JANUARY 2019 M. Sc. Thesis in Physics Engineering MUHAMMED HATIB

GAZİANTEP UNIVERSITY
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INVESTIGATION OF THERMOLUMINESCENCE PROPERTIES OF CALCITE MINERAL CONDUCTED BY BACTERIAL CALCIUM CARBONATE ($CaCO_3$) PRECIPITATION IN ORGANIC SOIL

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MUHAMMED HATIB

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Investigation of Thermoluminescence Properties of Calcite Mineral Conducted by Bacterial Calcium Carbonate ($CaCO_3$) Precipitation in Organic Soil

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Assoc. Prof. Dr. Hüseyin TOKTAMIŞ

By

Muhammed HATIB

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This is to certify that we have read this thesis and that in our consensus opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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Muhammed HATIB

ABSTRACT

INVESTIGATION OF THERMOLUMINESCENCE PROPERTIES OF CALCITE MINERAL CONDUCTED BY BACTERIAL CALCIUM CARBONATE ($CaCO_3$) PRECIPITATION IN ORGANIC SOIL

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The object of this study is investigation of thermoluminescence (TL) properties which are dose response, heating rate, reproducibility and fading of calcite mineral conducted by bacterial calcium carbonate ($CaCO_3$) precipitation in organic soil. The TL glow curves of the irradiated samples by using beta source ^{90}Sr-^{90}Y (≈ 0.04 Gy/s) were obtained for different dose levels between 2.4 Gy and 6.9 kGy. Trap parameters such as trap depth (E_a) and kinetic order (b) were obtained by using computerized glow curve deconvolution (CGCD) method, also the peak integral (n) was evaluated from TL signal by choose a specific dose at with 1°C/s heating rate β. The results for calcite show a clear TL glow curve with four main peaks located around 90, 140, 210 and 240 °C and good TL properties with good reproducibility, wide linear dose response and good fading. A good linearity behavior observed for the dose–response between 140 Gy and 2.3 kGy for the peaks 210 °C and 240 °C. The dosimetric peaks located between 200 and 250 °C are not affected by the storage time. The kinetic parameters of traps are calculated for two main peaks which located around 88 and 208 °C, the trap depth varies between 0.74 - 0.82 eV and 0.83 - 0.88 eV, kinetic order (b) varies between 1.24 -1.5 and 1.4 -1.5, respectively.

Keywords: Thermoluminescence, calcite mineral ($CaCO_3$), bacterial calcium carbonate ($CaCO_3$) precipitation

ÖZET

ORGANİK TOPRAKTA BAKTERİYAL KALSIYUM KARBONAT ($CaCO_3$) ÇÖKELMESİ SONUCU OLUŞAN KALSİT MİNERALİNİN TERMOLÜMİNESANS ÖZELLİKLERİNİN İNCELENMESİ

HATIB, Muhammed
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Danışmanı: Doç. Dr. Hüseyin TOKTAMIŞ

Ocak 2019
50 sayfa

Bu çalışmanın amacı organik toprakta bakteriyel kalsiyum karbonat ($CaCO_3$) çökelmesi ile oluşan kalsit mineralinin termolüminesans (TL) özelliklerinin incelenmesidir. ^{90}Sr-^{90}Y (≈ 0.04 Gy/s) beta kaynağı kullanılarak 2.4Gy ile 6.9kGy arasında farklı doz değerleri için numunelerin TL ışıldama eğrileri elde edildi. Tuzak derinliği (E_a) ve kinetik derece (b) gibi tuzak parametreleri ve ayni zamanda 1°C/s ısıtma oranında belirgin bir doz verilerek TL sinyalinden tepe altında kalan alan bilgisayarlı ışıldama eğrisi ayrıştırma (CGCD) metodu kullanılarak elde edildi. Bu çalışmanın sonuçlarına göre çalışmada kullanılan kalsit minerali iyi tekrarlanabilirliği, geniş doz cevap eğri aralığı ve oda sıcaklığında düşük sönümlemesi ile iyi bir termolüminesans özelliği göstermektedir. Deneyler sonucu elde edilen TL ışıldama eğrisi 90, 140, 210 and 240 °C civarlarında konumlanan dört ana tepeden oluşmuştur. 210 °C and 240 °C tepeleri için 140 Gy and 2.3 kGy doz aralığında iyi bir lineer doz cevap eğrisi gözlemlenmiştir. 200 ile 250 °C arasında konumlanan dozimetrik tepelerin TL ışık şiddetlerinin oda sıcaklığında ve karanlık ortamda numunelerin depolanma sürelerinden etkilenmediği görülmüştür. 88 and 208 °C civarında konumlanan iki ana tepenin tuzak kinetik parametreleri hesaplanmış ve sırasıyla tuzak derinliklerinin 0.74 - 0.82 eV ve 0.83 - 0.88 eV, kinetic derecelerinin 1.24 -1.5 and 1.4 -1.5 arasında değiştiği görülmüştür.

Anahtar kelimeler: Termolüminesans, Kalsit mineral ($CaCO_3$), bakteriyel kalsiyum karbonat ($CaCO_3$) çökelmesi.

To my parents, my wife, my child and freedom Syria

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I want to thank Assoc. Prof. Dr. Hüseyin TOKTAMIŞ, who is one of the most important persons that inspired me to complete the master's study by his knowledge, recommendations and wonderful dealing with me and all students. I want to thank Dr. Hanifi Canakci from civil engineering department and Dr. İbrahim Halil Kılıç from Biology department for providing powder samples.

I want to thank my mother, the person I trust, who is the only person will be happier than me for this certificate and to my father, I always believe with their praying to me, to my lovely wife and my lovely child, and to every martyr sacrificed for freedom of Syria.

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INTRODUCTION

1.1 Introduction

In the search of light history discovering, the first made by cavemen (prehistoric), chemists in mediaeval knew some minerals and fluorite showed a transient glow when heated in the dark. In 1663, Robert Boyle [1] talked about to the Royal Society of London of "observing a strange glimmering light" during heat a piece of diamond in the dark and used the term 'self-shining' to explain the phenomenon of luminescence [2-5]. Elsholtz [6] also, talking about similar observations with the fluorite (calcium fluoride) in 1676 [7] and Oldenberg reported studies on the same material [8].

In 1889, E. Wiedemann [9] introduced the "Thermoluminescence/ thermoluminescenz" after observation of light emission after thermal background (excitation), he was the first scientist used the term 'Thermoluminescence' in 1889. . In 18th century, TL of minerals such as rock crystal, amethyst, and calcite similar observations on TL when they heated in the dark, that reported by many authors [10-13]. This was the phenomenon of TL, more accurately Thermally Stimulated Luminescence (TSL), Wiedemann and Schmidth [14] detected TL of substances irradiated with cathode rays and investigated TL activators iron and rare earth elements. Thermoluminescence from natural specimens was first published by Trowbridge and Burbank in 1904 [15].

In the 1st quarter of the 20^{th} the researches related to TL of minerals and solid states started, extracted results refer to that the TL is becoming significant method to study the releasing energy from trap levels by exciting source as thermally ways.

Now more accurately can be defined thermoluminescence, which is emission of light from heated material (minerals, semiconductors, and complex biological systems) as a result of energy released from electrons previously trapped within the valance band, in other words, it frees the electrons, which produce light.

There are three essential conditions must be achieved for product TL, the samples studied must be either insulator or semiconductor, must exposure to radiation source to absorb

energy and, heating the samples to achieve emission of light means luminescence phenomena occurred after heating [16].

The intensity of thermoluminescence is proportional to two parameters which are temperature and absorbed energy by the material after irradiated by excitation source, the resulting curve is known as a TL glow curve, which sometimes consist of one or more glow peaks every one of this peak refer to trap levels (excited states).
Most solids under suitable excitation and suitable temperature may act as TL emitting material. The solid may be a mono crystal, polycrystals or amorphous. Some of the most comprehensively studied materials using TL as the technique are: alkali halides like KCl, KBr, KI and NaCl, Quartz and Calcite. A large number of studies has been reported for quartz of various forms like crystalline, fused silica etc. Minerals other than quartz that have been extensively studied are fluorite and calcite.

The aim of this study is to determine dose response, stability and kinetic parameters of TL peaks for calcite mineral conducted by bacterial calcium carbonate ($CaCO_3$) precipitation in organic soil (BCCP). There are several techniques to determine kinetic parameters from TL glow curves [17], computer glow curves deconvolution (CGCD) and peak shape (PS) are suitable techniques to estimate parameters for specific TL glow curve, because there are many TL glow curves for calcite mineral. The major positive feature of (CGCD) technique is the synchronous estimation of kinetic parameters for all peaks with no complicated process. The experiments shows four peaks at 90, 140, 210, 240 ^{o}C and 340 ^{o}C for high applied dose.

1.2 Luminescence process and Stokes Law

When material exposure to radiation source, some of its energy is absorbed and re-emitted as a beam of photons with longer wavelength (Stokes law). In luminescent treatment, wavelength of emitted photons are distinctive for a substance and not the applied radiation. The emitted light (beam photons) could be infrared, ultra-violet, or visible light. This treatment is cold emission, i.e. luminescence, does not include the emission of blackbody radiation. This process consist of two steps: (1) The ionization of electronic system of substances to higher energy level, and (2) emission of photons. The emission of light is proportional to time (τ_c) after absorption of the radiation occurred, depending on this parameter can be divide the luminescence process into two types: phosphorescence and fluorescence. In the fluorescence the characterized to time (τ_c) is

smaller of 10^{-8}s and does not depend on temperature but phosphorescence strongly depends on temperature and its characteristic time is bigger than 10^{-8} s.

The Phosphorescence phenomenon include two parts: (a) short period, the characteristic time is $\tau_c < 10^{-4}$ s, and (b) long period where $\tau_c > 10^{-4}$ s which is called thermoluminescence (TL), and its emission continues from minutes to 4.6×10^{9} years [16].

The family tree of luminescence phenomena is shown in figure1.1

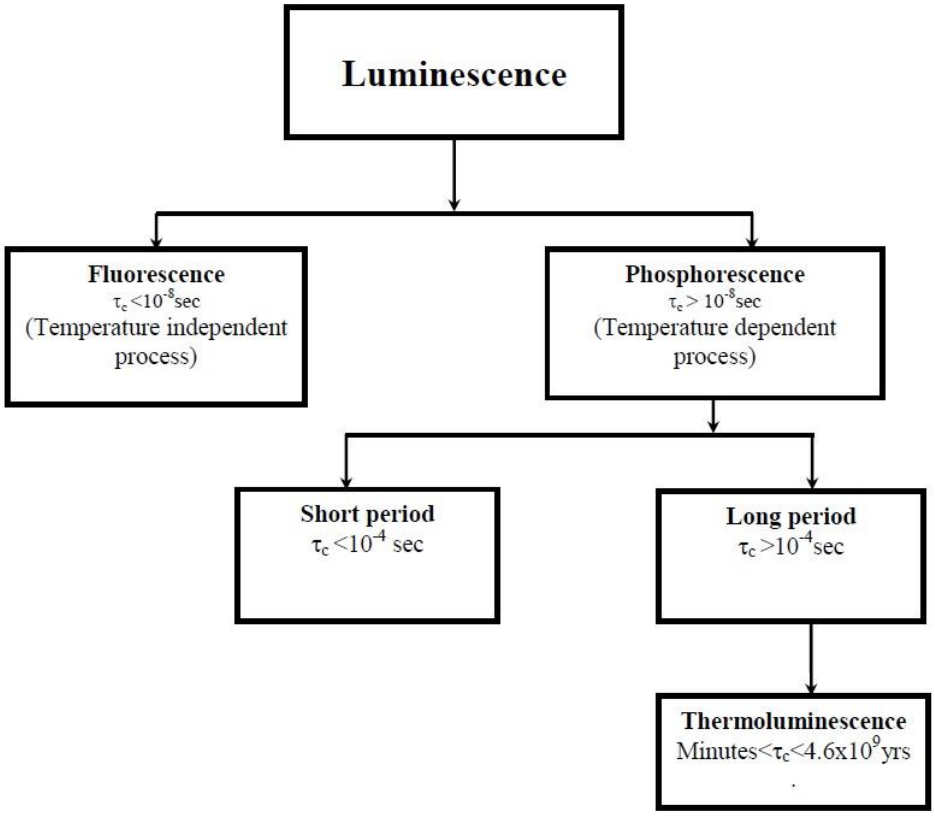


Figure 1.1 The luminescence phenomena classification depending on the characteristic time τ_c [16].

1.3 Thermoluminescence (TL)

The definition of Thermoluminescence phenomena (TL) is a luminescence process of an insulator or semiconductor which can be detected when the substance is thermally excited. The TL phenomena distinguished from the light spontaneously emitted from a material which it is heated to forever, also the black body radiation occur when the substance emits red radiation (infra) by increasing the temperature to higher degrees that coincides with increasing of intensity. TL, however, is the thermally induced emission of light after absorption of energy from radiation source. Depending on this definition there are fundamental conditions necessary for the production of TL which are, the substance

must be an insulator or a semiconductor with mention that the metals do not show luminescent properties, the substance must exposure to excitation source (radiation) specific period to absorbed energy and heating the substance is important to achieve emission of light leading to curve named TL glow curve [18].

1.4 Applications of Thermoluminescence

the present researches on TL refer to high applicability in different fields such as archaeology, analysis of defects in solids, radiation dosimetry, geology, forensic sciences, improve quality of some industrial products as glass and ceramics, and semiconductor products; biology and biochemistry for studying the properties (involving different chemical reactions) or contents of proteins and leaves. Moreover, TL has also interesting applications in space science, thermal stimulated luminescence (TSL) photography, radiation physics, petroleum exploration, etc. In this section, the applications of TL for defect analysis in solids and dosimetry are discussed briefly.

1.4.1 Studying defects in solids

There are lots of reports on the effect of impurities on the TL properties of various materials [19-21]. The TL has high sensitivity for effect of impurities or defects within the host material of a given sample and experiments on TL yields give high resolution and important information about properties of the different types of defect present within studied material [22-24]. This includes the position of the defect within the energy gap and sometimes the type of defect itself. In general the impurities excite the localized energy levels inside the forbidden gap, that effect directly on the processing and analyzing of TL. By analysis of TL glow curves, it can detect the properties of these defect levels. In addition to defect levels produced by external effect such as doping or irradiation, there are also those due to defects, such as lattice vacancies and interstitials inveterately present in the material. The presence of this type of imperfection in many materials is also important for the TL process. Recent research on defect analysis in various materials focusses on the determination of the position of the defect (trap) level just beneath the edge of the conduction band [25-27]. This can be achieved through analysis of TL glow curves by choosing various methods such as heuristic method, initial rise method, heating rate method, peak shape method and isothermal decay method.

1.5 Thermoluminescence dosimetry (TLD)

The TLD is one of the important application of TL and the first experiment was in 1953. After test atomic weapon LiF used to determine amount of radiation [22]. The competence of LiF for radiation dosimetry is mainly because of its high sensitivity and it was used as small pellets to measure internal radiation doses received by cancer patients treated with radioactive isotopes [28]. Other well-known TL dosimetry (TLD) phosphors in use today include Al_2O_3, $Li_2Ba_4O_7$, and Mg_2SiO_4 [29]. The absorption of radiation increases the level of TL observed from a given sample by filling the localized energy levels with trapped electrons while the absorption by heating to reduce the numbers of trapped electrons by de-trapping them. That means, the intensity of TL from the sample is the rate to the competition between filling traps by radiation and emptying traps by thermal excitation or heating. Depending on the relativity relation between intensity of TL and amount of absorbed energy from radiation source, the TL can used as a technique to measure of radiation dosimetery. It is necessary whether a material is suitable for dosimetric application or not, investigation of its TL properties with increase external radiation dose (ultra-violet, x-rays, β-rays, γ-rays, etc) is very important. In some TLD phosphors, the TL intensity grows linearly with dose [29]. In most materials used in radiation dosimetry, many different degrees observed of deviation from linearity, superlinearity (where the intensity growth is more than linear) and sublinearity (where the intensity growth is less than linear) can be observed from the TL response of a given TLD phosphor with dose [30, 31]. The other applications of Thermoluminescence can be shown in figure 1.2:

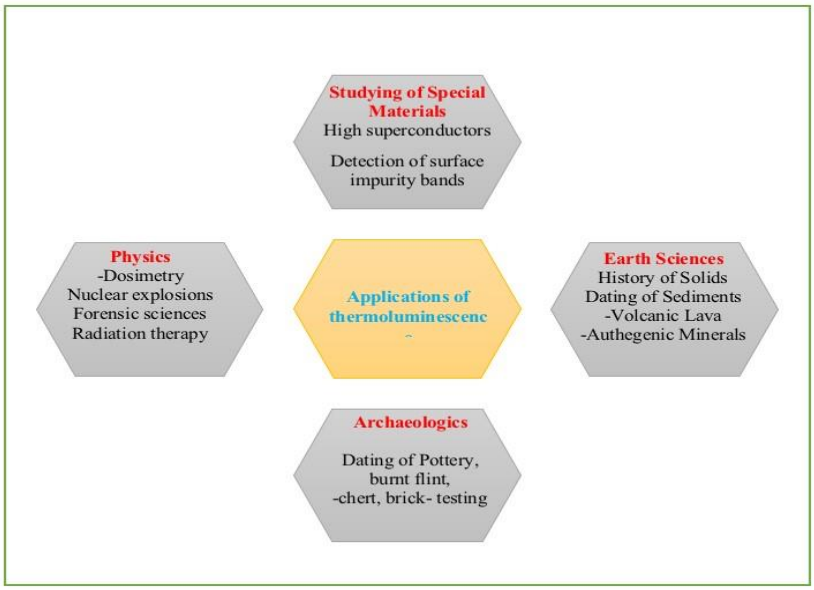


Figure 1.2 Applications of Thermoluminescence [34].

CHAPTER 2

THERMOLUMINESCENCE BASIC THEORY AND MECHANISM

To understand thermoluminescence phenomena, the process can be divided into two steps. First step is the change system from equilibrium state shown in figure 2.1 to non-equilibrium state after absorption energy from UV or external radiation source as shown in figure 2.2. In this part storage energy causes production of electron-hole pairs and trapped by centers inside band gap energy which located between valance band (VB) and conduction band (CB). These centers are due to existing impurities or radiation induced defects. The existence of impurities in the crystals lead to two types of defects called electron trap and hole trap and localized in band gap energy, close to conduction band and valance band respectively. In this step energy stored and electron-hole centers created because of the excitation from external radiation source as in figure 2.2.

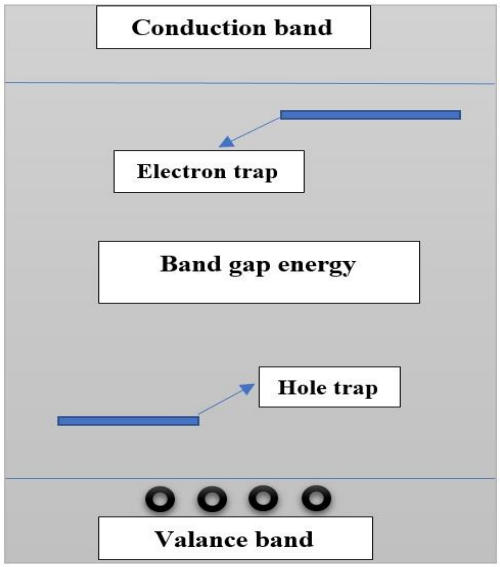


Figure 2.1 The equilibrium case of energy-levels

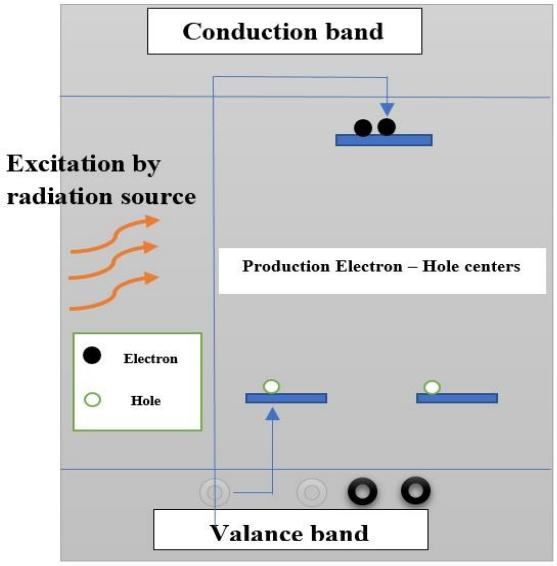


Figure 2.2 The excitation case of energy-levels in the first step of thermoluminescence mechanism

Then the second step is return to equilibrium case by releasing energy as photons beam with thermal excitation as shown in figure 2.3. In other words, thermoluminescence (TL) is the thermally induced emission of light after exposure to excitation source and absorb energy [32]. In the heating part as temperature is increased, the electrons in the electron traps are released to CB. After that, the electrons become free and have two probabilities tracks, either re-traps again or recombine with the hole located in the hole traps. When the recombination happened the results are emission of photons. In this case hole trap can named recombination center.

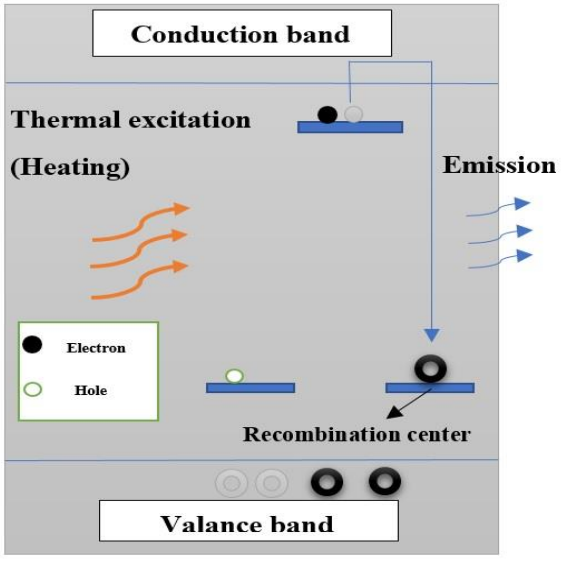


Figure 2.3 Releasing energy and return to equilibrium case in the second step of thermoluminescence mechanism.

2.1 Thermoluminescence Glow Curve

The TL glow curve is diagram of thermally emitted light (releasing energy) and the represent of the function between intensity and temperature [32]. The glow curve consist of one individual TL peaks and sometimes it may overlap as shown in figure 2.4.

The model of the TL glow curve may depend on the spectral response of the device which has a high sensitivity of light, the emission of light don't occur after cooling and heating unless the sample absorb energy during exposure to radiation source again. The distinct peaks in TL glow curve are found at different temperatures, which depending directly on the depth of electron traps in the crystal.

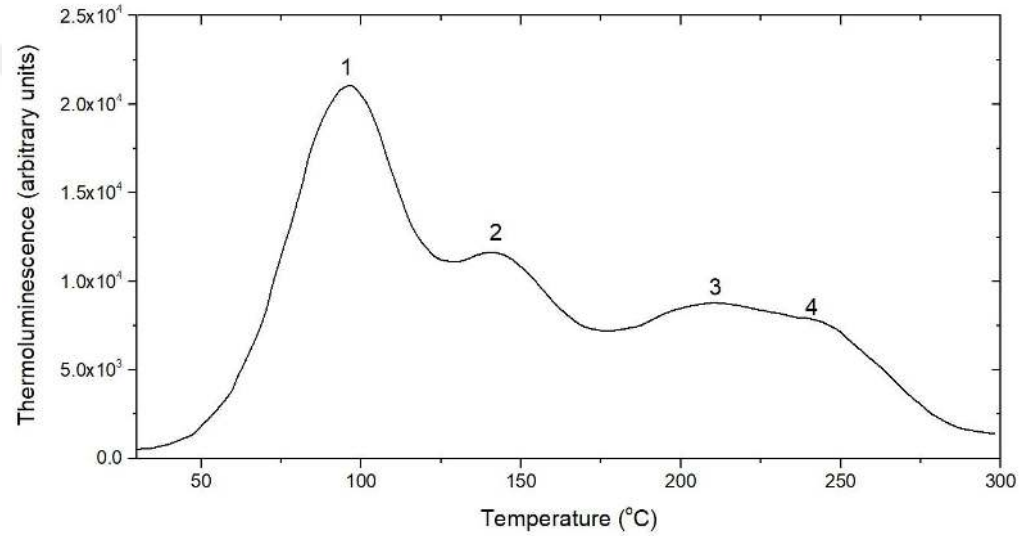


Figure 2.4 An example of TL glow curve of calcite mineral studied in the present study with several peaks

2.2 Simple Model of TL

the ideal and simple model to explain TL mechanism is two model levels such as in pure crystals in semiconductor and insulator, this levels located below bottom of C.B and above of top V.B as in figure 2.5. The levels indicated by T and R are empty in the equilibrium case, localized above and below the fermi level E_f, respectively. R level can represent a hope traps when the system excited and represent a recombination when the system heated, respectively. When the system excited by radiation source and absorption energy higher than band gap $h\upsilon > E_g$ leading to transition a, production electrons active and excited to conduction band (C.B) and holes in valance band (V.B).

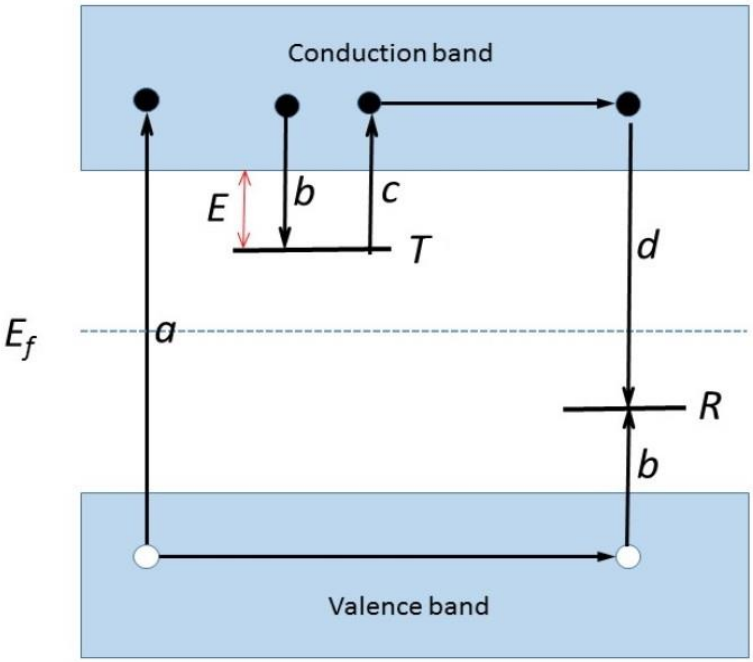


Figure 2.5 Simple model of energy levels in pure crystals with transitions: (a) generate pairs of electron – hole (e-h), (b) trapping of generated pairs e - h, (c) releasing electrons by thermally excitation, (d) recombination of pairs e-h and achieve emission of light. Black circles are electrons, white circles are holes. T is refer electron trap, R is refer to recombination center, E_f is Fermi level located in the mid of band gap, E_g is energy of band gap [34].

Two possibilities for this charge carriers, become trapped or recombine with each other that called direct recombination if happen, resulting energy which may induced other luminescent center sometimes that coincide with process of recombination. The luminescent center returns to the equilibrium case under the emission of light. When the time of emission of photons in the direct transition less than (10^{-8} s) called radioluminescence. in the semiconductors and insulator materials high percentage of pairs (e - h) are trapped in the T and R levels respectively, as in transition b.

Arrhenius equation give an information about possibilities to releasing an electron from trap level T per unit time. 2.1:

$$p = s \exp\left\{-\frac{E}{KT}\right\} \qquad 2.1$$

Where p is the possibility per unit time. The factor s is attempt-to-escape frequency from trap, is called frequency factor. The s factor independent of temperature the simple model, and constant related with lattice vibration frequency, between10^{12}-10^{14} s^{-1}. E is called trap depth refers to the trap depth, the energy necessary to excite system by mean excite an electron from the trap to the conduction band (as shown in Figure. 2.5). k is

Boltzmann constant equal (8.617×10^{-5} eV/K), and T is applied temperature in kelvin unit. The electrons trapped will stay much more time if the introduced energy not enough to release them at the beginning of irradiation that means the depth of trap level higher than of value KT_0 (T_0 is initial temperature) making the essential concentration of electrons in the trap levels T. Because of the electrons and holes generated in pairs and recombine in pairs, the essential concentration of holes will be also in recombination levels R. [34].

Increasing the temperature region above initial value T_0 results high probability of releasing electrons from traps levels into conduction band. That make the charge carrier flowing and leaving through conduction band in the system until pairs achieving recombination phenomena (e - h) in recombination center R. Return to equilibrium case leaves the center in one excited upper level results emission of photons which are coincide with return to ground levels and then consider the TL phenomena is happened.

2.3 First - order kinetics (Randall and Wilkins)

In 1945 assumed a mathematical expression for a peak obtained in the TL glow curve, and based on the energy band model, known a first-order kinetics [4]. If the temperature and number of trapped electrons in the trap levels are still constant, the n concentration will decreases with time t that make to write:

$$\frac{\mathrm{dt}}{\mathrm{n}} = -\mathrm{pn} \qquad 2.2$$

Integrating equation 2.2 can obtains:

$$n = n_0 \left[-se^{\left(-\frac{E}{KT}\right)}.t \right] \qquad 2.3$$

Where $n_0$is the number of trapped electrons at the initial time t_0=0, by consider assumptions:

- No electrons are released from the trap, when the TL material irradiated in low enough temperature.
- In recombination centers, the luminescence efficiency is no dependent on temperature.
- The recombination centers and concentrations of traps are no dependent on temperature.
- In the conduction band, the life time of the electrons is teeny.
- Negligible re-trapping during the heating stage.

At constant temperature, the intensity of luminescence emission becomes directly proportional to the ratio of release of electrons from the trap $\frac{dn}{dt}$:

$$I = -\frac{dn}{dt} = C.p.n = C.n.s.e^{-\frac{E}{KT}} \quad 2.4$$

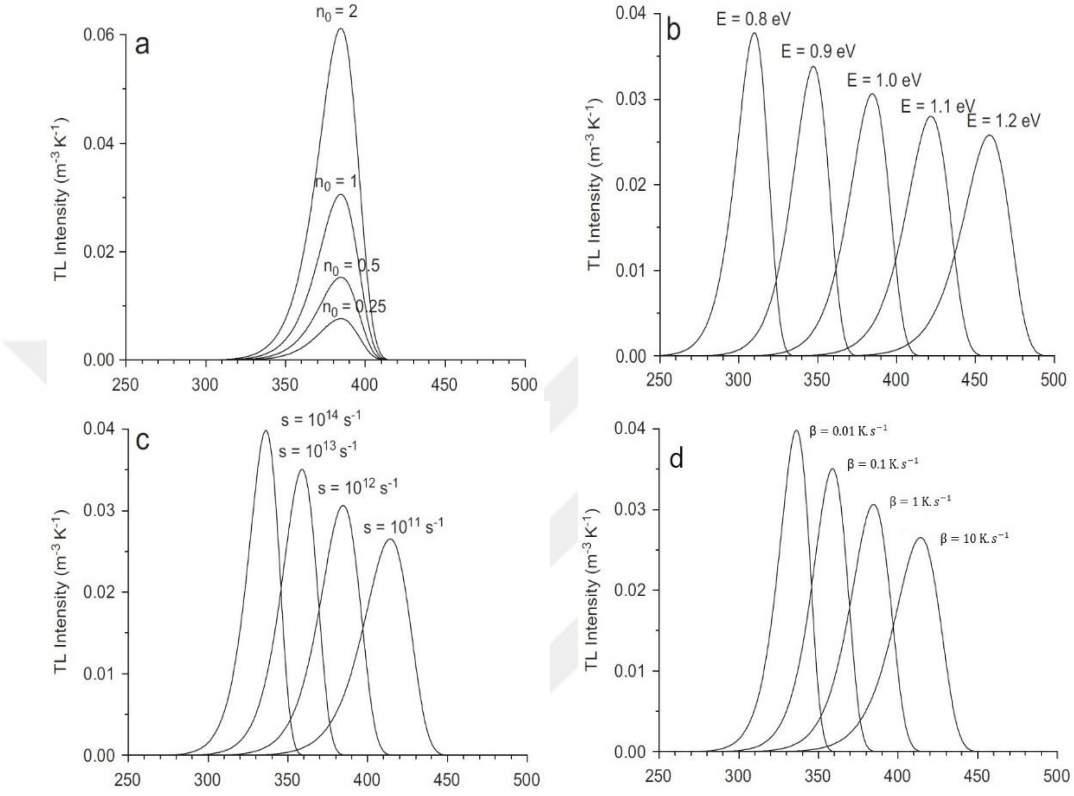


Figure 2.6 Properties of first kinetic-order thermoluminescence (TL) equation 2.4 effected by; (a) trap depth (E_a), (b) concentration of trapped charge carriers (n_o), (c) the escape frequency (s), and (d) the heating rate (β). Parameter values: ($n_0 = 1m^{-3}$) (E=1eV) ($s=1\times10^{12}s^{-1}$), of which one parameter is varied while the others are kept constant, and (β =1 K/s) for (a, b, and c) [34].

2.4 Second – order kinetics (Garlick and Gibson)

Garlick and Gibson assumed in phosphorescence that two probabilities for a free charge carrier either recombination or being trapped within a recombination center. The term of second order kinetic is to explain the behavior charge carrier which re-trapping is present [35]. They proposed that when electron escaping from the trap it has equal chance of either being recombining or re-trapped of with a hole in a recombination center.

$$I = -\frac{dn}{dt} = -\acute{S}.n^2.e^{-\frac{E}{KT}} \quad 2.5$$

Where $\acute{S} = \frac{s}{N}$ called previous exponential factor and constant; it is having dimensions of $cm^3\ sec^{-1}$.

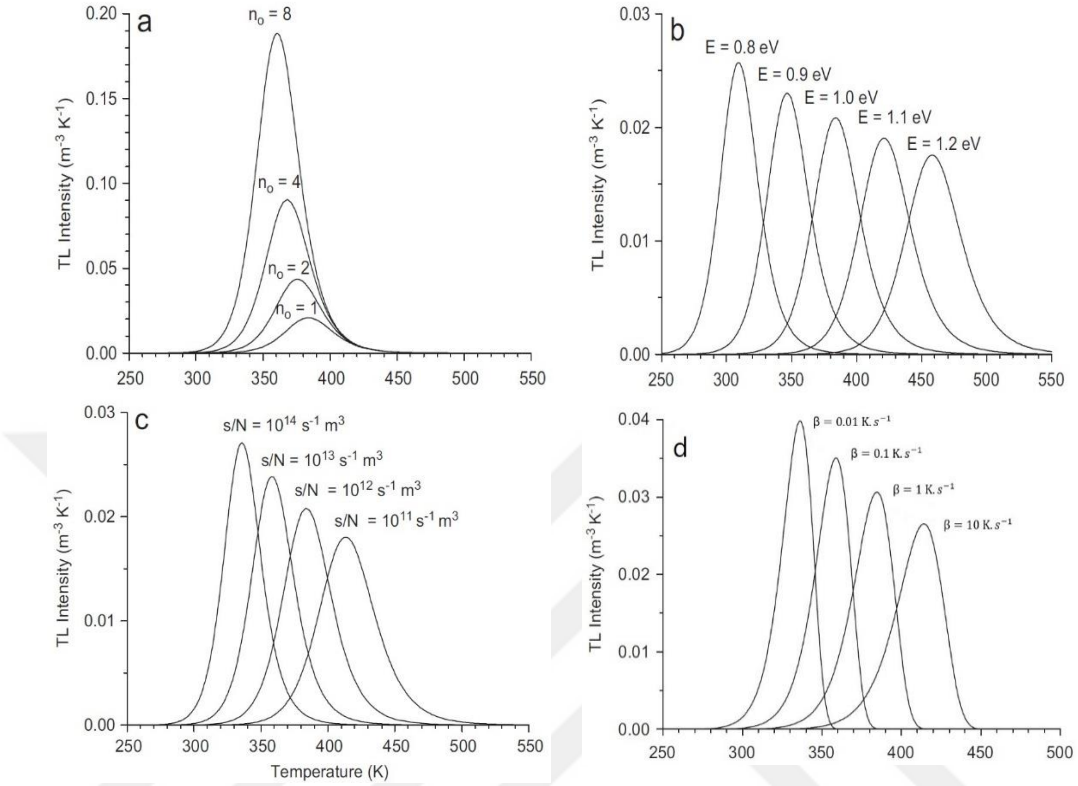


Figure 2.7 Properties of second kinetic-order TL equation 2.5 effected with: (a) trap depth (E_a), (b) concentration of the trapped charge carrier (n_o) after irradiation; (c) (s/N), and (d), the heating rate (β). Parameter values: (n_0 =1m^{-3}) (E =1eV) (s/N =1×$10^{12}s^{-1}m^3$), of which one parameter is changeable while the others are still constant, and (β =1 K/s) for (a, b, and c) [34].

2.5 General – Order Kinetic (May and Partridge)

The first and second order kinetics cannot explain the activity of glow peak, so, in (1964), May and Partridge [36] suggested a general-order expression to cover several cases.

$$I(T) = \frac{s''}{\beta}\, n_0 \exp^{\left\{-\frac{E}{kT}\right\}} \left[1 + (b-1)\frac{s''}{\beta} \times \int_{T_0}^{T} \exp^{\left\{-\frac{E}{kT}\right\}} d\acute{T}\right]^{\frac{-b}{b-1}} \qquad 2.6$$

Where is $s'' = s' n_0\,(b-1)$ with unit s^{-1}, this is general equation and can be changed to first when (b =1) and second-order when (b =2) as explained in figure:

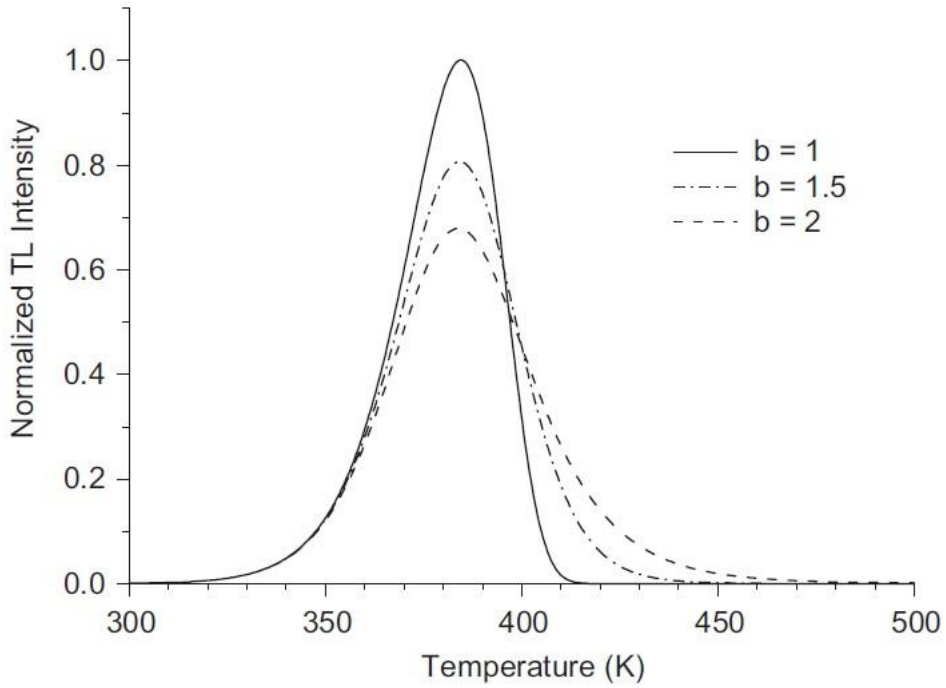


Figure 2.8 Glow curve represent First-order when (b =1) as in dark line, second-order when (b =2) as in dash point line and general-order (b =1.5) as in dash line, with trap depth1 eV, s =1 × 10^{12} s^{-1} and heating rate 1Ks^{-1}. The peaks are normalized to represent the first-order [34].

2.6 Methods studying of Trapping Parameters

After analysis the glow curve of thermoluminescence it can say there are four main parameters, which are conduction energy E_a and frequency factor s (trap parameters), which studied by analysis of properties of the trapping levels T and R. The determination of other two parameters can from experiment from TL signal by choose a specific dose at with constant heating rate β. There are different ways to evaluate this parameters from the TL glow curves [37-41].

It can classify the methods to two kinds depending on the glow curve if isolated or overlap, when glow curve isolated, the experimental methods is good to determine parameters like (Initial Rise Method (IR), Variable Heating Rates Method (VHR), Three Points Method (TPM), Isothermally Decay Method (ID), and Peak Shape Method (PSM). When the glow curve has overlapping peaks it is suitable to use computer glow curve deconvolution Method program, which become basic way to study the parameters from thermoluminescence glow curves [42]. The procedure of (CGCD) is began, by define location of the most accurate peaks in the TL glow curve and then estimate the parameters

E, s, and b by one of the mentioned method, theoretical curve can compute by equation of general-order for b ≠ 1, or equation of first-order for b =1.

In other words, first-order thermoluminescence kinetic:

$$I(T) = n_0 s\, exp^{\left(-\frac{E}{kT}\right)}\, exp^{\left[\left(-\frac{s\,kT^2}{\beta\ E} exp^{\left(-\frac{E}{kT}\right)}\right)*(0.9920-1.620\frac{kT}{E_a})\right]} \quad 2.7$$

Second-order thermoluminescence kinetic:

$$I(T) = n_0 s\, exp^{\left(-\frac{E}{kT}\right)}\ \left[1+\left(-\frac{(b-1)s}{\beta}\frac{kT^2}{E} exp^{\left(-\frac{E}{kT}\right)}\right)*(0.9920-1.620\frac{kT}{E_a})\right]^{\frac{b}{b-1}} \quad 2.8$$

Where, n_0 (m^{-3}) is the density of electrons which trapped in initial time (t = 0), s (s^{-1}) is the frequency factor for both first and the general orders, E_a (eV) is the depth of trap , T (Kelvin) is the absolute temperature, k (eVK^{-1}) Boltzmann's constant, β ($^oCs^{-1}$) is the heating rate and b is the kinetic parameter order.

Gathering peaks and background can produce formula to describe composite glow curve:

$$I(T) = \sum_{i=1}^{n} I_i(T) + a + b\ exp^{(T)} \quad 2.9$$

Where is I(T) the fitted TL glow curve, a is the factor which reflect value of dosimeters infrared and electronic noise for the background.

CHAPTER 3

PREPARATION OF SAMPLES AND EXPERIMENTAL PROCEDURES

3.1 Sample Preparation

All samples were provided from civil engineering department and had been used in the other study of Çanakçı et al. [43]. The samples were natural calcite minerals prepared by BCCP way which means bacterial calcium carbonate ($CaCO_3$) precipitation [43]. Generally calcite is the most diffusion soil carbonite, it is growing in root zones where CO_2 density are high and inherited from calcareous origin source materials [44] the microbial calcite can form by complex biochemical interactions, like the interaction between of B. Pasturii, ammonia and urease. Production of urease depend on the activity of microorganism in alkalophilic soil, this microorganism hydrolyzes urea to produce carbon dioxide (CO_2) and ammonia (NH_3) which make the PH in soil high, subsequently prepare the condition in organic soil to produce calcium carbonite ($CaCO_3$) [46] as shown in figure 3.1. Previous studies show that B. pasteurii has a high potential for urea production, which leads to carbonate production [47-49]. Table 3.1 shows the urease activity for different kinds of bacterial [47]

Table 3.1 The urease productions activity for different bacterial cultures.

Bacterial culture	Urease activity (Urea/ml)
Bacillus pasteurii NCIM 2447	17.5
Bacillus lentus 8773	10
Brevbacterium ammniagenes ATCC 6871	12.5

When the suitable conditions in environment, the urea get its energy from B. pasteurii to produce NH_3 and CO_2, that make the PH in surrounding is high. The three following interaction explain the hydrolysis of urea [47].

Two natural interactions happened in organic soil with presence water, this interactions as described in the equations 3.1 and 3.2, respectively [50]. they convert the NH_3 and

CO_2 to ions of ammonia NH^{4+} and carbonic acid HCO_3, with noting that the ions NH^{4+} responsible about the high value of PH that results ions of OH^- which create an ideal environment for the activity of bacteria and precipitate calcite[43].

$$2NH3 + H2O \longrightarrow 2NH_4{}^+ + 2OH^- \quad 3.1$$

$$CO_2 + OH^- \longrightarrow HCO_3^- \quad 3.2$$

In the solution the calcium ions Ca^{2+} interact with HCO^{3-} and OH^- to produce calcium carbonate $CaCO_3$ as in equation 3.3, the calcium ions come from dissolved calcium chloride $CaCl_2$ [50].

$$Ca^{+2} + HCO_3^- + OH^- \longrightarrow CaCO_3 + H_2O \quad 3.3$$

All chemical interaction process which occurs in the sand matrix is displayed in figure 3.1.

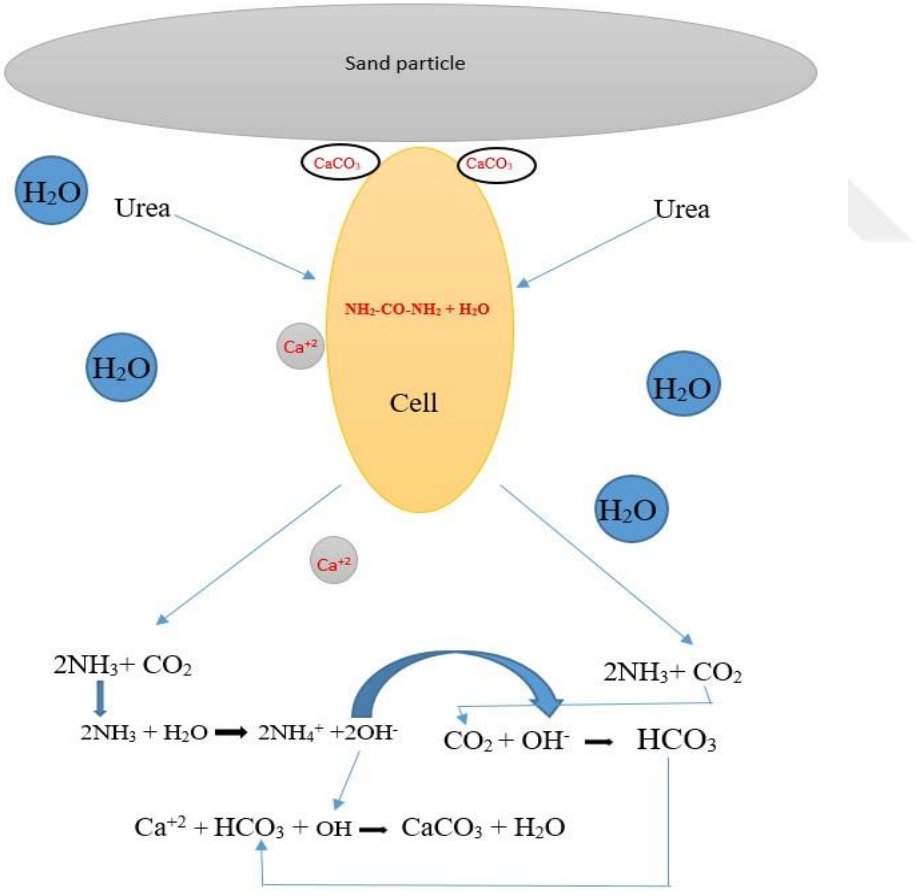


Figure 3.1 Diagram of biological calcite precipitation in the sand [43].

3.2 Experimental Procedure

The samples were irradiated with beta rays (β-rays) source at room temperature from a calibrated ^{90}Sr-^{90}Y source. The activity of this radiation source is 100 mCi. It is calibrated in 1994. The recommended life-time in laboratory is about 15 years. ^{90}Sr also emits beta particles with high energy from their products (^{90}Sr β-0.546 MeV and ^{90}Y β-2.27 MeV). Beta radiation can be absorbed from air atoms, making intensity decreases with distance very quickly, where the high range of Y90 beta particles in air is close to 9 meter.
The typical strength of a 100 mCi Sr^{90} β-source installed in a 9010 Optical Dating System is 2.64 Gy/minute (0.0438 Gy/Sec). The irradiation equipment is an additional part of the 9010 Optical Dating System which is purchased from Little More Scientific Engineering, UK [51].

Figure 3.2 Radiation sources of beta ray ^{90}Sr - ^{90}Y source (≈ 0.04Gy/s).

After exposure samples to beta radiation source they read out by a Harshaw QS 3500 manual type reader or (TLD reader) which connect to PC, there were installed Win-REMS program drawing TL signals which studied and analyzed [52].

Figure 3.3 Harshaw TLD reader system 3500.

TL glow curves were obtained from room temperature to 400 °C by heating rate from 1 °C.s^{-1} to 5 °C.s^{-1} by linearly increasing, Our irradiation source gives 0.04 Gy per second, the applied dose level on calcium carbonate samples were various between 2.4 Gy to 6.9 kGy. The TL reader diagram is shown in Figure 3.3.

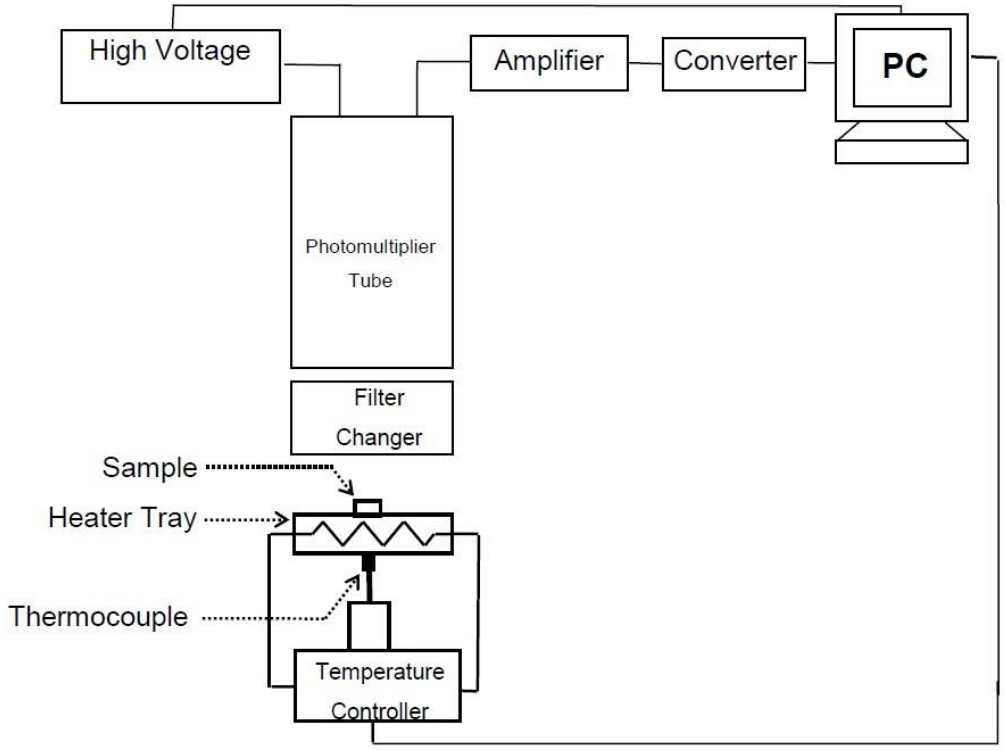


Figure 3.4 Essential scheme diagram of TL reader [18].

A glass filter has been placed in the reader between the photomultiplier tube and planchet to prevent emission infrared from the samples on reader. The device has a sample change drawer for inserting the cup which have powder sample and removing. Nitrogen is set around the area of the planchet to keep its lifetime and get high precision of signs for low exposure, also set nitrogen around planchet to remove humidity which formed during intensification through the Photo Multiplier Tube (PMT).

Also the typical time profile use to improve the accuracy of low-exposure reader and keep planchet life, the time profile (TTP) use to define three sectors shown in figure 3.5: preheat, acquire and anneal, all independent of time, pre-read anneal: variable from 0 to 1000 sec, linear slope: variable from 1°C to 50 °C per second, post read anneal variable from 0 to 1000 second, and the temperature (pre- read anneal variable from room temperature to 200 °C, post-read anneal can arrive to 400 °C.

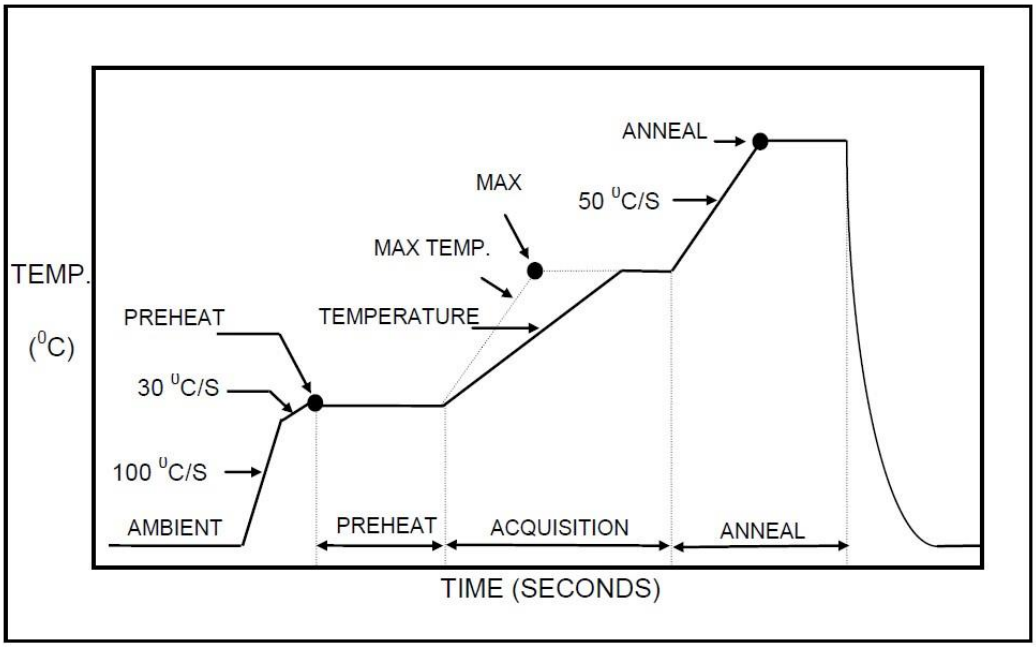


Figure 3.5 Typical time temperature profile (TTP) [64].

CHAPTER 4

RELATED STUDIES

There are many kinds of calcite minerals in natural area, have colors red, gray, green, blue, brown, yellow and orange, but when its color close to white that refer to high purity, also the calcite mineral can conduct by many chemical interactions or chemical precipitation like samples which conducted by bacterial calcium carbonate ($CaCO_3$) precipitation in organic soil [43], investigation of TL properties has been studied for many kinds of calcite by many different radiation sources.

In 2009, T. Dwijen Singh and S. Dorendrajit [53] studied parameters for green calcite samples. The TL glow curves obtained after exposure to gamma rays γ. The experimental results show three main peaks located around 413, 503 and 603K. The trap depth and order of kinetics are determined using the computerized glow curve deconvolution, the TL glow curves in all results tend to represent non-first order kinetics.

In 2015, Yassin A.R. [54] studied thermoluminescence dosimetry using natural calcite. The study was done to investigate the feasibility for use in gamma radiation dosimetry, The peak appeared at temperature of 283 ^oC on the TL glow curve was found to have a linear response to the doses over the range of 0.05–1000 Gy, especially after being annealed at 600 ^oC for 5 h before irradiation. Accordingly. the natural calcite is nominated as a good dosimeter for many dosimetric applications.

In 2006, R. G. Yildirim and E. Gün [55] studied thermoluminescence Properties of Calcite ($CaCO_3$). TL glow curve characteristics of samples of annealed at different temperature 400, 450 and 500 ^oC and unannealed has been studied after beta irradiation between dose levels 0.9 Gy and 864 Gy. The glow curves of annealed and unannealed samples show main peaks at 115, 254 and 380 ^oC, the measurement of the dose response and fading process are very useful in radiation dosimetry and archeological dating. The dose response for all peaks showed similar pattern, they showed strong linearity.

In 2003 V. Ponnusamy et al. [56] studied kinetics of thermoluminescent calcite. the thermo-stimulated luminescence (TSL) glow curve characteristics of five, blue colored calcite samples, the glow curves of annealed (600 °C) and un-annealed samples, irradiated with gamma dose of 500 Gy show three peaks at 145, 255 and 345 °C, respectively, all the samples were annealed in air atmosphere, in the temperature range from 200-700 °C with an interval of 50 °C, for 1 h duration, the kinetic parameters such as trap depth(E_a), frequency factor (s) and order of kinetics (b) evaluated by using partial heating, peak shape, isothermal and initial rise methods. The trapping centers are not affected by the annealing procedure and it follows second-order kinetics.

In 2014, J.M. Kalita and G. Wary [57] studied thermoluminescence study of X-ray and UV irradiated natural calcite and analysis of its trap and recombination level. Thermoluminescence (TL) of natural light-orange color calcite ($CaCO_3$) mineral in micro-grain powder form was studied at room temperature X-ray and UV irradiation under various irradiation times. TL was recorded in linear heating rate (2 K/s) from room temperature to 523 K. Trapping parameters such as depth of trap , order of kinetics, frequency factor have been evaluated by Computerized Glow Curve Deconvolution technique, Three electron trap centers estimated at depth 0.70, 1.30 and 1.49 eV from the conduction band. Due to simultaneous excitation of electrons from valence band to the trap level, TL intensity was found to increase with UV irradiation time.

In 2014, H. Toktamiş et al. [58] studied thermoluminescence of calcite extracted from natural sand used in making roasted chickpea. Three distinct TL peaks were observed at 130 °C, 230 °C and at 330 ^{o}C with small intensity. The dose response of the sample was carried out between 2.4 Gy and 9.8 kGy, linearity in dose response is observed for the values up to 0.6 kGy and above 0.6 kGy linearity is not preserved and dose response becomes sublinear, and the best reproducibility is obtained when the samples are annealed between 400 °C and 600 °C, thermoluminescence (TL) properties of the green emission band of calcite and concluded that it has good TL response within the γ- ray dose range of 0.01–104 Gy.

In 2016, J.M. Kalita, and G. Wary [59] studied the x- ray dose response under title "X-ray dose response of calcite-A comprehensive analysis for optimal application in TL dosimetry". The effect of various annealing treatments on dosimetric characteristics of orange calcite ($CaCO_3$) mineral has been studied. The TL from the samples were recorded

within temperature range (300–520 K) by the TL reader with (2 K/s) heating rate. Analysis on the dose response shows that the 573 K annealed sample showed sublinear dose response from 10 mGy to 1 Gy, the fading and reproducibility of this sample were good. This sample showed very less fading and good reproducibility, after X-ray irradiation post-annealing at 340 K for 6 min provides linear dose response from 10 mGy to 3.60 Gy, very less fading and good reproducibility. Analysis of TL glow curves confirmed that the 1.30 eV trap center in calcite crystal is the most effective trapping site for dosimetric application.

In 1989, S. Tatumi et al. [60] studied thermoluminescence dating of calcite deposits in a Brazilian cave. The thermoluminescence of secondary calcites found in a Brazilian cave was investigated. The glow peak observed at 240 °C was fitted with second order kinetics. This result indicates that the peak is stable enough to be used for dating the calcite samples investigated in the present work and no correction due to the spontaneous decay is needed.

In 1998, M. Urbina et al. [61] studied the dose rate effect in calcite. The TL signals in both irradiation types are initially supralinear but then becomes linear up to at least 7 kGy. The glow curves of gamma-irradiated calcites consist of peaks near 130 °C, 250 °C and 350 °C, TL glow curves of beta-irradiated samples show similar behavior to previous one but now the maximum of TL glow curves is placed at lower temperature, near 280 °C with shoulder at 350 °C.

CHAPTER 5

EXPERIMENTAL RESULTS

5.1 Chemical Composition of Calcite

In this chapter an explanation about compound of Calcite (Calcium carbonate) is given, the chemical structure of $CaCO_3$ is shown in figure:

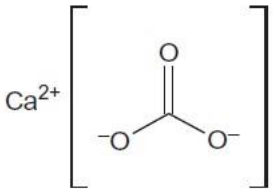
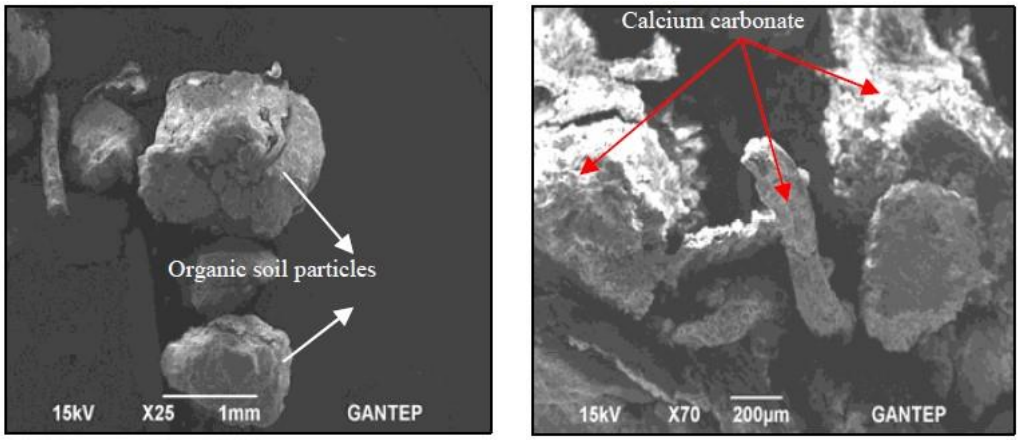


Figure 5.1 Chemical structure of $CaCO_3$.

Table 5.1 Compositions of $CaCO_3$

		%		
Compound	Molecular Formula	C	Ca	O
Calcium carbonate	$CaCO_3$	12.00	40.04	47.96

The Molecular Weight: 100.09 g/mol, it has Hexagonal Crystal. The SEM images of the organic soil before and after BCCP are given in Figure 5.2 a and b. The images reveal $CaCO_3$ crystals on the surface of the organic soil particles [43].



(a) (b)

Figure 5.2 Organic soil particles a) before treatment b) after treatment [43].

In this study four experiments are achieved: Dose Response, Heating Rate, Reproducibility or Cycle of Measurement and Fading, and also the kinetic parameters were calculated. In all experiments samples weighted about 15mg were used at room temperature.

5.2 Dose Response

The study of dose response was done at 1°C/s of heating rate. The all TL glow curves by different dose levels are shown in Figure (5.3.a and b). Experimental results showed that the position of peak temperatures between 2.4 Gy and 576 Gy dose levels is stable as shown in figure 5.4, with higher dose levels than 576 Gy new TL peak around 340ºC is appeared and the low temperature TL peak around 90ºC is disappeared as shown in figure 5.3 b. More accurately TL glow curves obtained between 2.4 Gy and 576 Gy applied dose levels show that there are four peaks located around 90, 140, 210 and 240 ºC. The shape of TL glow curve is not affected under this range of applied dose levels. As shown in figure 5.3b, the TL peak at 90 ºC is completely disappeared, the TL peaks at temperatures 210 ºC and 240 ºC are converged and merged in one peak at temperature ~225 ºC, that accompanied by appear new peak at temperature 340 ºC when applied higher dose levels. The relation between TL intensity and applied dose for the peaks 210 ºC and 240 ºC is linear between 140 Gy and 2.3 kGy as shown in the area under TL glow curve figure 5.5.

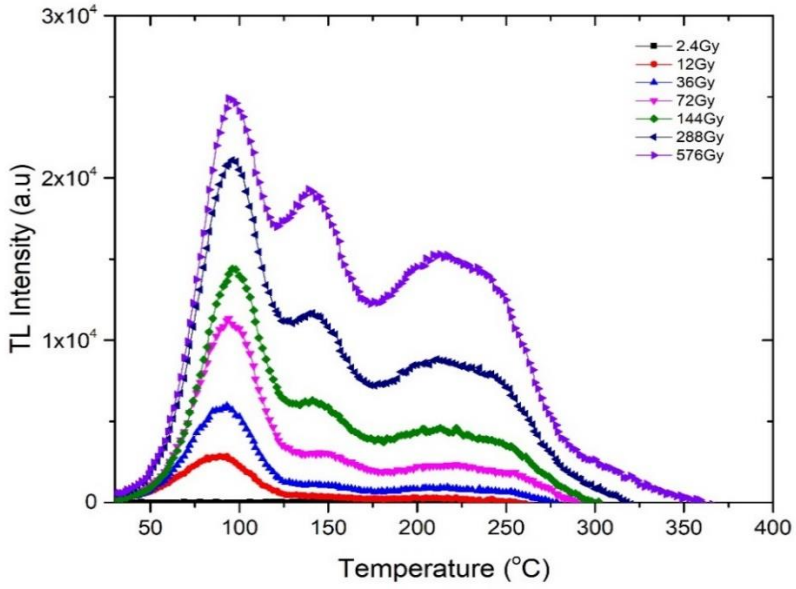


Figure 5.3a TL glow curves of calcite mineral applied dose levels (2.4Gy to 576 Gy) with heating rate (β =1ºC/s).

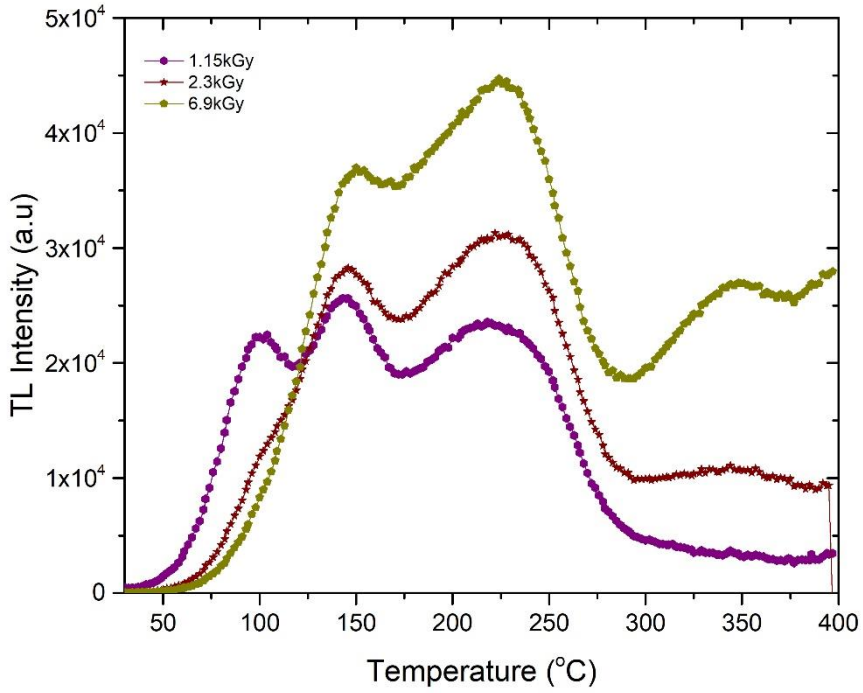


Figure 5.3b TL glow curves of calcite mineral applied dose levels (1.15 kGy to 6.9 kGy), heating rate (β=1°C/s).

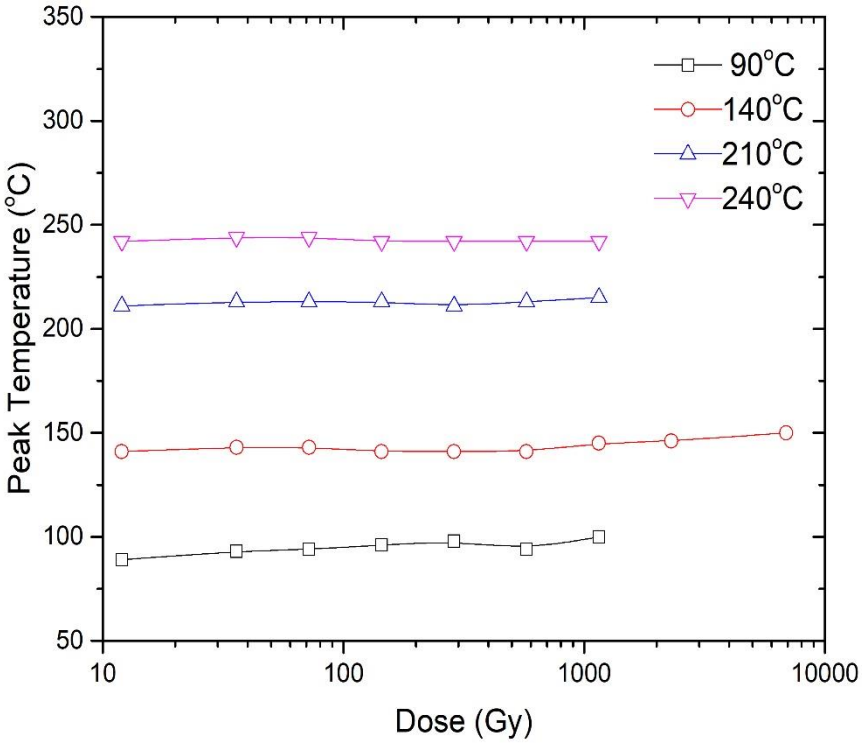


Figure 5.4 The effect of applied dose on TL peak temperatures.

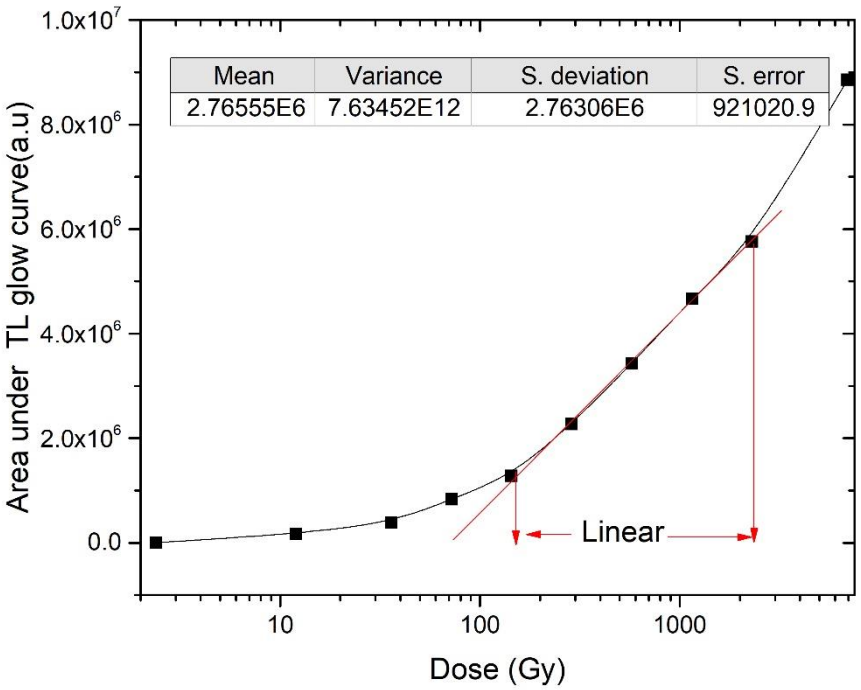


Figure 5.5 Area under TL glow curve.

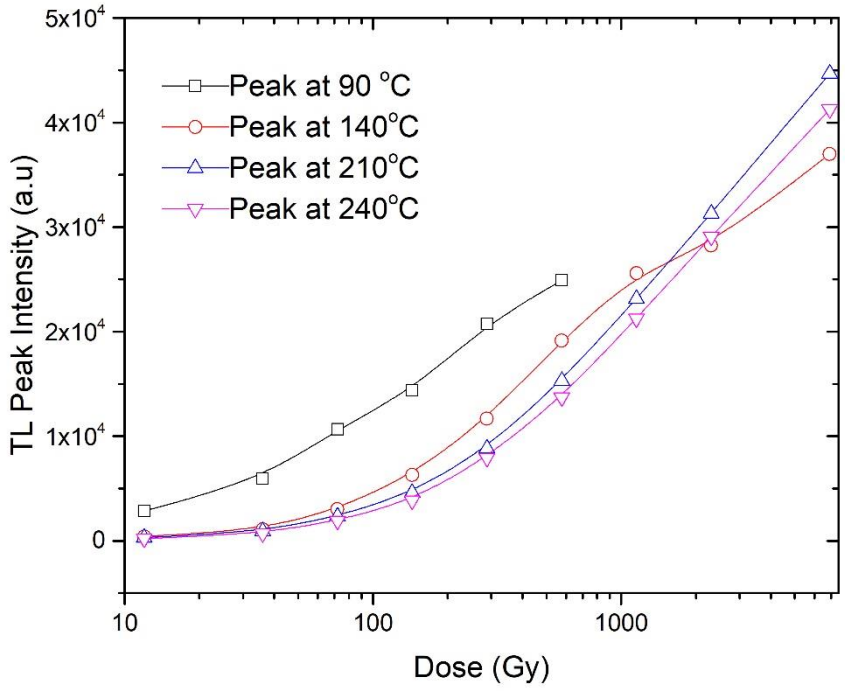


Figure 5.6 The TL peak intensities located around 90, 140, 210 and 240 ºC.

Figure 5.6 shows the variation of TL peak intensities for four peaks as a function of applied dose, generally the TL peak intensities increase linearly between 140 Gy and 2.3 kGy.

5.3 Heating rate experiment

It is necessary to study of the heating rate effect on the TL properties of the calcite mineral sample, because the heating rate is a dynamic factor which effect on the characteristics of TL glow curve. As the heating rate increases gradually, the peaks of glow curve will shifts to higher temperatures and the TL intensity will be decreased significantly [62-63]. After irradiating all samples about 36 Gy, the calcite minerals were readout at five different heating rates of 1, 2, 3, 4 and 5 °C/s. As a result no extra distinct peaks were produced with variation of heating rate, in other words there were no changes in the shape of the TL glow curve as in figure 5.7.

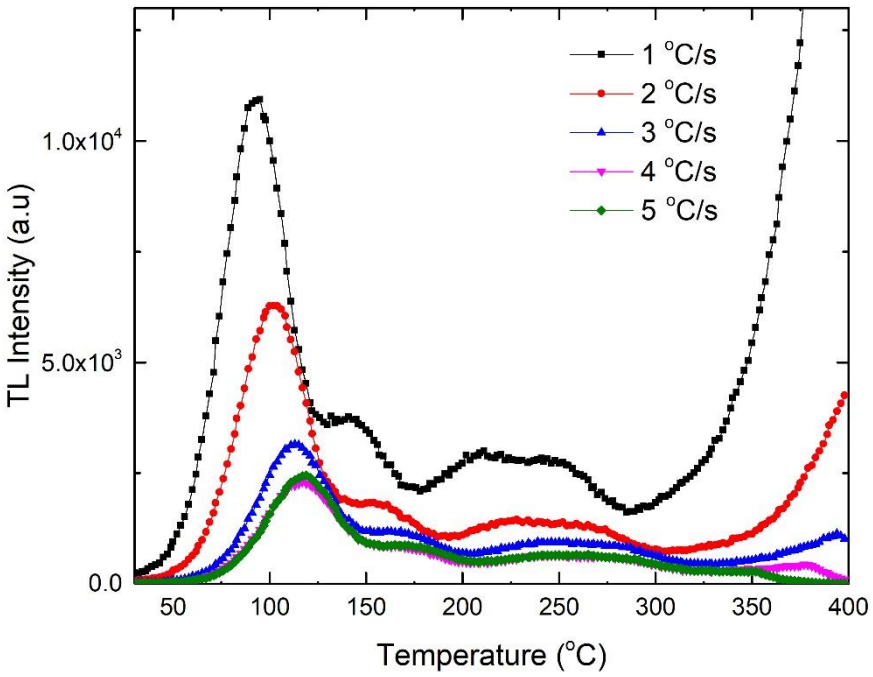


Figure 5.7 TL glow curve variation as a function of heating rate.

More accuracy, the TL peak intensity at 90 °C dramatically decreases, other TL peak intensities decrease slowly as shown in figure 5.8. Table 5.2 shows the TL peak intensities of four TL peaks at different heating rate. The TL peak located around 90 °C shifted to

higher temperature region about 28 ºC between 1 and 5 °C/s heating rate. The shifts of TL peaks located around 140 °C, 210 °C and 240 °C are 26 ºC, 33°C and 47 °C, respectively as shown in figure 5.9 and table 5.3, all these changes happen with keeping constant shape of TL glow curve for calcite.

Table 5.2. Values of intensities located around 90, 140, 210 and 240 ºC with different heating rate.

Heating rate	Peak at 90 ºC	Peak at 140 ºC	Peak at 210 ºC	Peak at 240 ºC
1	10836	3779	2997	2834
2	6274.3	1836	1453.5	1328
3	3151	1184	953.6	850.5
4	2302.5	847.5	634.5	583.5
5	2449.5	869.5	647.5	564.8

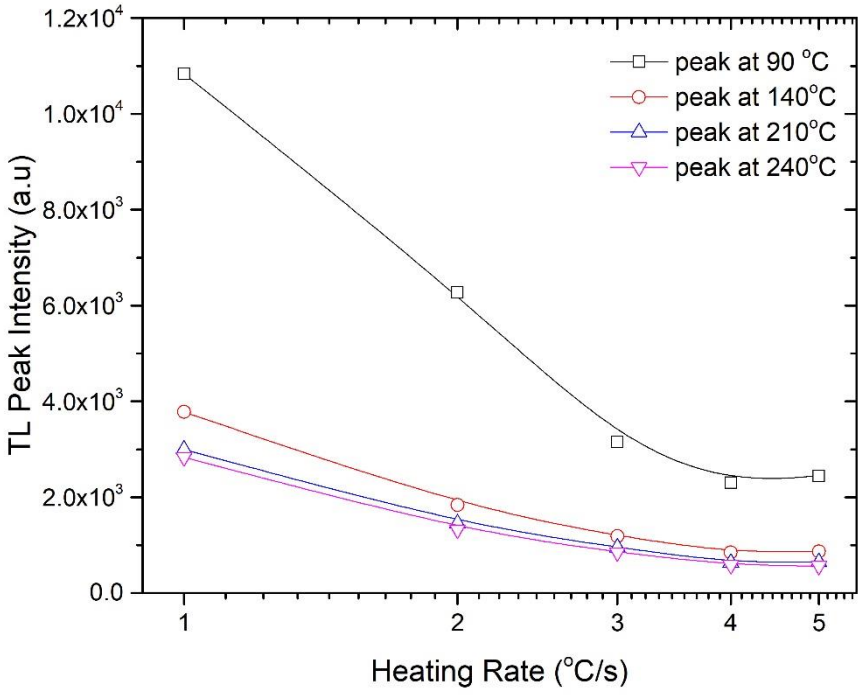


Figure 5.8 The effect of different heating rate on TL peak intensities located around 90, 140, 210 and 240 ºC.

Table 5.3 Values of temperature peaks located around 90, 140, 210 and 240 ºC with different heating rate.

Heating rate	Peak at 90 ºC	Peak at 140 ºC	Peak at 210 ºC	Peak at 240 ºC
1	91	141	211	241
2	100	154	228	265
3	113	161	238	281
4	117	167	242	283
5	119	167	244	289

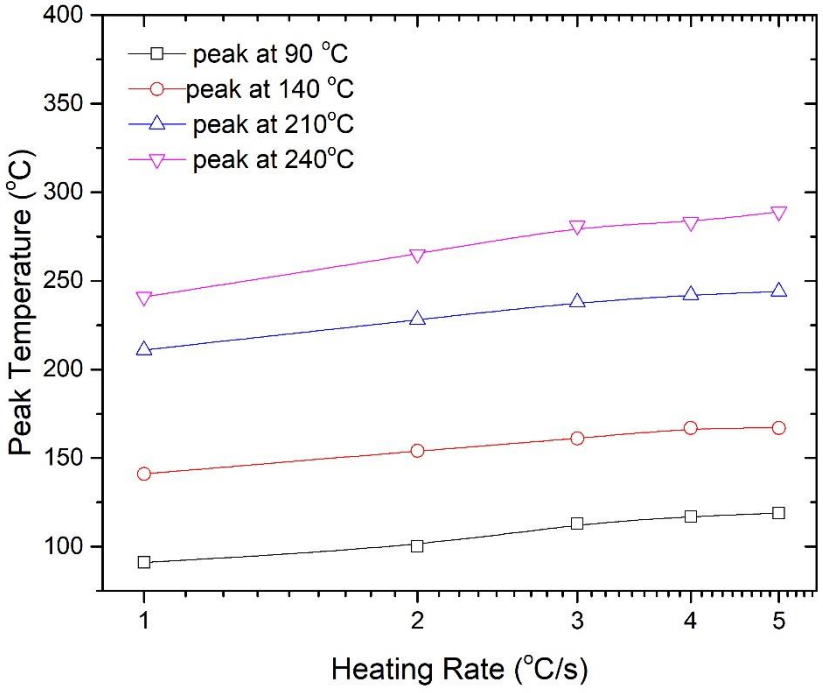


Figure 5.9. The effect of different heating rate on temperature peaks located around 90, 140, 210 and 240 ºC.

In figure 5.10 the area under the TL glow curve decreases until 4 °C/s and become stable.

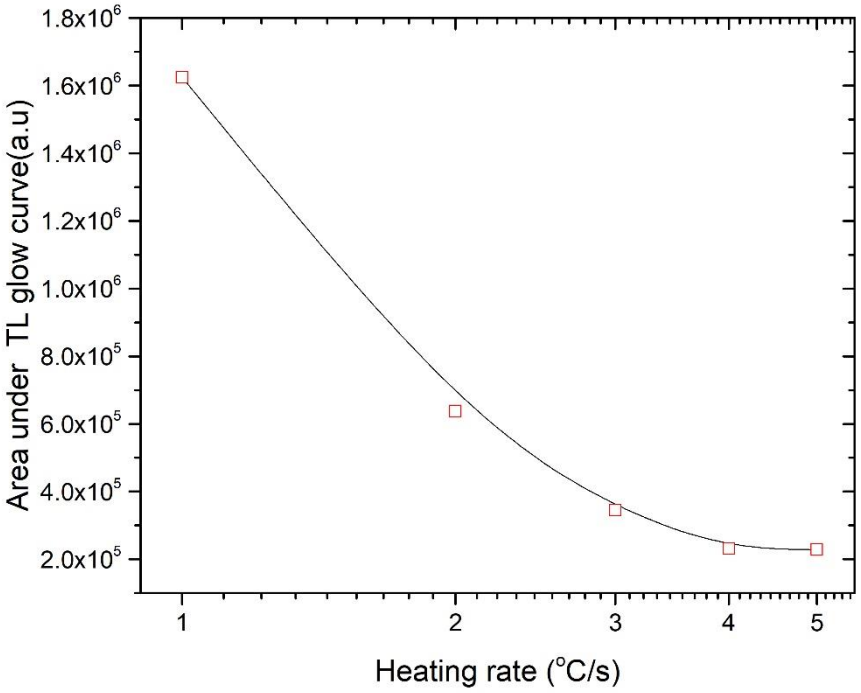


Figure 5.10 The area under the TL glow curve as a function of heating rate.

5.4 Fading experiment

Fading is the loss of stored intensity of thermoluminescene signals, it depends highly upon the depth of traps, when the sample read out from TLD reader. The sample is waited in dark room in the laboratory and irradiated with β-source at 36 Gy. The TL signal is found to be metastable by decreasing after irradiation, which means the signal has faded. In this study a decrease is observed in the TL peak intensity with increasing waiting time. The TL peak intensities at 90 ºC and 140 ºC fade completely after 24 and 336 hours storage time, respectively. No change is observed for other peaks located between 200 and 250 ºC as shown in figure 5.11 and 5.12. A stability observed for temperature peaks located around 90, 140, 210 and 240 ºC as a function of waited time as shown in figure 5.13.

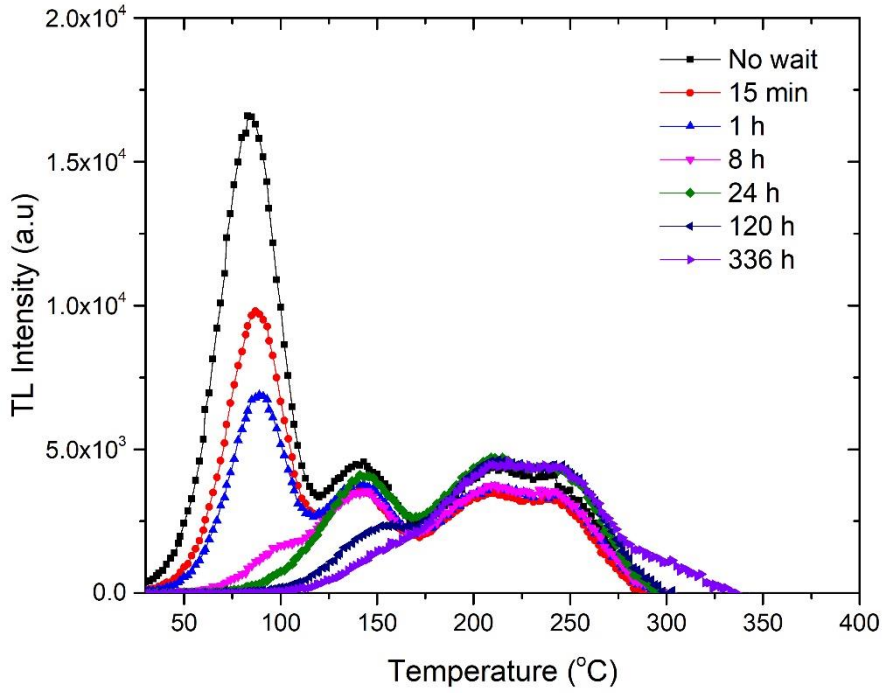


Figure 5.11 The variation of TL glow curve as a function of waiting time.

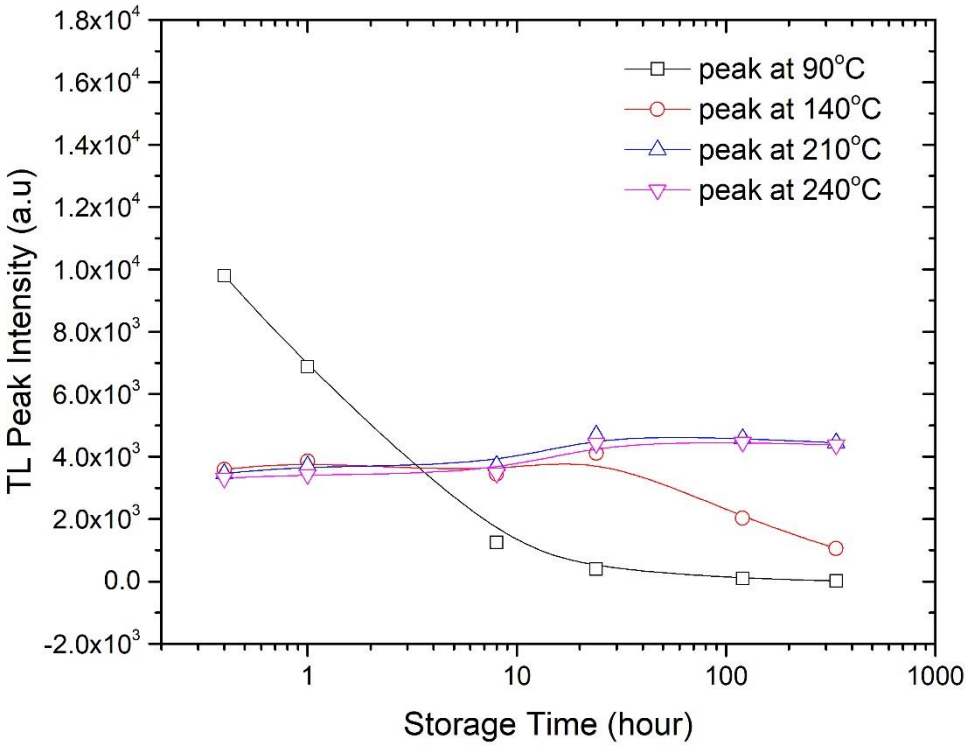


Figure 5.12 The effect of waited time on TL peak intensities located around 90, 140, 210 and 240 °C.

After 10 hours of waited time unexpectable increases was observed in TL peak intensities of peaks around 210 and 240 °C, but this increase is very small called anomalous fading. Anomalous fading is seen when the TL-signal decays significantly, even though it is not expected to do so thermally. It is believed that there are two major causes for this: quantum mechanical tunneling of the trapped charge to the recombination site, and localized transitions which do not take place via the delocalized bands [18].

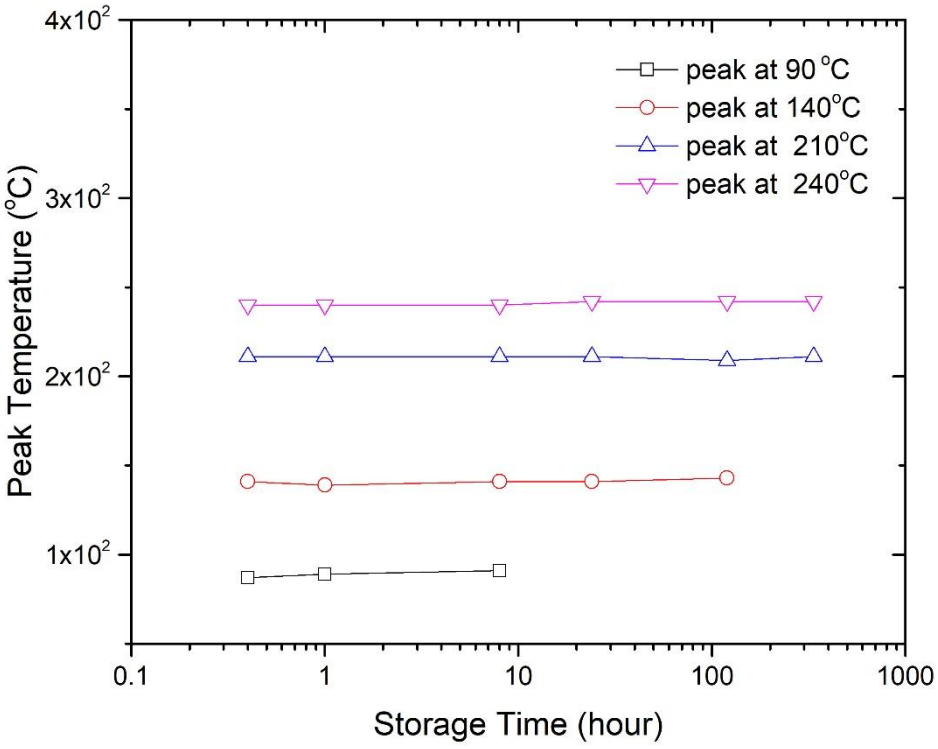


Figure 5.13 The effect of waited time on temperature peaks located around 90, 140, 210 and 240 °C.

The figure 5.14.a and b show that how the area under the peaks changes with increasing waited time. The TL glow curve is divided into two main region which are 30 – 150 °C and 150 – 400 °C. While the area between 150- 400 °C does not change, the area between 30-150°C decreases suddenly up to 100 minutes of waited time. Then no important change in area under the TL glow curve is observed.

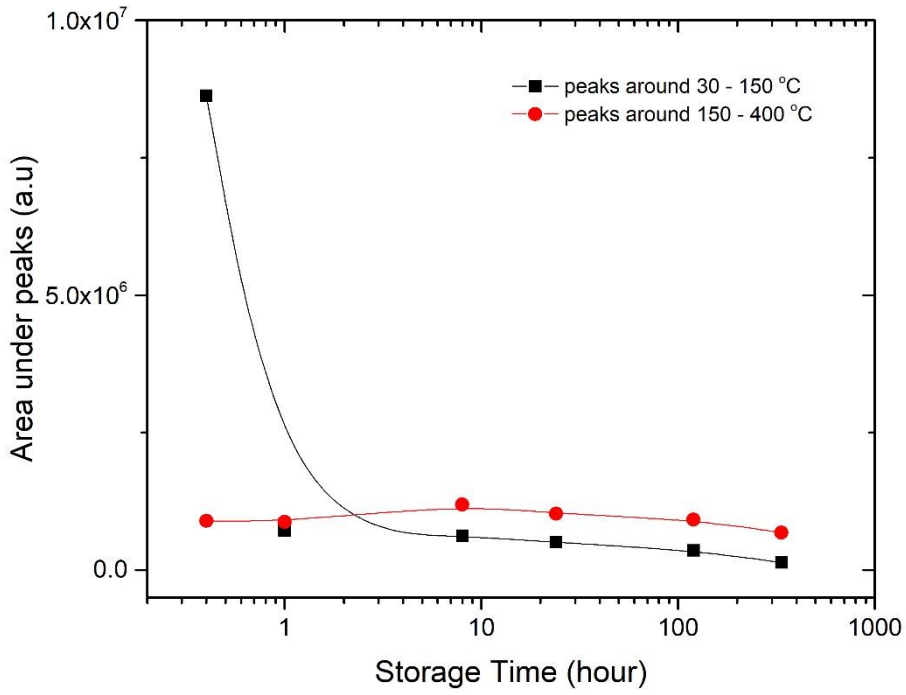


Figure 5.14.a. Area under TL glow curve as a function of waited time, divided to two parts: from 30 to 150 ºC and from 50 to 400 ºC, respectively.

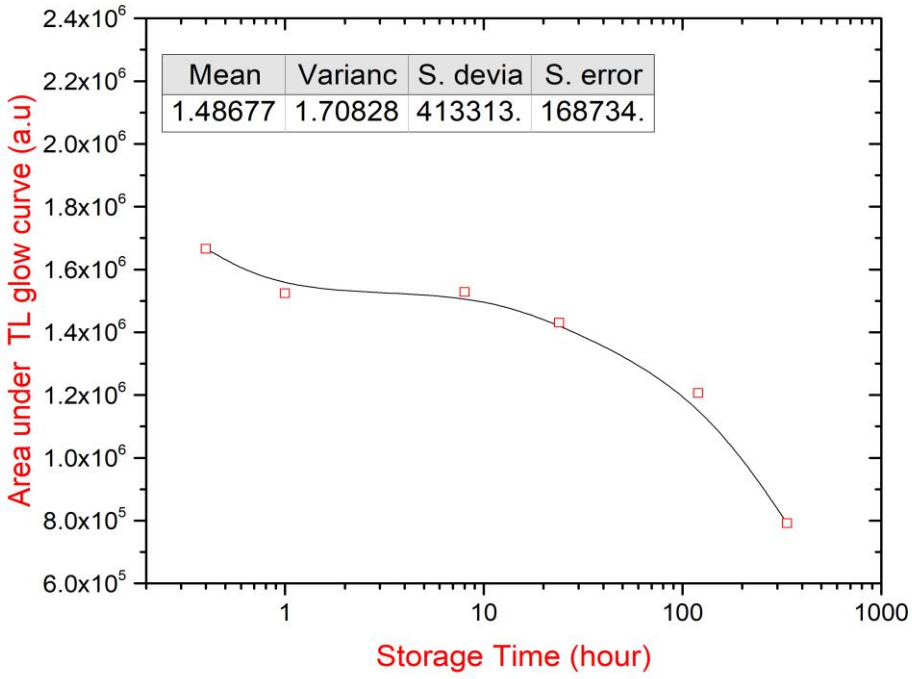


Figure 5.14.b Area under TL glow curve as a function of waited time.

5.5 Reproducibility experiment

Reproducibility is also known as cycle of measurements, refer to sensitivity of TL glow curve. A high similarity percentage of TL signals is the scale to classify as a good reproducibility. In this study the sample irradiated at 36 Gy and read out by TLD reader at 1°C/s. this cycle is repeated 8 times. As a result, there are no extra distinct peak produced at the end of each cycle as shown in figure 5.15. The TL peak intensities located around 140, 210 and 240 ºC are more stable than the TL peak intensities located around 90 ºC as shown in figures 5.16. In addition, no important shifting is observed in the position of peak temperatures as shown in figure 5.17. When the TL glow curve is divided into two parts, the area under the peaks located between 30- 125 ºC does not change. But a small fluctuation is observed in the area under the peaks located between 125 - 400 ºC as shown in figure 5.18.

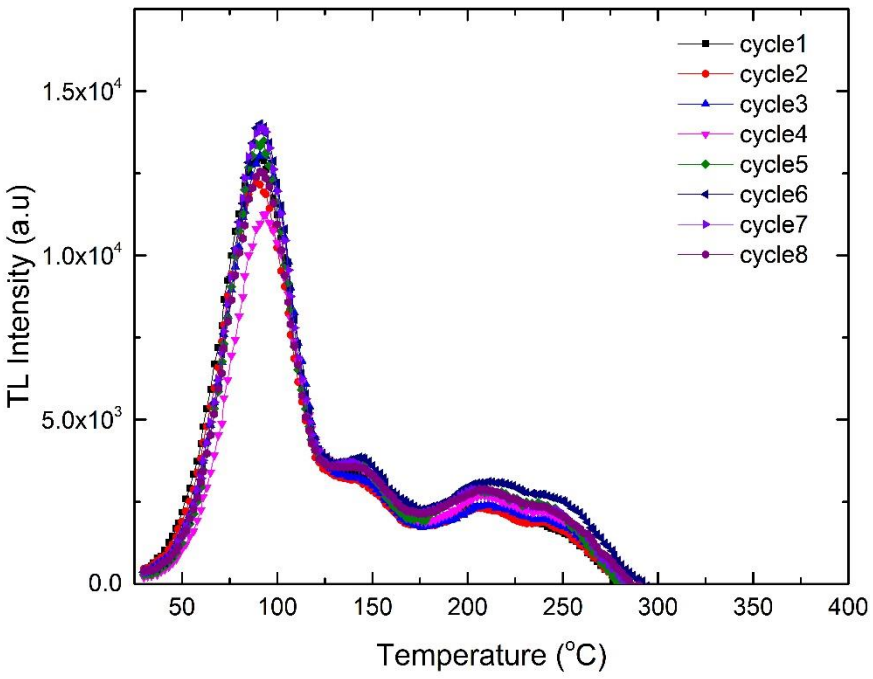


Figure 5.15 The TL glow curve variations with cycle of measurement.

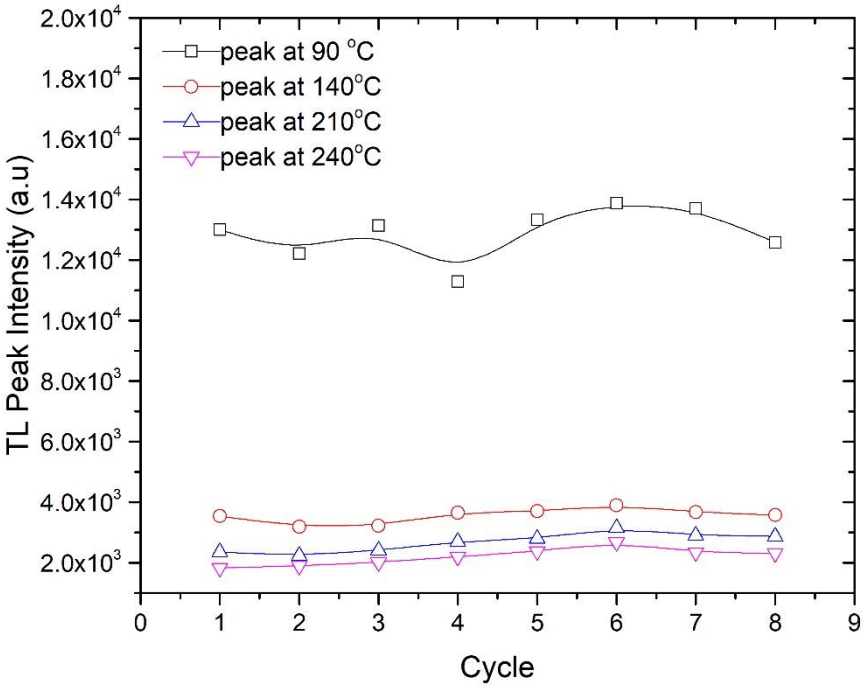


Figure 5.16 The effect of cycle of measurement on the TL peak intensities located around 90, 140, 210 and 240 ºC.

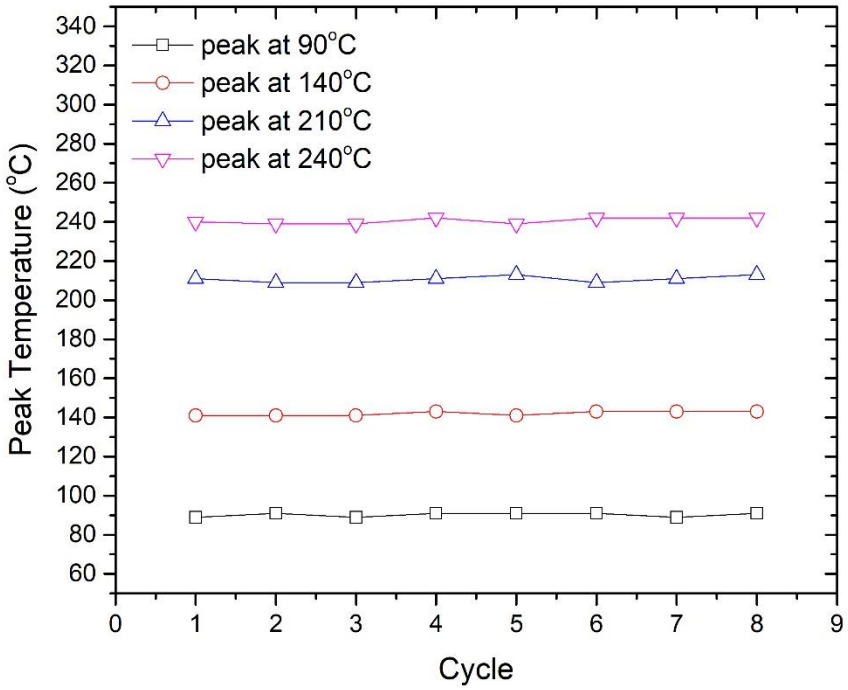


Figure 5.17 The effect of cycle of measurement on the peak temperatures located around 90, 140, 210 and 240 ºC.

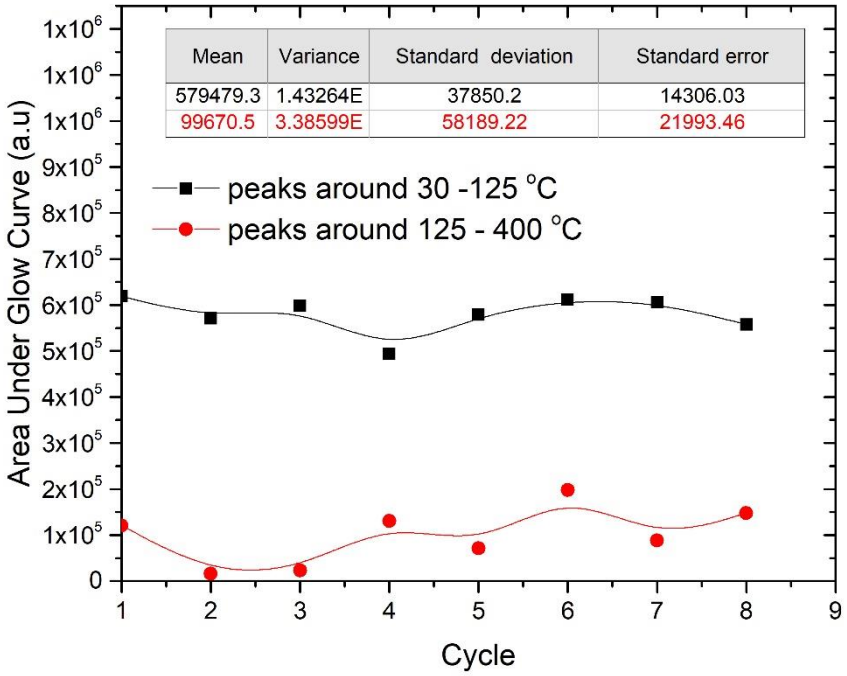


Figure 5.18 The variation of area under TL glow curve with cycle of measurement.

5.6 Determination of kinetic parameters

A different methods are widely used to determine kinetic parameters [37- 41]. Indeed there are overlapping peaks in TL glow curves of the sample used in the study. Therefore the Computerized Glow Curve Deconvolution (CGCD) method is most recently used to find individual peaks hidden in the TL glow curve. This way reduce experimental complexity and gives quite good estimation of TL kinetic parameters. In this study, it has been tried to obtain the kinetic parameters of the samples by using cycle of measurements experiments.

The TL glow curves are fitted to six satellite peaks between room temperature and 400 ^{o}C as in figures 5.19, 5.20, 5.21, 5.22, 5.23, 5.24, 5.25 and 5.26, with high FOM (Figure of Merit) values, because of the appearance of protrusion in curves making the fitting difficult. By this deconvolution method three kinetic parameters which are peak integral (n), trap depth E_a and kinetic order (b) of two main individual peaks are obtained and listed with the tables in the figures.

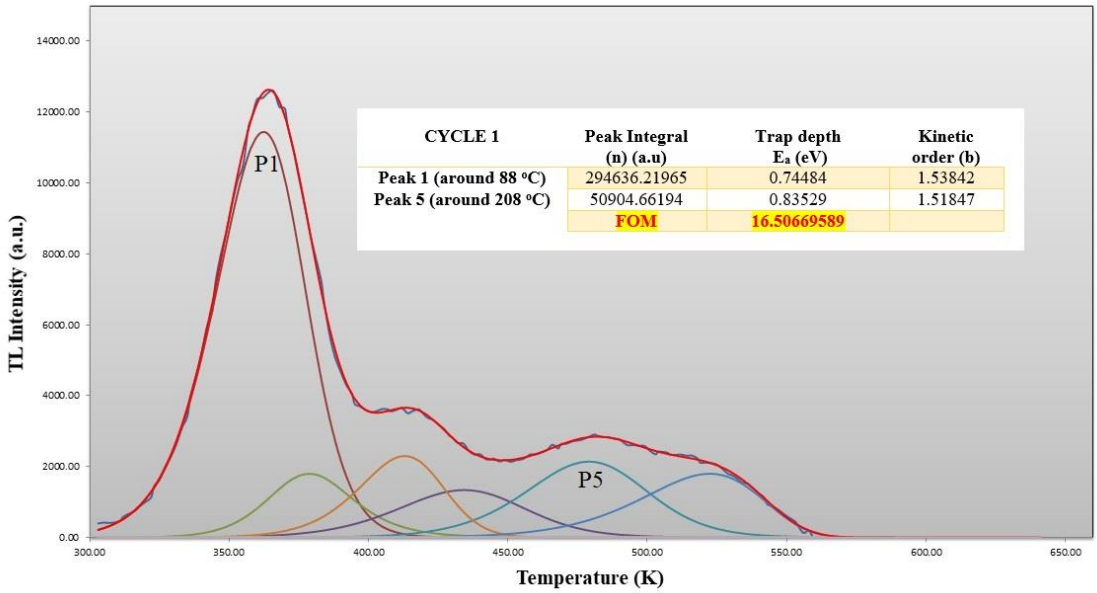


Figure 5.19 Fitted TL glow curve with kinetic parameters: trap depth E_a (eV), peak integral (n) and kinetic order (b) evaluated for two main peaks.

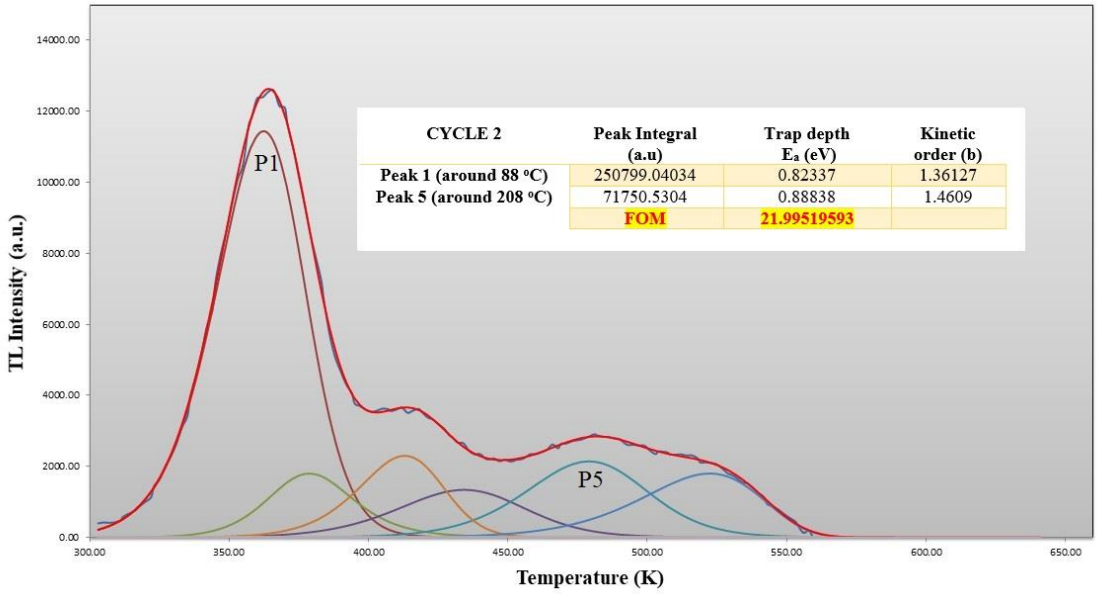


Figure 5.20 Fitted TL glow curve with kinetic parameters: trap depth E_a (eV), peak integral (n) and kinetic order (b) evaluated for two main peaks.

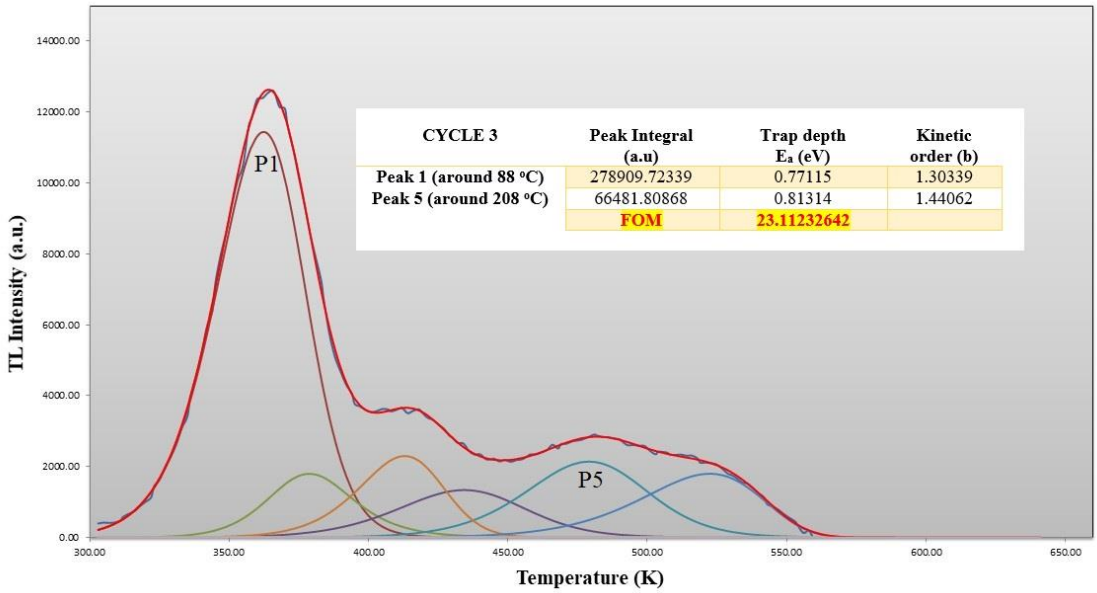


Figure 5.21 Fitted TL glow curve with kinetic parameters: trap depth E_a (eV), peak integral (n) and kinetic order (b) evaluated for two main peaks.

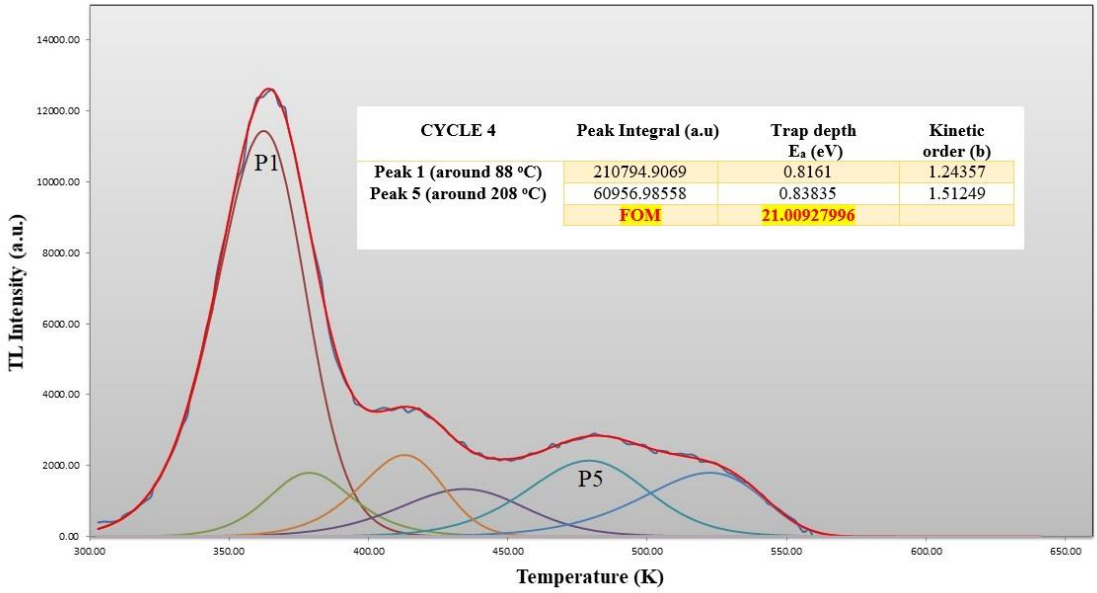


Figure 5.22 Fitted TL glow curve with kinetic parameters: trap depth E_a (eV), peak integral (n) and kinetic order (b) evaluated for two main peaks.

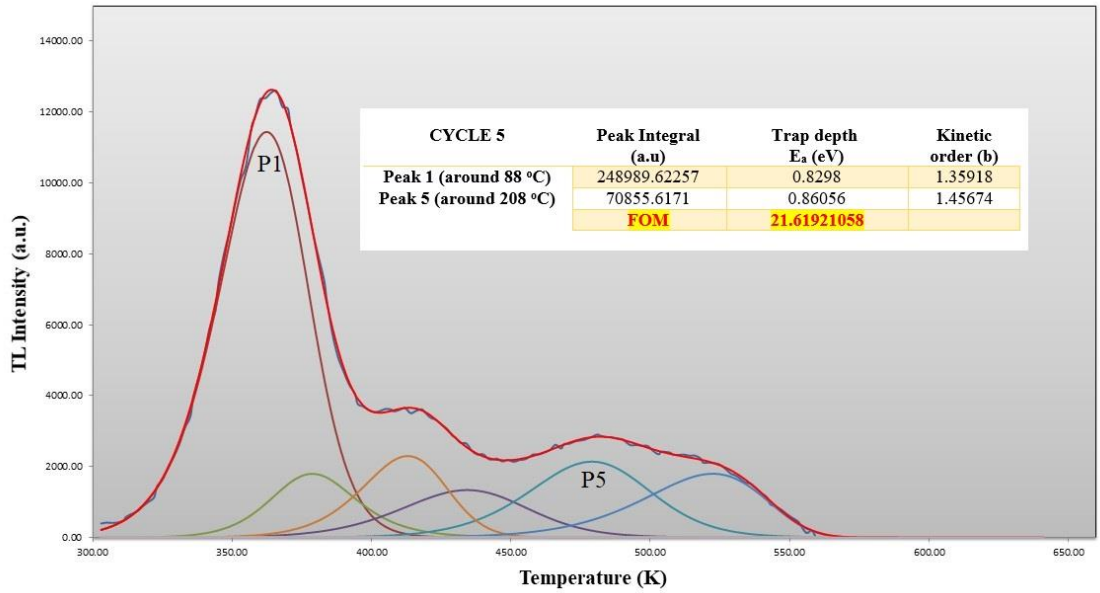


Figure 5.23 Fitted TL glow curve with kinetic parameters: trap depth E_a (eV), peak integral (n) and kinetic order (b) evaluated for two main peaks.

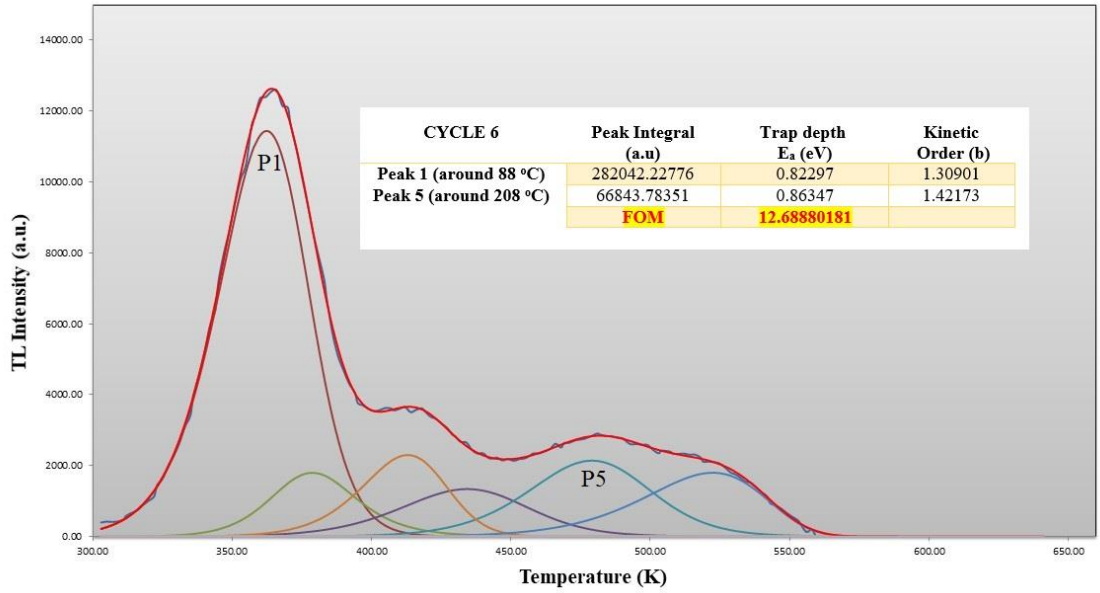


Figure 5.24 Fitted TL glow curve with kinetic parameters: trap depth E_a (eV), peak integral (n) and kinetic order (b) evaluated for two main peaks.

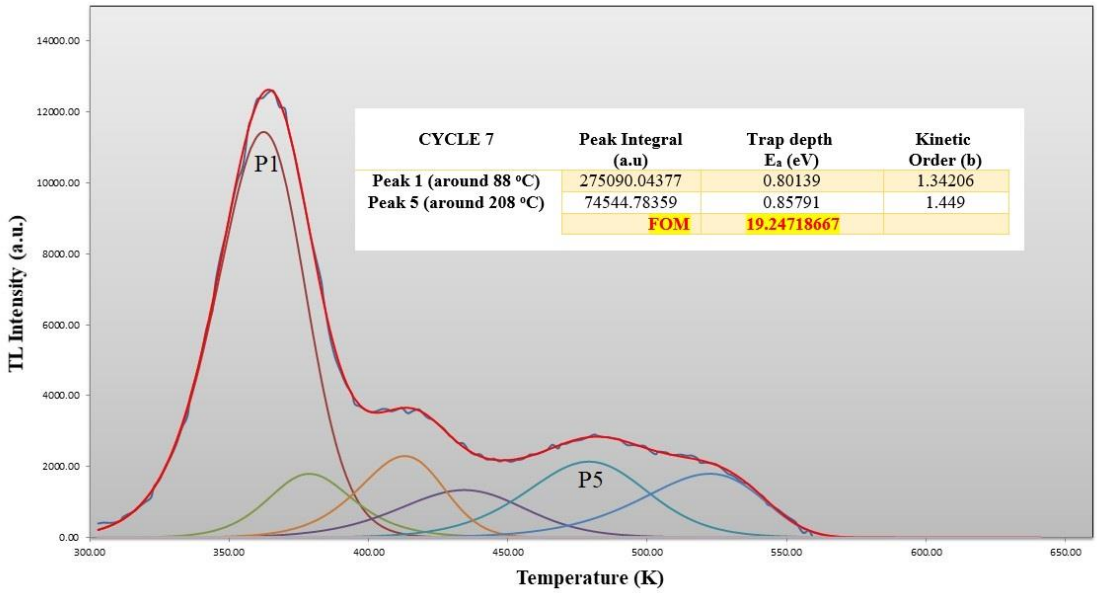


Figure 5.25 Fitted TL glow curve with kinetic parameters: trap depth E_a (eV), peak integral (n) and kinetic order (b) evaluated for two main peaks.

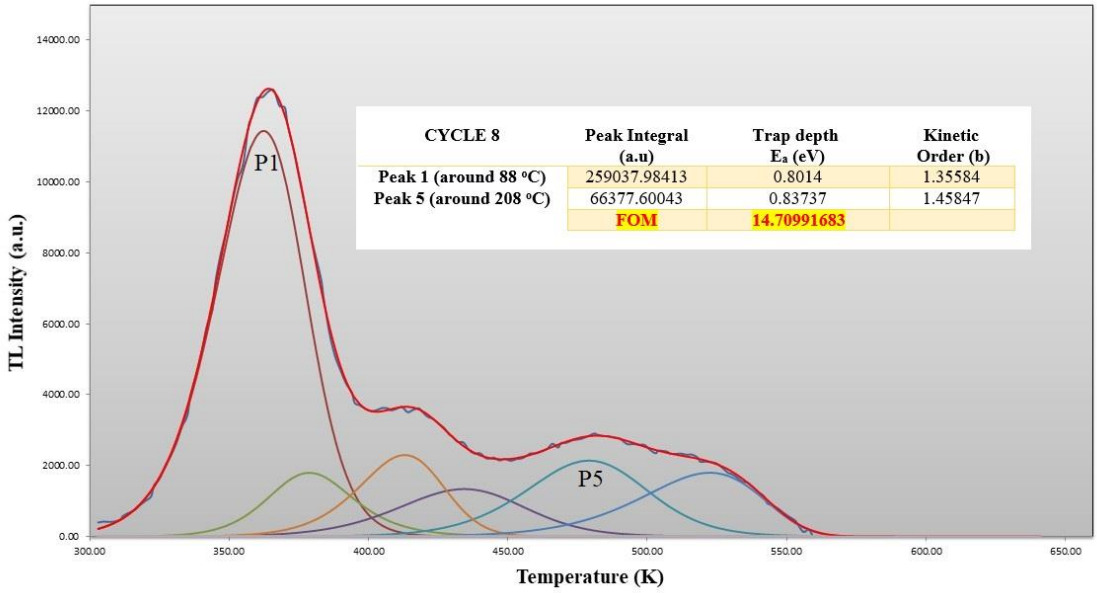


Figure 5.26 Fitted TL glow curve with kinetic parameters: trap depth E_a (eV), peak integral (n) and kinetic order (b) evaluated for two main peaks.

As a result, the peak integral for the peak around 208 °C doesn't change with varies of cycle of measurement, while the integral of Peak around 88 °C fluctuates as shown in figure 5.27. Trap depth varies between 0.74 eV and 0.82 eV for the peak around 88 °C, for the peak around 208 °C varies between 0.83 eV and 0.88 eV as shown in figure 5.28. The kinetic order (b) varies between 1.24 and 1.5 for the peak around 88 °C, and varies

between 1.4 and 1.5 for the peak around 208 ºC as shown in figure 5.29, the average values for peaks were 1.34 and 1.46, respectively. This indicates that the two main peaks chose in the TL glow curve fitted represent general kinetic - order.

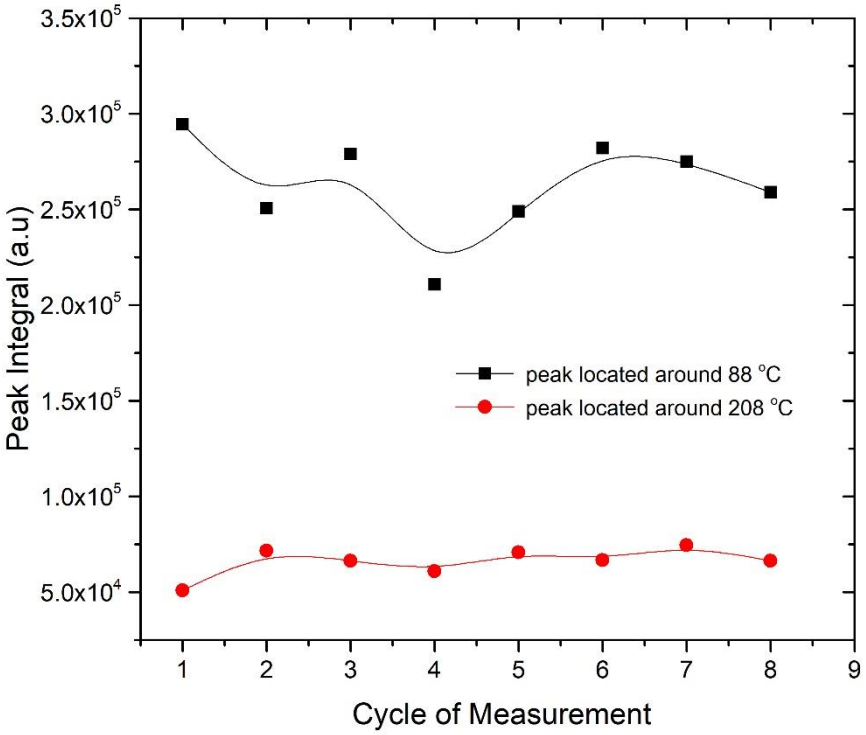


Figure 5.27 Variation of peak integral for peaks located around 88 ºC and 208 ºC withe cycle of measurements.

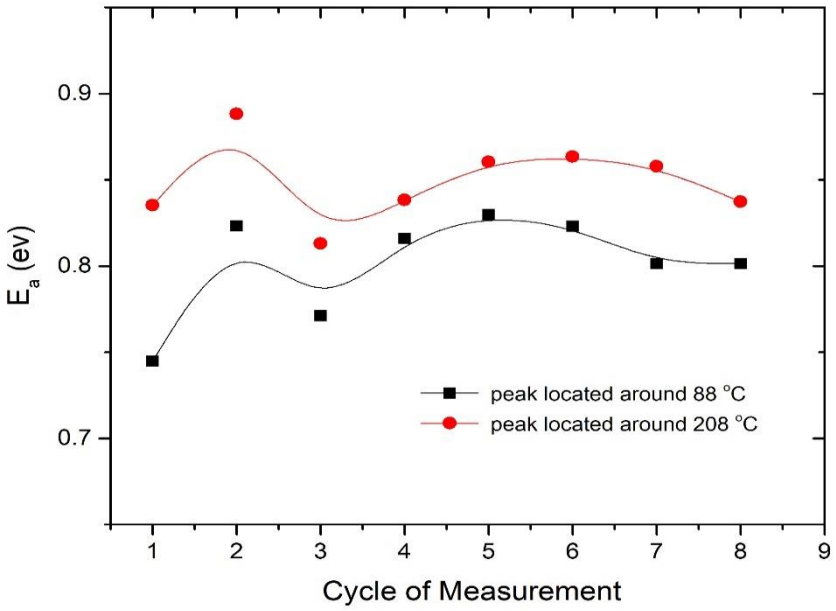


Figure 5.28 Variation of trap depth E_a for peak around 88 °C and peak around 208 °C with cycle of measurements.

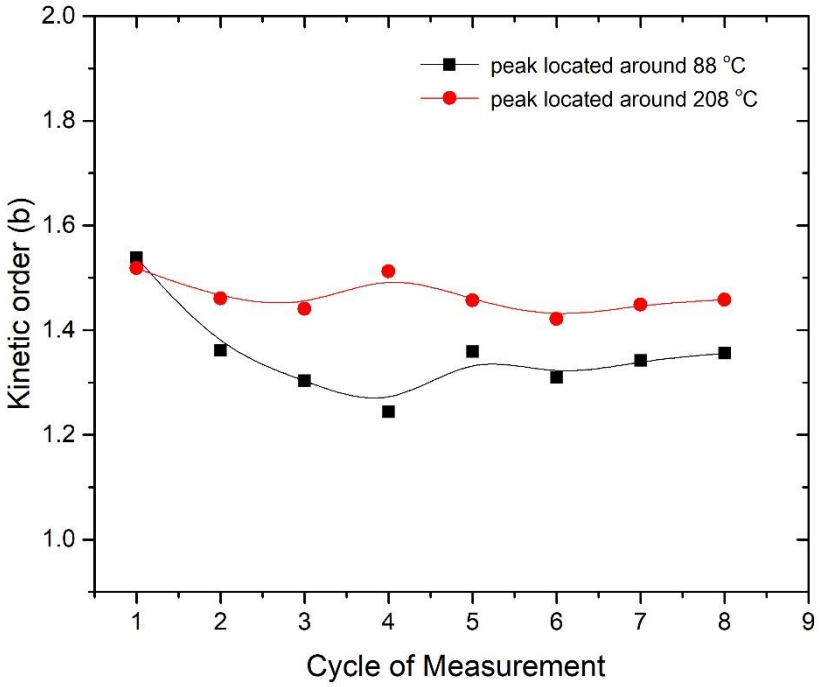


Figure 5.29 Variation of kinetic order (b) for peak around 88 °C and peak around 208 °C with cycle of measurements.

Table 5.4. Values of kinetic parameters: peak integral (n), trap depth E_a (eV) and kinetic order (b) for two peaks, around 88 °C and 208 °C.

CYCLE 1	Peak Integral (n) (a.u)	Trap depth E_a (eV)	Kinetic order (b)
Peak 1 (around 88 °C)	294636.21965	0.74484	1.53842
Peak 5 (around 208 °C)	50904.66194	0.83529	1.51847
	FOM	**16.50669589**	

CYCLE 2	Peak Integral (a.u)	Trap depth E_a (eV)	Kinetic order (b)
Peak 1 (around 88 °C)	250799.04034	0.82337	1.36127
Peak 5 (around 208 °C)	71750.5304	0.88838	1.4609
	FOM	**21.99519593**	

CYCLE 3	Peak Integral (a.u)	Trap depth E_a (eV)	Kinetic order (b)
Peak 1 (around 88 °C)	278909.72339	0.77115	1.30339
Peak 5 (around 208 °C)	66481.80868	0.81314	1.44062
	FOM	**23.11232642**	

CYCLE 4	Peak Integral (a.u)	Trap depth E_a (eV)	Kinetic order (b)
Peak 1 (around 88 ºC)	210794.9069	0.8161	1.24357
Peak 5 (around 208 ºC)	60956.98558	0.83835	1.51249
	FOM	**21.00927996**	

CYCLE 5	Peak Integral (a.u)	Trap depth E_a (eV)	Kinetic order (b)
Peak 1 (around 88 ºC)	248989.62257	0.8298	1.35918
Peak 5 (around 208 ºC)	70855.6171	0.86056	1.45674
	FOM	**21.61921058**	

CYCLE 6	Peak Integral (a.u)	Trap depth E_a (eV)	Kinetic Order (b)
Peak 1 (around 88 ºC)	282042.22776	0.82297	1.30901
Peak 5 (around 208 ºC)	66843.78351	0.86347	1.42173
	FOM	**12.68880181**	

CYCLE 7	Peak Integral (a.u)	Trap depth E_a (eV)	Kinetic Order (b)
Peak 1 (around 88 ºC)	275090.04377	0.80139	1.34206
Peak 5 (around 208 ºC)	74544.78359	0.85791	1.449
	FOM	**19.24718667**	

CYCLE 8	Peak Integral (a.u)	Trap depth E_a (eV)	Kinetic Order (b)
Peak 1 (around 88 ºC)	259037.98413	0.8014	1.35584
Peak 5 (around 208 ºC)	66377.60043	0.83737	1.45847
	FOM	**14.70991683**	

Table 5.5. Values of kinetic parameters: peak integral (n), trap depth E_a (eV) and kinetic order (b) for peaks of cycle 8.

CYCLE 8	Peak Integral (a.u)	Trap depth E_a (eV)	Kinetic order (b)
Peak 1 (around 88 ºC)	259037.9841	0.801404308	1.355844859
Peak 2 (around 105 ºC)	40017.81782	1.14038867	1.993438736
Peak 3 (around 139 ºC)	49589.11523	1.089980699	1.498112947
Peak 4 (around 160 ºC)	43202.87242	1.081159376	1.289724993
Peak 5 (around 208 ºC)	66377.60043	0.837373718	1.458467759
Peak 6 (around 242 ºC)	54658.23079	1.056535864	1.00000001

CHAPTER 5
CONCLUSION

The main object of this study is to investigate the thermoluminescence properties of calcite mineral ($CaCO_3$) which conducted by precipitation of bacterial calcium carbonate in organic soil, and obtain kinetic parameters of traps such as peak integral (n), trap depth E_a (eV) and kinetic order (b).

Four experiments were done: dose response, heating rate, fading and reproducibility, kinetic parameters were also evaluated by (CGCD) method depending on the TL glow curves resulted from reproducibility.

Officially, in dose response, the TL glow curve includes four peaks around 90, 140, 210, and 240 ^oC between dose levels 2.4 Gy and 576 Gy with 1^oC/s heating rate. When applied higher dose level such as 6.9 kGy, a new peak appears around 340 ^oC and peak around 90 ^oC completely disappeared. The shape of TL glow curve is same in the range of dose level between 2.4 Gy and 576 Gy, the new shape is observed with higher dose levels. The area under glow curve and TL intensity show linearity behavior between 140 Gy and 2.3 kGy for the peaks 210 ^oC and 240 ^oC.

In the experiment of heating rate (β), it was observed that the temperature peaks gradually shifted to higher temperature region. The peaks around 90, 140, 210 and 240 ^oC shifted to 119, 167, 244 and 289 ^oC, respectively with increasing heating rate from 1^oC/s to 5 ^oC/s. The TL intensities also decrease with different percentage, for example TL peak around 90 ^oC decreases about 57.5, 28.8, 21.1 and 22.4 % for heating rate range 2, 3, 4 and 5 ^oC/s, respectively, and a similar decrease in the other TL peak intensities is seen. In the other words, there is no change in TL glow curve shapes.

The third experiment of the study is to check how the TL glow curves change with waiting period. The TL peak around 90 ^oC fades dramatically, the TL peak intensity decreases about 59 % after 15 minutes waiting time in dark room and decreases about 41.5% after one hour, the peak completely disappears after 24 hours waiting time in same condition. The TL peak intensity around 140 ^oC completely disappears after 120 hours waiting time.

The fourth experiment is to check reproducibility of the samples. The sample irradiated at 36 Gy and read out by TLD reader at 1°C/s heating rate, this cycle is repeated eight times. There is no changing in TL glow curve. Therefore a good reproducibility is obtained for TL glow curves of calcite mineral

The final part of the study is to obtain kinetic parameters of the traps found in the samples by (CGCD) method. The kinetic parameters are trap depth E_a (eV), peak integral (n) and kinetic order (b). They are evaluated for two main peaks which are located around 88 ^oC and 208 ^oC. For TL peaks around 88 ^oC and 208 ^oC, the trap depth E_a (eV) varied between 0.74 - 0.82 eV and 0.83 - 0.88 eV, kinetic order (b) varied between 1.24 -1.5 and 1.4 and 1.5, respectively. The result shows the TL peak integral around 208 ^oC doesn't change with cycle of measurement, while it fluctuates for the TL peak around 88 ^oC.

Briefly, the calcite mineral conducted by bacterial calcium carbonate ($CaCO_3$) precipitation in organic soil (BCCP) shows a good thermoluminescence properties with good reproducibility, wide linear dose response and good fading. It has a clear TL glow curve with four main peaks located around 90, 140, 210 and 240 ^oC. It has linear dose response between 140 Gy and 2.3 kGy. The dosimetric peaks of the sample located between 200 and 250 ^oC are not affected by the storage period.

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