that occurred in our sample of unannealed synthetic quartz. In our study of the causes of sensitivity change, we heated the sample to 325°C in order to activate the sample. This step was made due to the fact that the luminescence signals are found only when the sample is heated at the temperature $\geq 300^\circ\text{C}$, figure 6.10. After activation, the experiment was done in the following steps:

1. The sample was given a high dose D of 21 Gy and heated to a temperature greater than that of the position of the main peak i.e 150°C to remove the induced TL.
2. A test dose d of 1 Gy was given to the same sample and the initial sensitivity S_0 was measured by heating the sample to 150°C. Figure 6.11 indicates the

initial sensitivity S_0 of the sample.

3. After measuring S_0 , the sample was activated by heating to 500°C . After activation, the same test dose of 1 Gy was given to the sample. The new sensitivity S_D was measured by heating the sample to 150°C . Figure 6.12 is the glow curve measured by heating to 150°C after a test dose of 1 Gy.

The comparison of two glow curves in figure 6.11 and 6.12 indicates that the sample was sensitized as $S_D > S_0$.

In order to investigate the cause of these sensitivity change, the sample was activated again by heating to 500°C . After activation, the same test dose of 1 Gy gave the intensity S'_D and S_D ($940 \text{ (a.u.)} > S'_D$ (809 (a.u.)) . The decrease of S'_D is consistent with the fact that the TL intensity decreases with repetition of measurement under the same conditions as shown in figure 6.8. This implies that the sensitivity changes is not due to heating to the activation temperature alone.

By using irradiation doses between the test dose d and a dose D and heating to 500°C , we investigated the sensitivity change further. In this experiment, we heated to 500°C to activate the sample. After each activation, the doses between d and D were given to the sample. After each dose, we heated at 150°C to measure the glow curve and from the curve the intensity of peak I was noted. Doses used were 5, 10, 12, 15 and 20 Gy. Figure 6.13 is the graph of the intensity of peak I after doses between 1 and 20 Gy and heating to 500°C . The increase of sensitivity with the increase of dose was obtained as indicated in figure 6.13. The increase of TL intensity with dose confirms that the change of S_0 to S_D is not caused by heating only but by the combination irradiation dose D and heating [2].

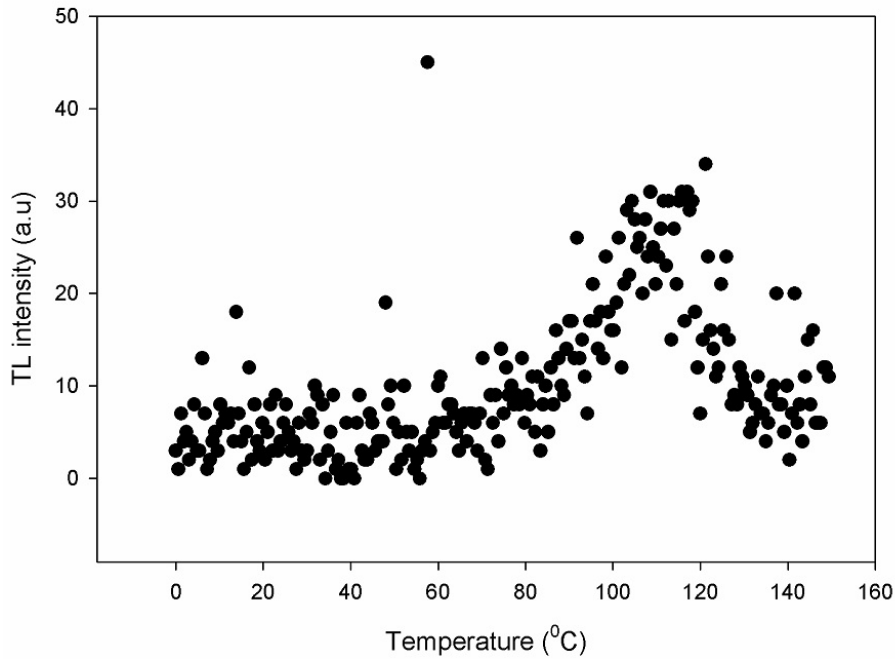


Figure 6.11: Glow curve of unannealed synthetic quartz measured by heating to 150°C after a test dose of 1 Gy to record the initial sensitivity S_0 of the main peak.

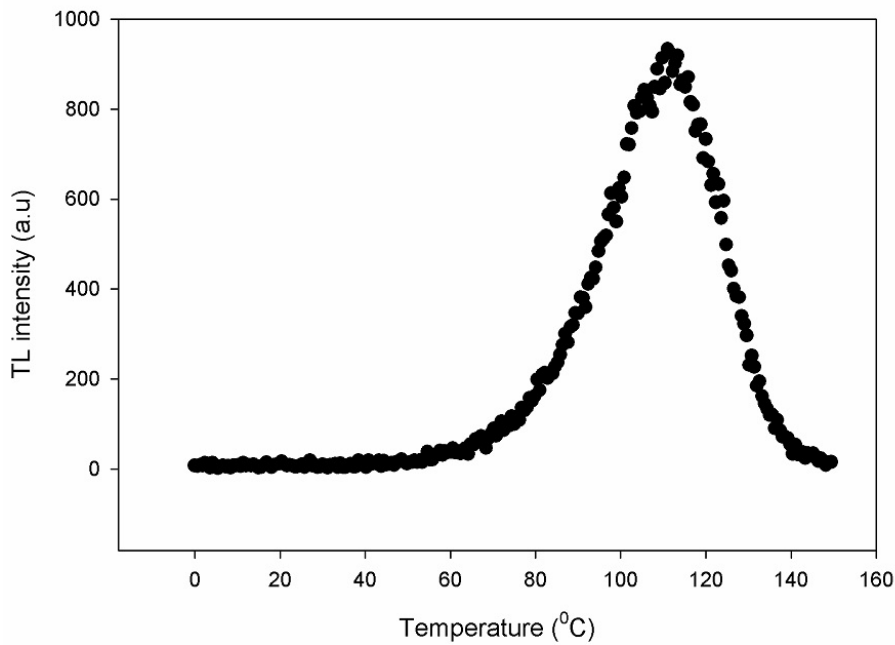


Figure 6.12: Glow curve of unannealed synthetic quartz measured by heating to 150°C after the same test dose of 1 Gy. Before irradiation the sample had been heated beyond the activation temperature i.e to 500°C.

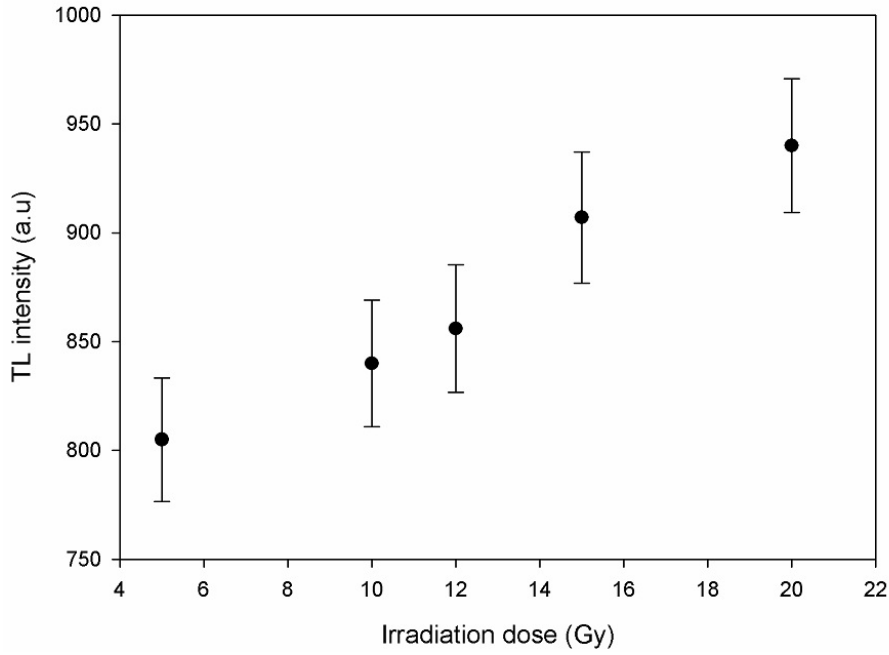


Figure 6.13: Graph of intensity of peak I in unannealed synthetic quartz against dose.

6.2.4 Effect of heating rate on the position and the maximum intensity of the main peak

In this section, we present results of measurements on the influence of heating rate on the position and intensity of the main glow peak of synthetic quartz. The investigations were made by measuring glow curves at various heating rate ranging from 0.5 up to 6°C s^{-1} after an irradiation dose of 31 Gy. The peak temperatures and TL maximum intensity corresponding to glow curves measured at each heating rate were noted.

6.2.4.1 The effect of heating rate on the position of the main TL peak in unannealed synthetic quartz

Figure 6.14 shows the behaviour of peak temperature as a function of heating rate for two different measurements. From the graph, it is clear that the peak position shifts to higher temperature with increase of heating rate.

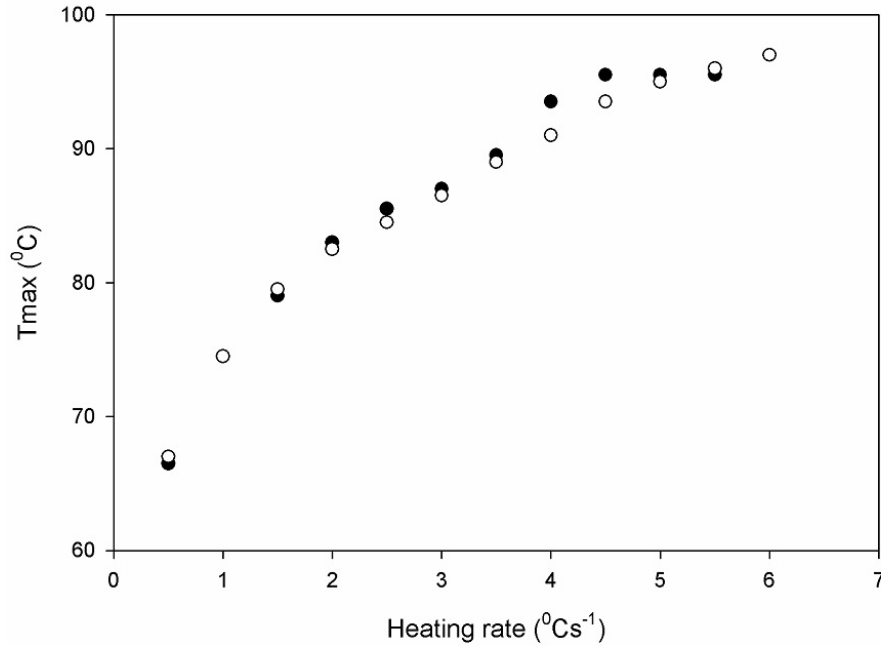


Figure 6.14: The effect of heating rate on the peak position of the main peak of the TL glow curve in unannealed synthetic quartz. All glow curves were measured after an irradiation dose of 31 Gy.

6.2.4.2 The effect of heating rate on the position of the main TL peak of annealed synthetic quartz

The position of peak I in unannealed synthetic quartz shifts to high temperature as heating rate increases as shown in figure 6.14. The same procedure as described in section 6.2.4 was applied on the sample of synthetic quartz annealed at 500°C for 10 minutes. The objective of this experiment was to study whether annealing affected the response of the position of peak I against heating rate. The result is shown in figure 6.15 which indicates that the position of the main peak for an annealed sample shifts to higher temperature when the heating rate increases. Both figure 6.14 and 6.15 from the unannealed and annealed sample respectively indicate that the position of the main peak shifts to higher temperature when the heating rate increases. This shift of the peak temperature with heating rate is expected from kinetics theory of the effect of heating rate on the peak position as indicated in the

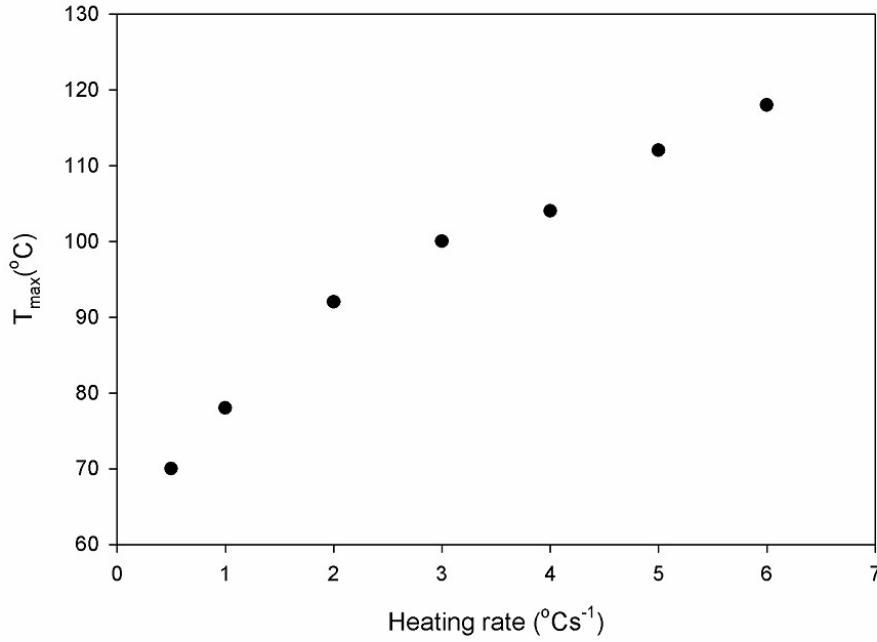


Figure 6.15: The peak temperature of the main peak against the heating rate in annealed synthetic quartz. In this measurement a dose of 31 Gy was used.

relation presented in equation 2.7. In this equation, the frequency factor s and the activation energy E are constants for a given dose [7, 37]. The change of the peak temperature is only due to the effect of changing the heating rate. The T_m read from the experimental glow curve might be systematically lower than the actual value. This deviation is probably due to thermal contact of the heater and the sample[38].

6.2.4.3 The effect of heating rate on the intensity of the main TL peak of unannealed synthetic quartz

Using the glow curves measured at different heating rates, the intensities corresponding to maximum temperature of the main peak were collected. After this collection, intensities were plotted as a function of heating rate and the resultant graph is presented in figure 6.16. Figure 6.16 shows the increase of TL intensity as the heating rate increases and then decreases as the heating rate continues to increase.

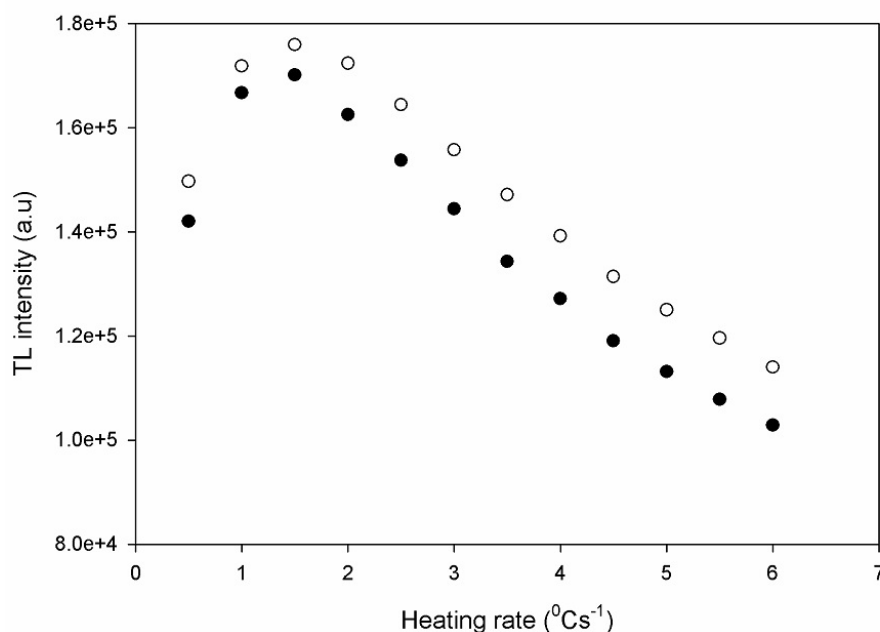


Figure 6.16: The effect of heating rate on the peak maximum intensity of the main peak of the TL glow curve in unannealed synthetic quartz. A dose of 31 Gy was used.

6.2.4.4 The influence of heating rate on the intensity of the main TL peak of annealed synthetic quartz

The intensity of peak I in an unannealed synthetic quartz increases and then decreases as heating rate increases as presented in the previous section. As was done in the previous section for an unannealed sample, the same procedure was applied for the sample annealed at 500°C for 10 minutes. The aim of this experiment was to study whether the response of TL intensity against heating rate was affected by annealing. The maximum intensities of the main peak measured at various heating rates were collected and plotted as function of heating rate as was done in the previous section. The graph of maximum TL versus heating rate is presented in figure 6.17. The observation from this graph is that the TL intensity increases at lower heating rates and then decreases with heating rate. Both samples of synthetic quartz, unannealed and annealed used in this investigation showed the same behaviour for both TL peak temperature and peak intensity. The increase of the peak temperature

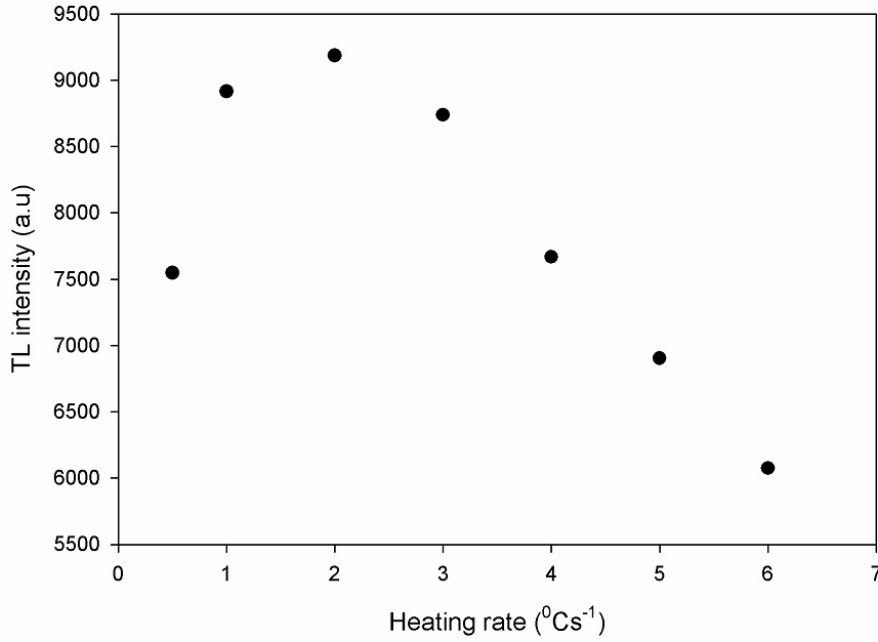


Figure 6.17: The behaviour of the peak maximum intensity of the main peak against the heating rate in annealed synthetic quartz. A dose of 31 Gy was used.

with heating rates and the increase followed by the decrease of TL intensity with heating rate. From theory of luminescence, we expect the constant intensity because the total number of emitted photons are constant since the same irradiation dose was used [39]. The increase of the TL intensity with heating rate requires further studies. The decrease of the TL intensity as heating increases is a sign of thermal quenching which is attributed to the competition between the radiative and non-radiative recombination [37, 39].

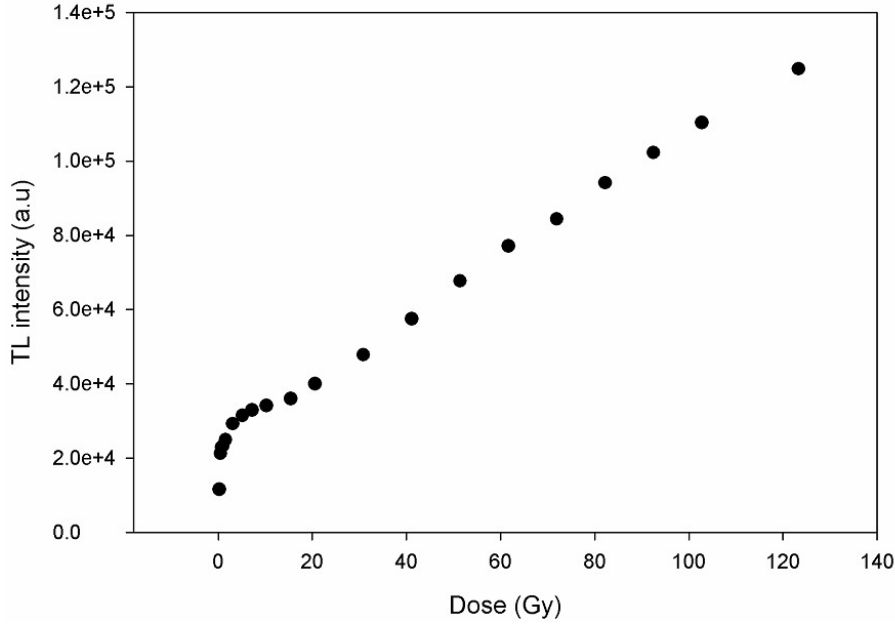


Figure 6.18: The thermoluminescence intensity against irradiation dose in unannealed synthetic quartz.

6.2.5 Dose response

One of the applications of thermoluminescence is in radiation dosimetry. This method is applied using insulator or semiconductor materials as dosimeters. One of the requirements for a material to be used as a dosimeter is linear response to irradiation which means that the measured TL intensity is proportional the applied dose [2, 3]. In this work, thermoluminescence dose response of peak I in an unannealed synthetic quartz and the sample annealed at 500°C for 10 minutes was investigated.

6.2.5.1 Dose response of the TL of the unannealed synthetic quartz

The sample of an unannealed synthetic quartz was irradiated from 0.2 up to 123 Gy and the TL intensities of peak I were collected at each dose. The intensity was plotted against the irradiation dose and the resultant graph is presented in figure 6.18. The results indicate that the thermoluminescence intensity of peak I increases with dose. For doses lower than 20 Gy, the response is non linear. At higher doses but less than

120 Gy, the behaviour changes to a linear response.

In order to determine the nature of the growth-curve, we tried to find an equation which gives the best fit to the dose response curve. The curve was approximately described as

$$y(D) = A(1 - \exp(-\eta D)) + cD, \quad (6.1)$$

where D (Gy) is the irradiation dose, A (arbitrary unit), η and c in (Gy^{-1}) are constants. Figure 6.19 is the dose dependence curve fitted with equation 6.1. The equation did not properly fit all the data in the curve. This lack of a general equation to describe the behavior of the growth nature of the TL intensity against dose response may be caused by many effects. One of the effects is that peak I has two overlapping peaks. The first overlapping peak (satellite peak) is in its initial rise region and the other overlapping peak (peak II) is in its high temperature side (see figure 6.2). The two overlapping peaks possibly contribute to the dose response by competition in capturing electrons. The other reason is that our sample undergoes sensitization upon heating to 500°C . When the sample is irradiated and heated, the increase of the TL intensity may be caused by both irradiation and thermal activation.

Figure 6.20 is the glow curve of unannealed sample measured at linear heating rate of 5°C s^{-1} after an irradiation dose of 180 Gy. The graph shows that the TL intensity of peak II grows faster with irradiation dose compared to the intensity of peak I. At higher dose, peak II becomes dominant in intensity.

6.2.5.2 Influence of irradiation dose on activation energy for the unannealed synthetic quartz

In the dose range between 0.5 up to 123 Gy, the influence of dose on the activation energy for the unannealed synthetic quartz was investigated. We used the initial rise method to calculate the activation energy of the main peak from glow curves measured at different doses. Figure 6.21 shows the activation energy against dose.

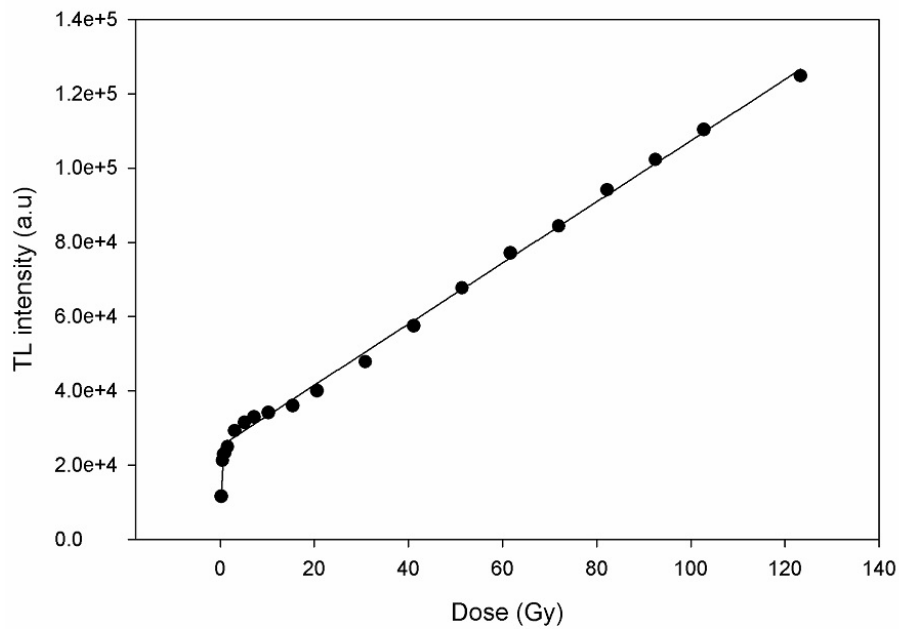


Figure 6.19: Graph representing the behaviour of the thermoluminescence intensity in unannealed synthetic quartz against irradiation dose fitted with a saturating exponential equation plus a linear equation.

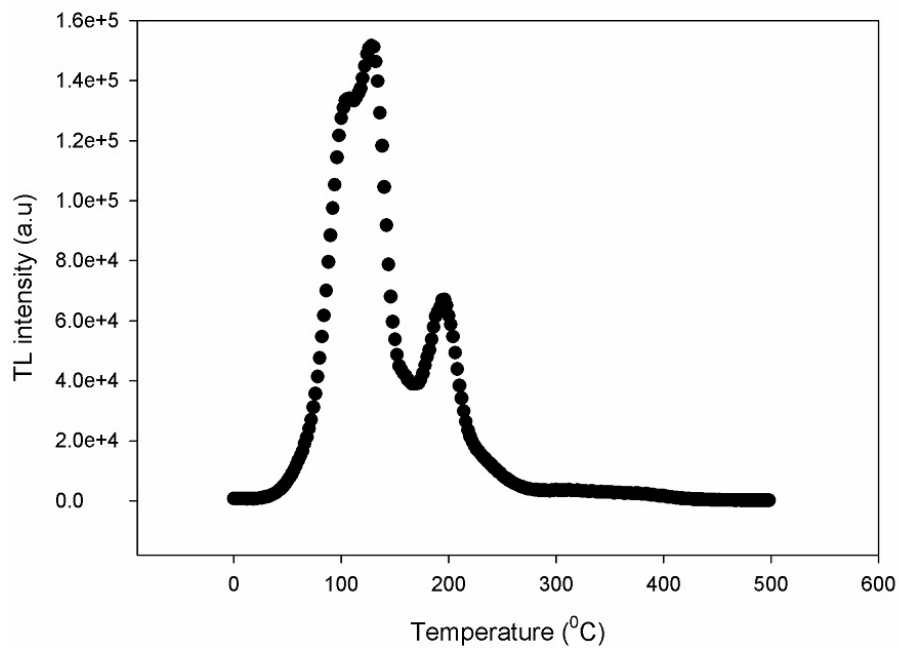


Figure 6.20: Glow curve of unannealed synthetic quartz measured after an irradiation dose of 180 Gy.

The graph indicates that increasing dose from 0.5 up to 123 Gy did not introduce new peak in the proximity of peak I since the activation energy of peak I did not change with irradiation dose.

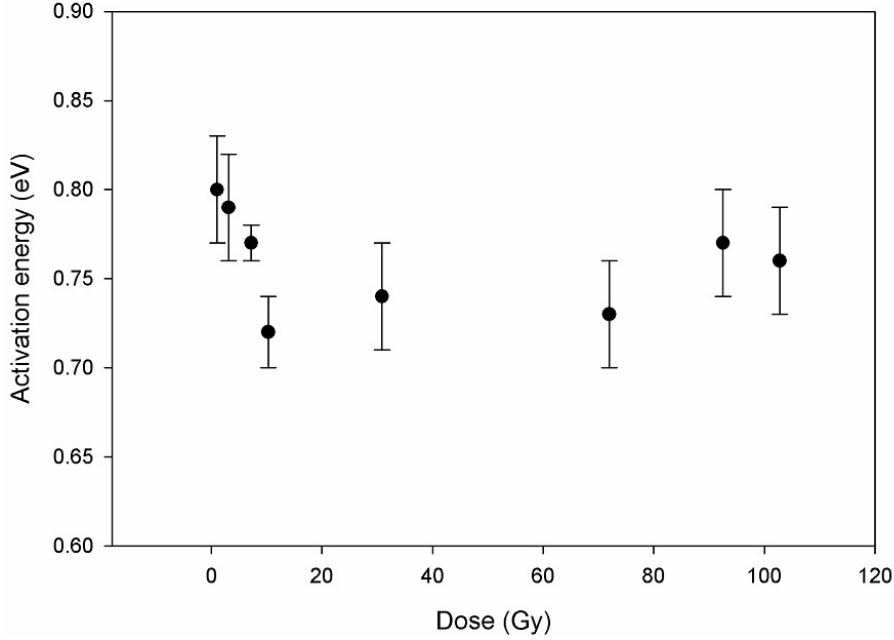


Figure 6.21: Graph of activation energy of peak I versus dose for the unannealed synthetic quartz.

6.2.5.3 Dose response of the TL of annealed synthetic quartz

The dose response of peak I for an unannealed sample was found to be possibly affected by the presence of overlapping peaks as discussed in the section 6.2.5.1. The nature of the dose response curve in an annealed synthetic quartz was investigated using the sample annealed at 500°C for 10 minutes. The aim of this experiment was to study the effect of annealing on the dose response curve. As for the unannealed sample, figure 6.22 indicates that the TL of the main peak increases with dose throughout the dose range of 0.5 up to 102 Gy used in this study. The faster increase of the TL intensity of peak II with dose compared to that of peak I was also observed in an annealed sample. Peak II of the glow curve in figure 6.5 becomes dominant

compared with the intensity of peak I for doses greater than 100 Gy as was seen for the unannealed sample, figure 6.20.

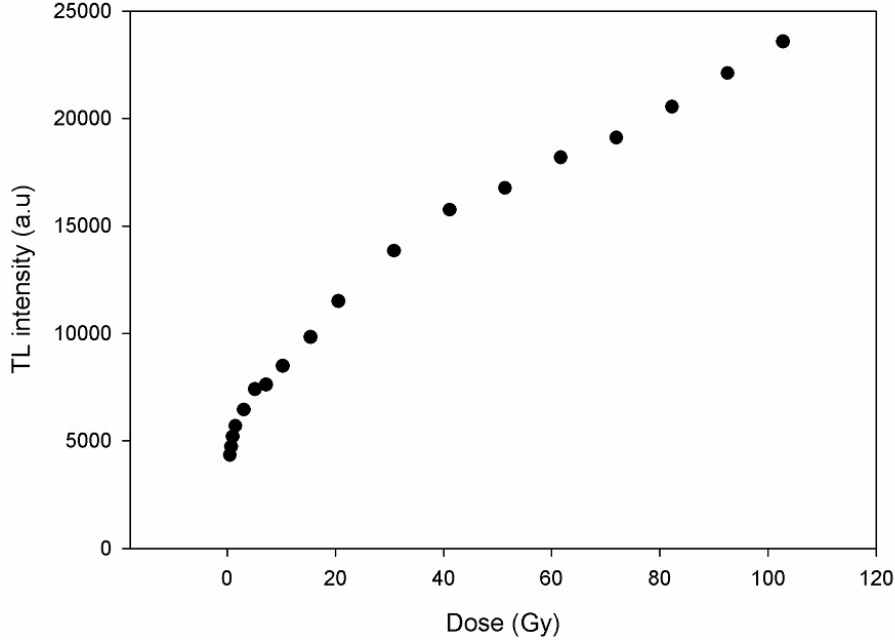


Figure 6.22: Graph of maximum intensity of peak I versus dose for the annealed synthetic quartz.

Unlike for the unannealed sample, the analysis showed that the dose response of the peak I of the annealed sample could be approximately described by the equation

$$y(D) = y_0 + aD^h, \quad (6.2)$$

where a and h in (Gy^{-1}) are fitting parameters, D in (Gy) is the irradiation dose and y_0 in (arbitrary unit) is the y - intercept. The solid line through data points in figure 6.23 is the best fit of equation 6.2.

The form of the dose response curve was studied by using superlinearity index $g(D)$ given by

$$g(D) = \left[\frac{Dy''(D)}{y'(D)} \right] + 1, \quad (6.3)$$

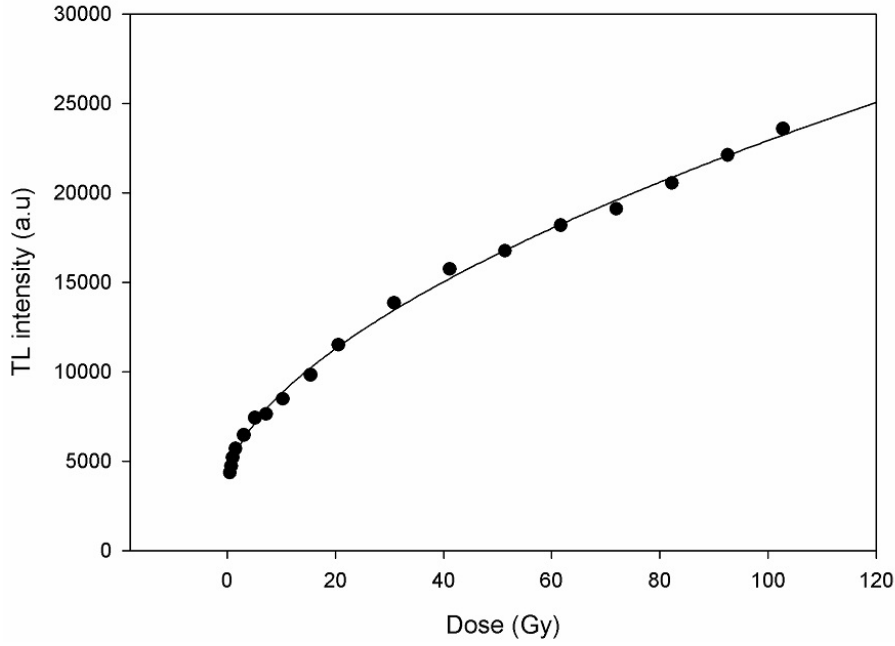


Figure 6.23: The dose response in annealed synthetic quartz. The dose response curve was fitted with equation 6.2.

where $y(D)$ stands for the equation describing the dose response and D is the irradiation dose. $y'(D)$ and $y''(D)$ are the first and the second derivative of $y(D)$ respectively. Figure 6.24 shows the graph of superlinearity index $g(D)$ against the irradiation dose. From the figure, two regions can be identified. First region is in the dose range of 0.5 up to 5 Gy. In this region the curve is approximately linear i.e., $g(D) \sim 1$. The second is in the range of 7 up to 102 Gy. In this second region the value of superlinearity index becomes greater than one ($g(D) > 1$) which implies that the dose response curve is superlinear with respect to the first region.

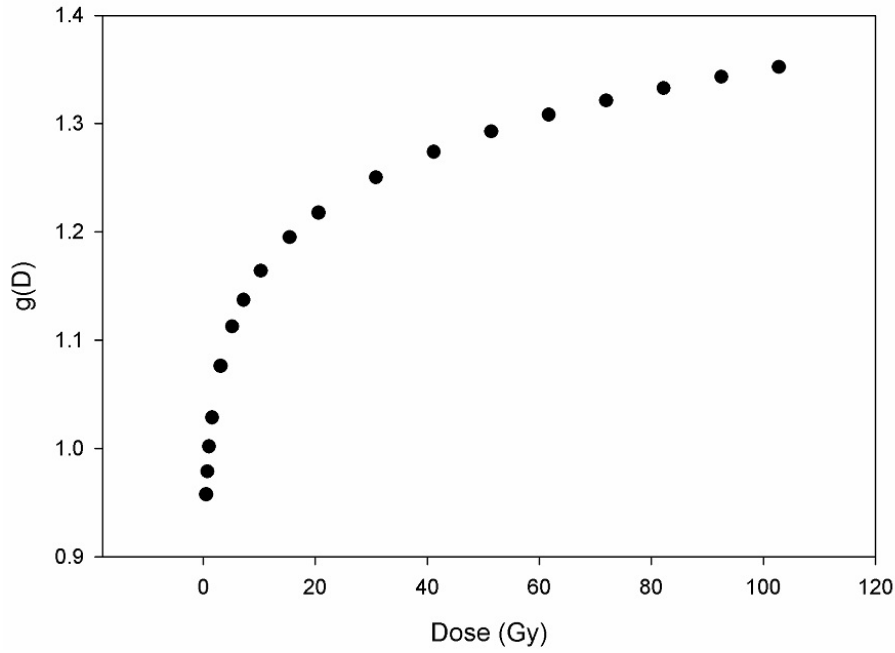


Figure 6.24: The superlinearity index $g(D)$ against dose for the annealed synthetic quartz.

6.2.5.4 Influence of dose on the activation energy of peak I for annealed synthetic quartz

The activation energy of peak I for the unannealed sample is constant for glow peaks measured following different irradiation doses as shown in figure 6.21. The objective of this experiment was to investigate the effect of annealing on the influence of dose on the activation energy in annealed synthetic quartz. As was done for the unannealed sample in section 6.2.5.2, the activation energy was determined using the initial rise method from glow curves measured at irradiation doses ranging from 0.5 to 102 Gy. Figure 6.25 shows the activation energy of peak I against irradiation dose for the annealed synthetic quartz. As for the unannealed sample, the results show that the activation energy is constant for different irradiation doses.

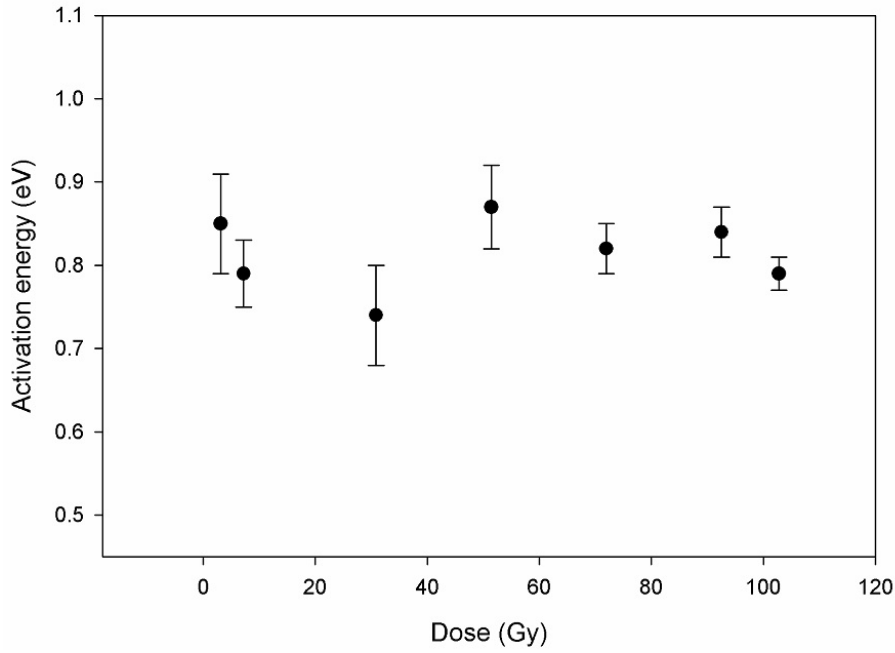


Figure 6.25: Graph of activation energy versus irradiation dose for annealed synthetic quartz. The corresponding glow curves were measured at 5°Cs^{-1} .

6.3 Kinetic analysis of peak I for unannealed synthetic quartz

This section presents the experimental results of trapping parameters calculated using different methods of kinetic analysis in order to better understand the mechanisms involved in the luminescence emission from quartz. These parameters are the order of kinetics b , the activation energy E and the frequency factor s .

6.3.1 The initial rise method

Glow curves measured from the unannealed synthetic quartz were analyzed in order to determine the trapping parameters of the trap responsible for peak I. The initial rise method as described in section 2.1 was applied on a glow peak measured at 5°Cs^{-1} by heating the sample to 500°C after an irradiation dose of 21 Gy.

Figure 6.2 is an example of a glow curve from unannealed synthetic quartz used in

this method of analysis. We found the values of activation energy from the slope of

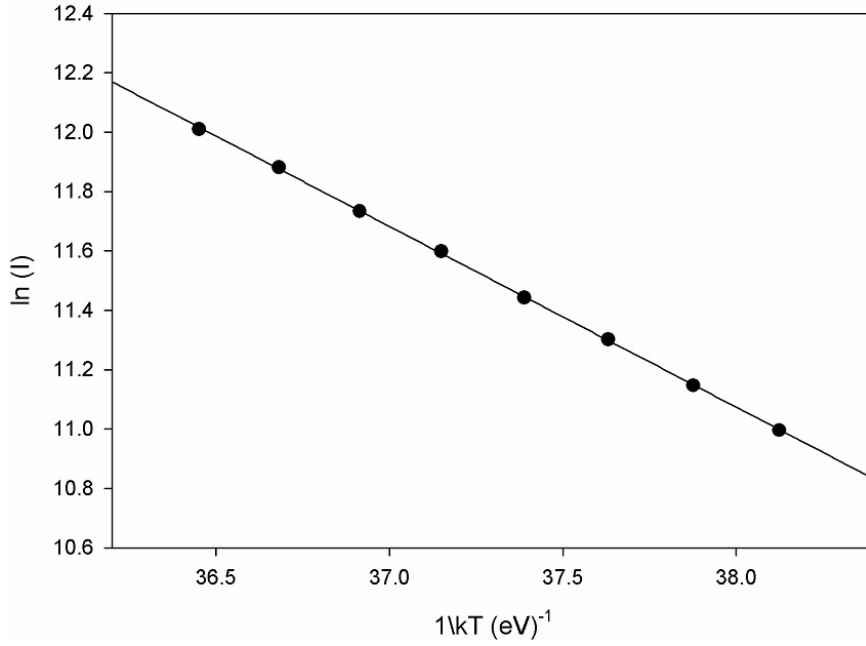


Figure 6.26: The graph of $\ln(I)$ versus $1/kT$ used in the calculation of the activation energy (E) using the initial rise method. The data was measured at 5°Cs^{-1} after an irradiation dose of 21 Gy.

the linear fit of $\ln(I)$ against $1/kT$ shown in figure 6.26. The slope of the fit gave the value of activation energy equal to $E = 0.61 \pm 0.01$ eV. Figure 6.27 shows the effect of repetitive measurement on the value of activation energy calculated using the initial rise method for 9 glow peaks measured at 5°Cs^{-1} following irradiation to 21 Gy. From figure 6.27, it is clear that all glow curves gave a consistent value of activation energy.

The value of E found in our study were compared with values reported in the literature from synthetic quartz. Petrov and Bailiff [40] reported that the value of activation energy of the main peak in synthetic quartz ranges from 0.80 to 0.99 eV. Yazici et al [41] reported 0.90 eV and Kitis et al [42] reported the value of about 0.79 eV.

The comparison indicates that our result is lower than the ones reported in the literature from synthetic quartz using the same method of analysis. The difference in

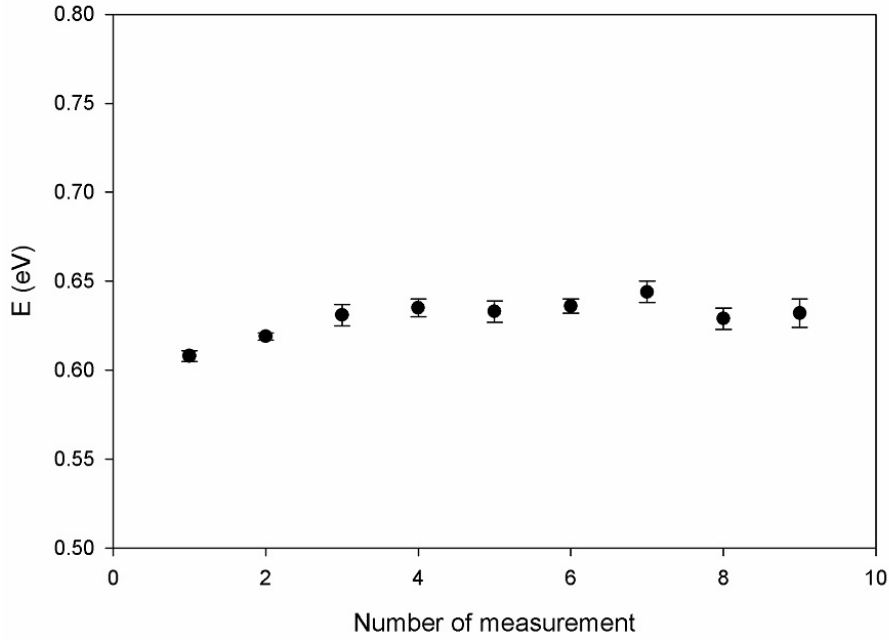


Figure 6.27: The activation energy calculated using the initial rise method as a function of repetitive measurement. The results are within each others' margins of error.

value could be attributed to the appearance of the satellite peak in the initial rise part of the main glow peak in our sample. We then used different methods of peak separation in order to get a well isolated main peak.

6.3.2 Peak separation methods

Two methods of peak separation were applied on the lower temperature part of the main peak of the glow curve. The purpose was to estimate the position of the satellite peak in the initial rise region of peak I, figure 6.2. The methods used were the $T_m - T_{stop}$ and $E - T_{stop}$ techniques as described in section 2.1.

6.3.2.1 $T_m - T_{stop}$ method

In this method, the sample was irradiated to 21 Gy and heated up to a temperature T_{stop} at the low temperature tail of the satellite peak i.e., 20°C and then cooled down. After cooling and without further irradiation, the sample was reheated up to 500°C

to measure the whole glow curve. From the glow curve, the temperature T_m of the first TL peak of the glow curve was noted. The value of T_{stop} was changed by 2°C from 20 up to 70°C . Figure 6.28 is the plot of T_m versus T_{stop} . Figure indicates that the first peak of the whole glow curve is at 78°C . This temperature is the position of the main peak when it is measured at 1°Cs^{-1} . The position of the satellite peak could not be clearly identified by this method. The reason is that the satellite peak is not a well defined peak and so it is difficult to estimate its peak temperature.

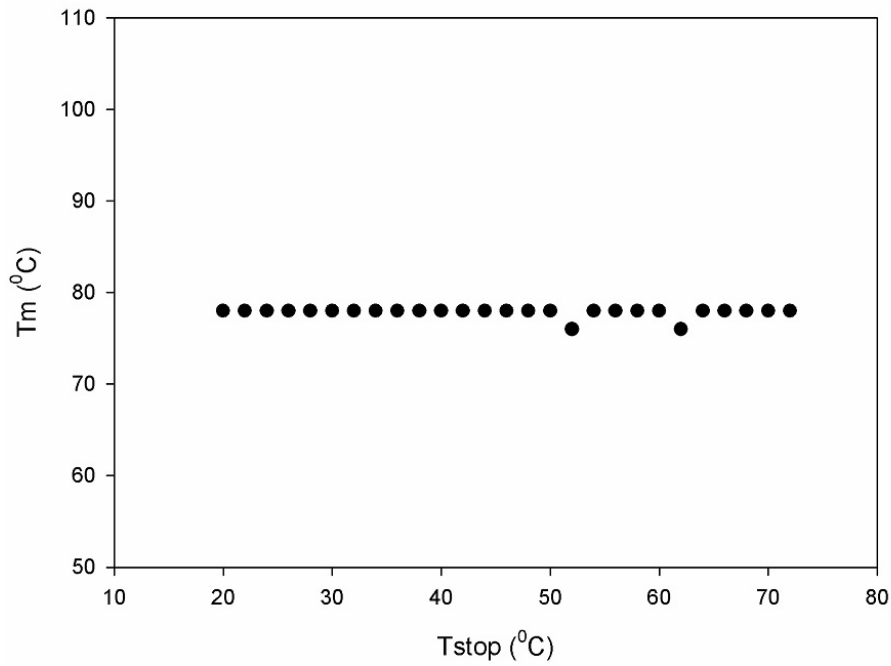


Figure 6.28: Variation of T_m with T_{stop} . Glow curves were measured at 1°Cs^{-1} after a dose of 21 Gy.

6.3.2.2 E - T_{stop} method

The second method of peak identification is called $E - T_{stop}$. In this method, the activation energy E of the peak measured after each T_{stop} was calculated using the initial rise method. The graph of E against T_{stop} will identify number of peaks due to the activation energy corresponding to the temperature to which the sample was heated [3]. Figure 6.29 shows the graph of E against T_{stop} . The resultant graph

shows two flat regions which implies that peak I is a composite of at least two peaks. The first peak has an activation energy of 0.6 eV found after T_{stop} between 20 and 30°C (first flat region) and the second has an activation energy of approximately 0.88 eV found after T_{stop} between 50 and 70°C (second flat region).

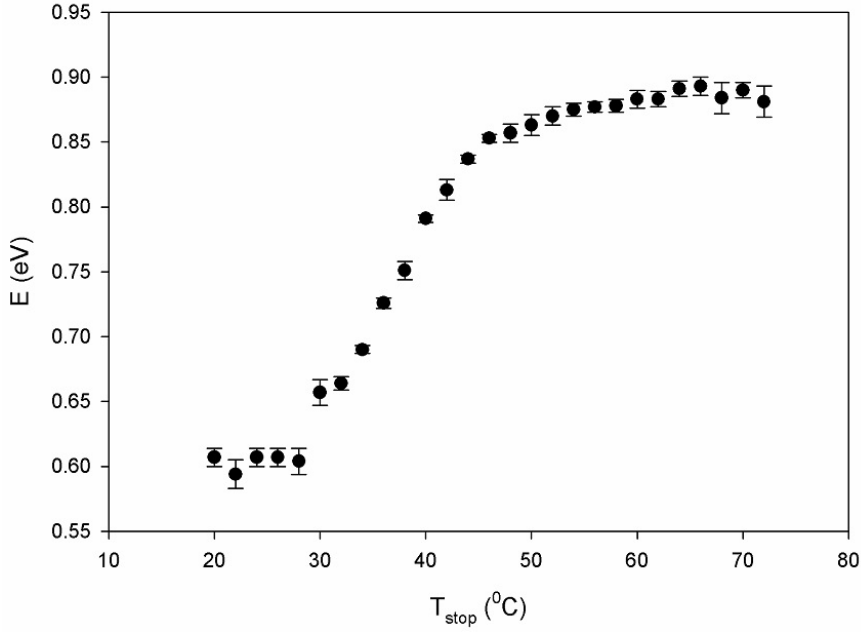


Figure 6.29: The graph of $E - T_{stop}$ plotted in the determination of the position of the satellite peak. These measurements were made at 1°Cs^{-1} after a dose of 21 Gy.

The values of the activation energy found in section 6.3.1 and the values of the first flat region of the graph in figure 6.29 are in the same range i.e., 0.6 eV. This implies that these energies are for the same peak i.e the satellite peak. The values of activation energy of the second flat region i.e., 0.88 eV is comparable with those reported in the literature for the main peak [41]. This implies that those two values are for two different peaks.

6.3.2.3 Investigation of the order of kinetics

Using the results from the $T_m - T_{stop}$ graph, the order of kinetics of the main TL peak of the unannealed synthetic quartz was deduced. The fact that the peak temperature T_m did not change with T_{stop} as presented in figure 6.28, implies that the peak

position does not depend of the initial concentration of the trap population [3, 7]. This behavior suggests that peak I follows first order kinetics.

6.3.3 Removal of the satellite peak

In order to analyze peak I separately, the satellite peak in its initial rise part was removed in two ways, by thermal cleaning and by isothermal cleaning.

6.3.3.1 Thermal cleaning method

In the thermal cleaning method, the sample was given a dose of 21 Gy. After irradiation, the sample was heated at 5°Cs^{-1} up to 80°C in order to remove the satellite peak. This temperature was chosen because the satellite peak was located approximately in the temperature range between 60 and 70°C in the glow curve measured at 5°Cs^{-1} (figure 6.2). The sample was then reheated without further irradiation up to 500°C to measure the whole glow curve. The glow curve recorded after thermal cleaning showed a clear rising edge of peak I as shown in figure 6.30.

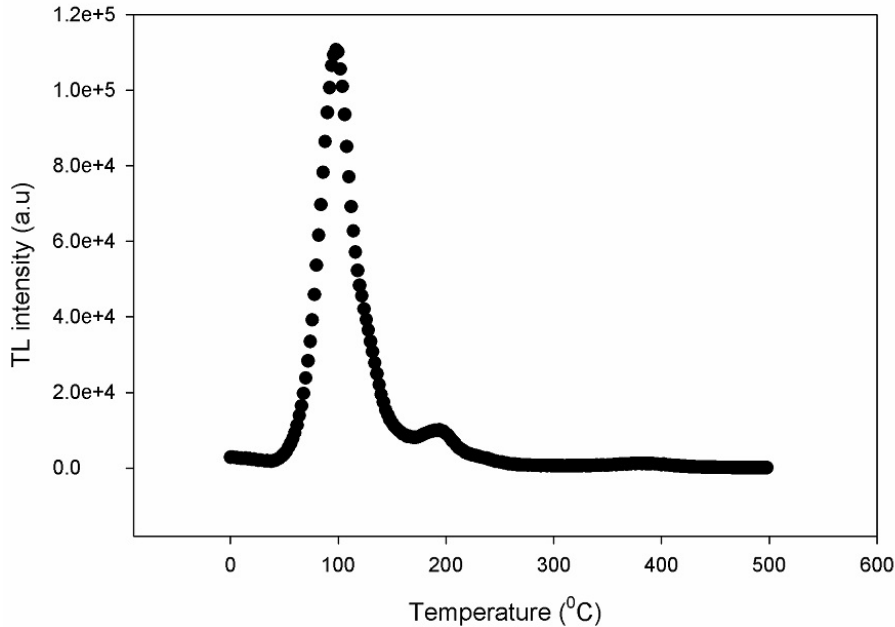


Figure 6.30: The glow curve measured at 5°Cs^{-1} after a dose of 21 Gy after thermal cleaning.

6.3.3.2 Isothermal cleaning method

In the isothermal cleaning process, the irradiated sample is heated to a specific temperature. The temperature should be lower than the maximum temperature of the peak to be cleaned. The sample is held at that temperature for a specific time. The next step is to record the whole glow curve.

In this method, the temperature and time have to be chosen such that the next peak will not be affected. The isothermal temperature for use was chosen by heating the sample to different temperatures T_{stop} . After each T_{stop} , the rest of the glow curve was measured. From the glow curve, the maximum intensity I_m of the main peak was noted for each T_{stop} . The values of I_{max} plotted against T_{stop} are shown in figure 6.31.

Figure 6.31 indicates that at isothermal cleaning temperatures $\geq 60^\circ\text{C}$, the intensity

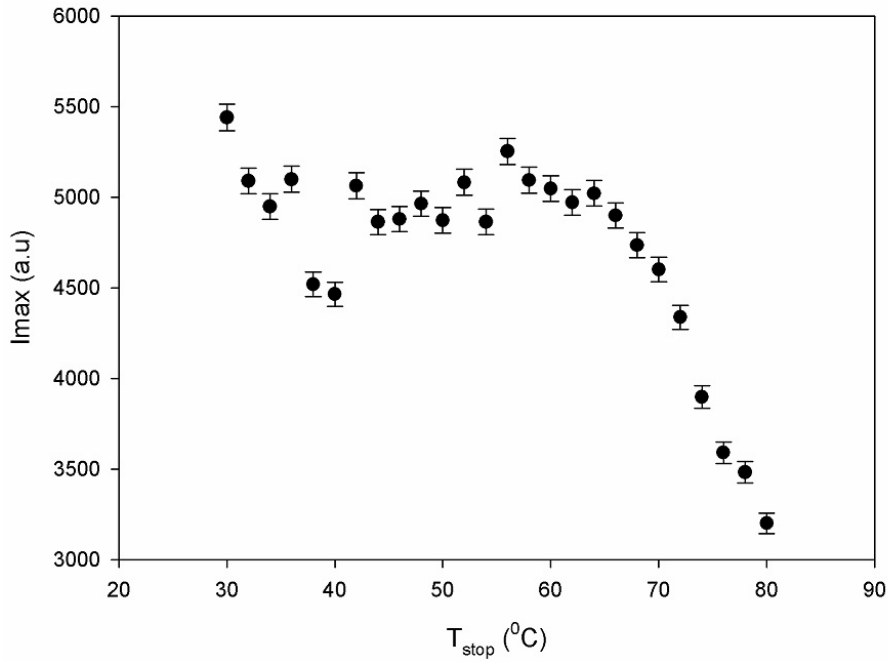


Figure 6.31: The change of the maximum intensity of the main peak as a function of T_{stop} .

of peak I started to be affected.

During this study, the isothermal cleaning temperature used was 40°C . The temperature was chosen because it is less than the maximum temperature of the peak to be

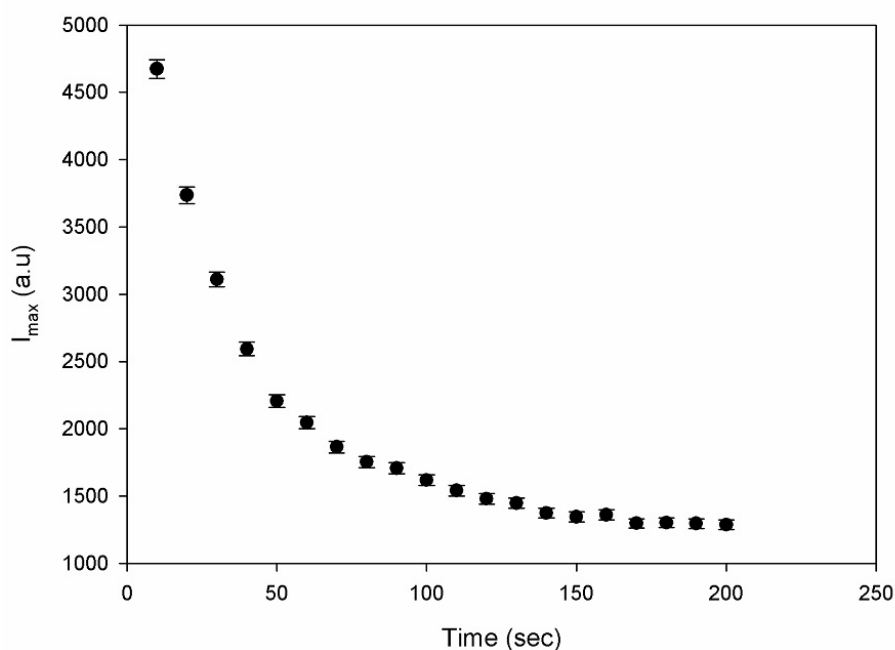


Figure 6.32: The graph of the change of the maximum intensity of the main peak as function of time to use in the choice of time to use in the isothermal cleaning process.

cleaned, satellite peak. This temperature is also in the range that cleans the satellite peak in the initial rise of peak I without affecting the intensity of peak I as shown in figure 6.31.

As for the temperature, the isothermal cleaning time should be chosen in the range which has no effect on the intensity of the next peak. The isothermal cleaning time was chosen by combining the chosen cleaning temperature i.e 40°C with different isothermal measurement times. The sample was heated to 40°C and held at that temperature for different times. At each holding time, the intensity $I_{\max}$ of the main peak was noted. Figure 6.32 is the graph of maximum intensity of peak I against isothermal measurement time. The graph shows that the increase of isothermal cleaning time reduces the intensity of the main peak. From the combination, we found that heating to 40°C and holding the sample at that temperature for 100 seconds cleaned completely the satellite peak. The glow curve measured after isothermal cleaning has a clear initial rise of the main peak as shown in figure 6.33.

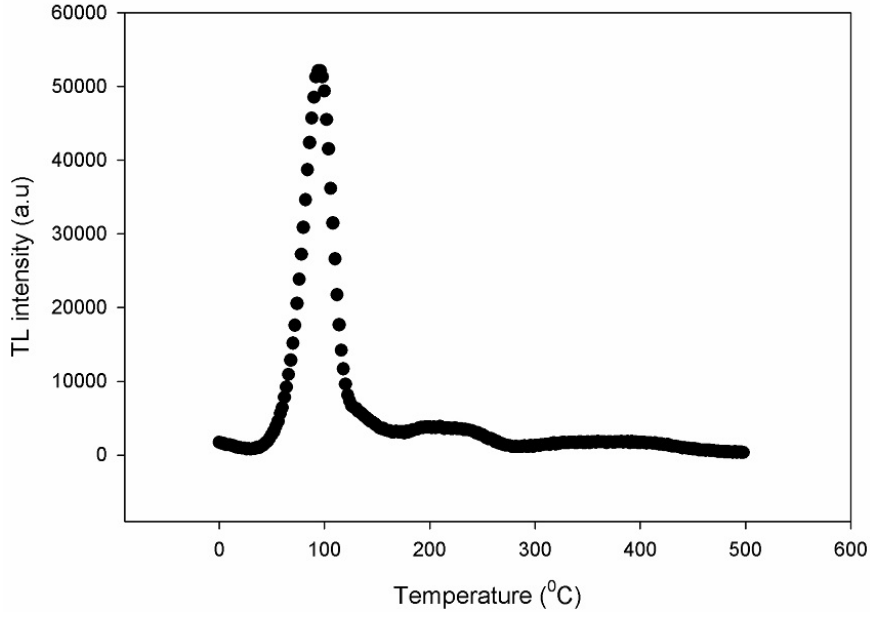


Figure 6.33: Glow curve of synthetic quartz measured after isothermal cleaning of the satellite peak. The cleaning was done at 40°C for 100 seconds. The glow curve was measured at a heating rate of 5°Cs⁻¹ after a dose 21 Gy.

6.3.4 Analysis of the thermally cleaned peak using the initial rise method

The initial rise method was used in order to determine the activation energy of the trap responsible for peak I. In addition, this section aims to investigate whether results from peak I after thermal cleaning are comparable with values of the activation energy reported in the literature as stated in section 6.3.1 ($\simeq 0.90$ eV) and value found using E-T_{stop} (0.88 eV, section 6.3.2.2). Using the initial rise method, the thermally cleaned peak was analyzed. Figure 6.34 is the plot of $\ln(I)$ against $1/kT$ used in this analysis. The activation energy is given by the slope of the straight line. The activation energy was calculated on peaks measured from three different samples. The values from each sample are 0.90 ± 0.01 , 0.92 ± 0.01 and 0.90 ± 0.01 eV for sample 1, sample 2 and sample 3 respectively. The values are in good agreement. The average of values from these measurements was found to be equal to 0.91 ± 0.01 eV.

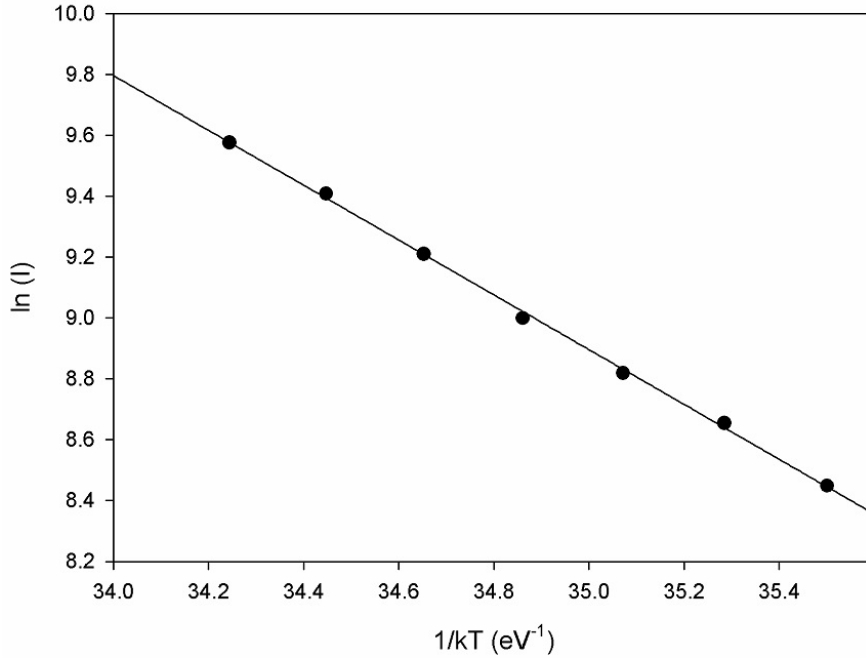


Figure 6.34: Determination of the activation energy (E) of the main peak after thermal cleaning using the initial rise method.

The results found after thermal cleaning were compared with the values reported by Yazici et al [41] which is 0.90 eV and those reported by Petrov and Bailiff [40] which is between 0.80 and 0.99 eV. Our results are comparable with these literature values. This implies that values of the activation energy from the uncleaned peak presented in section 6.3.1 were affected by the presence of the satellite peak as indicated by $E-T_{stop}$. The results also indicate that thermal cleaning removed completely the satellite peak.

6.3.5 Analysis of the isothermally cleaned peak using the initial rise method

For the purpose of investigating if the isothermal analysis method can be used as a method of thermal cleaning, glow peaks taken after isothermal cleaning were analyzed using the initial rise method. Figure 6.35 shows an example of the linear fit of $\ln(I)$ versus $1/kT$ for a peak measured after isothermal cleaning. The value of the

activation energy found from figure 6.35 is $E = 0.85 \pm 0.02$ eV. The results found using initial rise after isothermal cleaning are similar to the value found using the same method after thermal cleaning i.e 0.91 eV. The value is also comparable with the values reported in the literature as mentioned in the previous section. This is evidence that isothermal analysis can be used as method of thermal cleaning.

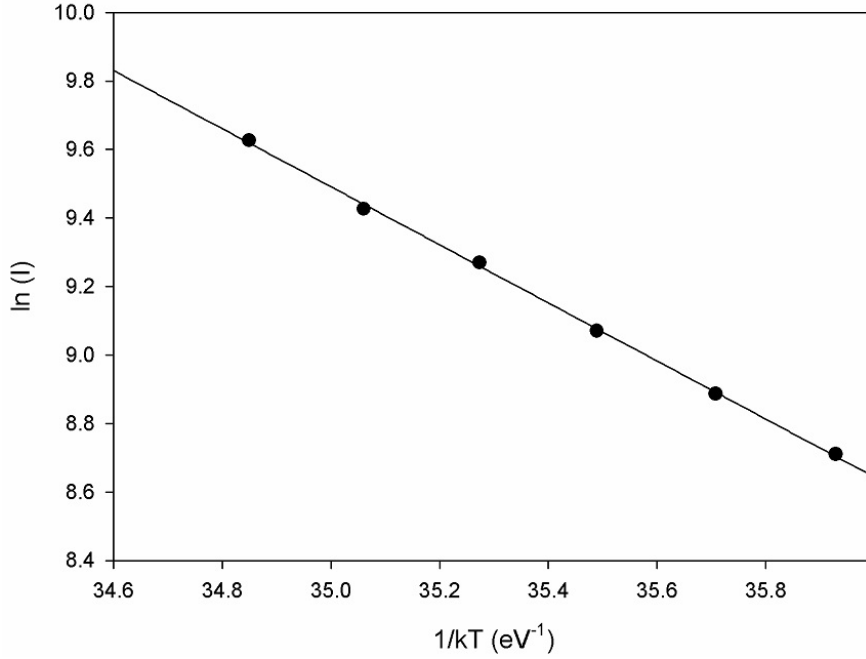


Figure 6.35: Application of the initial rise method on an isothermally cleaned glow peak. The graph was fitted with a linear equation to determine the value of the activation energy.

6.3.6 Analysis of the thermally cleaned peak using the various heating rate methods

The aim of this method was to use values of peak temperature measured at different heating rates in the evaluation of kinetic parameters. The various heating rate method (VHR) as discussed in section 2.3 is based on the shift of the peak position with heating rate. In this work, the heating rate was changed from 0.5 to 6°Cs^{-1} in steps of 0.5°Cs^{-1} . At each heating rate, the temperature corresponding to the peak

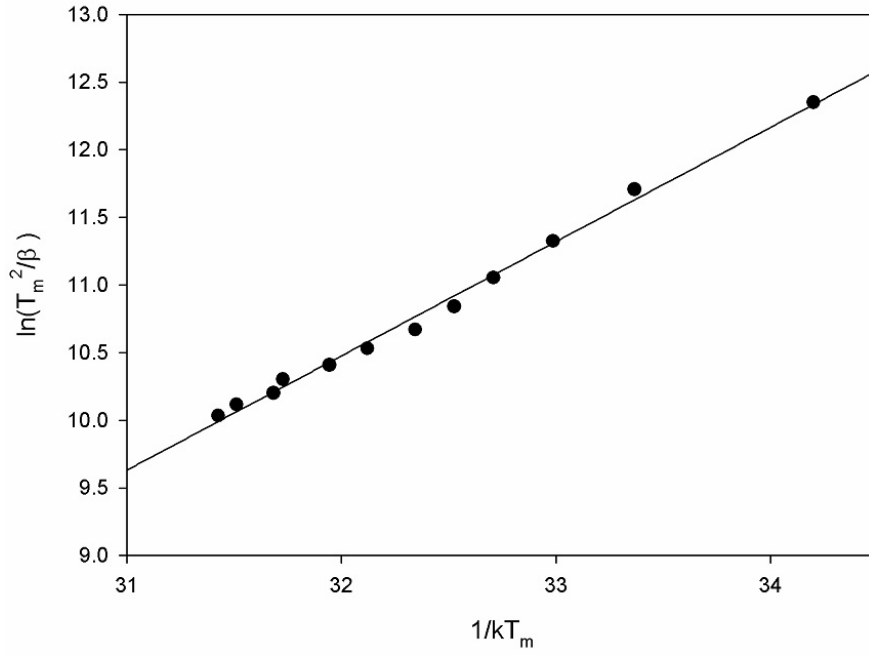


Figure 6.36: Graph of $\ln(T_m^2/\beta)$ versus $1/kT_m$ used in the determination of trapping parameters after thermal cleaning. The solid line is the best fit of a linear equation.

maximum after thermal cleaning was noted. The activation energy was determined by plotting $\ln(T_m^2/\beta)$ versus $1/kT_m$. Figure 6.36 is the graph of $\ln(T_m^2/\beta)$ against $1/kT$ fitted with a linear equation. Sometimes the difference in slope between points measured using higher and lower heating rates occurs. This difference is probably due to sample thickness which has an influence on the temperature gradient and temperature lag especially at high temperature [38]. From the slope of the graph in figure 6.36, the value of the activation energy was found to be $E = 0.85 \pm 0.02$ eV. The intercept of the graph is equal to $\ln(E/sk)$. In the determination of the value of the frequency factor s , the value of E found was substituted into the expression of the intercept. The value of frequency factor s was found to be equal to $s = 2.1 \times 10^{11} \text{ s}^{-1}$. The value of the frequency factor found is in the order of the Debye vibration frequency as expected by kinetics theory of solid state physics [2].

The method of a combination of two heating rates and corresponding maximum temperatures to determine the value of E was also used. These values were substituted

Table 6.1: Values of activation energy (E) obtained using the combination of two heating rates and two corresponding maximum temperatures.

Combinations of β ($^{\circ}\text{Cs}^{-1}$)	Activation energy (eV)
0.5 and 1	0.77
0.5 and 5	0.85
1 and 4	0.91
2.5 and 5	0.76
1.5 and 4.5	0.81

into equation 2.10 using different combinations. Five combinations were made and five values of activation energy were found. The values of E found at each combination are presented in table 6.1. All combinations gave values of E comparable with each other. The values are also in good agreement with values found using the initial rise method (section 6.3.4, 6.3.5).

6.3.7 Analysis of the isothermally cleaned peak using the various heating rate methods

The aim of this analysis was to determine kinetic parameters E and s , and compare them to the ones found from a thermally cleaned peak. This was done in order to confirm the use of isothermal analysis as a method of thermal cleaning. Values of T_m were found from TL glow peaks measured at different heating rates after isothermal cleaning. Figure 6.37 is the graph of $\ln(T_m^2/\beta)$ versus $1/kT_m$ for peaks measured after isothermal cleaning. The linear fit of the graph gave the slope $-E$ and the intercept of $\ln(E/sk)$. The value of the activation energy is $E = 0.78 \pm 0.02$ eV and the value of the frequency factor from the intercept is $s = 1.8 \times 10^{10} \text{ s}^{-1}$. This method gave results which are comparable with those from the various heating rate method of the thermally cleaned peak presented in the previous section. The results are also in good agreement with those from the initial rise method ($\simeq 0.90$ eV).

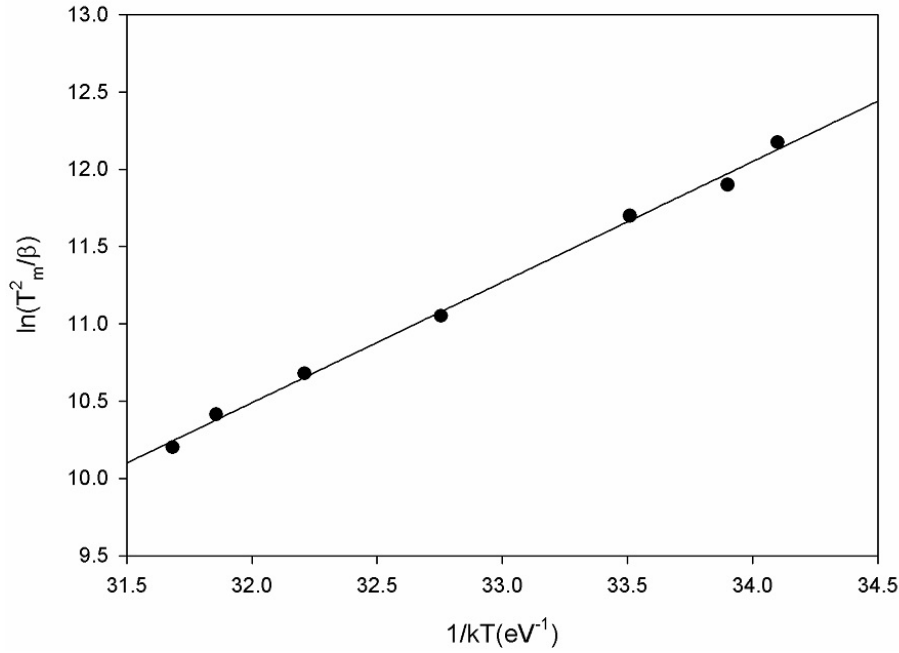


Figure 6.37: Graph of $\ln(T_m^2/\beta)$ against $1/kT_m$ used in the calculation of the trapping parameters of the isothermally cleaned peak using the various heating rate method of kinetic analysis.

6.3.8 Peak shape methods

The geometrical shape parameters of the cleaned peak I was also used to determine kinetic parameters using peak shape methods as discussed in section 2.4.

6.3.8.1 Analysis of the thermally cleaned peak using peak shape methods

The geometric shape parameters as defined in section 2.4 were determined from the glow peak after being thermally cleaned. We applied these methods to glow peaks measured from three different samples. The results gave the average value of geometrical factor $\mu = 0.44 \pm 0.03$ which implies that the main TL peak of unannealed synthetic quartz follows first order kinetics [2]. The results of the order of kinetics allowed us to determine the activation energy using equation 2.11. The values of C_γ and b_γ were deduced from table 2.1 by substituting the value of μ by 0.42 as was done by Pagonis et al [8] when the geometric factor μ indicates that the

Table 6.2: Values of the activation energy calculated used Chen's equation [2]. The glow curves were measured using different heating rates after isothermal cleaning of the initial rise part of peak I.

Heating rate ($^{\circ}\text{C/s}$)	μ	E_{ω} (eV)	E_{τ} (eV)	E_{δ} (eV)
0.6	0.42 ± 0.04	0.99 ± 0.05	0.98 ± 0.07	0.98 ± 0.10
1	0.43 ± 0.05	0.87 ± 0.04	0.89 ± 0.06	0.88 ± 0.08
2	0.43 ± 0.05	0.92 ± 0.04	0.97 ± 0.07	0.88 ± 0.08
3	0.46 ± 0.05	0.88 ± 0.03	0.96 ± 0.07	0.78 ± 0.06
4	0.44 ± 0.04	0.84 ± 0.03	0.90 ± 0.05	0.80 ± 0.06
Average	0.44 ± 0.05	0.90 ± 0.04	0.94 ± 0.06	0.86 ± 0.08

peak follows first order kinetics. Three value of the activation energy, E_{ω} , E_{τ} and E_{δ} were calculated for each of the three samples and the average activation energy for all samples are $E_{\omega} = 0.85 \pm 0.04$ eV , $E_{\tau} = 0.89 \pm 0.05$ eV and $E_{\delta} = 0.79 \pm 0.05$ eV. The results from all geometrical shape parameters ω , τ and δ for all samples are consistent with the results found using the initial rise, sections 6.3.4 and 6.3.5 and various heating rate methods, section 6.3.6 and 6.3.7.

6.3.8.2 Analysis of the isothermally cleaned peak using peak shape methods

We also measured glow curves using various heating rates after isothermal cleaning. We used each of these glow curves to determine the activation energy of peak I using peak shape methods. The analysis started by investigation of the order of kinetics using the value of the geometric shape factor μ . Table 6.2 shows values of trapping parameters found from peak I measured at different heating rates after isothermal cleaning. Our results indicate that the peak follows first order kinetics as μ is close to 0.42. The value of C_{γ} and b_{γ} in equation 2.11 were found using the same procedure as was done in the previous section and were used to calculate the value of activation energy E . The results of the activation energy in table 6.2 show that the values of activation energy calculated using the different geometric shape parameters are comparable.

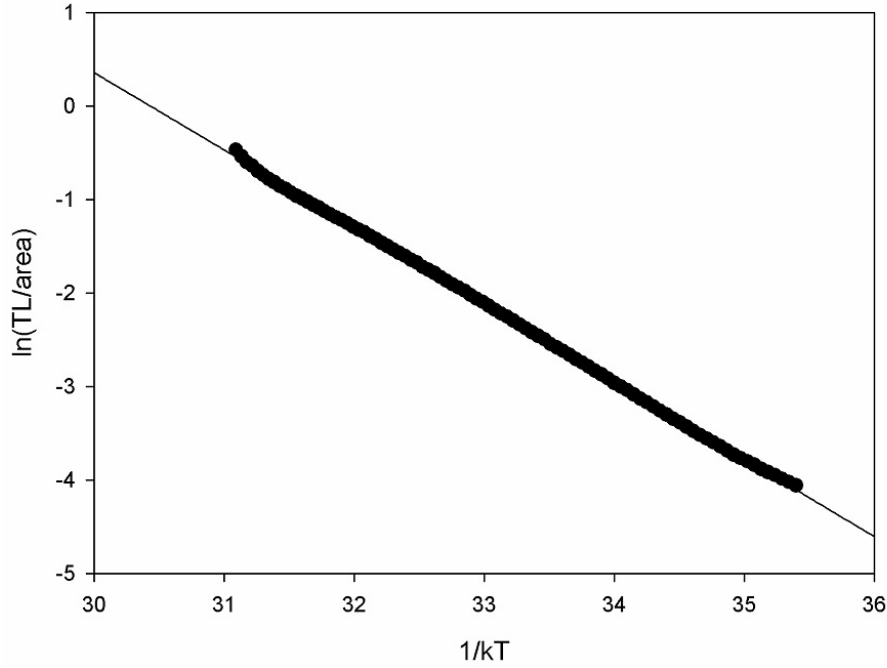


Figure 6.38: The example of the graph of $\ln (TL/area)$ versus $1/kT$ fitted with a linear equation. The peak was measured after an irradiation dose of 31 Gy and the order of kinetics was considered to be 1. The data was obtained using heating rate of 2°s_{-1} .

6.3.9 Whole curve method

In this method, the area of the glow peak was determined using the method described in section 2.2. The peak was transformed into a straight line by plotting the $\ln (TL/area)$ against $1/kT$. For first analysis we set $b = 1$. The fit of the transformed graph with a linear equation gave the value of activation energy E from its slope. The intercept $\ln (s/\beta)$ gave the value of frequency factor s .

6.3.9.1 Analysis by first order kinetics

Figure 6.38 is an example of the fit used in the determination of the trapping parameters using the whole curve method by considering first order kinetics. The method was applied to glow peaks measured at different heating rates from 0.5 up to 6°Cs^{-1} and the resultant value of E was plotted as function of heating rate. Figure 6.39

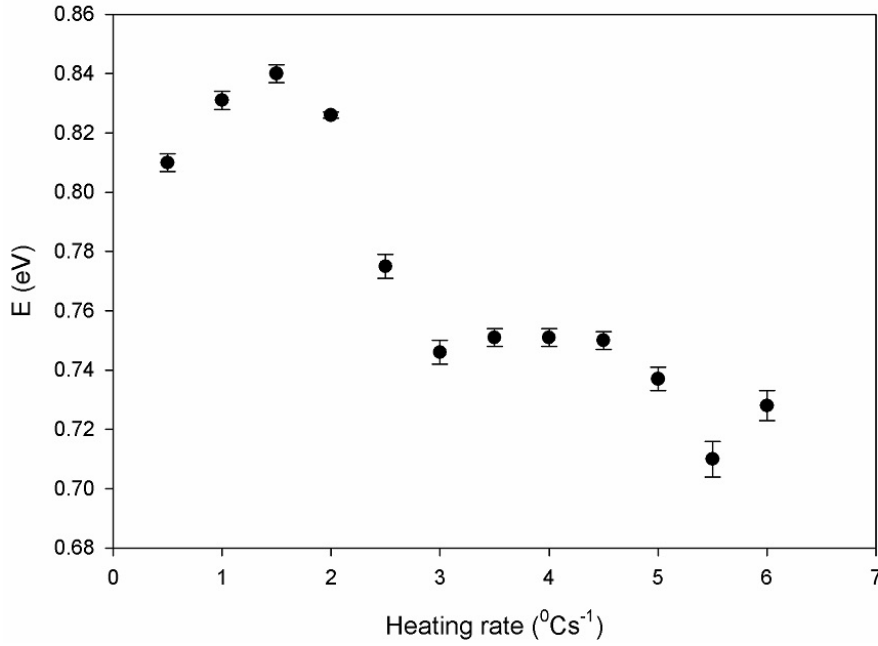


Figure 6.39: Apparent values of the activation energy calculated using the whole curve method plotted as a function of heating rate.

indicates that the activation energy of peak I decreases with heating rate. The apparent decrease could be possibly attributed to the fact that the main peak shifts faster to higher temperature while the peak II in figure 6.3 shifts slower to higher temperature. The peak II overlaps with the main peak at higher heating rates. The value of frequency factor s was calculated from the intercept $\ln(s/\beta)$ and equals $s = 1.7 \times 10^{11} \text{ s}^{-1}$.

6.3.9.2 Analysis by general order kinetics

Using general order kinetics, the order of kinetics b of the main peak was estimated. This analysis was done by plotting $\ln(TL/area^b)$ against $1/kT$. During this procedure, the exponent b was changed from 1 up to 2. The purpose of that change was to find the value of b which was best fitted by a straight line. The fit improved $b \rightarrow 1.1$, as shown in the figure 6.40. These results indicate that the peak indeed follows first order kinetics.

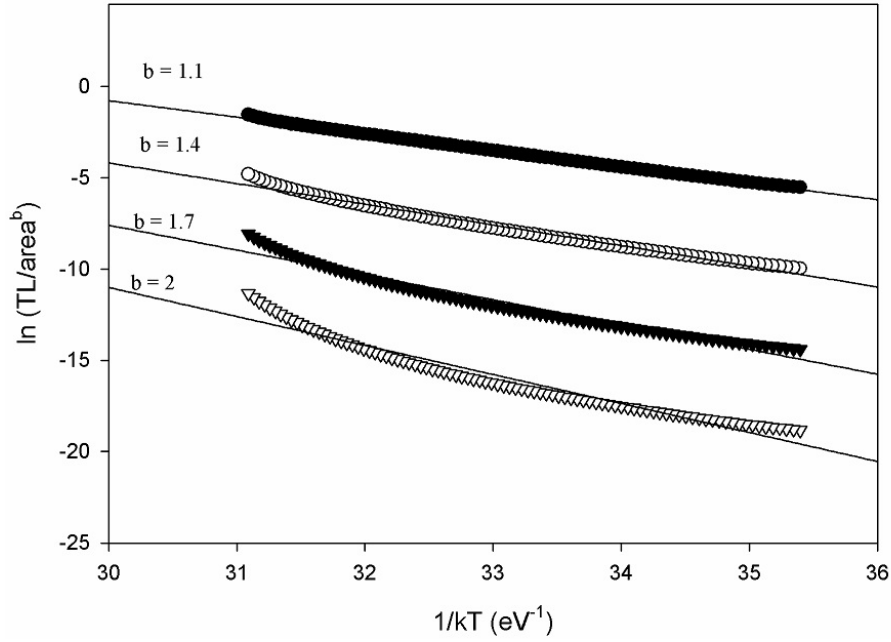


Figure 6.40: The plot used in the determination of the order of kinetics of the main peak using the whole glow peak method. The line through each dataset is a linear regression.

6.3.10 Isothermal analysis methods

Isothermal luminescence is thermally stimulated luminescence measured as function of time while keeping the temperature constant [3]. The methods of evaluation of trapping parameters from isothermal decay curves were discussed in section 2.5. Isothermal luminescence is a time dependent function. For first order kinetics, isothermal luminescence is described as an exponential decay as defined by equation 2.13.

6.3.10.1 Isothermal analysis of thermally cleaned peak

In this study, the experiment were begun by irradiating the sample to a dose of 31 Gy. After irradiation, the satellite peak in the rising edge of the main peak was removed by heating the sample to 80°C. After this, isothermal decay curves were measured at temperatures ranging from 50 up 75°C in steps of 5°C, for 100 seconds in each

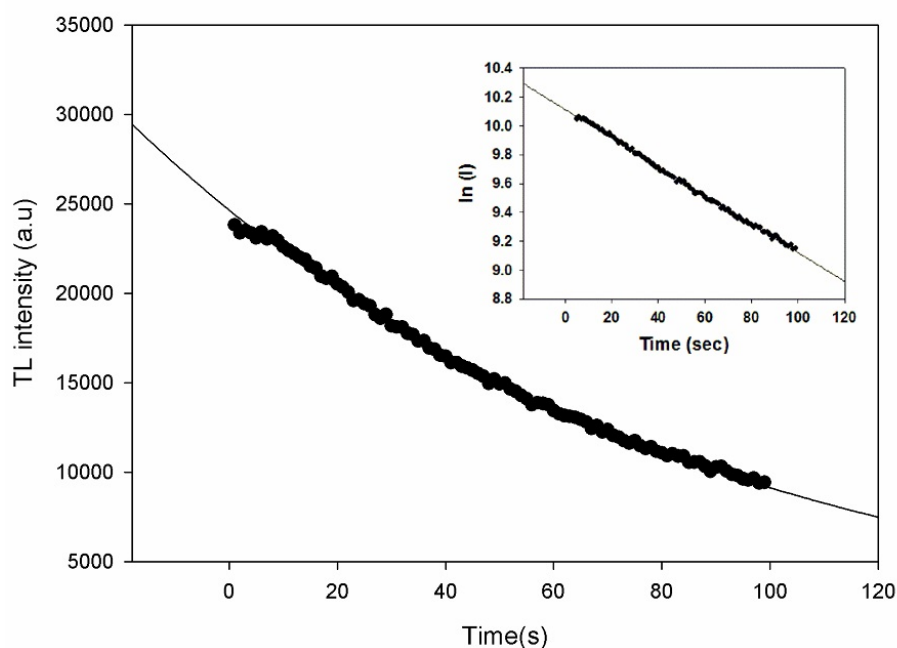


Figure 6.41: An isothermal decay curve measured at 55°C fitted with a simple exponential function. The inset is a graph of $\ln(I)$ versus time fitted with a straight line equation ($y = 0.01x - 10$).

case. Isothermal decay curve were measured at heating rate of 5°s^{-1} . Figure 6.41 is an example of an isothermal decay curve measured at 60°C for 100 seconds .

6.3.10.2 Analysis by first order kinetics

The isothermal decay curves were also used in the investigation of the order of kinetics of the main TL peak of unannealed synthetic quartz. This was done by fitting the isothermal decay curves with a simple exponential decay equation. Figure 6.41 represents an isothermal decay curve fitted with a simple exponential equation. From the fit we conclude that the main TL peak of the unannealed synthetic quartz follows first order kinetics since no additional parameters beyond the simple exponential equation were required to fit the decay adequately. This is confirmed by the inset of figure 6.41 where a straight line equation gave the best fit in a graph of $\ln(I)$ against time.

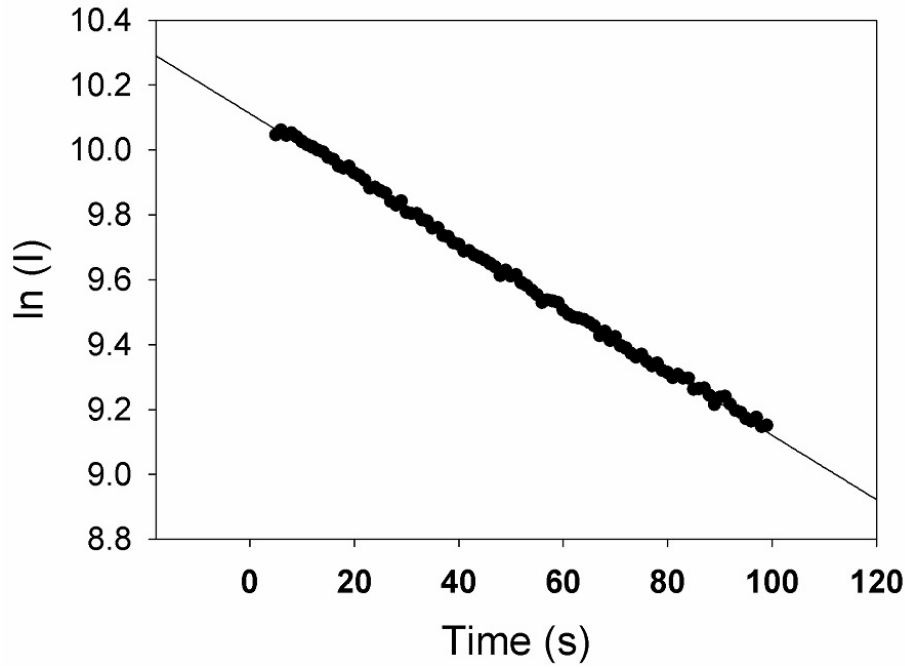


Figure 6.42: Example of the fit used in the determination of the decay constant p by fitting the transformed curve with a linear equation. The decay curve was measured at 55°C .

6.3.10.3 Calculation of trapping parameters

Isothermal decay curves measured at different temperatures were used to calculate the activation energy of the main peak. This was done by plotting the natural logarithm of TL intensity against time t . The graphs were then fitted with a linear equation and the decay constants p from each fit were found. Figure 6.42 is an example of a graph used in the determination of the decay constant p . Five measurements made at 50, 55, 60, 65 and 70°C were used in this method.

The activation energy E was determined by plotting the natural logarithm of the decay constants p versus $1/kT$ where T is the isothermal temperature and k is Boltzmann's constant. The resultant graph was fitted by a linear equation and the fit is given in figure 6.43. The slope of the fit gave the value of activation energy $E = 0.83 \pm 0.02 \text{ eV}$. The value of frequency factor s from the intercept equals $6.4 \times 10^{10} \text{ s}^{-1}$. These values are in good agreement with the values found using methods of kinetic

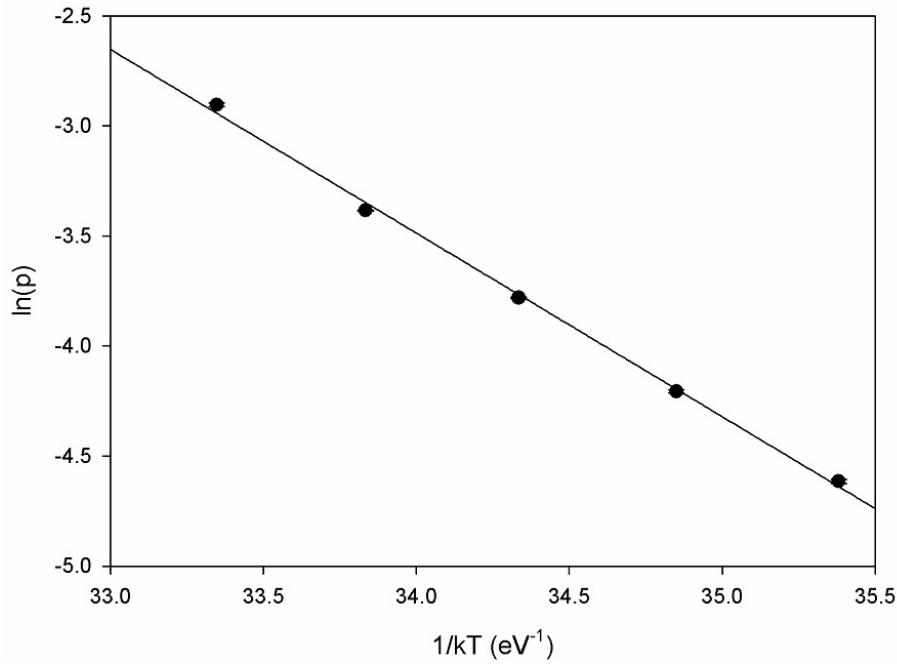


Figure 6.43: The graph of $\ln(p)$ versus $1/kT$ fitted by a linear equation. The solid line through the data points is the best fit of a straight line equation.

analysis used in this work i.e, initial rise method (0.90 eV) and various heating rate method (0.85 eV).

6.3.10.4 Analysis by general order kinetics

For a value of b which corresponds to the order of kinetics of the peak under study, we expect a straight line when we plot $[I(t)/I_0]^{\frac{1-b}{b}}$ against time t (section 2.5.2) [7]. In this work, several values of order of kinetics b were tried to find one which gave a straight line. The best straight line was found for $b = 1.2$ as indicated in figure 6.44. This value is close to 1 and confirms our other results that the main peak indeed follows the first order kinetics.

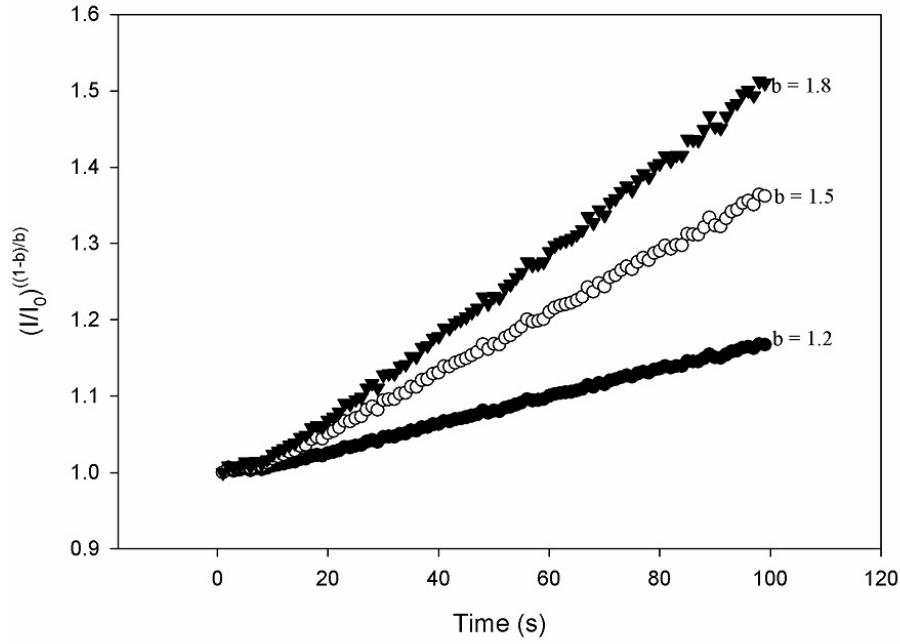


Figure 6.44: Determination of the order of kinetics using general order isothermal analysis. The original decay curve was measured at 55°C.

6.3.10.5 Analysis of isothermal decay curves using monotonic curve to glow curve transformation method

As discussed in section 2.5.3, isothermal luminescence decay curves can be transformed into the form of glow peaks. Figure 6.45 shows the results of transformation of decay curves measured at 65 and 70°C. Equation 2.18 was used to calculate the activation energy by combining two temperatures and the corresponding values of $\ln t$. Four combinations were made and the resultant values of activation energy E are presented in table 6.3. This method gave results which are in good agreement with the others found using other methods for example 0.89 eV from peak shape methods.

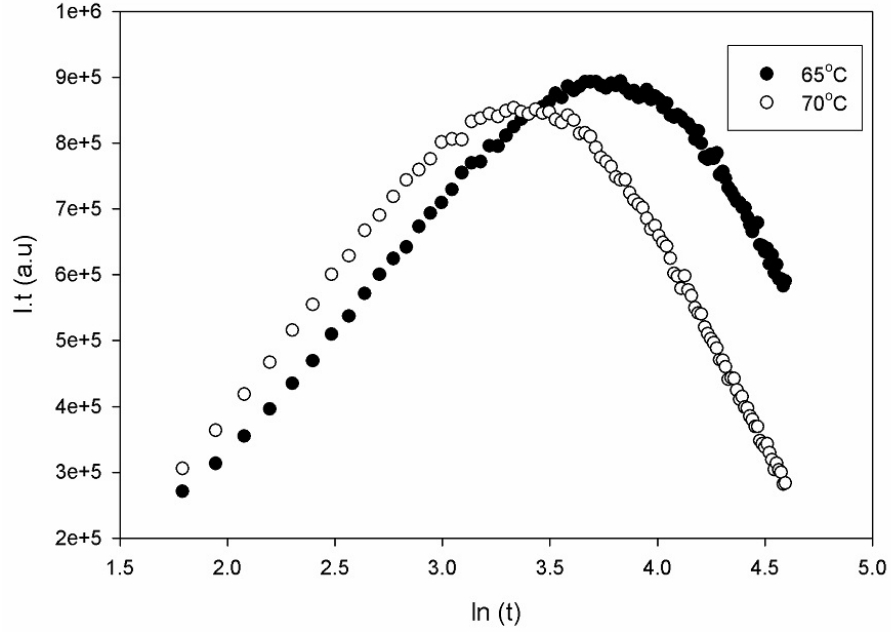


Figure 6.45: Schematic representation of the transformed isothermal decay curve into a peak-like form. The original decay curves were measured at 65°C and 70°C respectively.

Table 6.3: Values of activation energy found using the TL-like transformation method.

Temperature combinations ($^\circ\text{C}$)	Activation energy (eV)
65 and 70	0.79
70 and 75	0.95
60 and 70	0.98
65 and 75	0.87

6.3.11 Study of the isothermally cleaned peak using isothermal analysis

The isothermal method of analysis was applied to the peak cleaned using the isothermal technique. In our experiment, the same sample of powdered unannealed synthetic quartz was used. In this study, the isothermal cleaning was done at 40°C for 100 s as was chosen in the process described in section 6.3.3.2. After cleaning, the isothermal decay curves were then measured. The isothermal decay curves were recorded at different temperatures from 50-70°C in steps of 5°C for 100 seconds.

6.3.11.1 Analysis by first order of kinetics

Isothermal decay curves measured after isothermal cleaning were used in the determination of order of kinetics. The curves were fitted by a simple exponential equation. Figure 6.46 is the decay curve measured at 50°C fitted with a simple exponential equation. The equation gave a good fit to the curve. This implies that the peak under study follows the first order kinetics. A graph of $\ln(I)$ versus time confirms the results as it is fitted well by a straight line equation as shown by the inset of figure 6.46.

6.3.11.2 Analysis of order of kinetics using the general order method

The order of kinetics was also determined using the general order kinetics method. This was done by plotting $(I/I_0)^{(1-b)/b}$ versus time t , where b is the order of kinetics. To try to find a straight line, the value of b was varied. Here the value of b which gives the best fit i.e. for which R-squared is close to 1 is the order of kinetics of the glow peak. Figure 6.47 shows the graph of the transformed decay curve measured at 55°C for 100 seconds. The graph with $b = 1.1$ gave the best straight line. This confirms the results found from first order analysis that the main peak follows the first order kinetics.

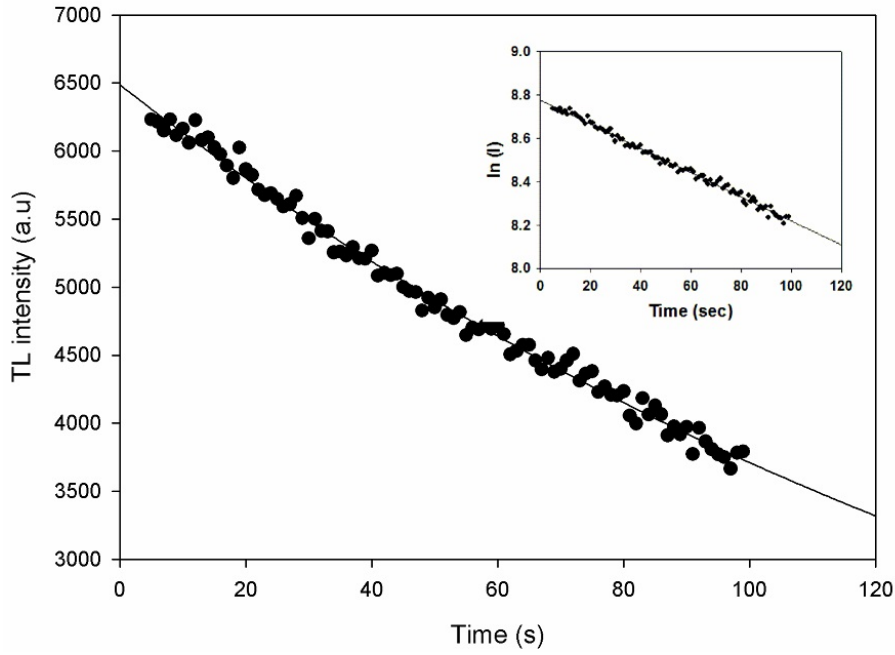


Figure 6.46: Graphs of isothermal decay data fitted with simple exponential equation. Graph was taken at 50 °C for 100 s. The decay curves were measured after isothermal cleaning. The inset is the plot of $\ln(I)$ versus time.

6.3.11.3 Determination of the activation energy

The decay curves measured after isothermal cleaning were used in the determination of the activation energy. We determined the decay constant p from graphs measured at different temperatures. Figure 6.48 is an example of a graph used to find the value of p by plotting $\ln(I)$ against time. The values of p were plotted as $\ln(p)$ versus $1/kT$ in order to find trapping parameters. Figure 6.49 is the graph of $\ln(p)$ versus $1/kT$ fitted with a straight line equation. The slope of the fit gave the value of the activation energy and the intercept gave the frequency factor. The activation energy was found to be $E = 0.99 \pm 0.02$ eV and frequency factor as $s = 2.9 \times 10^{13} \text{ s}^{-1}$. These values are comparable with other values from other methods we used in this work.

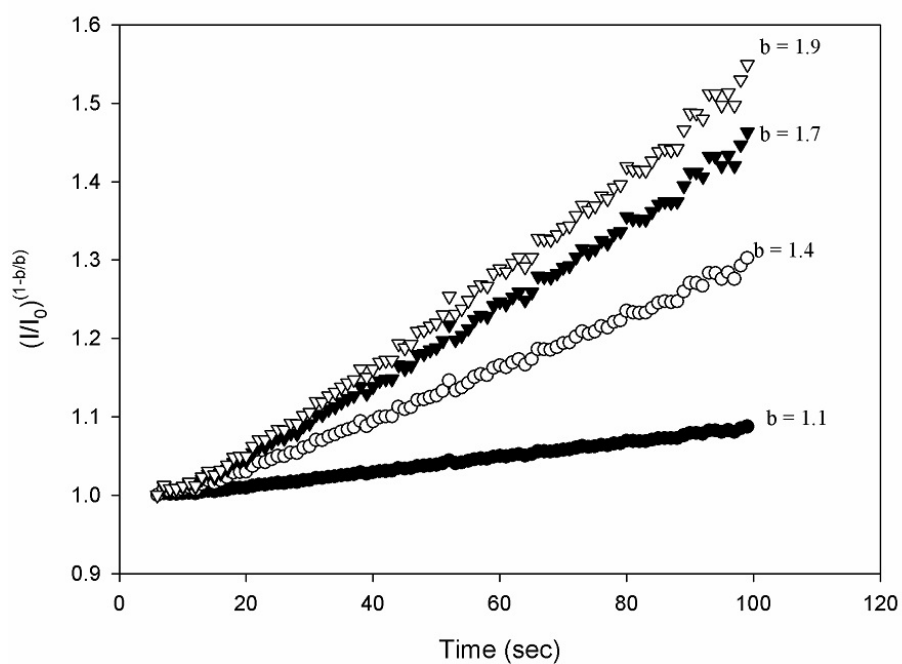


Figure 6.47: A graph of $(I/I_0)^{(1-b)/b}$ against t used to determine the order of kinetics. The value of $b = 1.1$ (solid circle) shows the best straight line. The decay curves were measured after isothermal cleaning of the satellite peak.

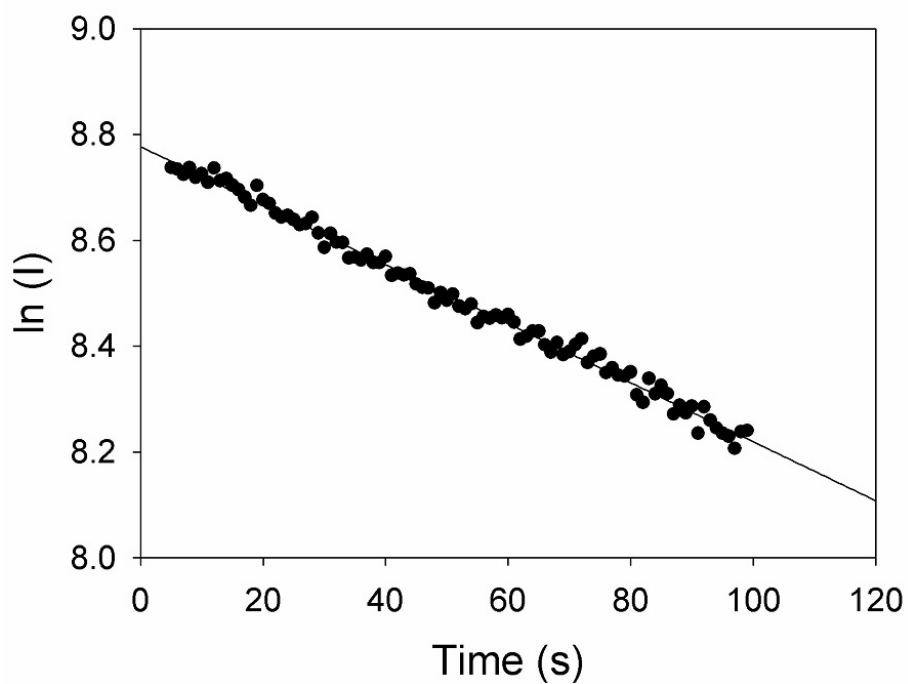


Figure 6.48: Graph of $\ln(I)$ versus time fitted with a linear equation in order to find p , the slope. Data were taken at 50°C for 100 seconds.

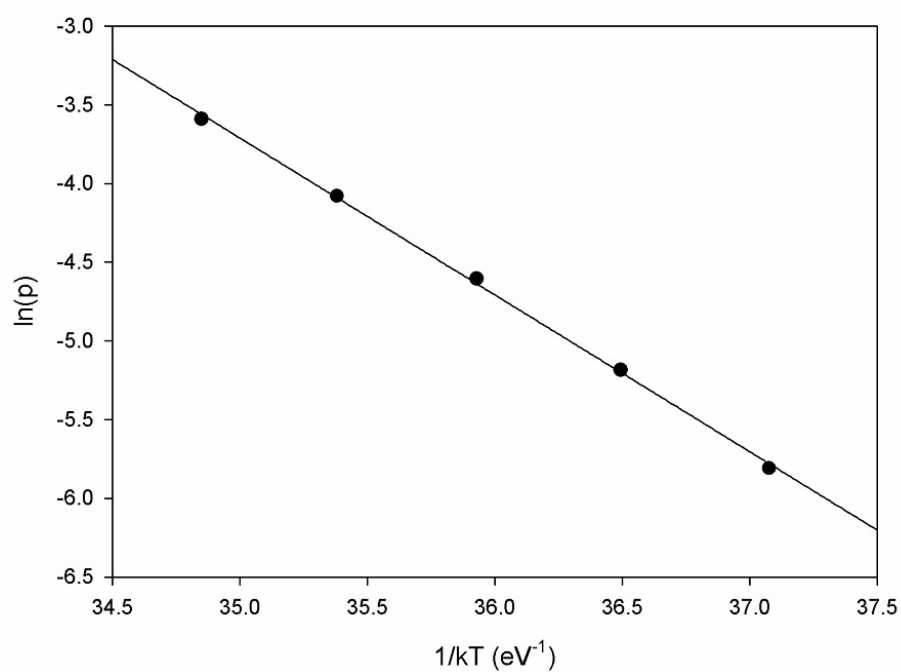


Figure 6.49: Graph of $\ln(p)$ against $1/kT$ fitted with a linear equation to find the activation energy of peak I after using isothermal analysis.

6.4 Kinetic analysis of the main TL peak of annealed synthetic quartz

This section presents experimental results related to evaluation of the trapping parameters of the main peak of the TL glow curve of synthetic quartz annealed at 500°C for 10 minutes. The objective of this analysis is to compare the kinetic parameters of the unannealed and annealed synthetic quartz in order to investigate the effect of annealing on the trapping parameters of the material.

The main peak in both unannealed and annealed synthetic quartz has a satellite peak in the rising edge as shown in figures 6.2 and 6.4 respectively. We applied the methods of kinetic analysis on both thermally and isothermally cleaned peaks of the annealed sample. Thermal cleaning and isothermal cleaning methods were described in sections 6.3.3.1 and 6.3.3.2 respectively.

6.4.1 Analysis of the thermally cleaned peak using the initial rise method

The use of the initial rise method in the analysis of peak I for an unannealed sample after thermal cleaning gave values of activation energy which are in good agreement with the reported values as was shown in section 6.3.4. With the aim of investigating the effect of annealing temperature on the activation energy of peak I, we applied this method on thermally cleaned peak I of a sample annealed at 500°C for 10 minutes. In this case, we applied the initial rise method on peaks measured at various heating rates i.e., 0.5, 1, 2, 3, 4 and 5°Cs⁻¹. Figure 6.50 is the plot of $\ln(I)$ versus $1/kT$ from a glow curve measured at 3°Cs⁻¹. The value of the activation energy given by the slope of the graph is $E = 0.79 \pm 0.03$ eV. Values of activation energy plotted as function of heating rate are presented in the figure 6.51. The results indicate that the activation energy does not change with heating rate.

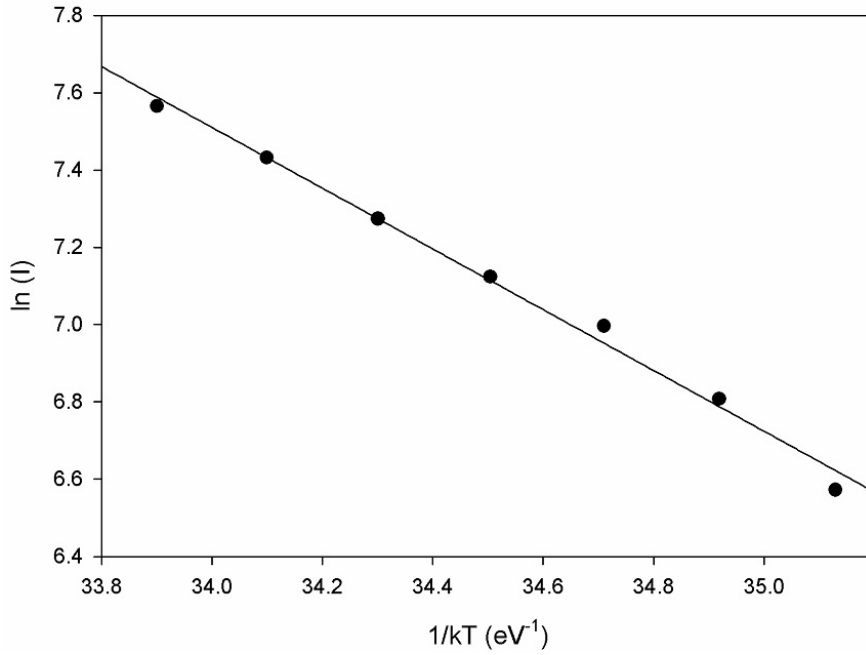


Figure 6.50: The graph of $\ln(I)$ versus $1/kT$ of the main peak for annealed synthetic quartz. The peak was measured after thermal cleaning.

The results in figure 6.51 from an annealed sample are comparable to the results in section 6.3.4 from an unannealed sample, and to the range reported in the literature, which indicates the activation energy E from the initial rise method analysis of thermally cleaned peak was not affected by annealing.

6.4.2 Analysis of the isothermally cleaned peak using the initial rise method

Application of the initial rise method on the isothermally cleaned peak of unannealed sample gave a value of E which is comparable with the value from the thermally cleaned peak as presented in section 6.3.4 and 6.3.5. This section aimed to investigate if the isothermal cleaning temperature and time as were chosen in section 6.3.3.2 will also clean the satellite peak and give the consistent results with those from thermally cleaned peak I for an annealed sample. In this analysis, peaks measured at various heating rates after isothermal cleaning were used. Figure 6.52 is one plot of $\ln(I)$

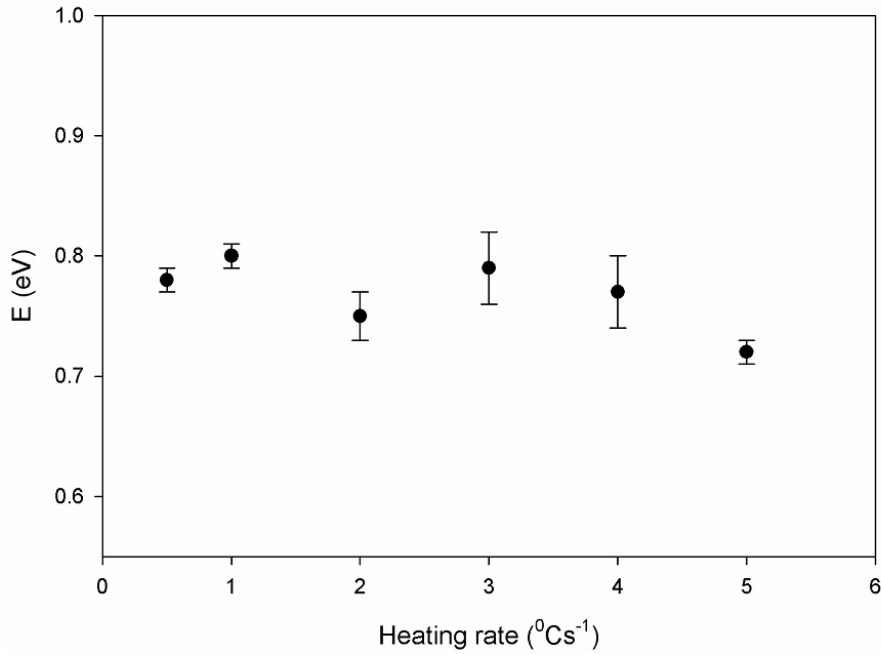


Figure 6.51: The activation energy of the main peak against the heating rate for the annealed synthetic quartz.

versus $1/kT$ used to determine E from the peak measured at 3°Cs^{-1} after isothermal cleaning. The graph gave the value of activation energy as $E = 0.86 \pm 0.03$ eV. Values of E corresponding to each heating rate are presented in table 6.4. Values of E in figure 6.51 and table 6.4 from thermally and isothermally cleaned peaks of annealed sample respectively are consistent.

The comparison of values of E from the thermally cleaned peak of an unannealed sample, section 6.3.4 and from the thermally cleaned peak of an annealed sample, section 6.4.1, shows that annealing did not affect the values of E calculated using the initial rise method. The same lack of effect was found in the isothermally cleaned peaks as presented in sections 6.3.5 and 6.4.2.

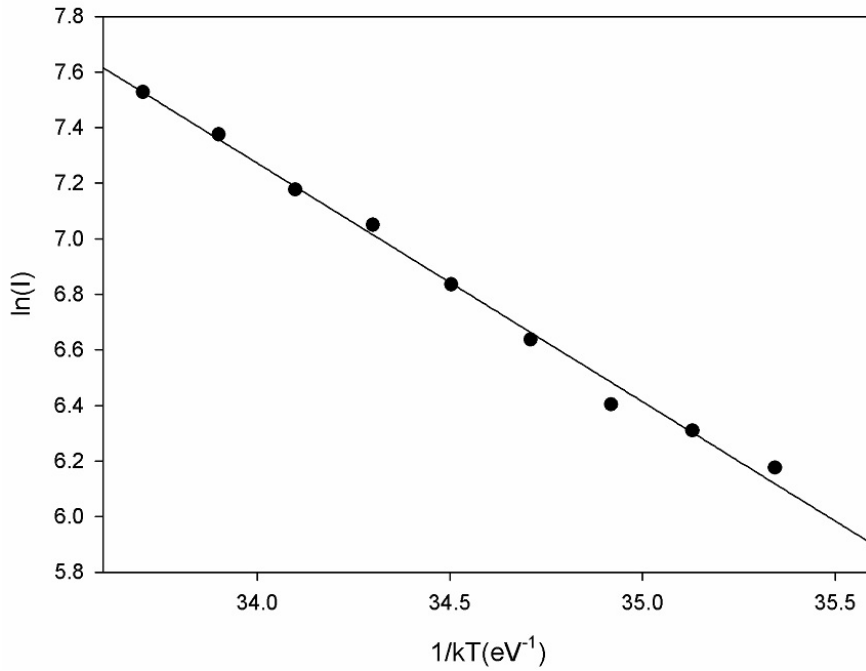


Figure 6.52: The graph of $\ln(I)$ versus $1/kT$ used in the analysis of the main peak for annealed synthetic quartz after isothermal cleaning.

Table 6.4: Values of the activation energy E calculated from isothermally cleaned glow peak measured at various heating rate using the initial rise method. The glow curves were measured from a sample of synthetic quartz annealed at 500°C for 10 minutes.

Heating rates ($^\circ\text{C/s}$)	Activation energy $E(\text{eV})$
0.5	0.87 ± 0.01
1	0.89 ± 0.02
2	0.90 ± 0.01
3	0.86 ± 0.03
4	0.83 ± 0.02
5	0.86 ± 0.02

6.4.3 Analysis of the thermally cleaned peak using the various heating rate method

The aim of this section is to investigate the effect of annealing temperature on determining trapping parameters of the trap responsible for the main peak using the shift of the peak position. As in the case of the unannealed sample in section 6.3.6, the various heating rate method was used to determine trapping parameters of an

annealed sample.

The position T_m of peaks measured at different heating rates after being thermally cleaned were noted. The measurements were repeated four times in order to find the average value of T_m which was used in the analysis. Figure 6.53 shows the graph used to determine the activation energy and the frequency factor for the main peak of the annealed sample. The value of activation energy E obtained from the slope is equal to 0.52 ± 0.02 eV. The frequency factor deduced from the intercept of the graph gave the value of the frequency factor as $1.3 \times 10^6 \text{ s}^{-1}$. The parameters found in this section are lower compared to values from various heating rate analysis of thermally cleaned peaks of unannealed sample, section 6.3.6 (0.85 ± 0.02 eV and $2.1 \times 10^{11} \text{ s}^{-1}$).

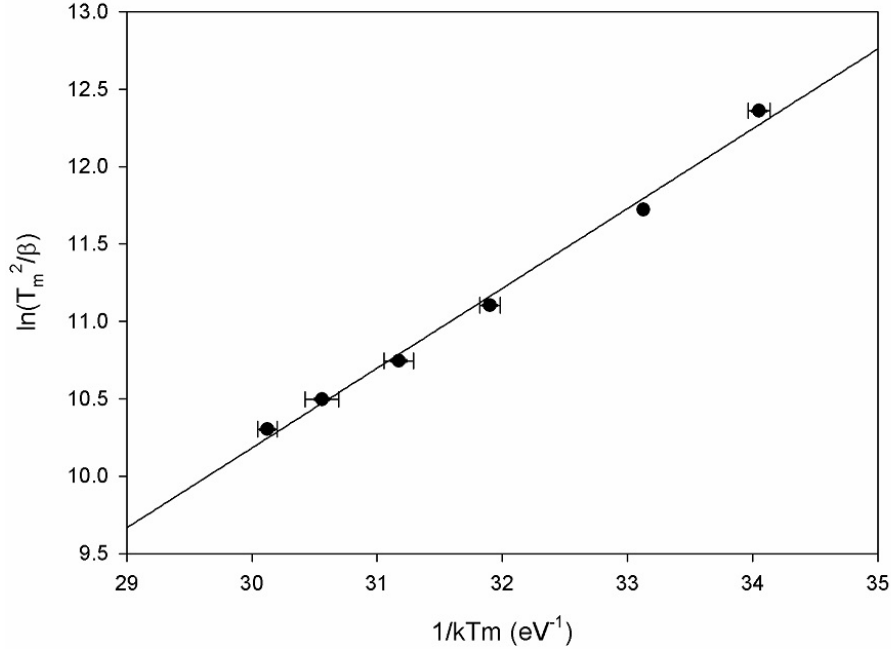


Figure 6.53: The plot of $\ln(T_m^2/\beta)$ versus $1/kT_m$ used in the determination of the trapping parameters of the main peak of an annealed sample after thermal cleaning.

The error bars in figure 6.53, are due to uncertainties in the maximum temperature.

The error bars in the y -axis, $\Delta \ln(T_m^2/\beta)$, is given as

$$\frac{d}{dT_m}(\ln(T_m^2/\beta)) = 2\Delta T_m/T_m, \quad (6.4)$$

where ΔT_m is the standard deviation of the four T_m values. The error bars on x -axis, $\Delta(1/kT_m)$, is given as

$$\frac{d}{dT_m}(1/kT_m) = (1/k) \times (\Delta T_m/T_m^2). \quad (6.5)$$

6.4.4 Analysis of the isothermally cleaned peak using the various heating rate method

The effect of annealing on the trapping parameters using the various heating rate method was further investigated using the isothermally cleaned peaks. The same procedure used on the isothermally cleaned peaks of an unannealed sample in section 6.3.7 was applied to the isothermally cleaned peaks of an annealed sample. Figure 6.54 is the graph of $\ln(T_m^2/\beta)$ versus $1/kT_m$ for the an annealed sample after isothermal cleaning. The value of the activation energy E was found from the slope of figure 6.54 to be equal to 0.56 ± 0.04 eV. From the intercept we found the value of frequency factor s to be $5.6 \times 10^6 \text{ s}^{-1}$. Here the various heating rate method gave lower values of trapping parameters for the annealed sample, (section 6.4.3 and 6.4.4) compared to values from the unannealed sample (section 6.3.6 and 6.3.7).

Underestimation of trapping parameters by the various heating rate method was explained by Pagonis et al [39] using a semi-localized transition model. In this model, stimulation of electrons to the conduction band takes place via intermediate localized excited state. In this case, the activation energy to stimulate the electrons to the conduction band is the sum of energies to stimulate the electrons from the ground to an excited state of the trap and the energy to stimulate the electrons from the excited state to the conduction band. The semi-localized transition model considers

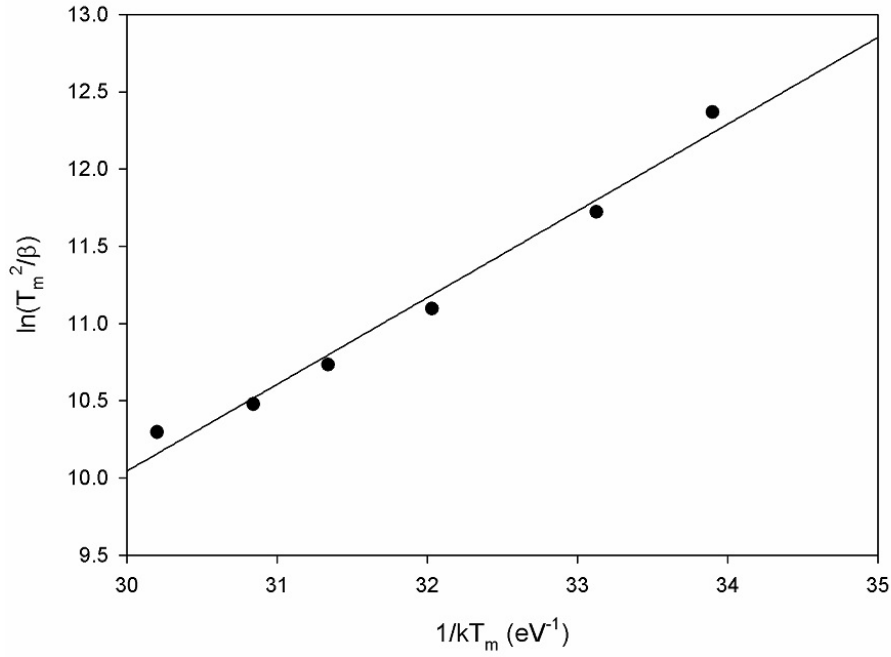


Figure 6.54: The heating rate method of analysis applied on the main peak for an annealed synthetic quartz. Glow curves were measured after isothermal cleaning.

two types of recombinations; a non radiative pathway directly from excited state of the trap to the recombination centre and conduction band pathway.

The various heating method gives accurate values of trapping parameters when the non-radiative recombination probability is small. In this case, these parameters are the sum of parameters for the first and second stage of thermal stimulation. The underestimation of trapping parameters is caused by high probability of non-radiative compared to radiative recombination probability. For the high non-radiative probability, kinetic parameters tends to the value of parameters from the stimulation of electrons from ground to excited states of the trap.

6.4.5 Analysis of the thermally cleaned peak using the peak shape methods

Analysis of the thermally cleaned peak I of the unannealed sample using peak shape methods in section 6.3.8.1 showed that the peak follows first order kinetics. The

values of activation energy were in good agreement with values from other methods. In this section, peak shape methods were applied on peaks measured from an annealed sample in order to study the influence of annealing on the shape parameters of the peak.

Table 6.5 shows values of the parameters calculated from peaks of annealed sample measured at different heating rates after thermal cleaning. The geometric factors μ calculated from these glow peaks indicate that the peak follows the first order kinetics since its value is close 0.42. The value of the activation energy was determined by substituting the value of coefficients C_γ and b_γ appearing in equation 2.11 for first order kinetics. The resultant values of E_ω , E_τ and E_δ are also presented in table 6.5. For the annealed sample, peak shape methods gave values of trapping parameters of peak I after thermal cleaning which are consistent with ones from the unannealed sample as shown in section 6.3.8.1 and table 6.5 respectively.

Table 6.5: The values of geometric factor μ calculated from thermally cleaned glow peak measured at various heating rate and the activation energies E_ω , E_τ and E_δ calculated from each peak. The glow curves were measured from the sample of synthetic quartz annealed at 500°C for 10 minutes.

Heating rates ($^{\circ}\text{C/s}$)	μ	E_ω (eV)	E_τ (eV)	E_δ
0.5	0.46 ± 0.05	0.91 ± 0.04	0.99 ± 0.08	0.81 ± 0.07
1	0.43 ± 0.05	0.89 ± 0.04	0.89 ± 0.06	0.86 ± 0.08
2	0.40 ± 0.04	0.90 ± 0.03	0.86 ± 0.05	0.93 ± 0.08
3	0.46 ± 0.04	0.93 ± 0.04	1.07 ± 0.07	0.83 ± 0.06
4	0.44 ± 0.04	0.90 ± 0.03	0.94 ± 0.06	0.86 ± 0.07
5	0.44 ± 0.04	0.93 ± 0.03	0.96 ± 0.06	0.89 ± 0.07
Average	0.44 ± 0.04	0.91 ± 0.04	0.95 ± 0.06	0.86 ± 0.07

6.4.6 Analysis of isothermally cleaned peaks using peak shape methods

The aim of this section is to study whether the agreement of trapping parameters found using peak shape methods between thermally cleaned peaks of unannealed and annealed samples also applies for the isothermally cleaned peaks.

Using procedures as presented in section 6.3.8.2 for the unannealed sample, values of the geometrical factor and activation energy from the isothermally peaks of annealed sample measured at various heating rates are presented in the table 6.6. The value of μ is close to 0.42 which indicates that first order kinetics for the main peak applies. The values of the activation energy from each method are consistent with each other and with the values from other methods. The values of activation energy

Table 6.6: The values of geometric factor μ , E_ω , E_τ and E_δ calculated from glow peak measured at various heating rates. The glow curves were measured from the sample of synthetic quartz annealed at 500°C for 10 minutes.

Heating rates ($^{\circ}\text{C/s}$)	μ	E_ω (eV)	E_τ (eV)	E_δ
0.5	0.43 ± 0.05	0.85 ± 0.04	0.86 ± 0.06	0.82 ± 0.07
1	0.46 ± 0.05	0.83 ± 0.04	0.91 ± 0.06	0.74 ± 0.08
2	0.43 ± 0.05	0.96 ± 0.04	0.97 ± 0.07	0.92 ± 0.08
3	0.46 ± 0.04	0.93 ± 0.03	1.02 ± 0.07	0.83 ± 0.06
4	0.44 ± 0.04	0.90 ± 0.03	0.93 ± 0.06	0.85 ± 0.07
5	0.41 ± 0.04	0.87 ± 0.03	0.91 ± 0.06	0.89 ± 0.07
Average	0.44 ± 0.05	0.89 ± 0.03	0.93 ± 0.06	0.84 ± 0.07

E_ω , E_τ and E_δ are in each others' margin of error as shown in tables 6.5 and 6.6 for peaks measured after thermal and isothermal cleaning respectively. Values of μ for thermally and isothermally cleaned peaks are also consistent and all indicate that the main peak follows first order kinetics. The error in the activation energy E and μ depends on the uncertainty in temperatures at half-maximum intensity used in the evaluation of geometrical shape quantities (ω , τ and δ).

A comparison of the results in section 6.3.8.1 and table 6.2 from thermally and isothermally peaks of unannealed sample with those in tables 6.5 and 6.6 from an annealed one shows that geometric shape parameters were not affected by annealing and the shape parameters are more consistent for annealed sample.

6.4.7 Study of the thermally cleaned peak using the whole glow curve method

The glow peaks of an annealed sample measured using different heating rates after thermal cleaning were transformed into a straight lines as was done for the unannealed sample in section 6.3.9. The main objective of this section was to investigate if the whole curve method analysis was affected by annealing.

6.4.7.1 First order kinetics

Figure 6.55 is an example of a graph used in the determination of the activation energy and the frequency factor using the whole curve method. The values of the

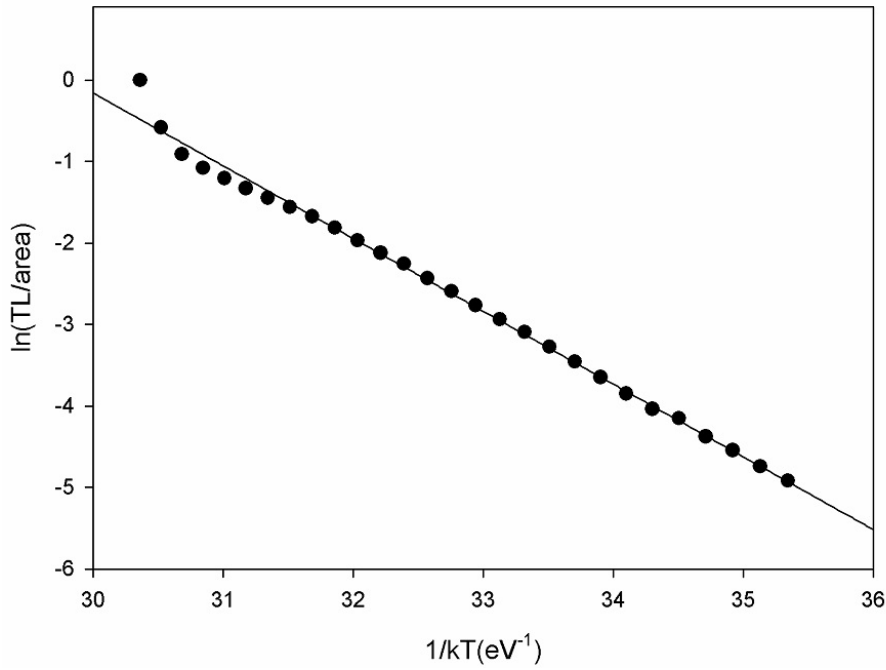


Figure 6.55: Graph of $\ln (TL/area)$ versus $1/kT$ fitted with straight line equation used in the determination of trapping parameters using the whole curve method. The original curve was measured at 2°Cs^{-1} after a dose of 31 Gy after thermal cleaning. The deviation from linearity at high temperature is probably due to the effect of an overlapping peak at high temperature side of the main peak.

activation energy and the frequency factor for each heating rate are presented in the

table 6.7. The analysis of peak I for the annealed sample using whole curve method gave the value of activation energy which is in good agreement with one of peak I for an unannealed sample shown in section 6.3.9.

Table 6.7: Values of the activation energy E and frequency factor s calculated from glow peaks measured at various heating rates. The glow curves were measured from a sample of synthetic quartz annealed at 500°C for 10 minutes.

Heating rates (°C/s)	activation energy E(eV)	Frequency factor (s ⁻¹)
0.5	0.84 ± 0.01	5.8 × 10 ¹⁰
1	0.87 ± 0.01	2.2 × 10 ¹¹
2	0.89 ± 0.01	7.3 × 10 ¹¹
3	0.91 ± 0.01	1.1 × 10 ¹²
4	0.82 ± 0.01	7.9 × 10 ¹⁰
5	0.78 ± 0.02	1.7 × 10 ¹⁰

6.4.7.2 Analysis of thermally cleaned peaks by general order kinetics

The general order method described in section 6.3.9.2 was applied on peak I of TL from an annealed synthetic quartz. Figure 6.56 shows the plot of $\ln(TL/area^b)$ against $1/kT$. Values of b close to 1 (i.e 0.9 and 1.2) gave the best straight line which implies that peak I follows first order kinetics.

6.4.8 Study of the isothermally cleaned peak using the whole glow curve method

The whole curve method gave consistent values of trapping parameters for peak I in both unannealed and annealed samples after thermal cleaning, section 6.3.9 and 6.4.7. This section aims to study whether the agreement of values of trapping parameters of peak I applies as well for peak I measured after isothermal cleaning.

6.4.8.1 First order kinetics

In this study, peaks of annealed synthetic quartz measured after isothermal cleaning were analyzed as was done in section 6.4.8 for the unannealed sample. Figure 6.57 is

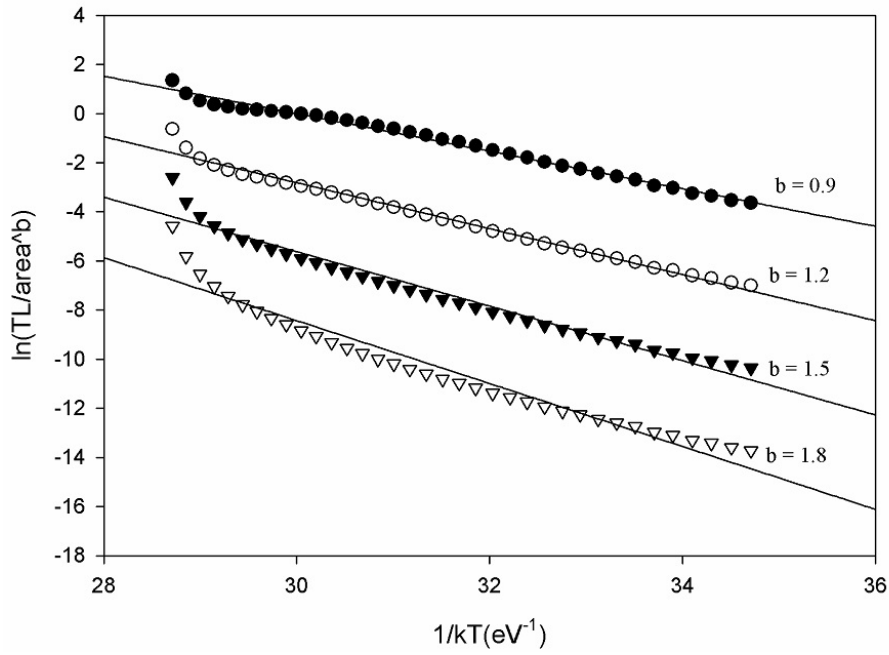


Figure 6.56: Graph of $\ln(TL/area^b)$ versus $1/kT$ used in the investigation of the order of kinetics. The original glow curve was measured at a heating rate of 4°Cs^{-1} after a dose of 31 Gy.

a graph of $\ln(TL/area)$ versus $1/kT$ of the main peak after isothermal cleaning. The analysis was done on glow curves measured at different heating rates and the values of kinetic parameters found are shown in table 6.8. Figure 6.55 and 6.57 show the deviation from linearity at high temperature. This deviation is probably due to the influence of the overlapping peak in the high temperature part of peak I.

Table 6.8: The values of activation energies E and frequency factor s calculated from glow peak measured at various heating rate after being isothermally cleaned. The glow curves were measured from the sample of synthetic quartz annealed at 500°C for 10 minutes.

Heating rates ($^\circ\text{C/s}$)	activation energy $E(\text{eV})$	Frequency factor (s^{-1})
0.5	0.86 ± 0.01	9.3×10^{10}
1	0.87 ± 0.01	2.1×10^{11}
2	0.86 ± 0.01	2.8×10^{11}
3	0.89 ± 0.01	7.0×10^{11}
4	0.92 ± 0.01	2.2×10^{12}
5	0.89 ± 0.01	8.8×10^{11}

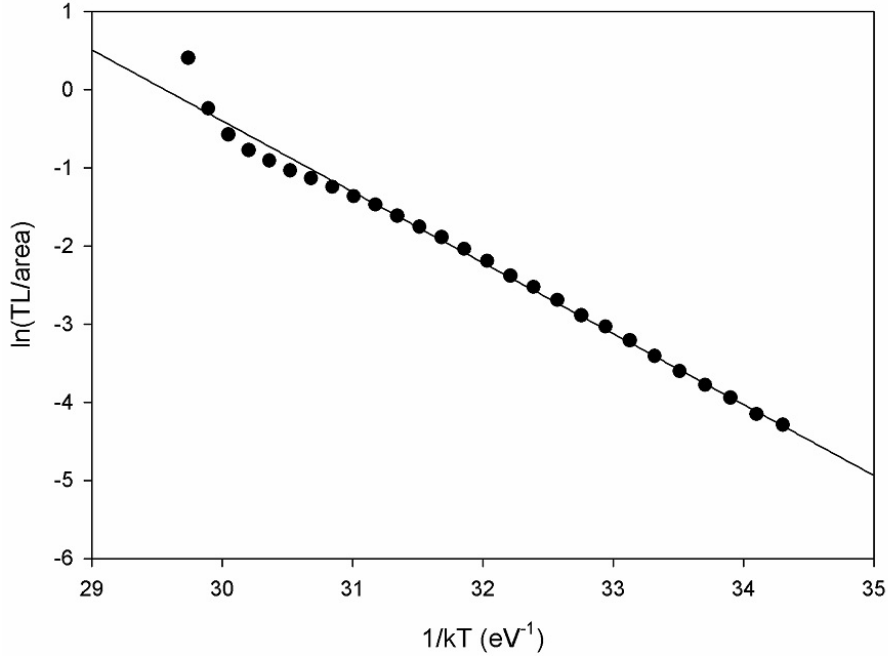


Figure 6.57: Graph of $\ln(\text{TL}/\text{area})$ versus $1/kT$ for the main peak after isothermal cleaning. The original glow curve was measured at heating rate of 4°Cs^{-1} after a dose of 30 Gy.

6.4.8.2 Investigation of the order of kinetics by general order method

The general order method of analysis was used to estimate the order of kinetics of the main peak of the annealed synthetic quartz after isothermal cleaning as was done for the unannealed sample in section 6.3.11.2. Figure 6.58 shows the graph of $\ln(\text{TL}/\text{area}^b)$ versus $1/kT$ for the main peak after isothermal cleaning. From the graph we concluded that peak I follows first order kinetics since values of b close to 1 i.e., 0.9 and 1.2 gave the best straight line. Whole curve analysis for the unannealed sample in section 6.3.9.2 and for an annealed sample in section 6.4.7.2 and 6.4.8.2 shows that peak I in both cases follows first order kinetics.

For the annealed sample, a comparison of the values of kinetic parameters in table 6.7 and table 6.8 from the thermally and isothermally cleaned peaks respectively are consistent. Table 6.7 and 6.8 shows values of trapping parameters from the annealed sample which are also consistent with those in section 6.3.9 from an unannealed

sample. Results from whole curve method indicate that trapping parameters were not affected by annealing.

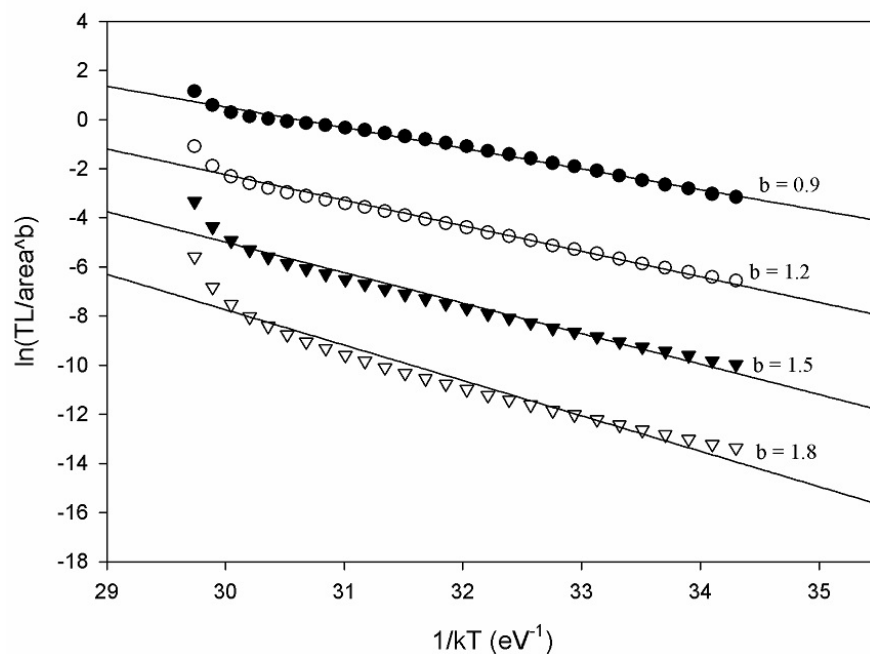


Figure 6.58: The plot of $\ln(TL/area^b)$ against $1/kT$ for the main peak after isothermal cleaning. The original glow curve was measured at $^{30}\text{Cs}^1$ after a dose of 31 Gy.

6.4.9 Analysis of peak I using isothermal analysis methods after thermal cleaning

The aim of this section was to investigate the effect of annealing temperature on trapping parameters using the isothermal analysis method. The kinetic parameters were determined using the procedures described in section 6.3.10.3. The main peak in an annealed synthetic quartz is at 115°C as shown in figure 6.5. Therefore at first the satellite peak in the initial rise part of the main peak was removed by heating to 75°C. After this thermal cleaning, isothermal decay curves were measured at different temperatures from 50 to 65°C for 100 seconds at each temperature.

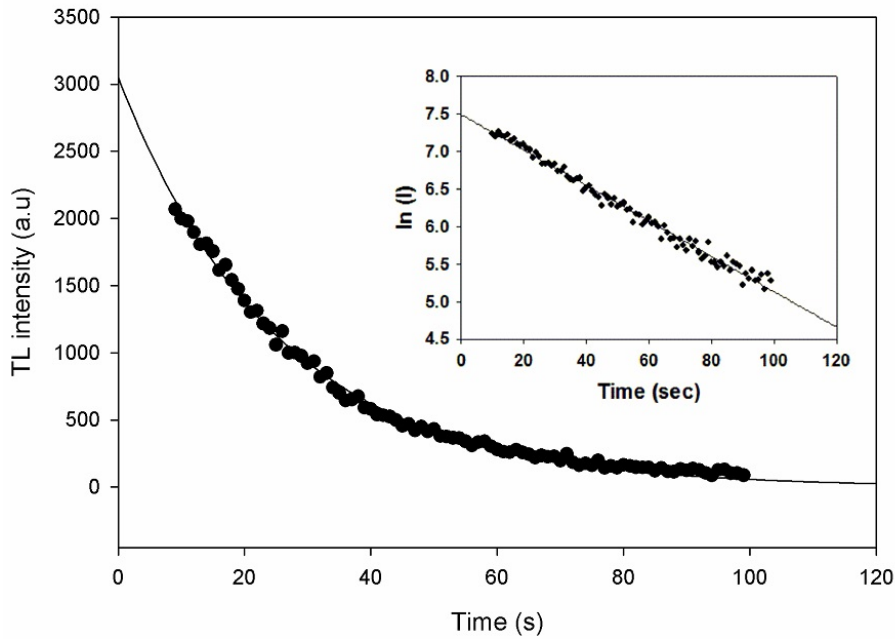


Figure 6.59: An isothermal decay curve measured at 65°C for 100 seconds after thermal cleaning. The curve is fitted with the simple exponential equation. The inset is a plot of $\ln(I)$ versus time.

6.4.9.1 Determination of order of kinetics using first order method

The order of kinetics was determined as was done for the unannealed sample in section 6.3.10.2. Figure 6.59 is the decay curve measured at 65°C after thermal

cleaning. In this investigation of the order of kinetics, the decay curve was fitted with a simple exponential equation. The isothermal decay curve was best fitted with a simple exponential equation which implies that the main peak follows first order kinetics, figure 6.59. These results were confirmed by plotting $\ln(I)$ versus time (inset, figure 6.59) and the resultant graph was again properly fitted by a straight line equation which implies that peak I indeed follows first order kinetics. First order isothermal analysis of the thermally cleaned peak of an annealed sample therefore gave results which is consistent with those from an unannealed sample described in section 6.3.10.2.

6.4.9.2 Determination of order of kinetics using the general order method

The fact that the main peak of an annealed synthetic quartz follows first order kinetics was investigated further using the general order kinetics. Figure 6.60 is the plot of $(I/I_0)^{(1-b)/b}$ versus time. The value of b was changed in order to get a best straight line. Figure 6.60 indicates that the peak follows first order kinetics since values of b close to 1 i.e., 1.2 gave a good straight line.

6.4.9.3 Determination of kinetic parameters

The processes applied on the thermally cleaned peak of an unannealed sample to determine its kinetic parameters using isothermal analysis method (section 6.3.10.3) were also applied on peak I from an annealed sample. In this analysis, the values of decay constant p were determined from decay curves by plotting $\ln(I)$ versus time. Figure 6.61 shows an example of the graph used in determination of p from the decay curve measured at 60°C. Values of p found from isothermal decay curves measured at different temperatures were used in the determination of trapping parameters. Figure 6.62 is the graph of $\ln(p)$ versus $1/kT$ used to determine trapping parameters of peak I from an annealed sample after thermal cleaning. The slope of the graph gave the value of $E = 0.91 \pm 0.03$ eV and the intercept gave the frequency factor s

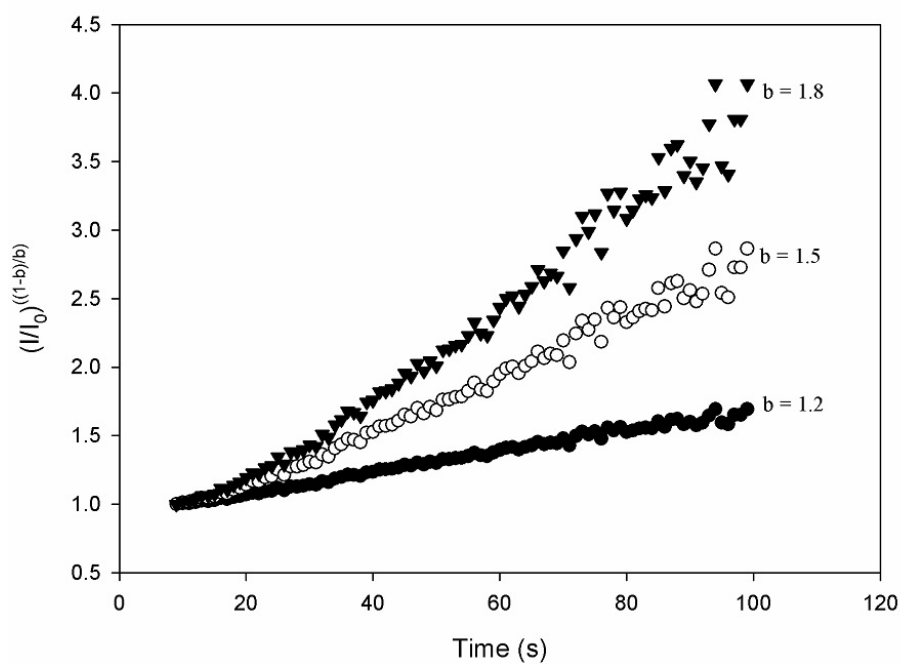


Figure 6.60: Graph used in the estimation of the order of kinetics of the main peak in an annealed synthetic quartz after thermal cleaning. The original glow curve was measured at 65°C for 100 seconds.

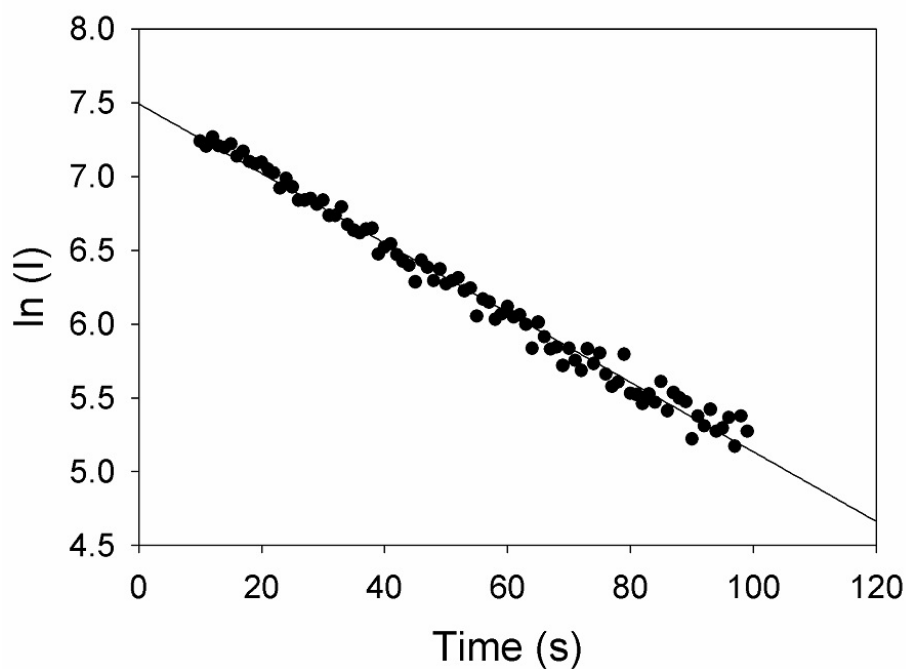


Figure 6.61: Graph used in the determination of the decay constant p for isothermal decay curves in the annealed sample measured after thermal cleaning. The original decay curve was measured at 60°C for 100 seconds.

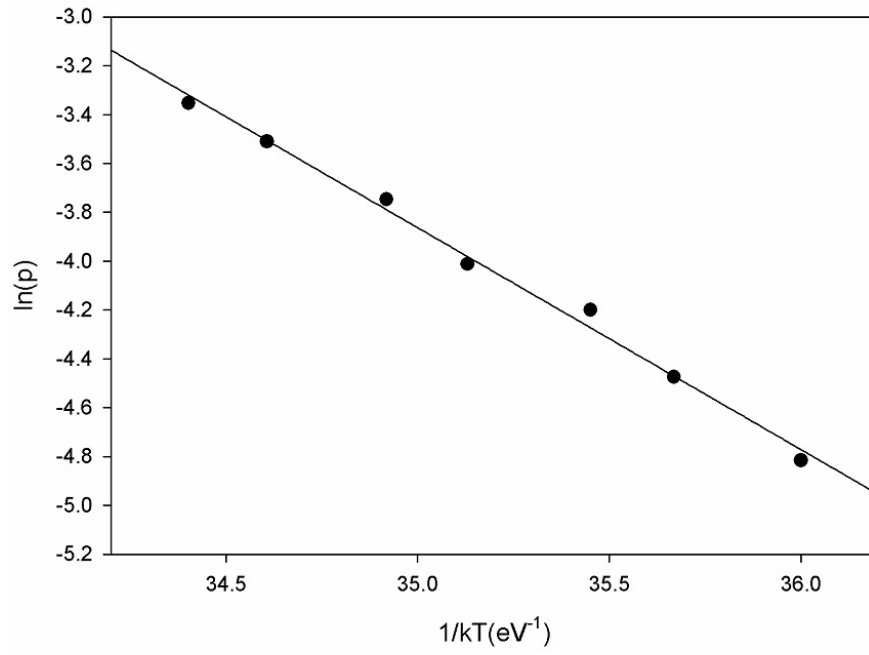


Figure 6.62: Graph used in the determination of the activation energy E of peak I for the annealed sample after thermal cleaning.

as $1.4 \times 10^{12} \text{ s}^{-1}$.

6.4.10 Analysis of peak I using isothermal analysis method after isothermal cleaning

The results in section 6.3.11.3 from the unannealed sample confirmed that isothermal luminescence can be used as a method of thermal cleaning. For the unannealed sample, holding the sample at 40°C for 100 seconds removed the satellite peak without affecting intensity of peak I as shown in section 6.3.3.2. Therefore the main objective of this section was to investigate whether the combination of isothermal cleaning temperature and time used on the unannealed sample would remove the satellite peak of peak I without affecting peak I itself in an annealed sample.

The overlapping peak in the initial rise part of the main peak was removed by heating at 40°C for 100 seconds as was done in section 6.3.11.3 for the unannealed sample. Isothermal decay curves were measured after isothermal cleaning at the same temperatures as in section 6.4.9. An example of an isothermal decay curve measured at 65°C for 100 seconds after isothermal cleaning is presented in figure 6.63.

6.4.10.1 Estimation of the order of kinetics of the main peak using first order method

As was done in section 6.3.11.1 for an unannealed sample, we used isothermal decay curves in the investigation of the order of kinetics of peak I from an annealed sample after isothermal cleaning. The order of kinetics of peak I was found to be first order since the simple exponential decay equation gave the best fit as shown in figure 6.63. The order of kinetics was further investigated by fitting a plot of $\ln(I)$ against time with a straight line equation. The straight line equation gave the best fit with the plot of $\ln(I)$ versus time as shown by the inset of figure 6.63. These results indicate that peak I of an annealed sample indeed follows first order kinetics.

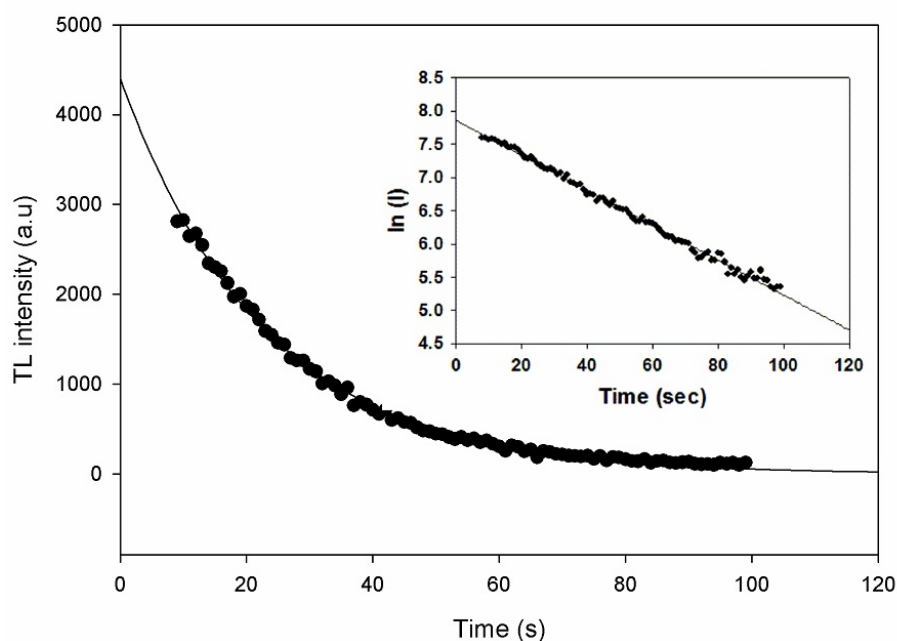


Figure 6.63: An isothermal decay curve measured at 65°C for 100 seconds after isothermal cleaning fitted with a simple exponential decay equation. The inset is the graph of $\ln(I)$ against time.

6.4.10.2 Determination of the order of kinetics of the main peak using the general order kinetics method

The order of kinetics was investigated further by using the general order kinetics methods. Figure 6.64 is the plot of $(I/I_0)^{(1-b)/b}$ against time used to estimate the order of kinetics of peak I after isothermal cleaning. The value of b was changed as was done in section 6.3.11.2 for the unannealed sample. The best straight line was given by $b = 1.2$ which implies that peak I follows first order kinetics. The results are consistent with those from an unannealed sample in section 6.3.11.2. The results also are in good agreement with results from other methods used in this study.

6.4.10.3 Determination of kinetic parameters

In this analysis, we followed the steps described in section 6.3.10.3 used in the analysis of the unannealed sample. Figure 6.66 is the graph used to determine trapping parameters of peak I of annealed sample measured after isothermal cleaning using

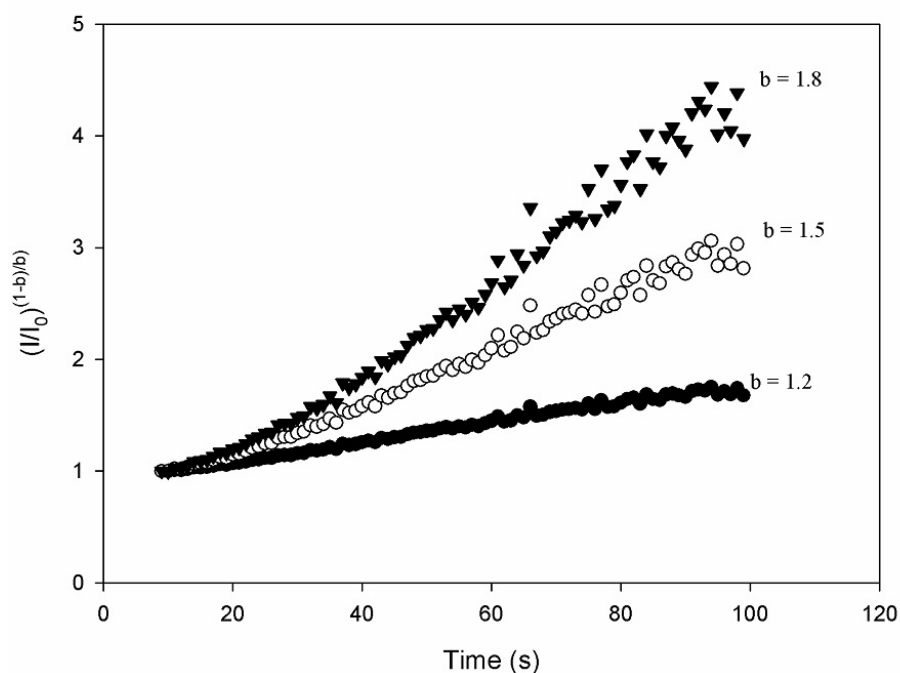


Figure 6.64: Graph of $(I/I_0)^{(1-b)/b}$ against time used in the estimation of the order of kinetics using general order isothermal analysis. The glow curve was measured at 65°C for 100 seconds.

isothermal analysis method. The slope of the linear fit of the resultant plot gave the value of $E = 0.97 \pm 0.03$ eV. The y -intercept gave the frequency factor $s = 1.6 \times 10^{13} \text{ s}^{-1}$. As for other methods of kinetic analysis, isothermal analysis gave values of trapping parameters for the unannealed sample (section 6.3.10.3 and 6.3.11.3) which are in good agreement with values from the annealed sample (section 6.4.9.3 and 6.4.10.3) for thermally and isothermally cleaned peaks respectively. This implies annealing had no effect on kinetic parameters.

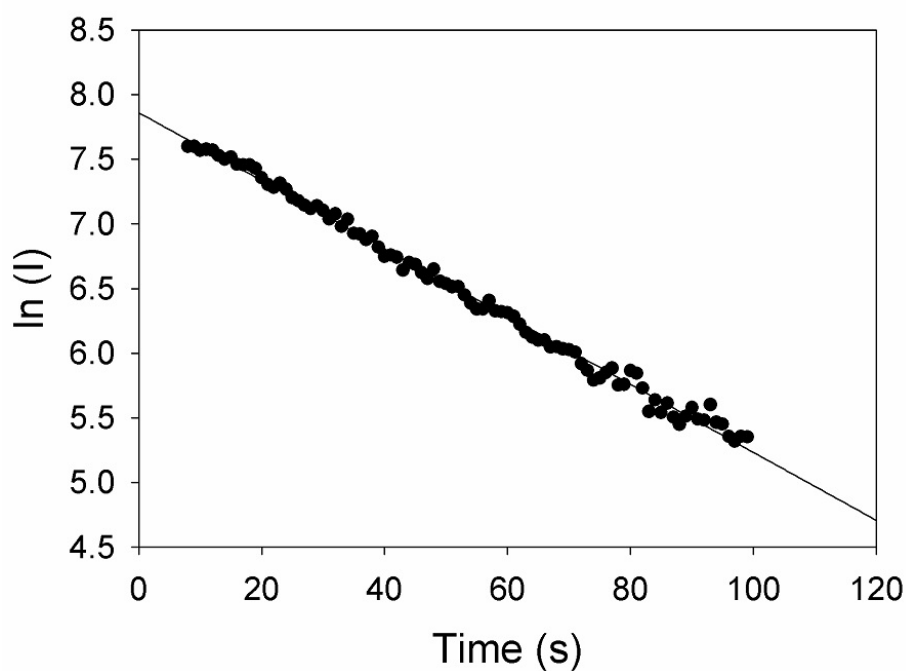


Figure 6.65: Graph used in the determination of the decay constants p for an isothermal decay curve measured after isothermal cleaning. The glow curve was measured at 60°C for 100 seconds.

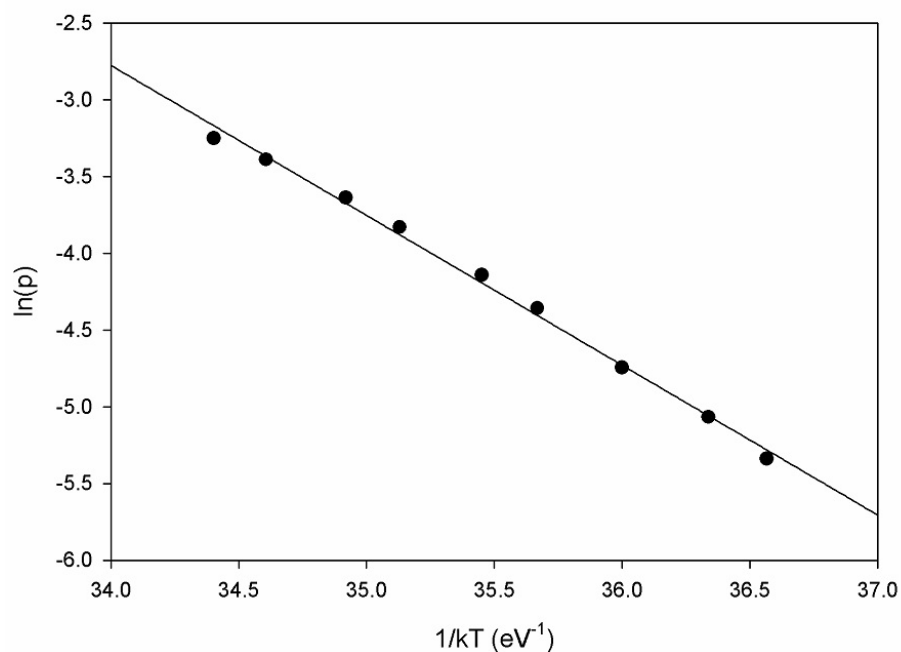


Figure 6.66: Plot of $\ln(p)$ versus $1/kT$ used in the determination of the activation energy E and frequency factor s . Isothermal decay curves were measured after isothermal cleaning.

6.4.11 Summary of the results from kinetic analysis

Table 6.9 summarizes results of trapping parameters i.e., activation energy E , frequency factor s and order of kinetics b from unannealed and synthetic quartz annealed at 500°C for 10 minutes. The analysis of TL for E , b and s was done using the initial rise (IR), various heating rate (VHR), peak shape (PS), whole curve (WCM) and isothermal analysis (ISL) methods.

For the unannealed sample, methods of kinetic analysis gave values of trapping parameters within each other's margin of error. Using the isothermal analysis, the unannealed sample gave values of kinetic parameters which are consistent with values from other methods of kinetic analysis. The various heating rate method used on the annealed sample underestimated the values of trapping parameters and explanations for this were given in section 6.4.3. Table 6.9 also shows good agreement between our results of the value of activation energy and values published in the literature.

Column 3 of table 6.9 shows the value of the geometric factor μ calculated using the peak shape method and the values are close to 0.42 i.e 0.44. These results indicate that peak I in both unannealed and annealed synthetic quartz follows first order kinetics. These results are confirmed with the values of b in column 4 found from whole curve and isothermal analysis methods where the values of b found are between 0.9 and 1.2 which also imply that for peak I first order kinetics applies. The analysis of peak I of synthetic quartz gave the value of frequency factor s , column 5 of table 6.9 which is in the order of the Debye vibration frequency which is expected by theory of solid state physics. Values of frequency factor are also consistent with published values.

Table 6.9 shows that values of the activation energy, order of kinetics and frequency factor for the unannealed and annealed synthetic quartz calculated using different methods of kinetic analysis are consistent. The results from various heating rate for annealed sample is lower compared to those for unannealed sample using the same

Table 6.9: Table of summary of the trapping parameters of peak I from both the unannealed and the annealed sample using different methods of kinetic analysis.

Method	E(eV)	μ	b	(s ⁻¹)	Reference
Unannealed					
IR	0.91 ± 0.01 ^a	0.44 ± 0.03	1	2.1× 10 ¹¹ ^a 1.8× 10 ¹⁰ ^b	Section 6.3.4
	0.85 ± 0.02 ^b				Section 6.3.5
VHR	0.85 ± 0.02 ^a				Section 6.3.6
	0.78 ± 0.02 ^b				Section 6.3.7
PS	0.85 ± 0.04 ^{a,x}				Section 6.3.8.1
	0.89 ± 0.05 ^{a,y}				
	0.79 ± 0.05 ^{a,z}				
	0.90 ± 0.04 ^{b,x}				Table 6.2
	0.94 ± 0.06 ^{b,y}				
	0.88 ± 0.08 ^{b,z}				
WCM	0.84 ± 0.01 ^a		1.1	1.7×10 ¹¹ ^a	Section 6.3.9
ISL	0.83 ± 0.02 ^a		1.2	6.4×10 ¹⁰ ^a	Section 6.3.10.3
	0.89 ^{a,Peak-like}				Table 6.3
	0.99 ± 0.02 ^b		1.2	2.9×10 ¹³ ^b	Section 6.3.11.3
Annealed					
IR	0.79 ± 0.03 ^a	0.44 ± 0.04	1	1.6× 10 ⁶ ^a 5.6× 10 ⁶ ^b	Section 6.4.1
	0.87 ± 0.02 ^b				Section 6.4.2
VHR	0.52 ± 0.02 ^a				Section 6.4.3
	0.56 ± 0.04 ^b				Section 6.4.4
PS	0.91 ± 0.04 ^{a,x}				Section 6.4.5
	0.95 ± 0.06 ^{a,y}				
	0.86 ± 0.07 ^{a,z}				
	0.89 ± 0.03 ^{b,x}				Section 6.4.6
	0.93 ± 0.06 ^{b,y}				
	0.84 ± 0.07 ^{b,z}				
WCM	0.85 ± 0.01 ^a		0.9	3.7×10 ¹¹ ^a	Section 6.4.7
	0.88 ± 0.01 ^b		0.9	7.3×10 ¹¹ ^b	Section 6.4.8
ISL	0.91 ± 0.03 ^a		1.2	1.4×10 ¹² ^a	Section 6.4.9.3
	0.97 ± 0.03 ^b		1.2	1.6×10 ¹³ ^b	Section 6.4.10.3
Published					
IR	0.90 ±0.01	0.46 ±0.01	1.32±0.09	1.9×10 ¹¹ 1.51×10 ¹¹	[41]
	0.79 ±0.11				[42]
	0.86 ±0.02				[40]
PS	1.02 ±0.03				[43]
VHR	0.94±0.10				[41]
	0.79±0.12				[42]
WCM	0.92± 0.09				[43]
ISL	0.82±0.04				[42]

^{a,b} : stand for values after thermal and isothermal cleaning respectively.

^{x,y,z} : stand for E_ω , E_τ and E_δ respectively found using peak shape methods.

Peak-like is the value found using transformation of isothermal curve into peaks.

method and other methods. Therefore annealing did not affect the trap responsible for the main peak of synthetic quartz. The effect of annealing was observed only on the intensity of the glow curve because the glow curve of the unannealed sample (figure 6.1) had lower intensity compared to that of the annealed sample (figure 6.4).

6.5 Phototransferred thermoluminescence

Phototransferred thermoluminescence (PTTL) of the unannealed synthetic quartz was investigated in this study. In our experiments, we exposed samples to a beta dose of 100 Gy. After irradiation, the shallow traps were depleted by preheating in order to remove peaks due to these shallow traps. The sample was then illuminated using 470 nm LEDs to induce the transfer of electrons from deeper to shallow traps. After illumination, the sample was heated up to 500°C to record the PTTL.

The phototransferred TL from the main peak was studied by removing in stages, the main peak at 94°C and subsequent glow peaks at 116, 175, 212, 280 and 348°C. The investigation of PTTL was initially based on the removal of the main peak by heating the irradiated sample to 100°C. After the heating and without further irradiation, the sample was illuminated by 470 nm LEDs. We used illumination times ranging from 3 to 1600 seconds. After illumination, the whole glow curve was measured by heating to 500°C. Figure 6.67 is the glow curve measured after removal of peak I and illumination for 20 seconds. The glow curve measured after removal of peak I and illumination did not show PTTL as shown in figure 6.67.

As described in section 6.1.1, the glow curve of synthetic quartz shows at least six peaks. In the next experiment, we investigated PTTL after removal of peak II. Peak II located at 116°C, was removed by preheating the sample to 135°C. The sample was then illuminated using the same illumination times as was done in our previous experiment. Figure 6.68 is the glow curve measured after removal of peak II and illumination for 20 seconds. Figure 6.68 shows that the illumination of the sample after removal of peak II did not give PTTL as well. Note that one sample was repeatedly irradiated with 100 Gy prior to different preheats.

Both glow curves measured after removal of peak I and peak II did not show the PTTL peaks as shown in figure 6.67 and 6.68 respectively. The absence of PTTL peak after removing the first two peaks can be attributed to the fact that electrons are

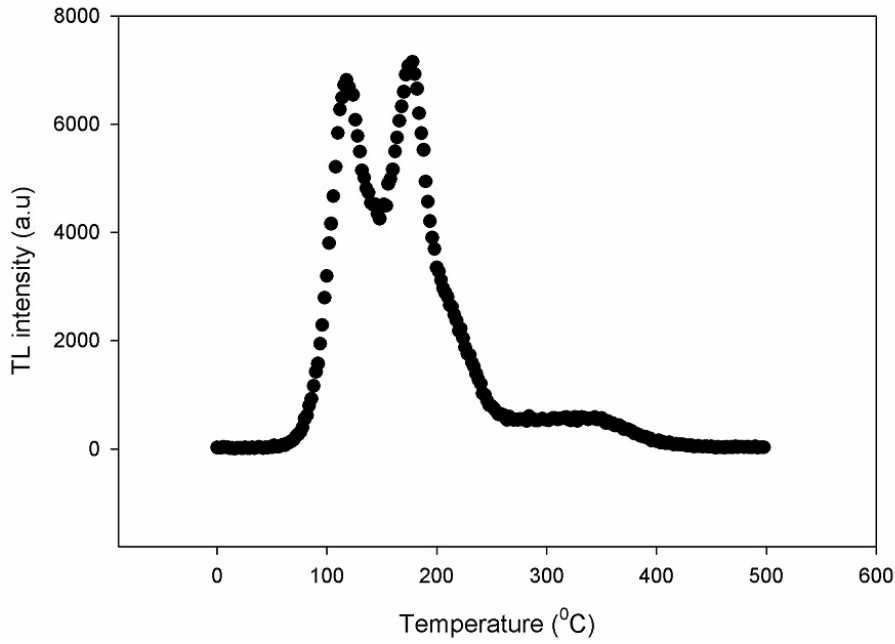


Figure 6.67: Glow curve of synthetic quartz measured after removal of peak I located at 94°C by preheating to 100°C and illumination for 20 seconds. No PTTL from peak I was observed.

captured by traps responsible for higher temperature peaks instead of being captured by the shallow trap.

Peak III is located at 175°C in the glow curve measured at 5°Cs⁻¹. Figure 6.69 shows the glow curve measured after removing peak III by preheating the sample at 185°C and illumination of the material for 20 seconds. From the figure, it is clear that illumination of the sample after removal of peak III produced the PTTL peak at the position of the main peak (84°C). This shows that the trap which was acting as a competitor was probably removed and the electrons from deep traps were now mostly captured by the shallow one.

PTTL was further investigated after removal of peak IV located at 212°C. The sample was preheated at 250°C in order to deplete the trap responsible for peak IV. After this preheat, the sample was illuminated using the same illumination times as were used after removal of first three peaks i.e., 3 to 1600 seconds. The illumination of the sample after removal of peak IV gave a clear PTTL peak at the position of peak

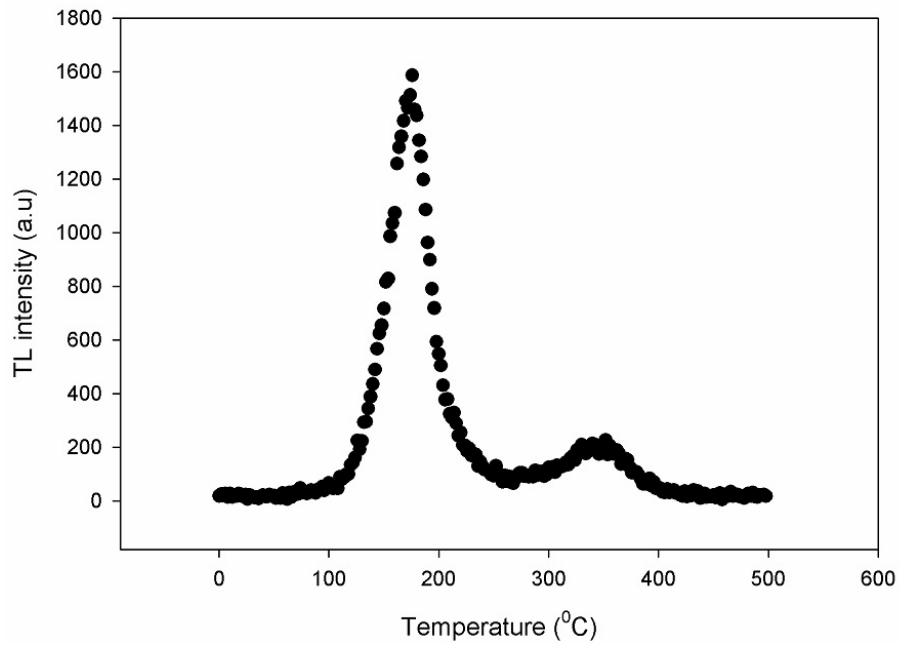


Figure 6.68: Glow curve of synthetic quartz recorded after preheat to 130°C to remove peak II located at 116°C followed by illumination for 20 seconds.

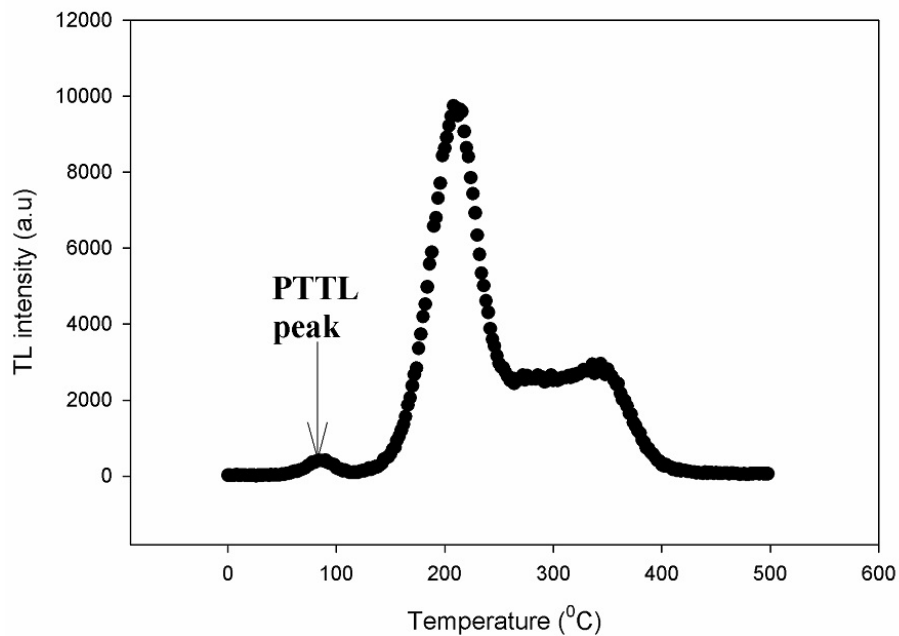


Figure 6.69: Phototransferred thermoluminescence peak at 84°C . Here the glow curve was measured after removal of peak III by preheating to 185°C and illumination by LEDs for 100 s.

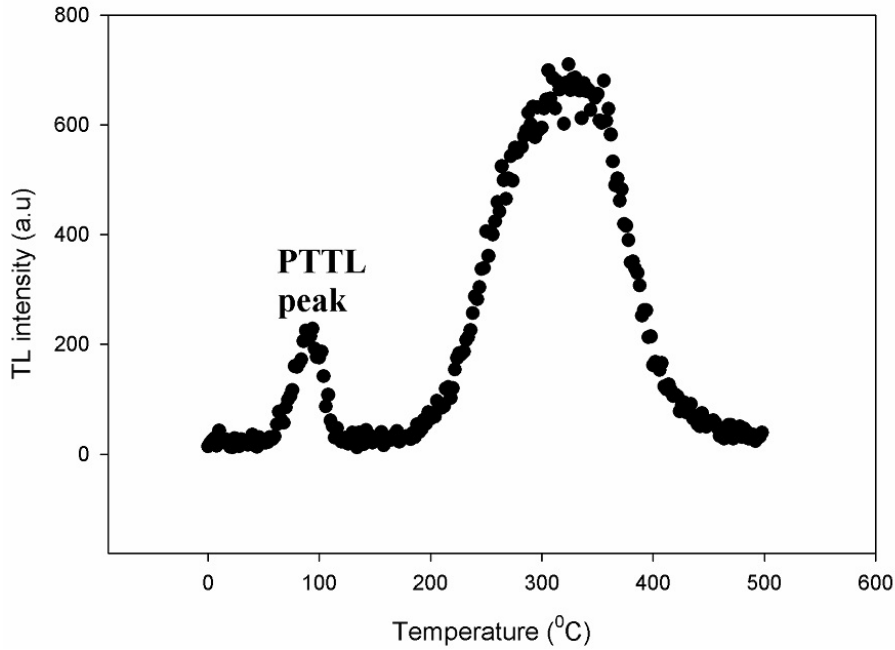


Figure 6.70: Glow curve measured after removal of peak IV located at 212°C by preheating to 250°C and illumination for 20 seconds. PTTL peak appeared at 88°C.

As shown in figure 6.70, Peak V was also removed by preheating to 300°C as the peak is located at 280°C and PTTL was investigated by measuring the whole glow curve following illumination. Figure 6.71 is an example of a glow curve measured after removal of peak V and an illumination time of 20 seconds. The removal of peak V and illumination also gave a PTTL peak at the position of peak I as shown in figure 6.71. Finally peak VI located at 348°C was removed by preheating to 450°C. This was done in order to investigate if the deep trap which acts as a donor is the trap responsible for peak VI. The illumination of the sample after removal of this peak gave a clear phototransferred peak at the position of the main peak as shown in figure 6.72. This implies that the donor traps are much deeper than that responsible for peak VI. The increase on the high temperature side of the graph in figure 6.72 was checked and is not a peak so is attributed to black body radiation caused by heating the material to high temperature since experiment found no new peak beyond 500°C. However, it is possible that this is a new PTTL peak. The removal of peaks

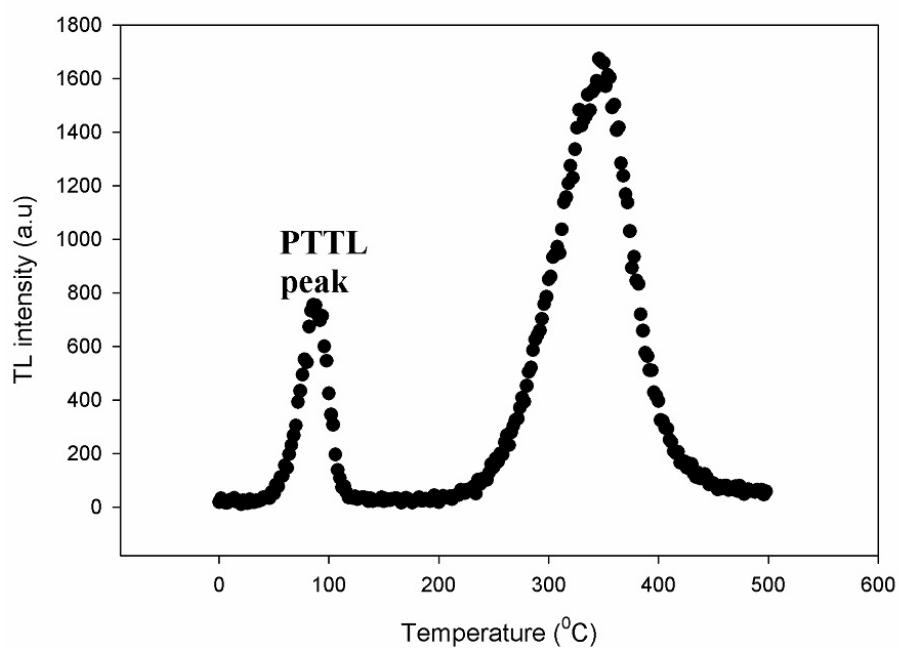


Figure 6.71: Glow curve of synthetic quartz measured after removal of peak V located at 280°C by preheating to 300°C and illumination for 20 s. The graph shows a PTTL peak at 86°C.

III, IV, V and VI together with illumination led to only peak I being reproduced by phototransfer.

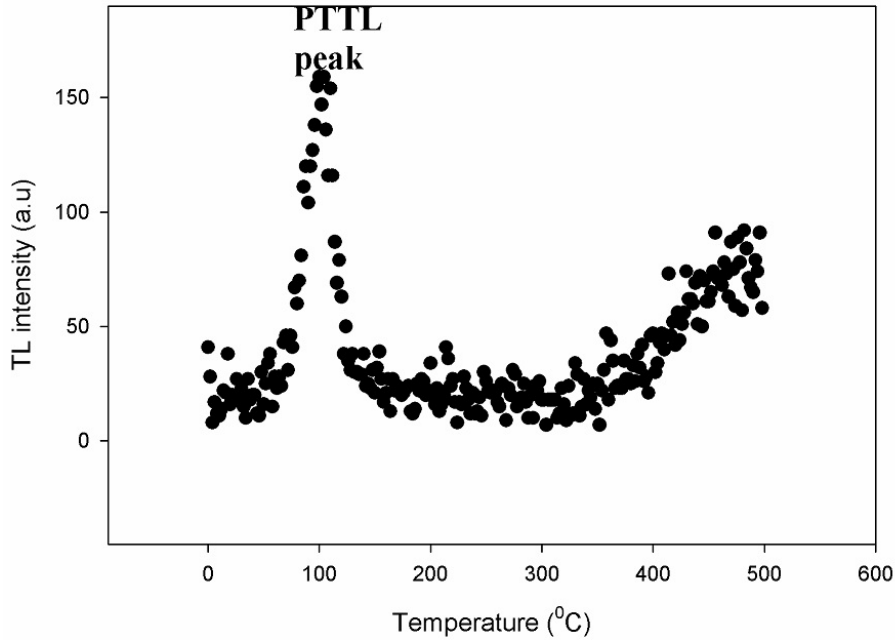


Figure 6.72: Glow curve from synthetic quartz showing the presence of a PTTL peak at 100°C. The glow curve was measured after removing peak VI located at 348°C by preheating to 450°C and illumination for 20 s.

6.5.1 Effect of illumination time on PTTL intensity for peak I

The purpose of this study was to investigate the dependence of the PTTL intensity on the illumination time for peak I. We started by collecting the PTTL intensity after removal of peak III at different illumination times and the resultant graph is presented in figure 6.73. The graph shows that PTTL intensity increases with illumination time. The PTTL intensity reached a maximum when the sample was illuminated for 20 seconds. The PTTL intensity decreased to a non zero steady state value for longer illumination times.

The intensity of the PTTL peak at 88°C in figure 6.70 was also studied as a function of illumination time after removal of peak IV. Figure 6.74 shows the PTTL intensity after removal of peak IV plotted as a function of illumination time. The resultant graph shows the same behavior as the graph plotted after cleaning peak III. The in-

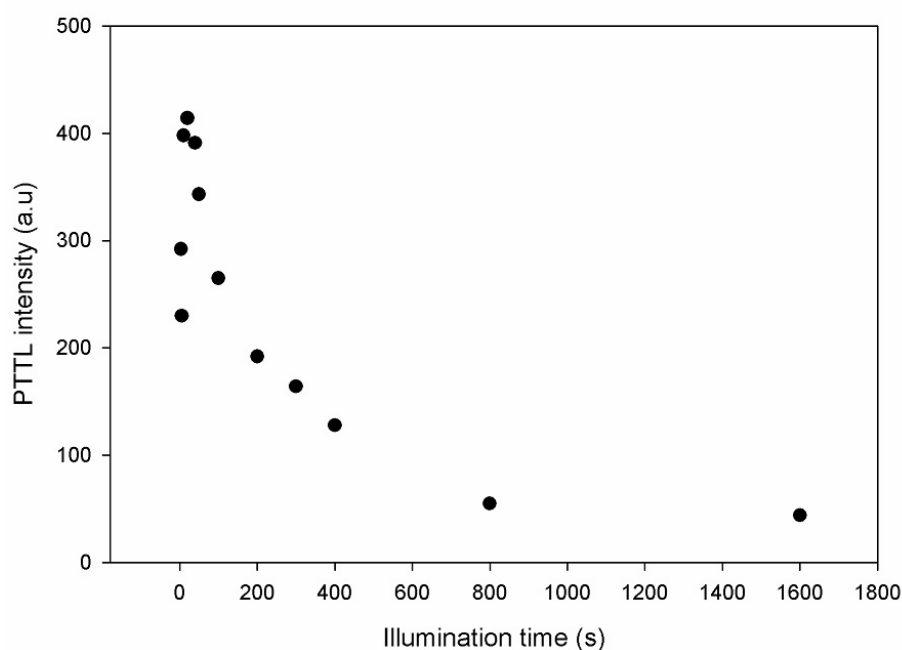


Figure 6.73: Phototransferred thermoluminescence intensity versus illumination time. The graph is for the PTTL peak that appears at the position of peak I (84°C) after removal of peak III.

tensity increases as illumination time increases and reaches a maximum at 20 s. The PTTL intensity decreased to a non zero almost constant PTTL intensity for longer illumination time.

In our next experiment, the maximum intensity of the PTTL peak after removal of peak V was plotted versus illumination time. Figure 6.75 shows the behaviour of the PTTL intensity versus illumination time after removal of peak V. The PTTL after removal of peak V showed a peak-shaped structure when plotted against illumination time. The PTTL intensity after removal of peak V is greater than that after removal of peak III and peak IV as shown in figures 6.73 and 6.75 respectively. The maximum intensity of the signal plotted after removal of peak V in figure 6.75 is almost two times greater than the maximum intensity in the graph after removal of peak III (figure 6.73).

The change of PTTL as a function of illumination time after removal of all six peaks was also studied. Peak VI located at 348°C was removed by preheating to 450°C and

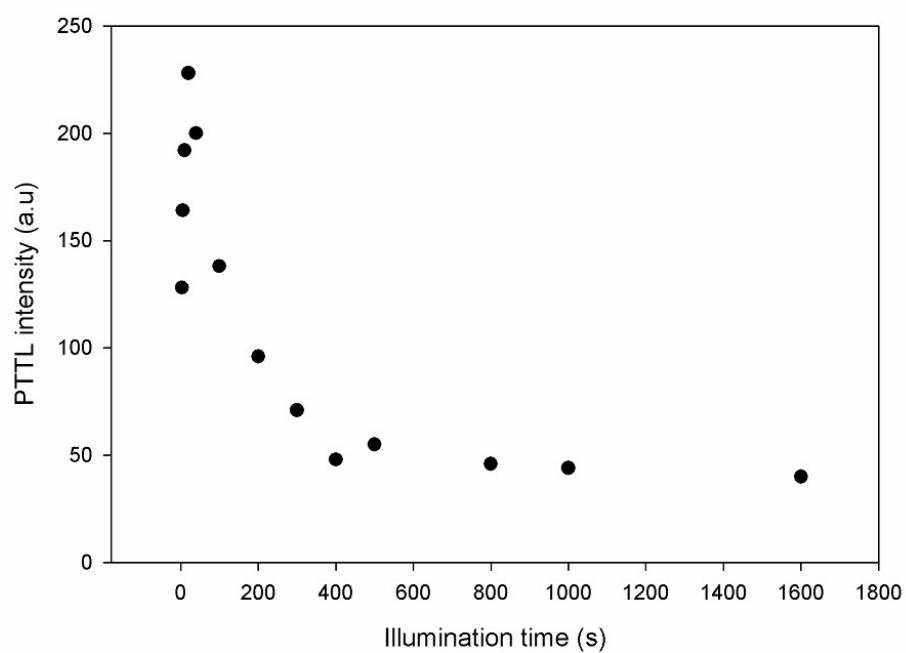


Figure 6.74: Intensity of the PTTL peak at 88°C versus illumination time. The PTTL peak was measured after removal of peak IV.

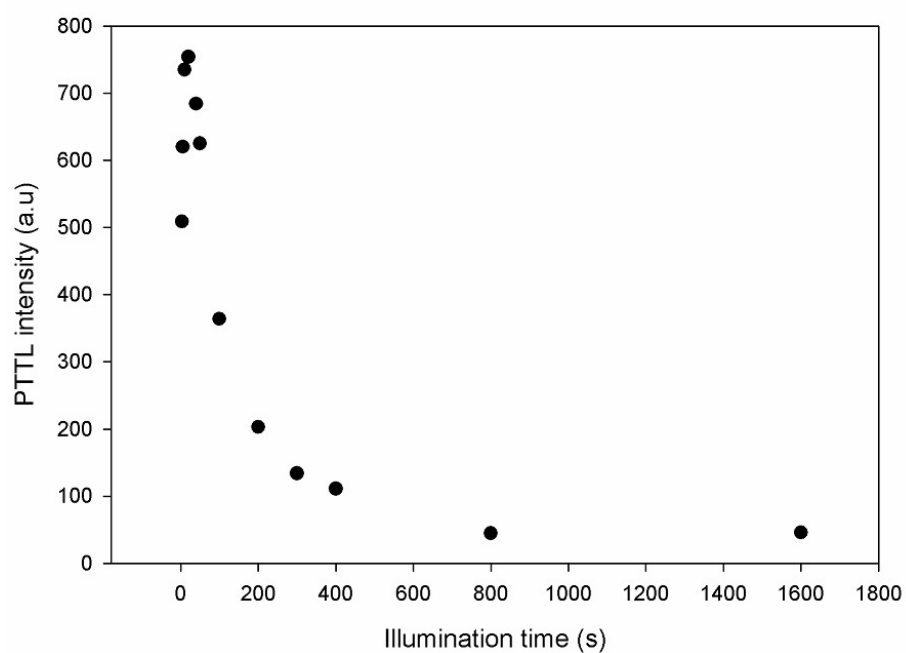


Figure 6.75: PTTL intensity versus illumination time. The intensity was collected from peak I in figure 6.71 for the glow curve measured after removal of peak V by preheating to 300°C and for different illumination times.

then the sample was illuminated for different times. Figure 6.76 shows the graph of PTTL versus illumination time after removal of peak VI. The PTTL intensity after removal of peak VI increased with illumination time. The PTTL reached its maximum at 50 seconds and then decreased to a non zero PTTL intensity as presented in figure 6.76.

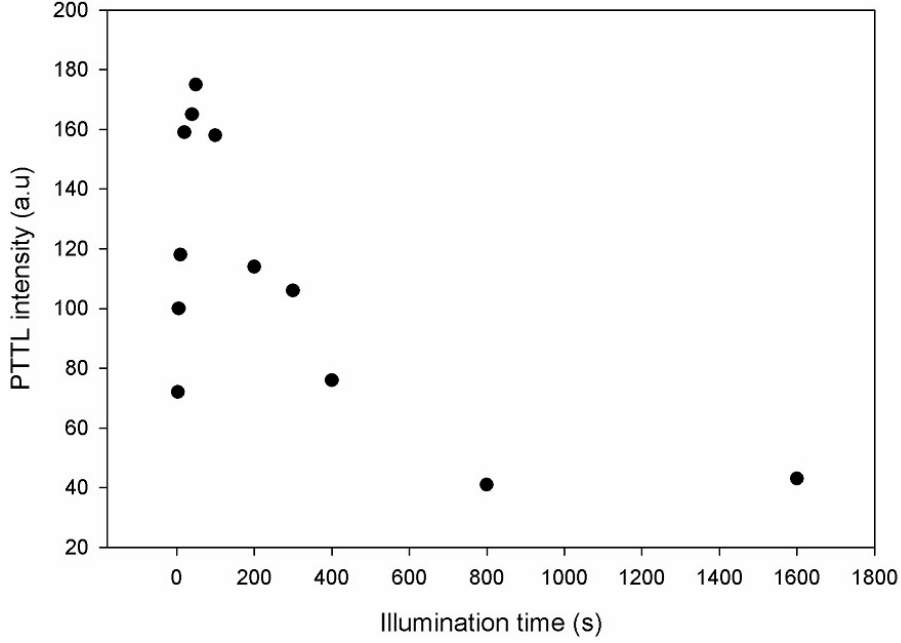


Figure 6.76: Graph of phototransferred luminescence intensity versus illumination time for peak I in figure 6.72 after removal of peak VI. An irradiation dose of 100 Gy was used before each measurement.

The behaviour of PTTL intensity against illumination time can be explained by the energy band diagram proposed by Alexander et al [14] given in figure 3.2. The diagram has one shallow trap (level 1), one optically active trap (level 2) and one optically inactive trap (level 3) with carrier concentrations of n_1 , n_2 and n_3 respectively. The diagram has also two hole centres, one radiative and the other non-radiative with carrier concentrations of m_4 and m_5 respectively.

According to the model, the PTTL follows the smaller of the concentration of electrons in the shallow traps (n_1) and holes in the radiative recombination centre (m_4). At the start of illumination, the number of electrons in the shallow trap is smaller

compared to that of holes in the radiative recombination centre and the PTTL intensity will increase as electrons in the shallow trap (n_1) increases. As illumination time increases, the concentration of holes in the radiative recombination centre decreases. The decrease is due to the recombination of holes with electrons and is the source of OSL signals during the illumination process. At longer illumination times, the concentration of electrons in the shallow trap (n_1) become greater than the concentration of holes in the radiative recombination centre (m_4). At this stage, the PTTL intensity will follow m_4 and will decrease as m_4 decreases. PTTL non-zero steady state is obtained for very long illumination times when the donor trap (level 2) is completely depleted and there are no more electrons to be stimulated from that trap [2, 44].

6.5.2 Dose dependence of PTTL

With the purpose of investigating whether the PTTL dose dependence and that of normal TL of synthetic quartz have the same behaviour, the illumination time was kept constant and the response of PTTL to different irradiation doses was investigated. The investigation was done by recording PTTL intensities for glow curves measured following different doses. For doses lower than 10 Gy, quartz did not show any detectable phototransfer. The PTTL signals first appeared at a dose of 10 Gy. By keeping the illumination time constant, peak III located at 176°C was removed by preheating to 185°C. The maximum intensity of the PTTL peak at 84°C, as in figure 6.69 was collected from glow curves measured after different doses. In this study, the highest dose used was 300 Gy. Figure 6.77 shows the graph of PTTL after removal of peak III against dose. The results show that the PTTL intensity increases with dose in this range. The PTTL dose response is approximately quadratic in the measurement range, since the best fit to data was given by a quadratic equation as shown in figure 6.77.

The PTTL peak and peak I of the normal TL gave different dose response curves.

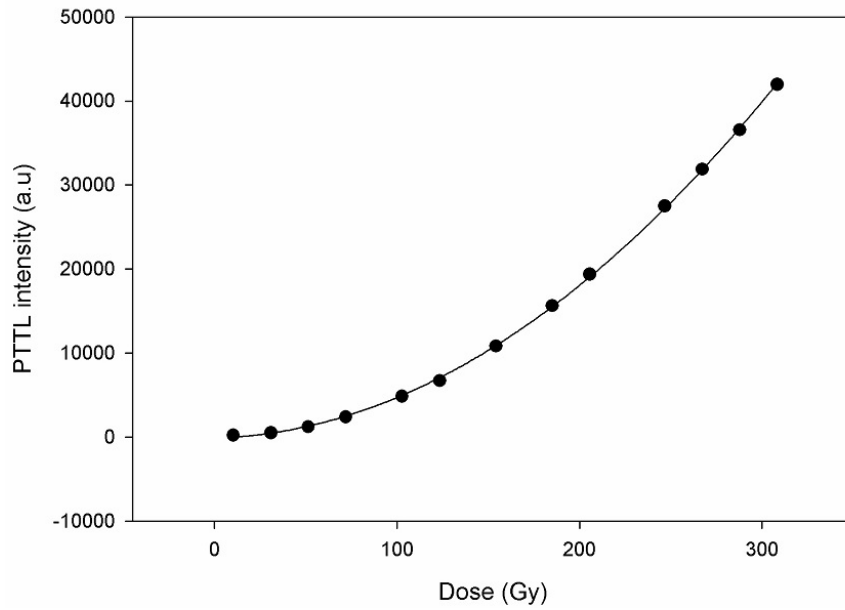


Figure 6.77: The dose response of the PTTL signals from peak I in synthetic quartz after removal of peak III. The line through the experimental data is the best fit of a quadratic equation.

The PTTL dose response curve was best fitted by a quadratic equation whereas the dose response curve of the normal TL peak did not have a general equation which fitted all the data. The main reason is that the PTTL peak is a completely separate peak whereas the normal TL peak I has overlapping peaks which can affect its dose response behaviour.

The PTTL dose dependence was further investigated after removal of peak IV situated at 212°C by preheating to 250°C. Using the same dose range as those used after removing peak III, the PTTL intensities from glow curves measured at different doses were noted. Figure 6.78 shows the graph of the PTTL from glow curves after removal of peak IV against dose. Figure 6.78 shows that the dose response curve of PTTL after removal of peak IV gave is roughly described by a quadratic equation.

In our next PTTL dose dependence study, we removed peak V located at 280°C by preheating to 300°C. Using a constant illumination time of 20 s, PTTL intensities were collected from glow curves measured after different doses. The PTTL intensities

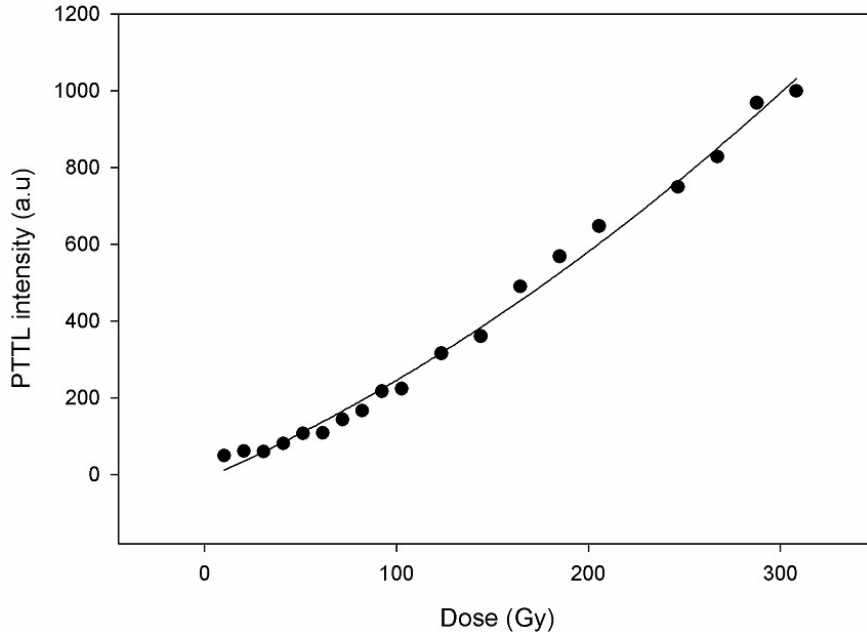


Figure 6.78: PTTL dose response in synthetic quartz after removal of peak IV. The line through the experimental data is the best fit of quadratic a equation of form $y = ax^2 + bx + c$.

were plotted against dose and the resultant graph is presented in figure 6.79. The PTTL dose response curve shows the data described by a quadratic equation as well.

6.5.2.1 Determination of the superlinearity index

In order to estimate the linearity of the dose response, the linearity index $g(D)$ given in equation 6.3 was used. By definition $g(D) > 1$; $g(D) = 1$ and $g(D) < 1$ imply superlinearity, linearity and sublinearity respectively. We used the superlinearity index to study quantitatively the dependence of the PTTL intensity on dose. This analysis was done on the dose dependence of PTTL intensity after removal of peak III. We calculated the superlinearity index $g(D)$ using equation 6.3 and we plotted $g(D)$ as function of dose. Figure 6.80 shows the superlinearity index of the PTTL intensity against dose. The value of superlinearity index is greater than 1 i.e., $g(D) > 1$ in the dose range used i.e., 10 up to 300 Gy as is clear in figure 6.80.

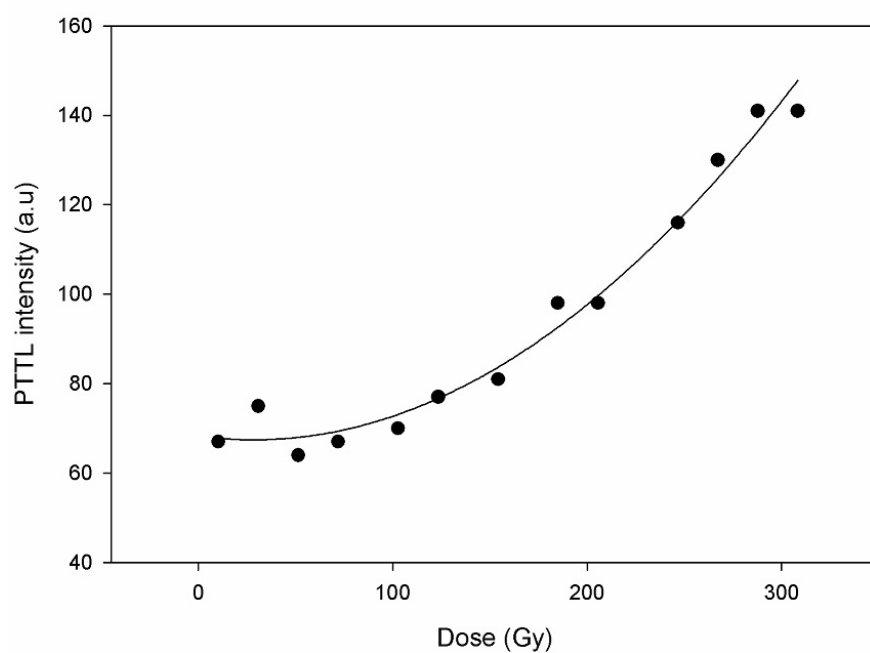


Figure 6.79: PTTL dose response in synthetic quartz after removal of peak 5. The line through the experimental data is the best fit of a quadratic equation.

This is quantitative evidence that the dependence of the PTTL intensity on dose is superlinear. The superlinearity is explained by the presence of competition either during heating or irradiation.

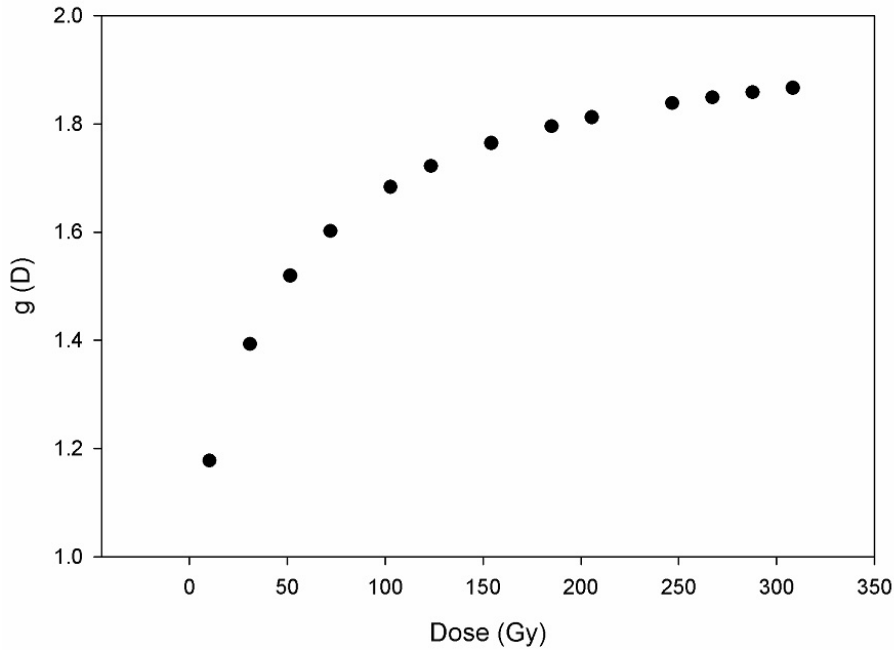


Figure 6.80: The superlinearity index $g(D)$ against dose. The index was calculated from the PTTL intensity measured after cleaning peak III and illumination of the sample for 20 seconds.

6.5.3 Fading

Fading is defined as the decline of luminescence intensity between irradiation and readout. The decrease is due to the loss of trapped charge during the delay [2]. In the investigation of fading of PTTL signals, the sample was irradiated with a beta dose of 100 Gy and illuminated with blue LEDs for 20 seconds. The PTTL was measured directly after illumination and after a delay of $\frac{1}{2}$, 1, 1.5, 2 and 3 hours. Figure 6.81 shows the plot of the PTTL intensity after removal of peak III against time delay. The results showed a decrease of the PTTL intensity with delay time.

Influence of delay between irradiation and measurement of PTTL in synthetic quartz was further investigated after removal of peak IV. Using the same time delay as was done after removal of peak III, PTTL intensities at each time delay were noted. Figure 6.82 shows the PTTL measured after removal of peak IV versus time delay. The figure shows that PTTL intensity fades with storage.

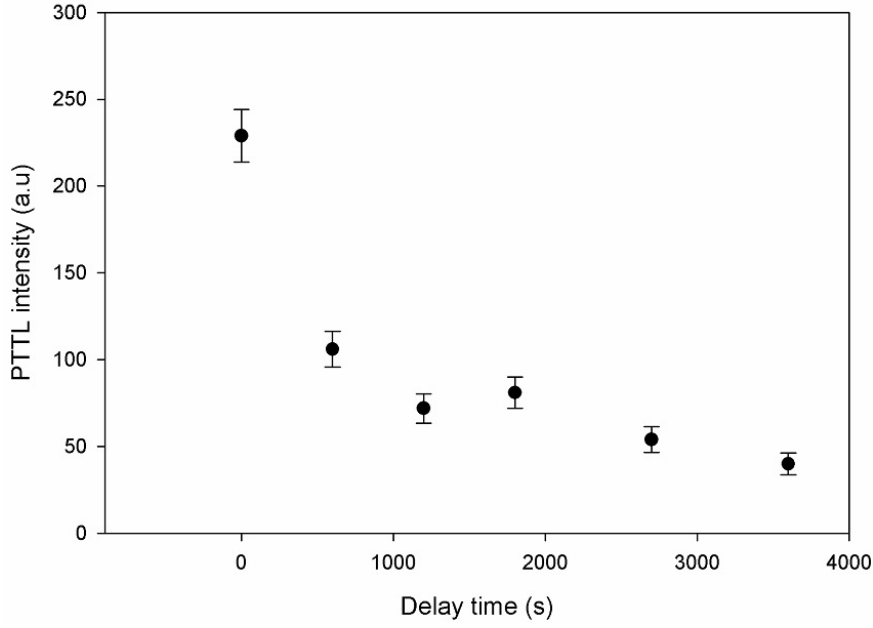


Figure 6.81: Graph PTTL intensity against the delay time. The PTTL intensity was measured after removal of peak III and illumination for 20 seconds each time.

In the next experiment, fading of PTTL signals was investigated after removal of peak V. The PTTL intensity collected from the PTTL peak in figure 6.71 after removal of peak V was plotted against time delay and the resultant graph is presented in figure 6.83. As for the PTTL intensity after removal of peak III and IV, figure 6.83 shows that the PTTL intensity after removal of peak V fades with time delay. The error bars was calculated using poisson' statistics due to the fact explained in section 6.2.2 and were given by the square root of the PTTL intensity.

The structure of the fading curves in figures 6.81, 6.82, and 6.83 seems to have the same structure as the phosphorescence curve (simple exponential) decay. From these graphs, we determined the half-life of the PTTL signals. The fading curve was fitted with a simple exponential equation as shown in figure 6.83. From the fit the value of the decay constant λ was found and was used in the estimation of half-life of PTTL signals. The half-life was found to be $T_{1/2} = 0.693/\lambda \simeq 1$ hour at room temperature.

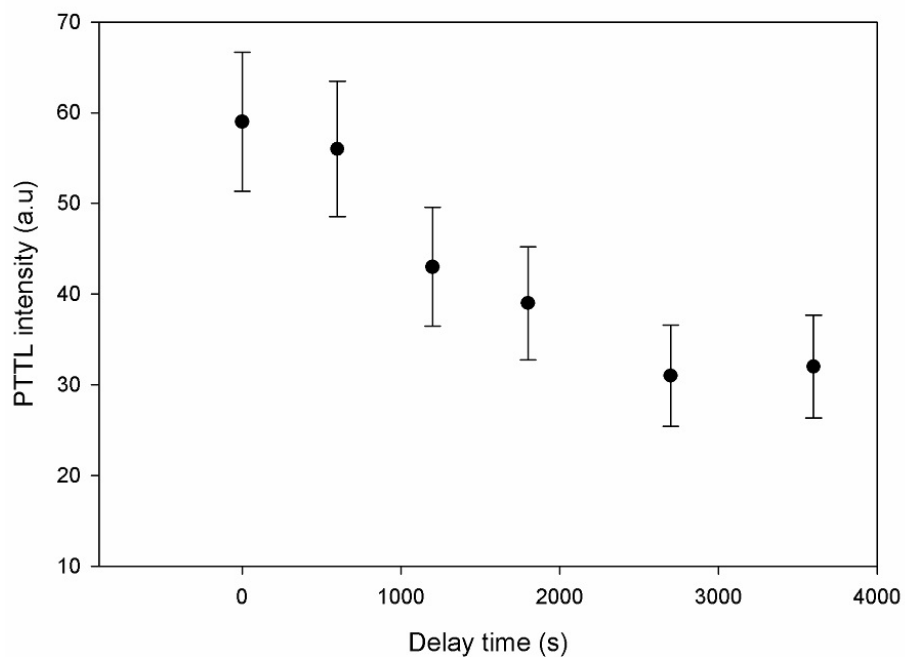


Figure 6.82: Graph of PTTL intensity against the delay time. The PTTL intensity was measured after removal of peak IV and illumination for 20 seconds.

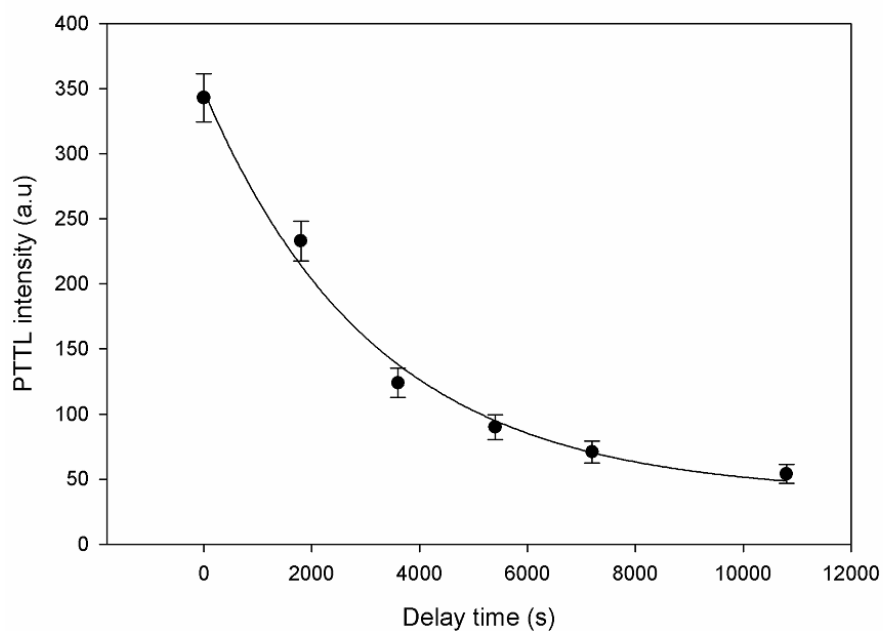


Figure 6.83: Graph PTTL intensity versus the delay time. The PTTL intensity was collected after cleaning peak V and illumination for 20 seconds. The line through the data is the best fit of an equation of form $y = a \exp(-\lambda t)$.

6.5.4 Kinetic analysis of the PTTL peak

The kinetic parameters of the phototransferred peak were determined in order to investigate whether the trap responsible for the normal TL of the main peak is the same as the one responsible for the PTTL peak. Due to the fact that the intensity of the PTTL peak is weak, we used only the various heating rate method of kinetic analysis. This method was chosen because it uses only the position of the maximum intensity which can be easily found from the experimental data.

6.5.4.1 Various heating rate analysis

In the measurements, the first four peaks were removed by heating the sample to 250°C. The sample was then illuminated for 20 seconds and the glow curve recorded by heating up to 500°C. The PTTL peak positions T_m were noted at heating rates of 0.5, 1, 2, 3, 4, and 5°Cs⁻¹ for the same illumination time and dose of 103 Gy. A graph of $\ln(T_m^2/\beta)$ against $1/kT_m$ was plotted and is shown in figure 6.84. The line through data points is the best fit of equation 2.8. From the fit the value of the activation energy was found as $E = 0.68 \pm 0.06$ eV. The value is similar to that of the normal TL peak using the the various heating rate after isothermal cleaning where $E = 0.78 \pm 0.02$ eV. The value of the frequency factor from intercept was found as $s = 4.2 \times 10^9$ s⁻¹ which is of the order of Debye vibration frequency.

The results of kinetic parameters of the PTTL peak are comparable with those of the normal TL peak I. This implies that during illumination, electrons are transferred from deep traps to the trap responsible for the main TL peak.

The maximum intensities of the PTTL peak measured after removal of peak IV by preheating to 250°C were collected from glow curves measured at different heating rates. Figure 6.85 shows the graph of intensity of PTTL peak versus heating rate. The results showed that PTTL intensity decreases as heating rate increases. This is the qualitative evidence that the PTTL peak is affected by thermal quenching. Note that intensities are shown in arbitrary unit in figure 6.85. Results of the influence of

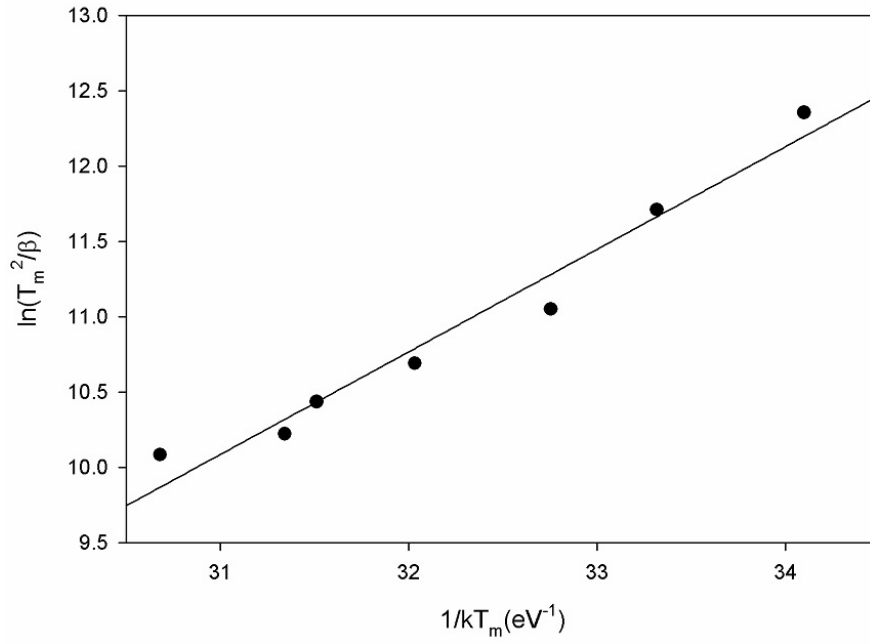


Figure 6.84: Graph used in the analysis of PTTL peak using the various heating rate method. The line through the data is the best fit of a linear equation.

heating rate on the normal TL intensity of the unannealed sample, figure 6.16 and on the PTTL intensity of peak I, figure 6.85 show that both peaks are affected by thermal quenching.

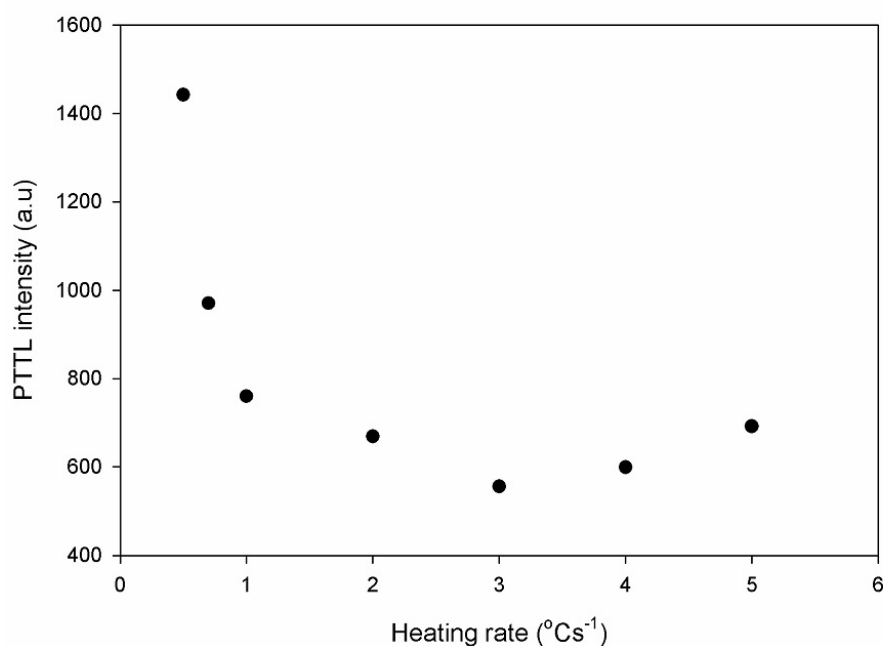


Figure 6.85: Graph of normalized PTTL measured after removal of peak IV, versus heating rate.

6.6 Analysis of radioluminescence of synthetic quartz

6.6.1 General observations

Figures 6.86 and 6.87 show the RL amplitude against emission energy for spectra from the unannealed and the sample annealed at 700°C respectively corresponding to different doses. The RL spectra of synthetic quartz show two broad emission regions for the unannealed and samples annealed at temperatures less than or equal to 700°C as shown in figures 6.86 and 6.87. The region between 2 and 3 eV and the second region between 3 and 4.5 eV. The RL amplitude of bands between 3 and 4.5 eV have higher RL intensity and increase faster with irradiation for samples annealed up to 600°C, figure 6.86 . For samples annealed at 700°C and higher, the emission bands between 2 and 3 eV become dominant and increase faster with irradiation compared to the emission bands between 3 and 4 eV, figure 6.87.

Figure 6.88 shows the RL intensity against energy for a sample annealed at 1000°C

for 60 minutes. Figure 6.88 shows that the emission band around 2 eV decreases with irradiation whereas the emissions between 3 and 4 eV increase with irradiation and gets to a point where there is no significant increase. The emission band around 2.7 eV increases with irradiation and then decreases with irradiation for dose greater than approximately 30 Gy, figure 6.88.

Figures 6.89 and 6.90 are graphs of RL intensity against energy measured from samples annealed at 700 and 800°C, for 10, 30 and 60 minutes each respectively. For samples annealed at temperatures less than or equal to 700°C, increasing the annealing time leads to increases the RL amplitude of the bands between 2 and 3 eV. The amplitude of the bands between 3 and 4 eV decreases with annealing time, figure 6.89. For the samples annealed at temperatures greater than 700°C, the RL amplitude of the whole spectrum increases with annealing time as shown in figure 6.90. In particular, in all samples annealed for 60 minutes at temperatures between 500 and 1000°C, the RL amplitude is enhanced with annealing temperatures as indicated in figure 6.91.

6.6.2 Effect of prolonged irradiation on RL intensity

For the unannealed sample, the main effect of the continuous irradiation is to increase the radioluminescence intensity of all bands in the spectrum as shown in figure 6.86. This increase is faster for low doses and gets to a point corresponding to 80 Gy where there is no more significant increase. This slow increase implies that the recombination centre involved is getting close to its saturation. The same effect was observed in samples annealed at 500, 600 and 700°C for 10, 30 and 60 minutes respectively as shown in figure 6.87 for the sample annealed at 700°C for 60 minutes.

The sample annealed at 800, 900 and 1000°C showed different irradiation response. Figure 6.88 shows examples of graphs measured at different doses from the sample annealed at 1000°C for 60 minutes. For this sample as for ones annealed at 800 and 900°C, the 2.7 eV emission band starts by increasing with irradiation, gets to

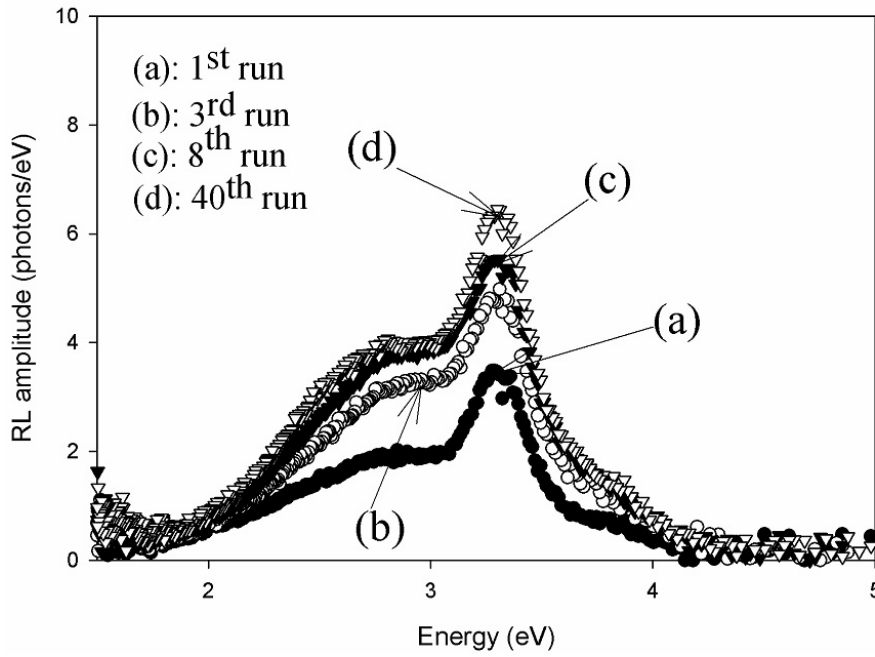


Figure 6.86: Radioluminescence spectra of unannealed synthetic quartz for continuous X-ray irradiation. Each run corresponds to a dose of 10 Gy.

a maximum point at corresponding to 30 Gy and then starts to decrease as dose is further increased. The 2.04 eV emission bands which are clear at higher annealing temperature showed completely the decrease of the RL amplitude with irradiation, figure 6.88.

The two last bands located at 3.4 and 3.9 eV showed an increase but then reached a point where there was no significant increase of RL amplitude. This effect may be explained by the effect of the radiation on the luminescence properties of materials. In addition to the production of luminescence emission, the interaction of the stimulating radiations with the material can cause different additional effects. These effects include radiation damage, trapping and detrapping effects which can cause the decrease or increase of RL signals [30].

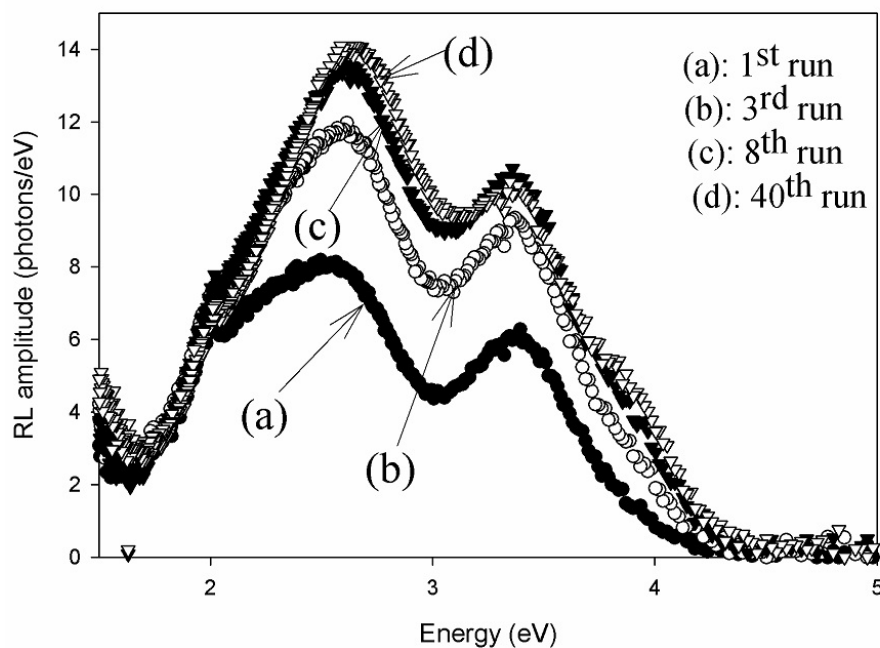


Figure 6.87: The effect of irradiation on radioluminescence spectra of synthetic quartz annealed at 700°C for 60 minutes. For each run, a dose of 10 Gy is imparted to the sample.

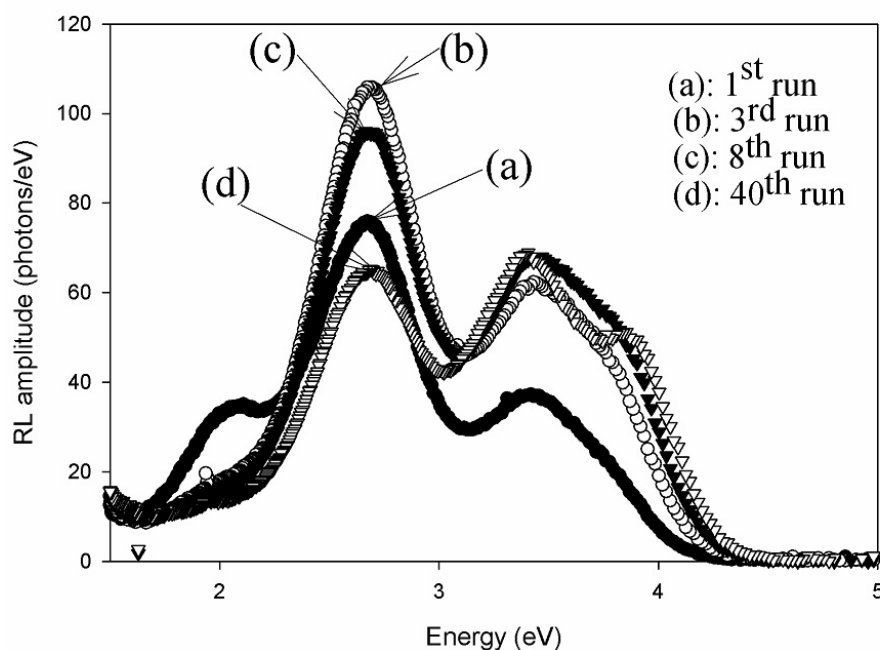


Figure 6.88: The effect of irradiation on radioluminescence spectra of synthetic quartz annealed at 1000°C for 60 minutes. Each run corresponds to the dose of 10 Gy.

6.6.3 Effect of annealing time on RL amplitude

The effect of annealing time was also investigated for constant annealing temperature. Figure 6.89 is the plot of RL intensity versus energy measured from the unannealed sample and samples annealed at 700 for 10, 30 and 60 minutes respectively. From figure 6.89, it is clear that the emission bands between 2 and 3 eV have lower intensity for the unannealed sample and the intensities increase with annealing time. The emission band around 3.4 eV increases for the unannealed sample, gets to a maximum for annealing for 10 minutes, and then started to decrease for annealing times of 30 and 60 minutes. Figure 6.89 also indicates that the emission band around 2 eV is affected by annealing time as the band becomes clearer at higher annealing duration. This effect is different from that in samples annealed at 800°C and higher. For samples annealed beyond 700°C, the RL amplitude of all emission bands increases with annealing time, as indicated in figure 6.90. The change of RL emission bands with annealing temperature correspond to a change in luminescence lifetime with annealing temperature, for the same sample [45]. This probably is due to the change in recombination centre.

6.6.4 Effect of annealing temperature on RL amplitude

Spectra measured from the unannealed sample, and samples annealed at 500, 600, 700, 800, 900 and 1000°C, were used to study the effects of annealing temperature on radioluminescence of synthetic quartz. The analysis were performed by making the annealing time constant and changing the annealing temperature.

Figure 6.91 shows RL spectra measured for unannealed and samples annealed at different annealing temperatures. Figure 6.91 indicates that the unannealed sample has the lowest RL intensity and the intensity increases with the annealing temperature. The annealing process indicates that the emission spectra are composites of many bands which, start to separate as the annealing temperature increases. The spec-

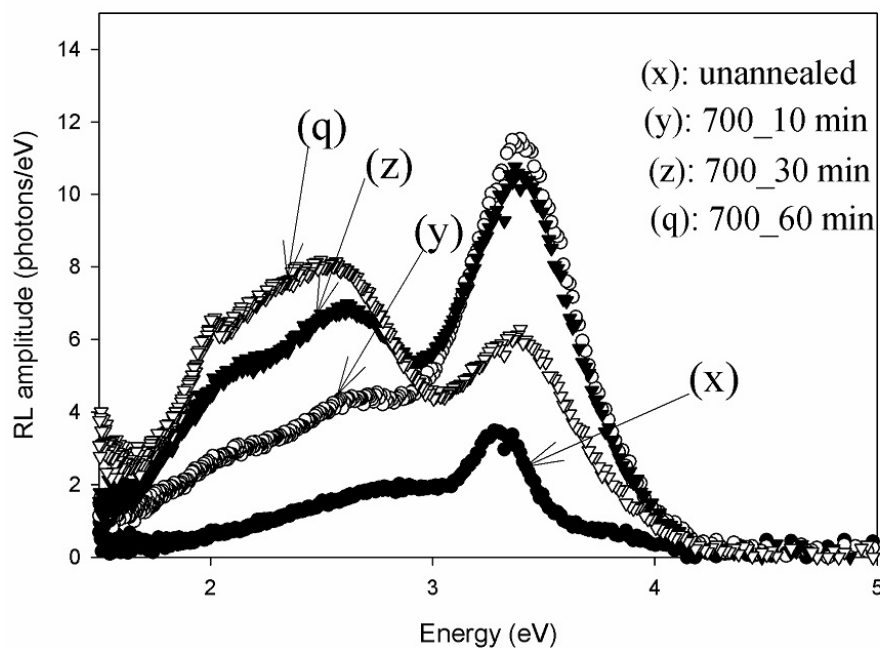


Figure 6.89: The effect of duration of annealing on radioluminescence spectra of unannealed synthetic quartz. Samples were annealed at 700°C for 10, 30 and 60 minutes. Data for an unannealed sample is included for comparison

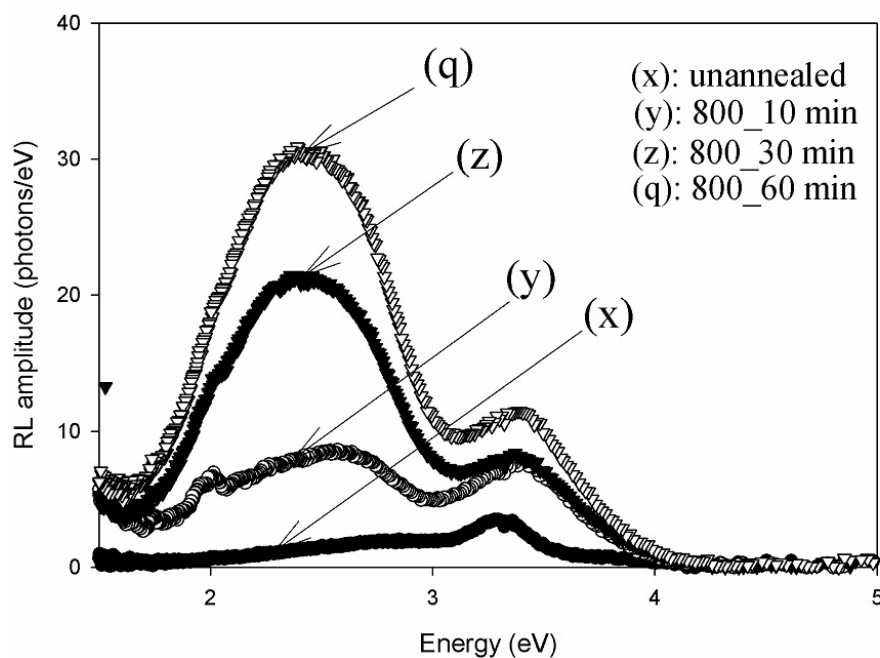


Figure 6.90: The effect of annealing time on radioluminescence spectra of unannealed synthetic quartz. Samples were annealed at 800°C for 10, 30 and 60 minutes. Data for an unannealed sample is shown for comparison.

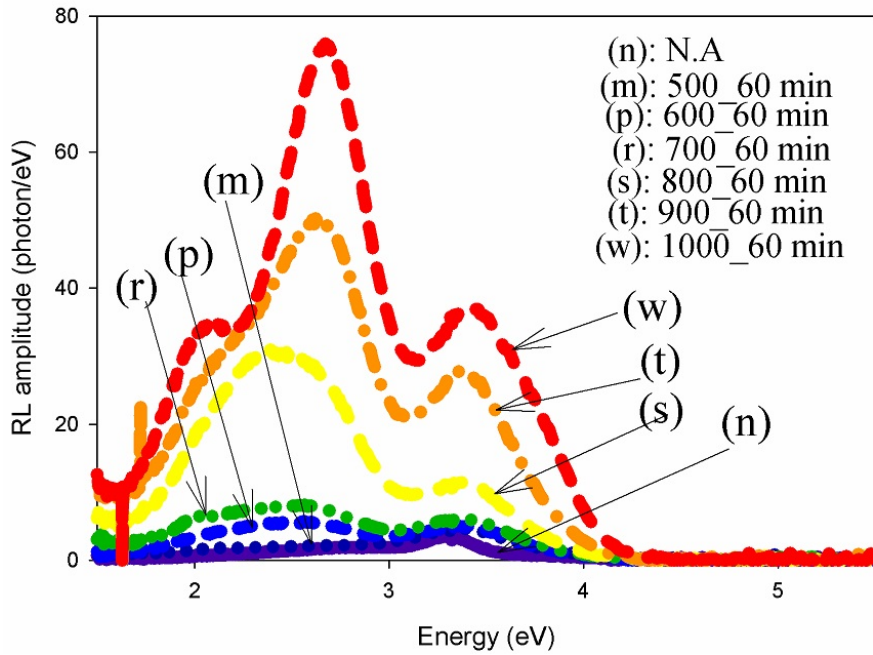


Figure 6.91: The effect of the annealing temperature on radioluminescence of synthetic quartz. The graph shows spectra measured from the unannealed (N.A) and samples annealed at 500, 600, 700, 800, 900 and 1000°C for 60 minutes.

trum from the sample annealed at 1000°C for 60 minutes shows that the spectrum is a composite of more than four emission bands. The increase in RL amplitude of the emission bands after annealing can be interpreted as being caused by an increase in concentration of recombination centres or the decrease of competitors centres due to the annealing process [31].

6.6.5 The deconvolution of spectra

The RL spectrum of synthetic quartz annealed at 1000°C for 60 minutes was used to estimate the energy and the number of the emission bands. This estimation was done by deconvoluting the RL spectrum into its Gaussian components. The deconvolution was done by fitting the whole spectrum with a sum of seven Gaussians of form $y = \frac{a}{\pi^{1/2}\omega} \exp[-2(\frac{x-x_0}{\omega})^2]$. a , ω are the area and the width of the emission bands respectively and x_0 is the energies corresponding to maximum amplitude of the bands.

Figure 6.92 is the spectrum measured from the sample annealed at 1000°C for 60 minutes fitted with sum of seven Gaussian functions. The figure shows that experimental results were properly fitted by the sum of seven Gaussians. The deconvolution of the RL spectrum showed that the spectrum is indeed a composite of seven emission bands. The Gaussian fit is in good agreement with the experiment curves and the results reported by Pagonis et al [29] but for natural quartz. The results from the deconvolution indicate the existence of emission bands located at energy positions indicated in table 6.10. Using the results from the fit, the emission bands were regenerated and are presented in figure 6.92. The spectra energies found in our deconvolution have also been reported in natural quartz by Pagonis et al [29] except for a difference in the first emission band reported at the energy around 1.9 eV whereas our experiment gave that emission at the energy of 2.04 eV.

Table 6.10: The energy and full width at half-maximum for the seven RL emission bands used in the deconvolution of RL spectra.

Bands	Energy (eV)	Wavelength (nm)	FWHM (eV)
O	2.04	607	0.47
A	2.54	487	0.37
B	2.77	446	0.37
X	3.04	407	0.74
C	3.40	363	0.50
M	3.75	330	0.36
D	3.91	316	0.40

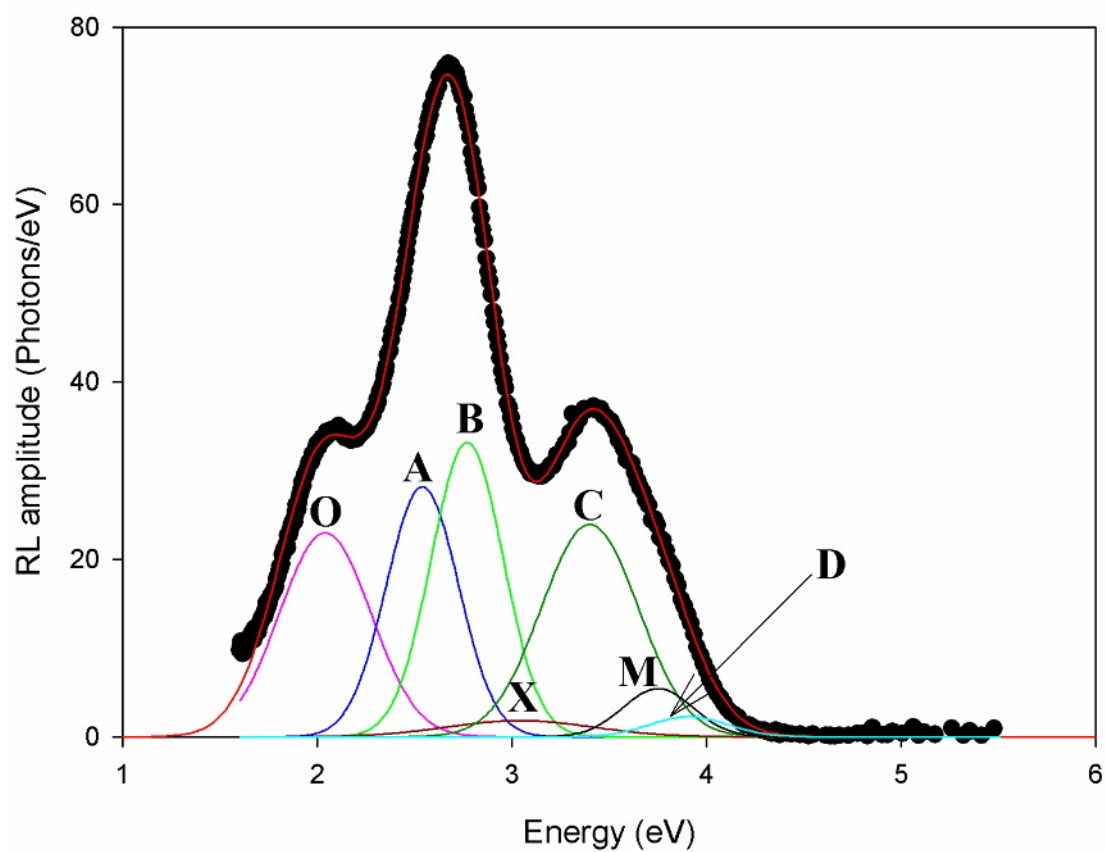


Figure 6.92: Deconvolution of the RL spectrum using the Gaussians. The peaks were regenerated using the parameters of seven components found from the deconvolution.

Chapter 7

Conclusions

The aim of this project was to study the mechanisms of thermoluminescence in synthetic quartz and to discuss the results in terms of the physical characteristics of point defects involved. The unannealed synthetic quartz shows a glow curve with low intensity when it is measured after irradiation without preheat before dose. When the sample is preheated before dose, the measured glow curve has higher intensity. This implies that, the sample was activated by heating the sample to 500°C. Unannealed synthetic quartz showed a change of sensitivity due the combination of irradiation and heating. This implies that during heating, the holes produced by irradiation were transferred from non radiative to the radiative recombination centres which account for the increase in sensitivity for the next cycle. For the annealed sample, the sample irradiated without preheat gave a glow curve with higher intensity. In this case in addition to defect equilibrium re-establishment, the annealing played the role of activation.

Thermoluminescence of unannealed synthetic quartz showed a glow curve with six peaks at 94, 116, 176, 212, 280 and 348°C when measured at a heating rate of 5°Cs⁻¹. The presence of these six peaks in the TL glow curve indicates the existence of six electron traps (defects) responsible for each peak which is located in the forbidden band. The TL of the annealed sample shows the presence of seven electron traps

since its glow curve shows seven peaks at 115, 148, 214, 246, 300, 348 and 412°C. For the measurements made on the same sample using the same dose but at different heating rates, the results showed that the position of peak I increases with heating rate. This effect was observed on both unannealed and annealed samples. The increase of peak position is due to the direct relationship between heating rate and peak temperature. The measurement at various heating rates also showed the increase followed by the decrease of the peak intensity as heating rate increases. The increase of the intensity with heating rate requires further investigation. The decrease of TL intensity as heating rate increases is a sign of thermal quenching. Glow curves measured at the same heating rate but at different doses showed that the intensity of the main peak increases with dose for both unannealed and annealed sample. These results showed that the activation energy does not depend on the irradiation dose which implies that irradiation did not introduce new peaks in the proximity of peak I. Dose response of TL from both samples requires further investigation in order to find the reasons why their dose response curves are different. In kinetic analysis, two methods of thermal cleaning were used in order to remove the satellite peak in the initial rise region of peak I. These were thermal and isothermal cleaning methods. All methods of thermal cleaning gave a clear rising edge of peak I. This implies that isothermal luminescence can be used as method of thermal cleaning. Kinetic analysis of the cleaned main peak in both unannealed and annealed samples showed that peak I follows first order kinetics. The trap responsible for the main peak has an activation energy of approximately of 0.90 eV with the frequency factor of the order 10^{11} s^{-1} . All methods of kinetic analysis used in this study gave comparable values of kinetic parameters for both unannealed and annealed samples except various heating rates methods which underestimated those parameters (E and s). These values are also comparable with those reported in literature for the same material using the same methods. The results of our study showed that kinetic parameters did not change with annealing. Further investigation is required in order

to find more explanations of the reason why various heating rates gave the values of kinetic parameters lower than those from other methods for annealed sample.

Unannealed synthetic quartz shows PTTL only after removing the first three peaks of the glow curve. The cause of lack of PTTL after removing first two peaks requires further investigation. The presence of PTTL after removal of first three peaks implies that the electrons are transferred from deep traps to shallow traps when the sample is illuminated. The PTTL intensity shows a peak-shaped structure when plotted against illumination time. The PTTL versus illumination behaviour is explained by the fact that the intensity follows whichever is the minimum of electrons in shallow trap or holes in the radiative recombination centre. For lower illumination times, the concentration of electrons in the shallow trap is low and increases with illumination which causes the increase of PTTL for lower illumination time. For higher illumination times, the concentration of holes in the radiative recombination centre is low and decreases as illumination times increases which causes the decrease of PTTL intensity.

The PTTL shows the superlinear dose response in the dose ranging between 10 and 300 Gy. The activation energy of the PTTL peak is 0.68 eV and the frequency factor of the order of 10^9 s^{-1} . These values are consistent with the values of normal main TL peak. These results indicate that electrons are transferred by illumination from deep traps and are captured by the trap responsible for the main peak. The measurements of PTTL at various heating rates showed that the maximum intensity of PTTL peak decreases as heating rate increases which implies that PTTL from peak I is affected by thermal quenching. The PTTL intensity fades with storage and its half-life is approximately 1 hour.

The deconvolution of RL spectra of synthetic quartz gave seven emission bands in the visible region of the electromagnetic spectrum. The emission bands are located between 2.04 eV (315 nm) and 3.94 eV (607 nm). For the unannealed and samples annealed to temperatures less than 800°C, RL amplitude increases with continuous

irradiation. The increase of RL amplitude with irradiation implies that irradiation increases the concentration of holes in recombination centres. For the sample annealed to temperatures greater than 700°C , irradiation increases 2.04 eV band and emission bands between 3 and 4.5 eV. The 2.7 eV band increases for doses less than 30 Gy and decreases at higher irradiation doses. The decrease of RL amplitude with irradiation may be explained by the detrapping effects which causes the decrease in RL amplitude. This requires further examination.

For the sample annealed to temperatures less than 800°C , the RL amplitude increase with annealing time for the emission bands between 2 and 3 eV. The emission bands between 3 and 4 decreases as annealing time increases. These results indicate that for samples annealed at temperatures less than 800°C i.e. $500, 600, 700^{\circ}\text{C}$, annealing time increases the concentration of holes in the centres responsible for the bands between 2 and 3 eV. The concentration of holes in the centres responsible for emission bands between 3 and 4 eV decreases as annealing time increases. Annealing time increases the concentration of holes in all centres for samples annealed to temperatures greater than 700°C i.e. $800, 900$ and 1000°C which causes an increase of all spectra. All emissions of the spectra increased with annealing temperature which indicates that the annealing process increased the population of all recombination centres.

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