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INVESTIGATION OF THERMOLUMINESCENCE CHARACTERISTICS OF MARBLES

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CEMİL ÖZBAY

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Cemil ÖZBAY

ABSTRACT

INVESTIGATION OF THERMOLUMINESCENCE CHARACTERISTICS OF MARBLES

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M.Sc. in Engineering Physics

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The dosimetric characteristics of any TL material mainly depend on the sensitivity, energy response and the kinetic parameters quantitatively describing the trapping emitting centers responsible for the TL emission. Thus, a reliable dosimetric study of a thermoluminescent material should be based on a good knowledge of its kinetic parameters. Evaluation of kinetic parameters, i.e. the activation energy $E_a$of the traps involved in the TL emission, the kinetic order *b*, and the frequency factor *s*, associated with the glow peaks. In the given study, the additive dose (AD), variable heating rate (VHR), peak shape (PS) and computerized glow deconvolution (CGCD) methods were used to determine the kinetic parameters glow peaks of Marble(white and pink). The results of the analysis show that Marbles (white and pink) have a first order glow peak of E_a=0.56 eV at 140℃ and E_a=0.55 eV at 145℃, respectively.

Key Words: Natural materials (Marbles), kinetic parameters, heating rate.

ÖZET

MERMERLERİN TERMOLÜMİNESANS KARAKTERİSTİĞİNİN İNCELENMESİ

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Dozimetrik bir malzemenin termoluminesans özellikleri, temelde malzemenin doz hassasiyetine, enerji cevabına ve termoluminesans ışıldama eğrilerini oluşturan tuzak parametresi değerlerine bağlıdır. Güvenilir bir dozimetrik çalışma için bu tuzak parametrelerinin, kinetik derecesi b, aktivasyon enerjisi E_a ve frekans faktörü s'in belirlenmesi oldukça önemlidir. Bu çalışmada değişken doz, farklı ısıtma hızları, tepe şekli ve bilgisayarlı ışıma eğrisi ayrıştırma yöntemleri kullanılarak Mermerlerin (beyaz ve pembe) tuzak parametre değerleri hesaplanmıştır. Analiz sonuçları Mermerlerin (beyaz ve pembe) sırasıyla 140℃'de birinci dereceden 0.56 eV ve 145 ℃'de birinci dereceden 0.55 eV enerjiye sahip bir ışıldama tepesine sahip olduklarını göstermektedir.

Anahtar Kelimeler: Doğal malzemeler (Mermeler), kinetik parametreler, ısıtma hızı.

To my parents, to my Supervisor: Assist. Prof. Dr. Rabia Güler YILDIRIM,

Assist.Prof.Dr. Vural Emir KAFADAR and to all humanity.

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CHAPTER 1

INTRODUCTION

1.1 What is Luminescence

The term luminescence means luminous emission which is not thermal in origin i.e. luminescence is 'cold light', light from other sources of energy, which takes place at normal and lower temperature. In luminescence, some energy sources kicks an electron of an atom of its ground state (lowest energy) into an excited state (higher energy) by providing extra energy, then as this excited state is not stable electron jumps back to its ground state by discharging this energy in form of light[1-3].

We can observe the luminescence phenomenon in nature like, in glowworms, fireflies, and in certain sea bacteria and deep-sea animals. This phenomenon have been used in several fields by scientists from different discipline all over the world like, Archaeology, Geology, Biomedical, Engineering, Chemistry, Physics, and several Industrial Application for Quality Control, Research and Developments.

1.1.1 Luminescence and Stoke's Law

In the process of luminescence, the material can be absorbed and re-emitting some of its energy in the light of a longer wavelength when the radiation falling on it (Stoke's law). In the process of luminescence wavelength of the emitted light is the characteristic of a luminescent substance and not on the incident radiation. The emitted light could be visible light, ultra-violet, or infrared light. This cold emission i.e. luminescence, not including the emission of blackbody radiation thus requires two steps [1-3].

1) The excitation of electronic system of a solid material to higher energy state and

2) Subsequent emission of photons or simply light.

The emission of light takes place at characteristics time 'τ_c' after absorption of the radiation, this parameter allows us to sub classify the process of luminescence into

fluorescence and phosphorescence as shown in figure 1.1. Hence, if the characteristic time 'τ_c' is less than 10^{-8}sec, then it is known as Fluorescence & if the characteristics time 'τ_c' is greater then that of 10^{-8}sec, them it is known as Phosphorescence. A large number of substances both organic and inorganic demonstrate the property of luminescence, but principal materials used in several application of luminescence, requires inorganic solid insulating materials such as alkali and alkaline earth halides, Quartz (SiO_2), Phosphates, Borates, and Sulphate etc. Luminescence solids are usually referred to as Phosphors [1-3]. The Fluorescence emission is seen to be spontaneous as 'τ_c'<10^{-8}sec, thus fluorescence emission is seen to be taking place simultaneously with absorption of radiation and stopping immediately as radiation ceases. But then, phosphorescence is characterized by delay between the radiation absorption and the time 'τ_{max}' to reach full intensity. Also phosphorescence is seen to continue for some time after the excitation has been removed.

If the delay time is much shorter it is more difficult to distinguish between fluorescence and phosphorescence. Hence phosphorescence is subdivided into two main types, namely, short period (τ_c<10^{-4}sec) & long-period (τ_c>10^{-4} sec) phosphorescence. Fluorescence is essentially independent of temperature, whereas decay of phosphorescence exhibits strong temperature dependence [1-3].

1.2 What is Thermoluminescence

Thermoluminescence as mentioned by McKeever et al. is one of the processes in thermally stimulated phenomena [4]. In a general view, thermoluminescence is a temperature stimulated light emission from a crystal after removal of excitation. However, microscopically, it is much more complicated. In this chapter, the thermoluminescence mechanism will be discussed in detail. With the developing technology, thermoluminescence has several application areas such as, radiation dosimetry, age determination and geology.

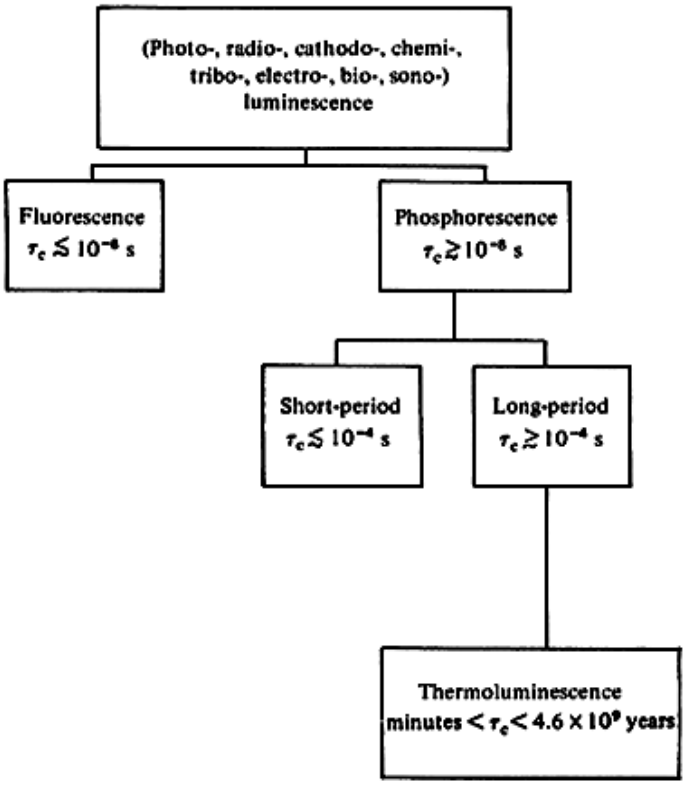


Figure: 1.1 Fluorescence and phosphorescence time table [1]

1.2.1 History of Thermoluminescence

The studies on thermoluminescence go back to the seventeenth century, when scholars like Johann Sigismund Elsholtz, Robert Boyle and Henry Oldenburg conducted experiments on minerals to see their radiation due to heating. George Kaspar Kirchmaier, who regarded the phosphorus as a green stone powdered and mixed with water and glows when heated, and Nathaniel Grew, who used the name Phosphorus metallorum, are other scientists who demonstrated interest in the concept.

Among the eighteenth century researchers, Dufay is the first to be acknowledged for his findings on thermoluminescence. He referred to lighting as a kind of burning. He worked on many materials, primarily chlorophane, and found out that too much heating would lead to loss of thermoluminescence of the material. A famous scientist, Canton brought Dufay's studies to a new level, by raising the temperature of phosphorus even further and discovering a new type of light, which he referred to as the thermoluminescence of artificial phosphorus.

Studies on thermoluminescence continued in the nineteenth century. Researcher, Heinrich claimed that almost all substances could emit light, provided that they are in powder form and subject to moderate heating. Another researcher Theodor von Grotthus dealt specifically with the fluorspar, and demonstrated resemblance between thermoluminescence and essence; both are made of positive and negative parts. Later, scientist David Brewster opposed to Grotthus, arguing that the luminescence property cannot always be regained on exposing the minerals to light.

Other researchers who studied thermoluminescence in the nineteenth century are Pearsall, who tried to find a relation between colour and thermoluminescence; Specia, who invalidated Pearsall's findings; Napier, who experimented on the chalks; Wiedmann and Schmitt, who attributed the thermoluminescence characteristic to cathode rays [3].

1.2.2 Thermoluminescence Mechanism

Thermoluminescence can be described by two stages. First stage is the change of the system from equilibrium to metastable state by absorption of energy from UV or ionizing radiation. Second stage is relaxation of the system back to the equilibrium by energy release such as light with the help of thermal stimulation. Hence, thermoluminescence (TL) is the thermally stimulated emission of light following the previous absorption of energy from radiation [3]. In this chapter, these stages and output of this light emission will be discussed briefly.

1.2.2.1 Energy Storage

There are two ways for the stabilization of this absorbed energy: electronic excitation and displacement damage. At the end of both processes, radiation-induced defects are formed in the material structure. Radiation-induced defects are localized electronic states occupied by non-equilibrium concentration of electrons [5]. Alias, before irradiation, materials have localized electronic energy states and after irradiation, some of these states are occupied by a non-equilibrium concentration of electrons. Thus, these occupied states are called radiation-induced defects. According to McKeever, when investigations are taken into consideration, they demonstrate that the cause of defect creation is electronic excitation rather than non-ionizing displacement damage.

Energy storage caused by electronic excitation takes place by the electron-hole pair production and excitation creation. Electron-hole pair production is the formation of mobile holes and electrons in the crystal structure of the material after radiation. In addition, there exists a mid gap state caused by defects which may be made by preexisting impurities or radiation induced defects. This gap is found between the two energy bands; called conduction band and valence band. The valence band is the outer most energy level and comprises electron-hole pairs in ground state of the solid. However; in the conduction band, electrons are free to move and have ability to produce electric current.

According to thermoluminescence phenomena it is assumed that there are two kinds of imperfections called electron trap and hole trap in the crystal which are localized at mid gap states [3, 4, 6]. In the mid gap, the electron trap is believed close to the conduction band and the hole trap is far from the valence band.

Figure 1.2 illustrates the energy storage mechanism. Then irradiation, the electrons pass from valence band to conduction band and hole becomes positively charged area in the valence band. While electron reaches the conduction band, electron find its way into an electron trap and hole occupies its associated trap. Hole traps are called luminescence center in this process [3, 4, 6, 7].

1.2.2.2 Energy Release

Excitation with an increase in temperature or giving light, results in release of the stored energy. Moreover, state of the material changes from metastable to ground. When heat is increased, the electron trapped in the electron trap is released to conduction band. After that electron is free to retrap or recombine with the hole found in the hole trap. The recombination of the electron with the hole in hole trap results in the emission of photons. In this case hole trap is called as recombination center [3]. This process is seen in the figure 1.3.

1.2.2.3 Glow Curve

After the energy release, the output of the emitted light as a function of temperature is called thermoluminescence glow curve [3].

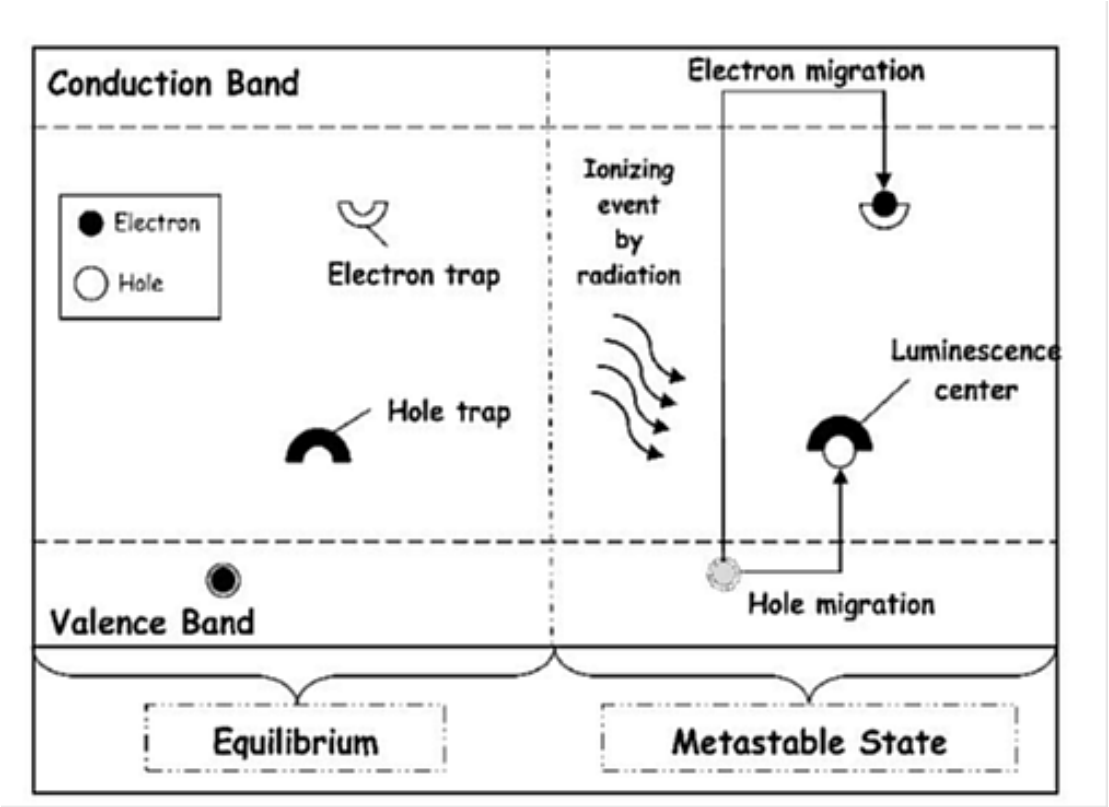


Figure 1.2 Energy-level diagram of the energy storage stage for TL Processes.

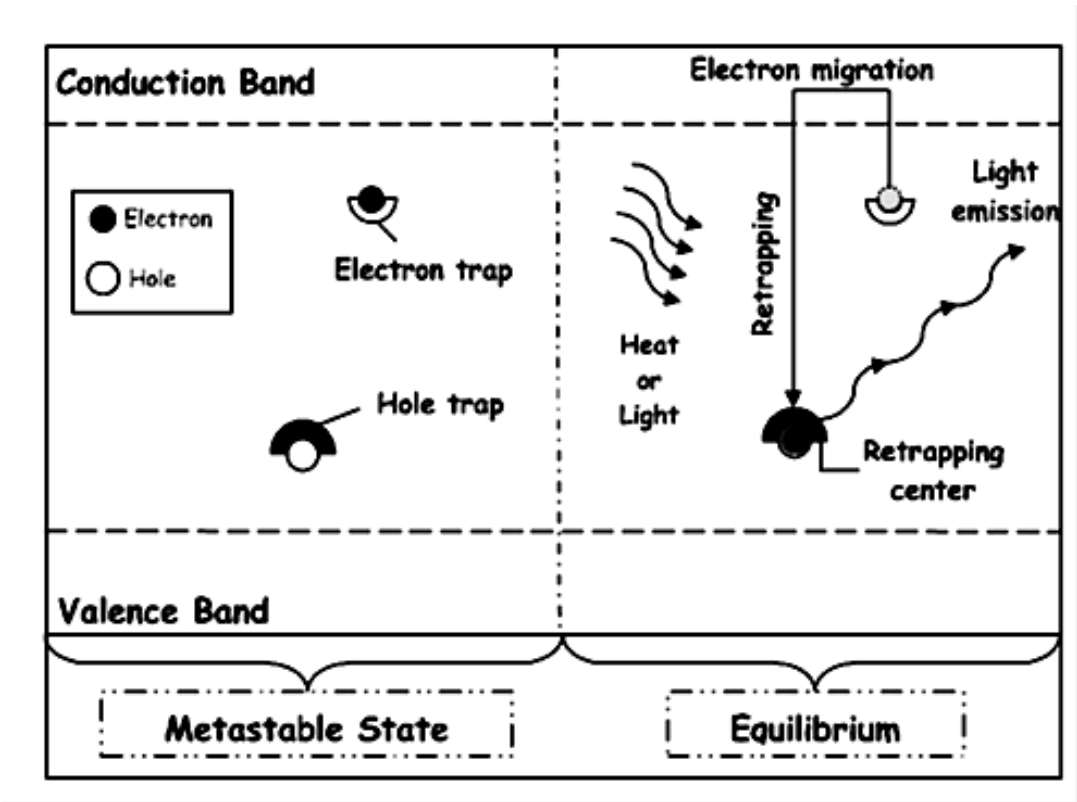


Figure 1.3 Energy-level diagram of the energy release stage for TL Processes.

Shape of the glow curves is one or more peaks of emitted light and some of them may overlap. Magnitudes and looks of the glow curves may change depending on the spectral response of the light sensitive device, several filter usage between the sample and the detector and heating rate. Furthermore, when the sample is irradiated it has only one shot effect. A second thermoluminescence emission cannot be recorded by cooling and reheating it unless it is not irradiated again.

1.2.3 Thermoluminescence Applications

The thermoluminescent materials used in the industry have three major areas; radiation dosimetry, age determining and geology. The radiation dosimetry measures the dose that is absorbed by the sample that is exposed to irradiation. Radiation dosimetry has three subgroups; personnel dosimetry, medical dosimetry and environmental dosimetry.

Personnel dosimetry has three sub categories; extremity dosimetry, whole-body dosimetry and tissue dosimetry. The first one focuses on body parts that are exposed to radiation such as hands, arms or feet while the whole-body focuses on the tissue below the surface of the body or the critical organs. It measures the dose absorbed in these parts of the body by dealing with gamma and X- rays (greater than 15 KeV) and neutrons which are penetrating rays. Tissue dosimetry, which is also called skin dose, measures the dose absorbed by skin. On the other hand, rather than dealing with penetrating radiation, it focuses on non-penetrating radiation such as beta particles or <15 KeV X-rays. In order for these measurements to be done, a thermoluminescence dosimetry (TLD) material that is equivalent to the human tissue is needed. The TLD material should absorb the same dose or amount of radiation as the human tissue would do in the same area within the same radiation levels.

Medical dosimetry intends to measure the effects of a TLD that is placed into the appropriate places within human body. By doing so, before exposing the patient, to ionizing radiations for treatment procedures or diagnosis, measurements can be made upon these TLD. From the data obtained, possible additional treatments or dose control can be implemented. It is impossible to do so by means of other than radiation dosimeter. The major variables that determine patient doses include imaging modality, technical factors and in the case of fluoroscopy, beam time [8]. In addition to these factors, the size of the patient is also a determining factor. Medical dosimetry has two

categories; diagnostic radiology and radiotherapy. The radiation used here may be X-rays (near 10 KeV level), gamma rays, beta particles, protons and other heavy particles and neutrons [4].

Again, the TLD material needs to be tissue equivalent and highly sensitive. The latter is needed for measurements done in laboratory conditions that require the possible smallest size of TLD material. Other than these properties, the TLD should not be toxic. Recommended diagnostic reference levels for medical imaging modalities have been published by the ICRP [8].

Environmental dosimetry deals with the radiation present in the environment due to human kind. Due to applications like nuclear power stations, waste disposals, usage or processing of nuclear fuels and disastrous nuclear power plant malfunctions introduce high levels of radiation into the environment. Thus, it becomes essential to monitor the radiation released to the environment continuously.

TLD's are used for environmental dosimetry applications. On the other hand, the performance criteria for TLDs in this application are different from those required for personal monitoring. They are still needed to be highly sensitive, more preferably extremely sensitive and this time it is not essential for TLDs to be tissue equivalent. Because the environment is exposed to radiation for a long time continuously, environmental dosimetry measures the values within a long period. Thus, the TLDs should be structurally intact and stable in long term.

In recent years, with the help of cutting edge technological innovations, space flight with astronauts has been possible. Radiation exists in space and since there is no more an atmosphere to protect from galactic cosmic rays, it is important to measure the radiation at these space flights. In addition, from the astronauts on board, the radiation is also harmful for the digital equipment of the vehicles. The radiation sources are galactic cosmic rays of which the main component is high-energy protons and heavy charged particles from the solar wind [7]. In order to measure the effects of these radiation sources, TLDs are used.

Thermoluminescence is used in age determining processes of materials, as it became an established method of age determination. A famous scientist, Daniels and his coworkers are the first to suggest the use of thermoluminescence for this purpose. They argued that there are already radioactive elements within the rocks, such as uranium,

thorium and potassium and these elements assigned a natural thermoluminescence to the rocks. From this radioactivity an accumulation, which is called ‘geological’ dose, takes place in the material. If the rate of irradiation from the radioactive minerals is established, and if the rate of thermal release of the thermoluminescence during the rock’s irradiation can be shown to be negligible, then the length of time over which the rock has been irradiated (i.e., its ‘geological age’) can be determined from the ratio of absorbed dose over dose rate [1, 8].

Thermoluminescence was used for age determination of rock formations however; it was not used for archeological dating until natural thermoluminescence was found in ancient samples. Because of the effects of heat on thermoluminescence, thermoluminescence of the pots diminished to zero during its bakery. Whereas, the surroundings of the pot does not change. And it is naturally radioactive itself with elements like uranium, thorium and potassium. Hence, the pot continues to be exposed to radioactivity and will absorb a certain amount of it, which will be measured to get the archeological age of the pottery. Thermoluminescence is now an established way of age determination.

CHAPTER 2

THERMOLUMINESCENCE THEORY

2.1 Basic Concepts of Thermoluminescence (TL) in Solids

The phenomenon of thermoluminescence (TL) of minerals was known empirically as early as 1663. It was in this year that Sir Robert Boyle described to the Royal Society about "Experiments and Considerations upon Colours with Observations on Diamond That Shines in the Dark" (1663) and depicted how, upon warming a diamond in contact with his body in the dark, he saw a flash. This reflects the definition of thermoluminescence. Not only diamonds but a large number of minerals give off light energy upon warming. Well-known substances are quartz, feldspar, calcite and flint. But the phenomenon of thermoluminescence itself was not sufficient to be used as a dating method. It was necessary to establish the mechanisms, which are responsible for resetting the dating clock and link the intensity of the emitted light energy to a time scale. Three centuries later the first law of thermoluminescence was established, which states that the thermoluminescence of minerals is approximately proportional to the irradiation dose to which they had been exposed [9].

The first application of this phenomenon for dosimetric purposes was from Daniel et al [10]. In spite of that phenomena of TL have been known for a long time in order to develop new thermoluminescence materials, it has been implemented a lot of researches to understand and improve the characteristics of the materials. In these days, a TLD is the dosimetric technique which is established well with applications in the domains like (personnel, environmental and clinical dosimetry). Thermoluminescence is the physical phenomenon in which a solid sample absorbs energy while irradiated at a given temperature, and releases this energy in the form of light while heating the sample. The emitted light is recorded as intensity vs. temperature in the shape of one or more TL peaks. Under favorable conditions, the emitted TL light intensity is proportional to the absorbed dose, and so using an appropriate calibration, one can

evaluate the applied dose in the given radiation field. The TL signal may be the intensity at the maximum or the area under the TL glow peak, which are usually nearly proportional to each other. In “regular” dosimetric applications, one can choose an appropriate material with reproducible results in repeated measurements, linear dose dependence for the kind of radiation in question as well as dose-rate independence and long time stability.

TL is a luminescence phenomenon of an insulator or semiconductor which can be observed when the solid is thermally stimulated. TL should not be confused with the light spontaneously gave off from a substance when it is heated to incandescence. At higher temperatures (say in excess of 200°C) a solid emits (infra) red radiation of which the intensity increases with increasing temperature. This is thermal or black body radiation. TL, on the other hand, is the thermally stimulated emission of light following the previous absorption of energy from radiation. According to this phenomenon, the three essential factors necessary for the production of TL can be deduced.

Firstly, the material must be an insulator or semiconductor–metals do not exhibit luminescent properties.

Secondly, the material must have at some time absorbed energy during exposure to ionizing radiation.

Thirdly, the luminescence emission is triggered by heating the material [4].

A thermoluminescent material is a material that absorbs some energy which is stored during exposure to ionizing radiation. While the material is heated, the stored energy is released in the form of visible light as shown in figure 2.1. In fact that TL does not refer to thermal excitation, but to stimulation of luminescence in a sample which was excited in a different way. TL material cannot emit light again by simply cooling the sample and reheating it other time. It should first be re-exposed to ionizing radiation before it produces light again. The storage capacity of a TL material makes it suitable for dosimetric applications.

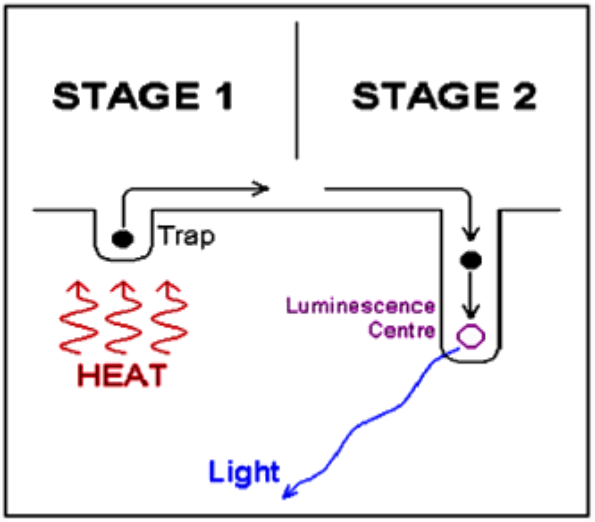


Figure 2.1 The phenomena of thermal excitation of luminescence.

2.2 The One Trapping—One Recombination Centre Model

An explanation of the observed TL properties can be obtained from the energy band theory of solids. In an ideal crystalline semiconductor or insulator most of the electrons reside in the valence band. The next highest band that the electrons can occupy is the (C.B), separated from the valence band by the so-called forbidden band gap. The energy difference between the delocalized bands is *E*g. In contrast, whenever structural defects occur in a crystal, or if there are impurities within the lattice, there is a possibility for electrons to possess energies which are forbidden in the perfect crystal. In a simple TL model two levels are assumed, one situated below the bottom of the (C.B) and the other situated above the top of the (V.B) (see figure 2.2). The highest level indicated by *T* is situated above the equilibrium Fermi level *(E*f) and so empty in the equilibrium state, i.e. before the exposure to radiation and the creation of electrons and holes. It is thus a potential electron trap. The another level (indicated by *R*) is a potential hole trap and can function as a recombination centre. The absorption of radiant energy with $h\nu > E$g results in ionization of valence electrons, producing energetic electrons and holes which will, after thermalisation, produce free electrons in the conduction band and free holes in the valence band (transition *a*). The free charge carriers recombine with each other or become trapped [11]. In the case of direct recombination an amount of energy will be released which may excite a luminescent centre (which may coincide with the recombination centre).

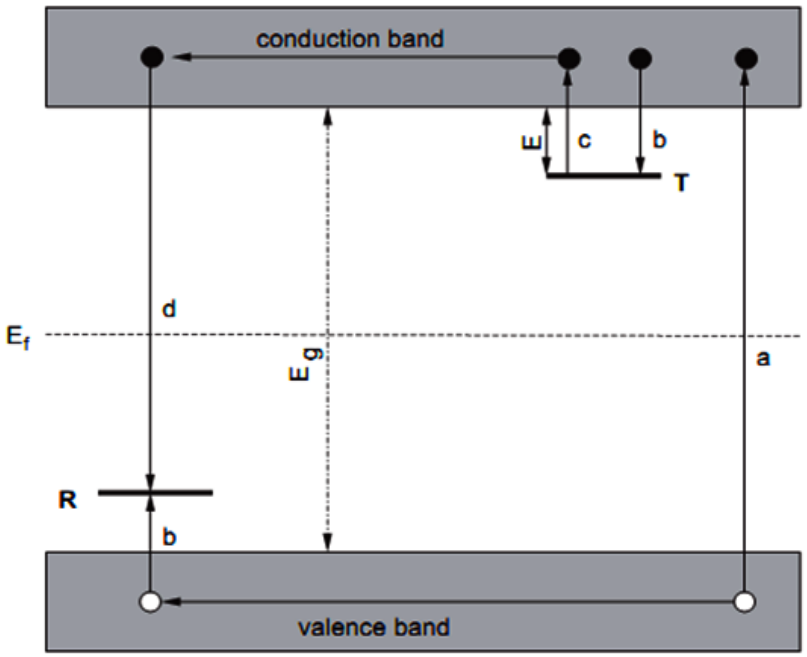


Figure 2.2 The electronic transitions in a thermoluminescence material are shown from the energy band model according to a simple (two-level) model, and (a) generation of electrons and holes; (b) electron and hole trapping; (c) electron release due to thermal stimulation; (d) recombination. Solid circles are electrons, open circles are holes. And the level T is an electron trap, level R is a recombination centre, Ef is Fermi level, Eg is the energy band gap [11].

The luminescent centre relaxes (returns to the ground state) under the emission of light. The phenomenon of direct ($<10^{-8}$ s) recombination of free electrons and holes under emission of light is called radioluminescence. On the other hand, in semiconductors and insulators a certain percentage of the charge carriers are trapped: the electrons at T and the holes at R (transition b). The Arrhenius equation describes the probability per unit time (p*)* for releasing an electron from the trap:

$$p = s \ \exp\left\{-\frac{E}{kT}\right\} \tag{2.1}$$

Where s is the frequency factor or attempt to-escape factor. In the simple model s is considered as a constant (not temperature dependent) with a value in the order of the lattice vibration frequency, namely 10^{12}-$10^{14}s^{-1}$. E is the depth of the trap or activation energy, the energy needed to release an electron from the trap into the (C.B) (see Figure2.2). The other symbols have their usual meaning: k=Boltzmann's constant=8.617×10^{-5}eV/K; T the absolute temperature.

The trapped electrons will stay in the trap for a long period of time if the depth of trap is much bigger than (kT_0), where (T_0) is the irradiation temperature, until radiation exposure there will exist a lot of electrons population which are trapped, But must be exist at the level (R) an equal trapped holes population, due to the creation and annihilation the (electrons and holes) in pairs. So that in the normal equilibrium the Fermi level (Ef) is located above the level (R) and below the level (T). The reaction track is always open for returning to the state of the equilibrium, but because the equilibrium disturbance was performed during exposure to the ionizing radiation at low temperature in comparison with (E/k), and the rate of relaxation that is specified by the equation (2.1) is small. Thus, the non-equilibrium state is metastable and presence for indefinitely and governed by the rate parameters activation energy (E) and frequency factor (s) [11].

The equilibrium can come back quickly by increasing the heat level of the thermoluminescence substances higher than (T_0). This will increase the probability of detrapping and the electrons will now be released from the trap into the conduction band. The charge carrier migrates through the conduction band of the crystal until it undergoes recombination at recombination centre R. This centre of recombination is a luminescent centre in the simple model, where the (electron and hole) recombination go out from the centre to one of the higher excited states, and come back to the ground state after emitting light, i.e. thermoluminescence (TL).

And the thermoluminescence intensity I(t) in photons per second at any time (t) during the heating is commensurate with rate of holes and electron recombination at the centre of recombination (R). If the concentration of holes trapped at (R) is (m (m^{-3})), can be written the intensity of the thermoluminescence (TL) as the:

$$I(t) = -\frac{dm}{dt} \tag{2.2}$$

Where (-) indicates a decrease of holes. Here, we assume that each recombination produces a photon and that all produced photons are detected. The rate of recombination will be proportional to the concentration of free electrons in the (C.B) n_c and the concentration of holes m:

$$I(t) = -\frac{dm}{dt} = n_c m A_m \tag{2.3a}$$

At the constant A_m the probability of recombination (p) expressed in units of volume per unit time which is supposed to be independent of the temperature. The rate of change of the concentration of trapped electrons *n* is equal to the rate of thermal release minus the rate of retrapping

$$-\frac{dn}{dt} = np - n_c(N - n)A_n \tag{2.3b}$$

Where N is the concentration of electron traps and A_n is the probability of retrapping ($m^{-3}s^{-1}$). Likewise the rate concentration of free electrons is equal to the rate of thermal release minus the rate of retrapping and the rate of recombination:

$$\frac{dn_c}{dt} = np - n_c(N - n)A_n - n_c m A_m \tag{2.3c}$$

Equations (2.3a) - (2.3c) described the charge carrier traffic in the case of release of a trapped electron from a single electron trap and recombination in a single centre. For TL produced by the release of holes the rate equations are similar to equation (2.3). These equations form the basis of many analyses of TL phenomena. There is no a general analytical solution and these equations must be solved by some simplifying assumptions for developing an analytical expression. An important assumption is that at any time

$$\left|\frac{dn_c}{dt}\right| \ll \left|\frac{dn}{dt}\right| ; \quad \left|\frac{dn_c}{dt}\right| \ll \left|\frac{dm}{dt}\right| \tag{2.4}$$

This assumption is called by Chen and McKeever [14] the quasi equilibrium (QE) assumption since it requires that the free electron concentration in the (C.B) is quasi stationary. The trapped electrons and holes are produced in pairs during the irradiation. Charge neutrality dictates therefore:

$$n_c + n = m \tag{2.5}$$

Which for $n_c \approx 0$ means that n ≈ mand

$$I(t) = -\frac{dm}{dt} \approx -\frac{dn}{dt} \tag{2.6}$$

Since $dn_c/dt \approx 0$ one gets from equations (2.3a) and (2.3b) [11]

$$I(t) = \frac{mA_m ns \ \exp\left\{-\frac{E}{kT}\right\}}{(N-n)A_n + mA_m} \tag{2.7}$$

2.2.1 First-Order Kinetics

Analytically, we can't solve the equation (2.7), but it can be solved by adding the additional simplifying assumption. Randall and Wilkins [12, 13] assumed negligible retrapping during the heating stage i.e. they assumed $mA_m \gg (N-n)A_n$. Under this assumption equation (2.7) can be written as

$$I(t) = -\frac{dn}{dt} = sn \ \exp\left\{-\frac{E}{kT}\right\} \tag{2.8}$$

This differential equation describes the charge transport in the lattice as a first-order process. If the temperature is kept constant, $p = s \exp(E/kT)$ is constant and the intensity can be found from equation (2.8) by integration

$$I(t) = I_0 \exp(-tp) \tag{2.9}$$

Where I_0 is the initial intensity at time $t = 0$. At a constant temperature the decay is thus a simple exponential function of time. The phenomenon is called phosphorescence. But if the temperature varies in time (p) is not longer a constant and the solution of the differential equation (2.8) becomes

$$I(t) = -\frac{dn}{dt} = n_0 s \exp\left\{-\frac{E}{kT(t)}\right\} \times \exp\left\{-s\int_0^t \exp\left\{-\frac{E}{kT(t')}\right\}dt'\right\} \tag{2.10}$$

Where n_0 is the total number of trapped electrons at time $t = 0$. As the temperature increases, the intensity initially increases (retrapping of the trapped charge carriers and recombination takes place which initiates luminescence), than reach a maximum and finally decreases (as the number of charges carriers becomes depleted). The intensity has thus the shape of a peak and (if derived from equation (2.8)) is called a first-order glow peak. Usually TL is observed as the temperature is raised as a linear function of time according to:

$$T(t) = T_0 + \beta t \tag{2.11}$$

Where β is the constant heating rate and T_0 is the temperature at time $t = 0$. This gives for the intensity as function of temperature

$$I(t) = -\frac{1}{\beta}\frac{dn}{dt} = n_0 \frac{s}{\beta} \exp\left\{-\frac{E}{kT}\right\} \times \exp\left\{-\frac{s}{\beta}\int_{T_0}^{T} \exp\left\{-\frac{E}{kT'}\right\} dT'\right\} \qquad (2.12)$$

Equation (2.12) is the famous Randall–Wilkins expression of the first-order for a peak of a single glow. The peak has a characteristic asymmetric shape being wider on the low temperature side than on the high temperature side [11].

On the low temperature side, i.e. in the initial rise of the glow peak, the intensity is dominated by the first exponential (exp (−E/kT)). Therefore, if I am plotted as function of 1/T, a straight line is expected in the initial rise temperature range, with the slope of −E/k, from which the activation energy E is readily found.

The properties of the Randall–Wilkins equation (2.12). It can be noted that the temperature at the peak maximum,T_m stays fixed. This is a characteristic of all first-order TL curves. The condition for the maximum can be found by setting dI/dt =0 (or, somewhat easier from d ln I (T)/dt = 0). From this condition we can obtain the following equation

$$\frac{\beta E}{kT_m^2} = s \exp\left\{-\frac{E}{kT_m}\right\} \qquad (2.13)$$

The equation n_0 does not appear which shows that T_m indeed does not depend on n_0. In the application in dosimetry n_0 is the parameter of paramount importance since this parameter is proportional to the absorbed dose. It is simple to see that the area under the glow peak is equal to n_0 since

$$\int_0^{\infty} I(t)dt = -\int_0^{\infty} \frac{dn}{dt} dt = -\int_{n_0}^{n_\infty} dn = n_0 - n_\infty \qquad (2.14a)$$

and n_∞ is zero for $t \to \infty$.

It is worthwhile to note that of the four parameters the activation energy (E) and the frequency factor (s) are the major physical parameters. They are called the trapping parameters and are fixed by the properties of the trapping centre. The other two parameters can be chosen by the experimenter by choosing a certain dose (n_0) and by read-out of the signal at a certain heating rate (β). Investigation of a new TL material

will thus start with studying the glow peak behaviour under variation of the absorbed dose and the heating rate.

Hoogenboom et al. [15] have derived an expression for I_m, the intensity at the peak maximum, for a first-order Randall–Wilkins glow peak

$$I_m = n_0 \frac{\beta E}{k T_m^2} e^{-g_m} \tag{2.14b}$$

With g_m=g(x) =x$e^x$$E_2$(x) with E_2(x) the exponential integral of second-order and x= E/kT_m. Setting g_m= 1 will give an under estimation of $I_m$up to 10%. From equation (2.14b) it can be shown that the peak height is not only proportional to (n_0) but also to the heating rate (β). (In fact not strictly proportional since in varying (β) the peak temperature T_m and the function $g_m$vary as well but the effect caused by (β) is by far dominant).

Sunta et al. [16] has developed a test to see whether the QE assumption has been fulfilled based on changes of the geometry factor $\mu_g$of the glow peak measured at several heating rates. A system that satisfied the QE assumption will see a peak symmetry that will not change with heating rate.

The evaluation of equation (2.12) is hampered by the fact that the integral on the right-hand side is not elementary in the case of linear heating. Chen [17] has shown how the integral can be approximated by asymptotic series. In practical applications it is convenient to describe the glow peak in terms of parameters which are easy to derive experimentally, namely the intensity of at peak maximum I_m and the temperature at the maximumT_m. Kitis et al. [18] have shown that equation (2.11) can be quite accurate approximated by

$$I(T) = I_m \exp\left[1 + \frac{E}{kT}\frac{T - T_m}{T_m} - \frac{T^2}{T_m^2} \times \exp\left\{\frac{E}{kT}\frac{T - T_m}{T_m}\right\}(1 - \Delta) - \Delta_m\right] \tag{2.15}$$

Where (Δ= 2*kT /E)* and (Δ_m= 2*k*T_m*/E)*. This expression may be convenient for peak fitting purposes [11].

2.2.2 Second-Order Kinetics

The possibility in which the retrapping dominates was considered by Garlick and Gibson [19]. It means that $mA_{\mathrm{m}} \ll (\mathrm{N}-\mathrm{n})A_{\mathrm{n}}$. Further they assume that the trap is far from saturation, i.e. $N \ll n$andn = m. By these assumptions equation (2.7) becomes

$$\mathrm{I(t)} = -\frac{\mathrm{dn}}{\mathrm{dt}} = \mathrm{s}\frac{A_{\mathrm{m}}}{\mathrm{N}A_{\mathrm{n}}}\mathrm{n}^2 \exp\left\{-\frac{\mathrm{E}}{\mathrm{kT}}\right\} \tag{2.16}$$

We see that now d*n*/d*t* is proportional to n^2, which means a second-order reaction. With the additional assumption of equal probabilities of recombination and retrapping, $A_{\mathrm{m}} = A_{\mathrm{n}}$, equation (2.16) can be solved if a certain temperature profile is assumed. If we assume a constant temperature (phosphorescence decay) integration yields:

$$\mathrm{I(t)} = \frac{\mathrm{I_0}}{(1+\mathrm{n_0}\alpha\mathrm{t})^2} \tag{2.17}$$

With $\alpha = \mathrm{s/N}\ \exp\ (-\mathrm{E/kT})$. This kind of decay is termed second order. It can be considered as a special case of Becquerel's decay law. It is seen that for this case of second-order kinetics the decay is not exponential but hyperbolic. Assuming a linear heating profile (according to equation (2.11)) integration of equation (2.16) gives

$$\mathrm{I(T)} = \frac{\mathrm{n_0^2}}{\mathrm{N}}\frac{\mathrm{s}}{\beta}\exp\left\{-\frac{\mathrm{E}}{\mathrm{kT}}\right\}\left[1+\frac{\mathrm{n_0 s}}{\mathrm{N}\beta}\times\int_{\mathrm{T_0}}^{\mathrm{T}}\exp\left\{-\frac{\mathrm{E}}{\mathrm{kT'}}\right\}\mathrm{dT'}\right]^{-2} \tag{2.18}$$

This is the Garlick–Gibson TL equation for second-order kinetics. The main feature of this curve is that it is nearly symmetric, with the high temperature half of the curve slightly broader than the low temperature half with a characteristic value of μ_g=0.52. This can be understood from the consideration of the fact that in a second-order reaction significant concentrations of released electrons are retrapped before they recombine, in this way giving rise to a delay in the luminescence emission and spreading out of the emission over a wider temperature range.

The initial concentration $\mathrm{n_0}$ appears here not merely as a multiplicative constant as in the first-order case, so that its variation at different dose levels change the shape of the whole curve. $\mathrm{T_m}$ decreases as $\mathrm{n_0}$ increases. It can be derived [20] that the temperature shift can be approximated by

$$T_1 - T_2 \approx T_1 T_2 \frac{k}{E} \ln f \tag{2.19}$$

Where T_1 is the temperature of maximum intensity at a certain dose and T_2 is the temperature of maximum intensity at an (f) times higher dose. From Eq. (2.19) it follows further that for a given increase of the dose the shallower the trap, i.e. the smaller E, the larger the peak shift.

Note that, similarly to the first-order case, the term dominating the temperature dependence in the initial rise is exp (−E/kT). So the 'initial rise method' for the determination of the trap depth can be applied here as well.

Also for second-order kinetics the glow peak shape, equation (2.18), can be approximated with a function written in terms of maximum peak intensity I_m and the maximum peak temperature T_m[18].

$$I(T) = 4I_m \exp\left(\frac{E}{kT}\frac{T - T_m}{T_m}\right) \times \left[\frac{T^2}{T_m^2}(1 - \Delta) \times \exp\left\{\frac{E}{kT}\frac{T - T_m}{T_m}\right\} + 1 + \Delta_m\right]^{-2} \tag{2.20}$$

With Δ and Δ_m are the same meaning as in equation (2.15) [11].

2.2.3 General-Order Kinetics

The forms of the (first-order) and the (second-order) of the equation of the thermoluminescence (TL) have been derived by using the specific, simplifying assumptions.

However, when these simplifying assumptions do not hold, the TL peak will fit neither first- nor the second-order kinetics. May and Partridge [21] used in the case of (general-order kinetics) an experimental expression for the kinetics of the general-order (TL), and this is

$$I(t) = -\frac{dn}{dt} = n^b s' \exp\left\{-\frac{E}{kT}\right\} \tag{2.21}$$

Where the dimension of (s') is $\left(m^{3(b-1)}s^{-1}\right)$ and (b) is defined as the general-order parameter and is not necessarily 1 or 2. Integration of equation (2.21) for b ≠1 yields

$$I(T) = \frac{s''}{\beta} n_0 \exp\left\{-\frac{E}{kT}\right\}\left[1 + (b-1)\frac{s''}{\beta} \times \int_{T_0}^{T} \exp\left\{-\frac{E}{kT'}\right\} dT'\right]^{-\frac{b}{b-1}} \quad (2.22)$$

Where ($s'' = s' n_0^{b-1}$) is in unit(s^{-1}). The equation (2.22) includes the second-order case (b=2) and reduces to equation (2.12) when $b \rightarrow 1$. It should be observed that according equation (2.21) the dimension of (s') should be ($m^{3(b-1)}s^{-1}$) that means that the dimension changes with the order (b) which makes it difficult to interpret physically. However, the case of the general-order is useful for intermediate cases can be dealt with and it running smoothly to the first-order when $b \rightarrow 1$ and to the second-order when $b \rightarrow 2$. For any non-first-order kinetics the temperature of the peak maximum is dependent of the initial concentration of charge carriers (n_0). The temperature shift can be approximated by following equation;

$$T_1 - T_2 \approx T_1 T_2 \frac{k(b-1)}{E} \ln f \quad (2.23)$$

Where T_1 is the temperature of maximum intensity at a certain dose and T_2 is the temperature of maximum intensity at an (f) times higher dose.

Also for general-order kinetics a function written in terms of maximum peak intensity I_m and the maximum peak temperature T_m has been derived [22].

2.2.4 Advanced Models

The model of the one trap-one center explains all the properties of the thermoluminescence (TL) phenomenon and interprets the behavior of the shape of the glow peak in accordance with the difference of the dose and heating rate. On the other hand, there is no existing TL material known that accurately is described by the simple model. This does not mean that the simple model has no meaning. But in opposite it has helped us to interpret a lot of features that can be considered like the variations of the one trap–one centre model. There is no room to discuss all the advanced (more realistic) models in detail. The reader is referred to the text book of Chen and McKeever [14] for a deeper and quantitative treatment. Here, only some models are very briefly mentioned in order to get some idea about the complexity of the phenomenon in a real TL material.

Generally, it will appear more than one single electron trap of real thermoluminescence material and it is not to be active all the traps in the range of temperature in which the sample is heated. A thermally disconnected trap is one which can be filled with electrons during irradiation but which has a trap depth which is much greater than the active trap such that when the specimen is heated only electrons trapped in the active trap (AT) and the shallow trap (ST) (see figure 2.6(a)) are freed. Electrons trapped in the deeper levels are unaffected and thus this deep electron trap (indicted in figure 2.6 (a) with DET) is said to be thermally disconnected. But its presence has an impact on the trapping filling and ultimately on the glow peak shape [24].

In Section 2.1 it was assumed that the trapped electrons are released during heating while the trapped holes are stable in the recombination centre. A description in which the holes are released and recombine at a centre where the electrons are stable during heating is mathematically identical. In contrast, the situation will change if both electrons and holes are released from their traps at the same time at the same temperature interval and the holes are being thermally released from the same centers as are acting as recombination sites for the thermally released electrons and vice versa (see figure 2.6 (b)). The equation (2.2) is invalid in this case. New differential equations should be drafted. Analysis of this complicated kinetic model reveals a TL glow curve which retains the simple Randall–Wilkins (equation (2.12)) or Garlick–Gibson (equation (2.18)) shape, depending upon the chosen values of the parameters. On the other hand, the (E) and (s) values used in equation (2.12) and equation (2.18) in order to obtain a fit on this complicated kinetic model need further interpretation.

Other process which might happen is a recombination without a transition of the electron into the conduction band (figure 2.6(c)). Here, the electron is thermally stimulated into an excited state from which a transition into the recombination centre is allowed. This means that the trap has to be in the proximity of a centre.

The transition probability may strongly depend on the distance between the two centers. Under certain assumptions an expression for the TL intensity can be derived [24] which has the same form as equation (2.12) but with s replaced by a quantity related to the probability for recombination. This means that these localized transitions are governed by first-order kinetics.

Finally, we will mention the possibility that the defect which has trapped the electron is not stable but is involved in a reaction with another defect (figure 2.6(d)). The result may be that at low temperature the trap depth is changing while the trapped electron concentration is stable. At higher temperatures electrons are involved in two processes: the escape to the conduction band and the defect reaction.

Piters and Bos [25] have defect reactions incorporated into the rate equations and glow curves simulated. It appears that the simulated glow curves can be very well fitted by equation (2.12) it is clear that (again) the fitting parameters do not have the simple meaning of trap depth and escape frequency.

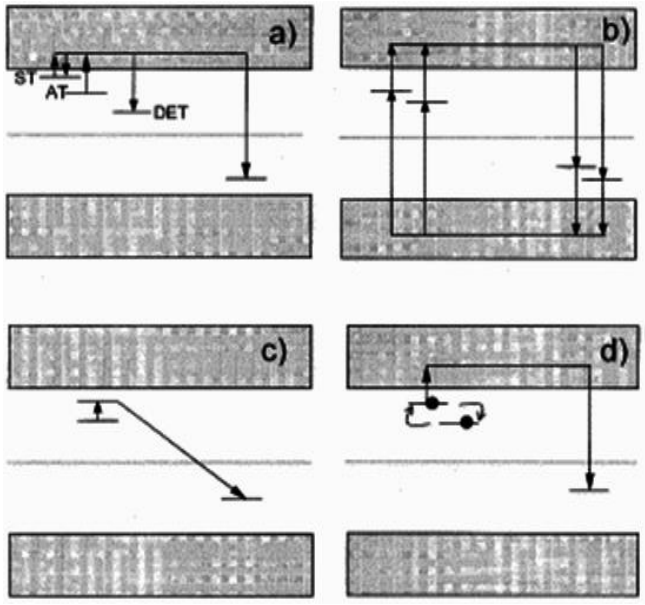


Figure 2.6 Advanced models describing the thermally stimulated release of trapped charged carriers including: (a) Where (ST) is a shallow trap , (DET) is a deep electron trap and (AT) is an active trap; (b) two centres of recombination and two active traps; (c) is a localized transition; (d) explains the defect interaction (center of trapping interacts with another defect).

CHAPTER 3

THERMOLUMINESCENCE ANALYSIS

3.1 Trapping Parameter Determination Methods

The determination of trapping parameters from thermoluminescence glow curves has been a subject of interest for half a century. There are different methods for evaluating the trapping parameters from the glow curves [12-13, 24, 26-30].

When one glow peak is highly isolated from the others, the experimental methods such as initial rise, variable heating rates, isothermally decay, and peak shape methods are suitable methods to determine these parameters. In contrast in most materials, the glow curve consists of different peaks as in the APSQ. In case of overlapping peaks there are essentially two ways to obtain these parameters, the first one is the partial thermal cleaning method and the second one is the computer glow curve deconvolution program. In most cases, the partial thermal cleaning method cannot be used to completely isolate the peak of interest without any perturbation on it. Thus, the computer glow curve deconvolution program has become very popular method to evaluate trapping parameters from TL glow curves in recent years [31].

3.1.1 Peak Shape Method

The first peak shape method was developed by Grossweiner [27], later Chen [26] modified Halperin and Braner's equation [28] for calculating (E) values. Chen [32] derived expression for evaluating (E) using numerical approximations. The Chen method is useful for a broad range of energies ranging between 0,1 eV and 2.0 eV and pre-exponential factors between $10^5 s^{-1}$ and $10^{13} s^{-1}$and it does not make any use of literature procedures. Moreover, the method does not need any knowledge of the kinetics order which is directly found from the peak slope. Its method is based on the shape of TL peak, similarly to the Lushchik [33] and Halberin – Braner method [34].

For simplicity, the parameters involve in a well resolved peak are here reported in figure 3.1

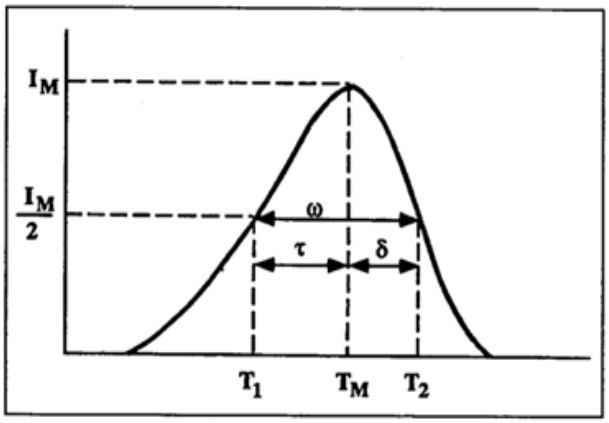


Figure 3.1 Parameters characterizing of single peak.

Where T_m,T_1 and T_2: are respectively the peak temperature at the maximum and the temperatures on either side of the temperature at the maximum, corresponding to half intensity,

$\tau = T_M - T_1$: is the half-width at the low temperature side of the peak,

$\delta = T_2 - T_M$: is the half-width towards the fall-off of the glow peak,

$\omega = T - T_1$: is the total half-width,

$\mu_g = \delta/\omega$ is the symmetrical geometrical factor (shape parameter).

The order of kinetics (b) can be estimated by means of shape parameters. Chen [30] found that (μ_g) is not sensitive to changes in (E) and (s), but it changer with the order of kinetics (b). It has been shown that the ranges of (μ_g)varies from 0,42 for b=1 to 0,52 for b=2 in case of linear heating. Interpolating and extrapolating the constants appearing in the equations for the first and second order, Chen gave a general expression which summarizes all the previously given expressions.

$$E_\alpha = c_\alpha \left(\frac{kT_M^2}{\alpha}\right) + b_\alpha(2kT_M) \qquad (3.1)$$

With α is τ, δ or ω. The values of $c_\alpha$and $b_\alpha$are summarized as:

$c_\tau = 1.51+3.0(\mu_g - 0.42)$ $\qquad$ $b_\tau = 1.58+4.2(\mu_g - 0.42)$

$c_\delta = 0.976+7.3(\mu_g - 0.42)$ $\qquad$ $b_\delta = 0$ $\qquad$ (3.2)

c_ω= 2.52+10.2(μ_g– 0.42) b_ω=1

With

μ_g= 0.42 for 1^{st}order

μ_g= 0.52 for 2^{nd}order

Chen [35] calculated a graph of μ_g, ranging from 0.36 to 0.55 for values of *b* between 0.7 and 2.5 which can be used for the evaluation of b from a measured μ_g.

Other graph has been proposed by Balarin [36] which gives the kinetics order as a function of $\gamma = \delta/\tau$.

Once the activation energy is obtained, one can find the frequency factor using the following equation

$$s = \left(\frac{\beta}{T_M^2}\right)\left(\frac{E}{k}\right)\left(\frac{1}{1+(b-1)(\frac{2kT_M}{E})}\right)\exp\left(\frac{E}{kT_M}\right) \qquad (3.3)$$

3.1.2 CGCD Method

Deconvolution computer glow curve (CGCD) method has the features of the experimental ways in that they can be used in largely interlaced-peak glow curves without the need for heat treatment. And it is one of the most important ways for determining the trapping parameters of the thermoluminescence (TL) glow curves.

In this study, a CGCD program was used to analyze the glow curve of APSQ. The program was developed at the Reactor Institute at Delft, The Netherlands [37].This program is capable of simultaneously deconvoluting as many as nine glow peaks from glow curve. Two different models were used in the computer program. In the first model, the glow curve is approximated from first order TL kinetic by the expression,

$$\mathrm{I(T)} = \mathrm{n_o s}\exp\left(-\frac{E}{kT}\right)\exp\left[\left(\frac{s\ k\mathrm{T}^2}{\beta E}\exp\left(-\frac{E}{kT}\right)\right)\times\left(0.9920-1.620\frac{kT}{\mathrm{E}_\alpha}\right)\right] \qquad (3.4)$$

In the second model, the glow curve is approached with general order thermoluminescence (TL) kinetics by using the below expression,

$$I(T) = n_o s\ \exp\left(-\frac{E}{kT}\right)\left[1 + \left(-\frac{(b-1)s\ kT^2}{\beta E}\exp\left(-\frac{E}{kT}\right)\right) \times \left(0.9920 - 1.620\frac{kT}{E_\alpha}\right)\right]^{\frac{b-1}{b}} \quad (3.5)$$

where ($n_o(m^{-3})$) is the concentration of trapped electrons at t=0, (s (s^{-1})) is the frequency factor for first-order and the pre-exponential factor for the general-order, E (eV) the activation energy, T (K) the absolute temperature, k (eVK^{-1}) Boltzmann's constant, β(℃ s^{-1}) heating rate and (b) the kinetic order.

The summation of overall peaks and background contribution can lead to composite glow curve formula as shown below

$$I(T) = \sum_{i=1}^{n} I_i(T) + a + b\exp(T) \quad (3.6)$$

Where I (T) is the fitted total glow curve, allows for the electronic noise contribution to the planchet and dosimeters infrared contribution to the background. Starting from the above equation (3.8), the least square minimization procedure and also FOM (figure of Merit) was used to judge the fitting results as to whether they are good or not. i.e.

$$FOM = \sum_{i=1}^{n} \frac{|N_i(T) - I(T)|}{A} = \sum_{i=1}^{n} \frac{|\Delta N_i|}{A} \quad (3.7)$$

Where $N_i(T)$ is i-th experimental points (total n=200 data points), I (T) is i-th fitted points, and A is the integrated area of the fitted glow curve. From many experiences [17,41], it can be said that if the values of the FOM are between 0.0% and 2.5% the fit is good, 2.5 % and 3.5% the fit is fair, and > 3.5% it is bad fit.

To have a graphic representation of the agreement between the experimental and fitted glow curves, the computer program also plots the function,

$$X(T) = \frac{N_i(T) - I_i(T)}{\sqrt{I_i(T)}} \quad (3.8)$$

Which is a normal variable with an expected value 0 and σ=1 where $\sigma^2(T) = I_i(T)$.

3.1.3 Heating Rate Method

Various heating rates are another important method to determine (E), and the peak temperatures will be different when heating the sample at two several heating rates (β_1) and (β_2). It can be written the above equation (3.14) for each heating rates and dividing the equation for (β_1 and T_{m1}) by the equation for ($\beta_2$and T_{m2}) and reordering, one obtains an obvious equation to calculate the activation energy (E)

$$E = k\frac{T_{m1}T_{m2}}{T_{m1} - T_{m2}}\ln\left[\left(\frac{\beta_1}{\beta_2}\right)\left(\frac{T_{m2}}{T_{m1}}\right)^2\right] \tag{3.9}$$

The basic feature of the method of the heating rate is that it only needs data that should be taken at a maximum peak (T_m,I_m) which, in case of a large peak surrounded by smaller satellites, can be sensibly accurately identified from the glow curve. Moreover the problems which are due to thermal quenching, are not effect on the calculation of (E) as with the initial rise method.

When one used the various heating rates for the first-order kinetics, can be obtain the following expression:

$$\ln\left(\frac{\mathrm{T_m^2}}{\beta}\right) = \left(\frac{\mathrm{E}}{\mathrm{k}}\right)\left(\frac{1}{\mathrm{T_m}}\right) + \text{constant} \tag{3.10}$$

Plotting ln (T_m^2/β) against ($1/T$) a linear plot is obtained with slope equal to (E/k). Hence it is possible to evaluate (E). In addition, and extrapolating to ($1/T_m = 0$), a value for ($ln\ (sk/E)$) is obtained from which frequency factor (s) can be calculated by entering the value of (E/k) obtained from the slope. This various heating rate method is applicable for general-order kinetics which contains the second-order case. For the general order case, one can plot (ln $[I_m^{b-1}(T_m^2/\beta)^b]$) against ($1/T_m$), whose slope is equal to (E/k).

CHAPTER 4

EXPERIMENTAL PROCEDURE

The materials, equipments and experimental procedures used in this work were described below.

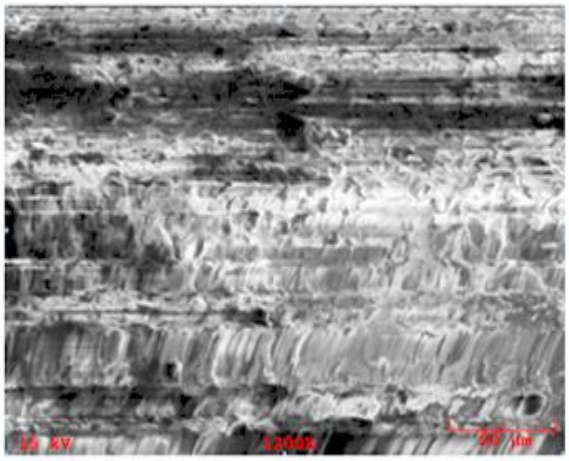
4.1 Materials

The samples used in this study were pink and white marbles obtained from Gaziantep and Mersin city. The data and graph of these marbles is taken Electron Microscope in the below figure 4.1 and 4.2

4.2 Experimental Procedure and Equipments

The samples were first annealed to wipe any remaining information and then cool rapidly in the air at (75 ℃/min) to the temperature of the room. All the annealing treatments were implemented with specially designed oven of microprocessor-controlled electrical which is able to control the temperature within (± 1.0℃). The samples were irradiated at room temperature with beta rays from a calibrated ^{90}Sr-^{90}Ysource. The β-source activity is about (100 mCi). Strontium–90 emits high - energy beta particles from their daughter products (^{90}Srβ -0.546 MeV together with ^{90}Yβ - 2.27 MeV). Beta radiation is absorbed by air, since its intensity reduced with distance much more quickly than inverse square law calculations would indicate. The maximum range of Y–90 beta particles in air is roughly 9 meters. 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 for fine grains of aluminium, or 3,3 Gy/min=0.055 Gy/Sec for 100 m quartz on stainless steel.

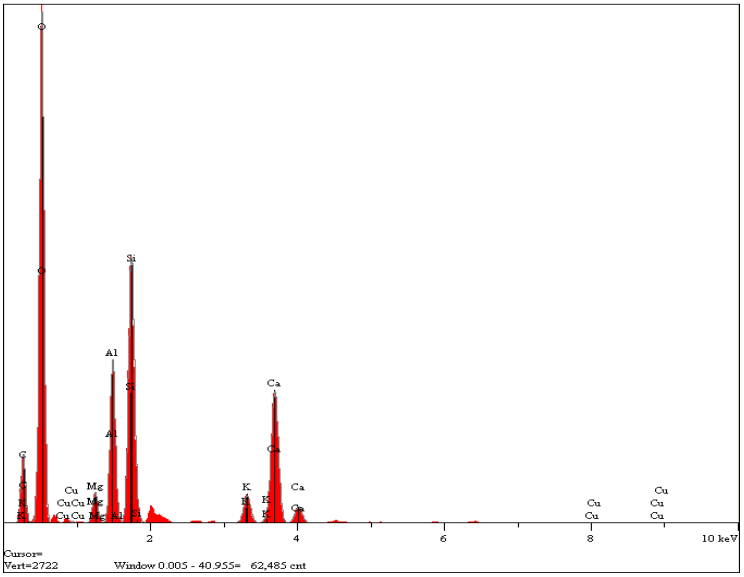
The equipment of irradiation is an additional part of the 9010 Optical Dating System which is purchased from Little More Scientific Engineering, UK [38].



(a)

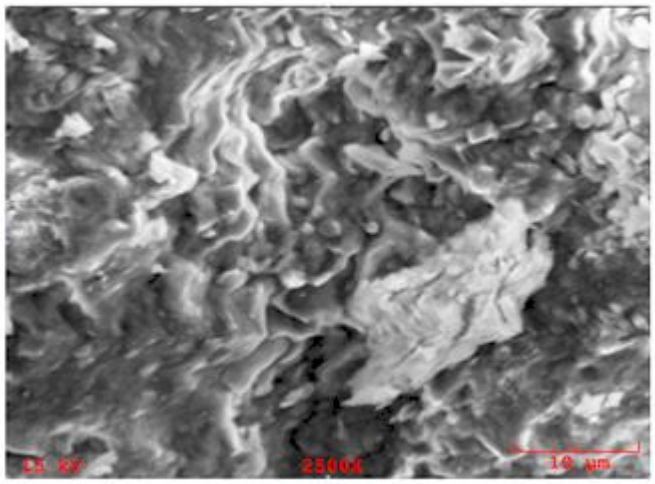
Elt.	Line	Intensity (c/s)	Conc	Units	Error 2-sig	MDL 3-sig	
C	Ka	27.87	12.128	wt.%	2.098	0.264	
O	Ka	215.01	55.603	wt.%	0.684	0.196	
Mg	Ka	14.19	1.419	wt.%	3.754	0.096	
Al	Ka	77.54	6.909	wt.%	1.257	0.086	
Si	Ka	133.30	11.731	wt.%	0.915	0.082	
K	Ka	16.92	1.832	wt.%	2.901	0.071	
Ca	Ka	84.67	9.912	wt.%	1.103	0.077	
Cu	Ka	0.80	0.465	wt.%	15.660	0.132	
			100.000	wt.%			Total

(b)



(c)

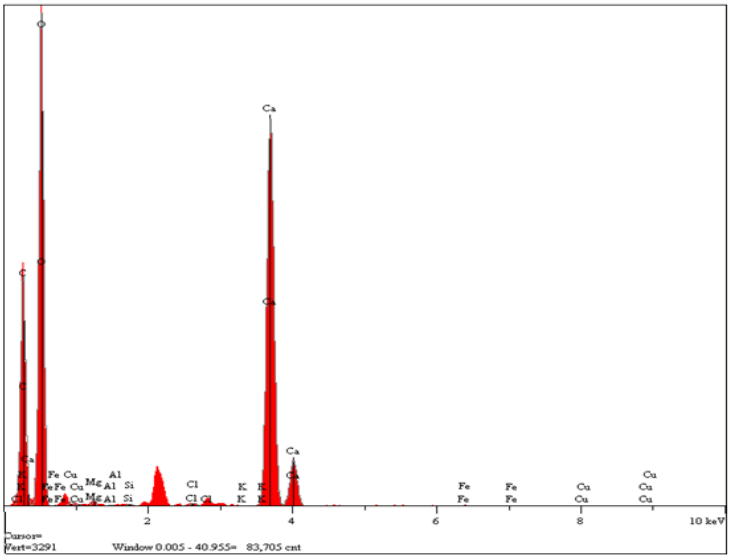
Figure 4.1 The data and graph of white marble is taken Electron Microscope (a, b, c,).



(a)

Elt.	Line	Intensity (c/s)	Conc	Units	Error 2-sig	MDL 3-sig	
C	Ka	129.22	17.220	wt.%	0.901	0.102	
O	Ka	263.18	58.844	wt.%	0.626	0.209	
Na	Ka	1.20	0.114	wt.%	32.672	0.112	
Mg	Ka	2.97	0.209	wt.%	14.086	0.085	
Al	Ka	0.98	0.059	wt.%	48.024	0.074	
Si	Ka	1.36	0.075	wt.%	34.682	0.065	
Cl	Ka	2.40	0.141	wt.%	17.213	0.060	
K	Ka	0.00	0.000	wt.%	-1.#IO	0.000	
Ca	Ka	312.46	22.932	wt.%	0.558	0.070	
Fe	Ka	0.80	0.149	wt.%	27.379	0.098	
Cu	Ka	0.68	0.259	wt.%	25.599	0.146	
			100.000	wt.%			Total

(b)



(c)

Figure 4.2 The data and graph of pink marble is taken Electron Microscope (a, b, c,).

The irradiated samples were read out by a reader of Harshaw QS 3500 manual type that is connected to a PC where studied and analyzed the signals of thermoluminescence. It economically provides high reliability. The basic block diagram of reader is illustrated clearly in the figure 4.3. It always has been installed the standard filter of clear glass in the reader between the planchet and photomultiplier tube to eliminate the emitted infrared lights from the reader plus samples. All functions are divided between the reader and the specialized software Shell of the TLD that are running on the computer. All data storage, instrument control, and operator inputs are performed on the PC. Signal acquisition and conditioning are performed in the reader. As such, and can be analyzed each glow curve by using a best-fit computer program depends upon a procedure of a Marquardt algorithm minimization, related to expressions of the first-order and general-order kinetics. The individual peaks present in the curve are resolved by the program, giving the best values for the parameters of different peak. The instrument includes a sample change drawer for inserting and removing the TLD elements. The reader uses contact heating with a closed loop feedback system which produces adjustable linearly lifted temperatures from (1℃) to (50℃) per second accurate to within (± 1℃) to (600 ℃) in the standard reader.

The Time Temperature Profile (TTP) is user defined in three segments. Pre-heat, Acquire, and Anneal, each with independent times (Pre-read anneal: adjustable 0 Sec to 1000 Sec, Linear ramp: adjustable from (1℃) to (50℃) per second, Post-read anneal: (0 Sec to 1000 Sec)) and temperature (Pre-read anneal: room temperature to (200℃), Post-read anneal: up to (400℃)). Figure 4.4 demonstrates the profile of the typical time temperature. For improving the low-exposure reading accuracy and to extend planchet life, the 3500 provides for nitrogen to flow around the planchet. Through the elimination of oxygen in the salinity, flow of nitrogen eliminates unwanted TL signal caused by the oxygen. Nitrogen is also directed through the photo-multiplier tube (PMT) chamber to eliminate moisture caused by condensation.

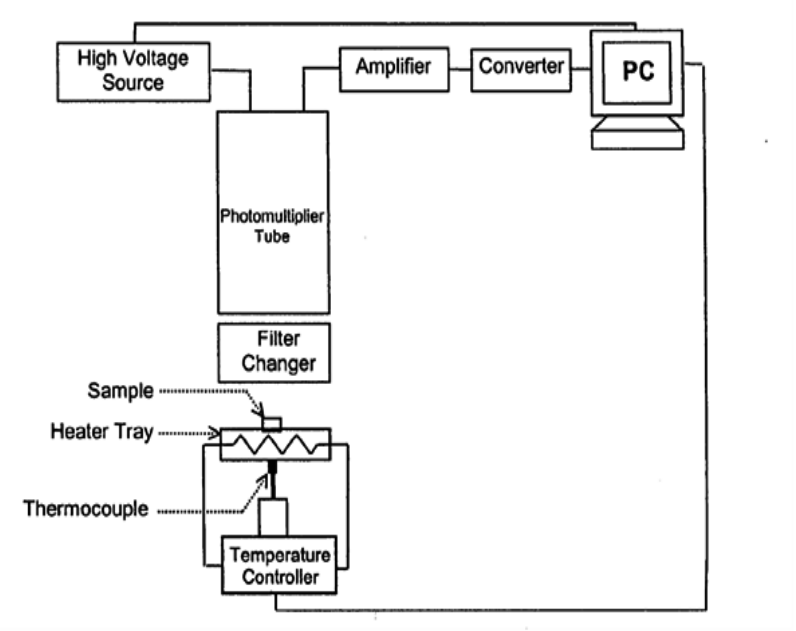


Figure 4.3 Basic block diagram of TL reader [38].

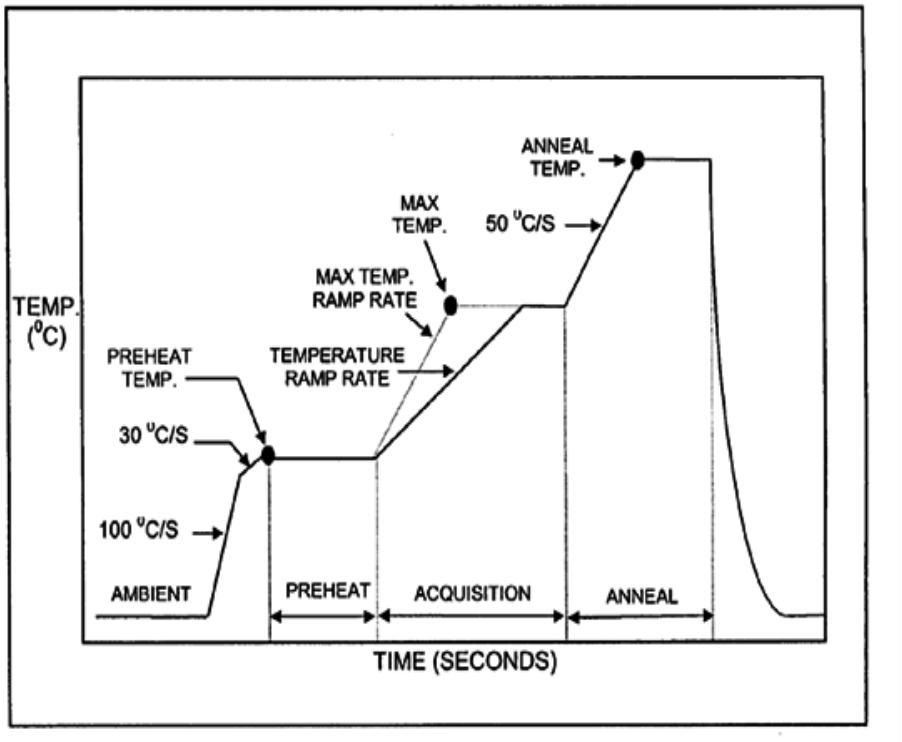
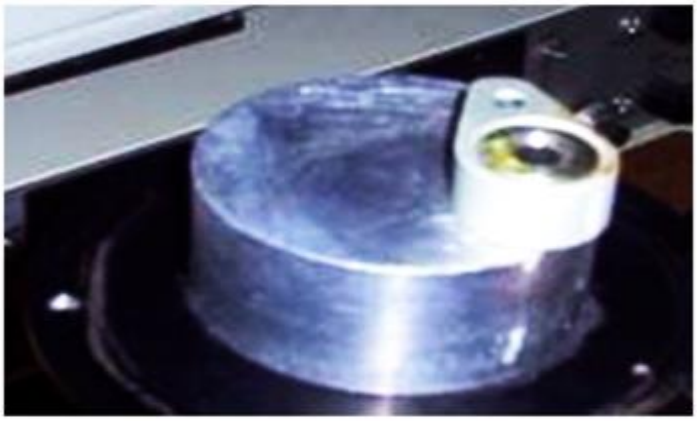


Figure 4.4 Typical time temperature profile (TTP) [38].



(a)

(b)

(c)

Figure 4.5 Experimental equipments (a) ^{90}Sr-^{90}Y β-source (b) 9010 Optical Dating System (c) Harshaw TLD System 3500.

CHAPTER 5

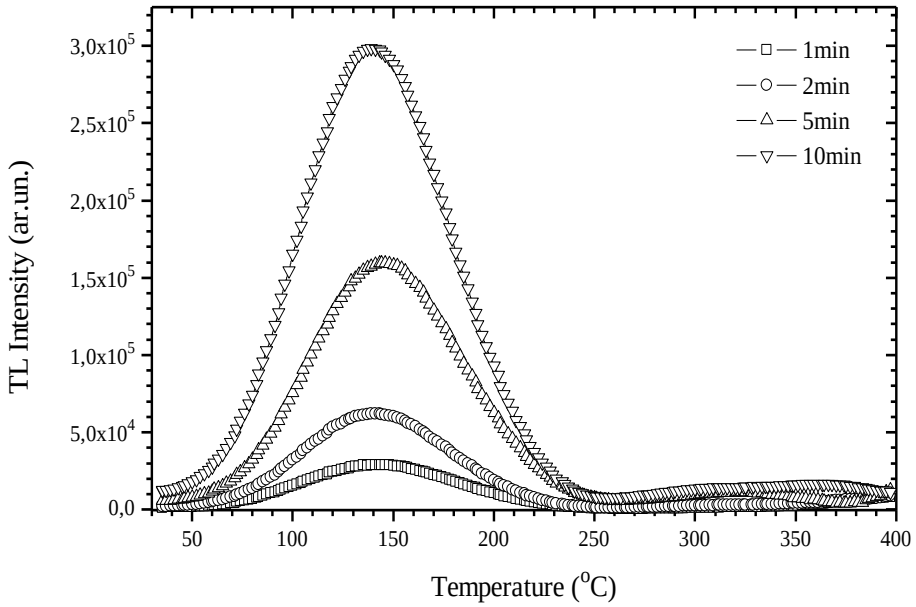
EXPERIMENTAL RESULTS

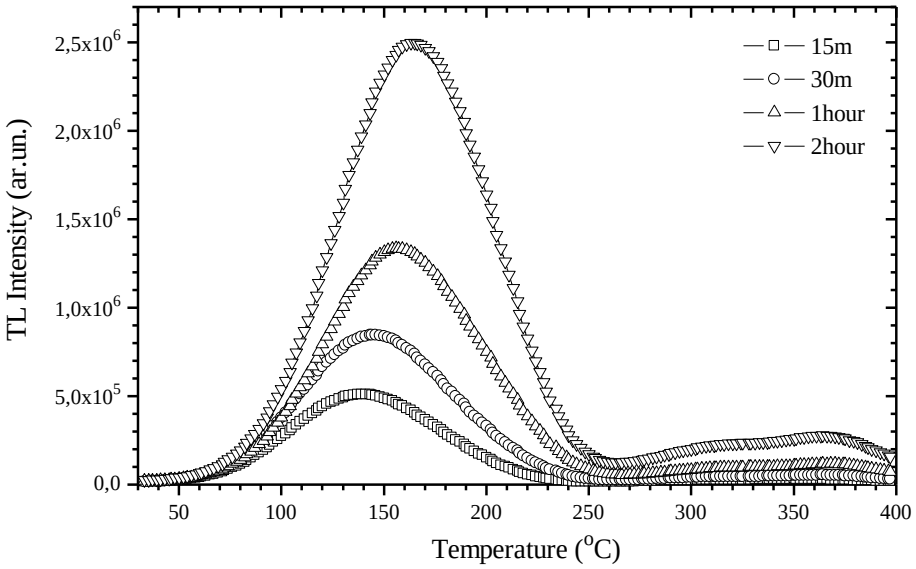
Thermoluminescence (TL) is a useful and sensible method to record radiation information in insulators and it is extensively used in several fields such as; radiation dosimetry and archaeological dating, also to examine the crystalline defects and lately in the sensing of phase transitions [1]. The thermoluminescence (TL) event has been studied for ages. It has been done a great deal of study to get a better understanding and enhance the properties of the substances and also to grow a new thermoluminescence material. Now, (TLD) is an established dosimetric way with measured dose used in areas like (personnel, clinical and environmental dosimetry). TLD depends on materials which give off light while they are heated [39].

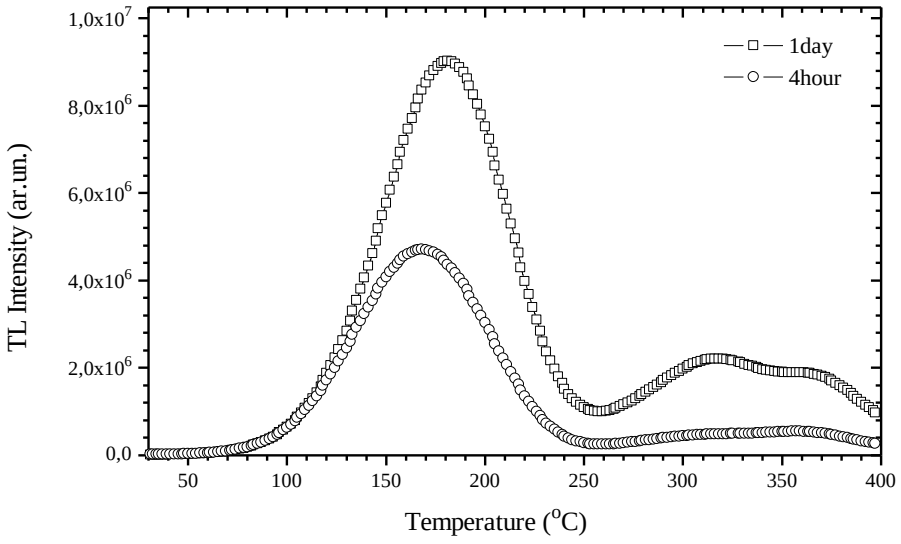
The determination of (E_a) and (s) primarily relies on the prior knowledge of (b) and exact number of glow curve [40]. The investigations were based on the principle of different characteristic response patterns of glow peaks during irradiation. In most situations, the glow peaks grow linearly at low-level exposure. No significant discrimination in the shapes of overlapped peaks can be observed at this situation. As the exposure level increases, the growth of TL peaks would behave in different patterns. Some are still linear while others are supralinear or sublinear. Therefore, the highly overlapped glow peaks become distinguishable through a series of high-level irradiations. In theory of thermoluminescence (TL) [18], supposed to alter the glow peak temperatures solely with the heating rate for (b=1). Hence, for a constant heating rate (β), the peak temperature should not be affected by other experimental parameters and should be quite constant in the extent of the experimental precariousness. Whereas, for ($b\neq1$) and below the trap saturation points {n_0 (concentration of trapped electrons) <Nt (concentration of traps)}, it is generally received that the peak temperatures are shifted to the lower-temperature side with increasing dose levels.

The pink and white marbles were irradiated at several doses between (≈2,4 Gy) and (≈3,5 kGy) to check the dose dependency influence on the peak positions. Some of the chosen glow curves after several dose levels can be shown in figure 5.1. The experimental observations have clearly shown that there were no significant changes in the peak temperature of glow peak white and pink marbles with increasing dose level. The positions of peak temperature of this peak are within the experimental imprecision (±4 ℃) for all the doses. This point clearly indicates that the all peaks in the glow curve of calcite should have the first-order kinetics. The additive dose experiments the measured glow curves were as well as utilized for calculating the trapping parameters of the peak shape method. This method is based on the shape and full width at half maximum (FWHM=T_2-T_1) of a single glow peak and the values of E_a were determined by the modified peak shape (PS) method of Chen [41]. According to this technique, the (*b)* of a single peak is easily obtained by means of the geometric factor {μ_g= (T_2-T_m) / (T_2-T_1)} and (μ_g) changes with the order of kinetics (*b)* from (≈0.42 to ≈0.52) where these two limits correspond to first-order and second-order kinetics, respectively. The kinetic parameters have also identified by using Gartia, Singh & Mazumdar peak shape (PS) method in addition to Chen's peak shape (PS) method [26] which needs the previous information of the kinetics order.

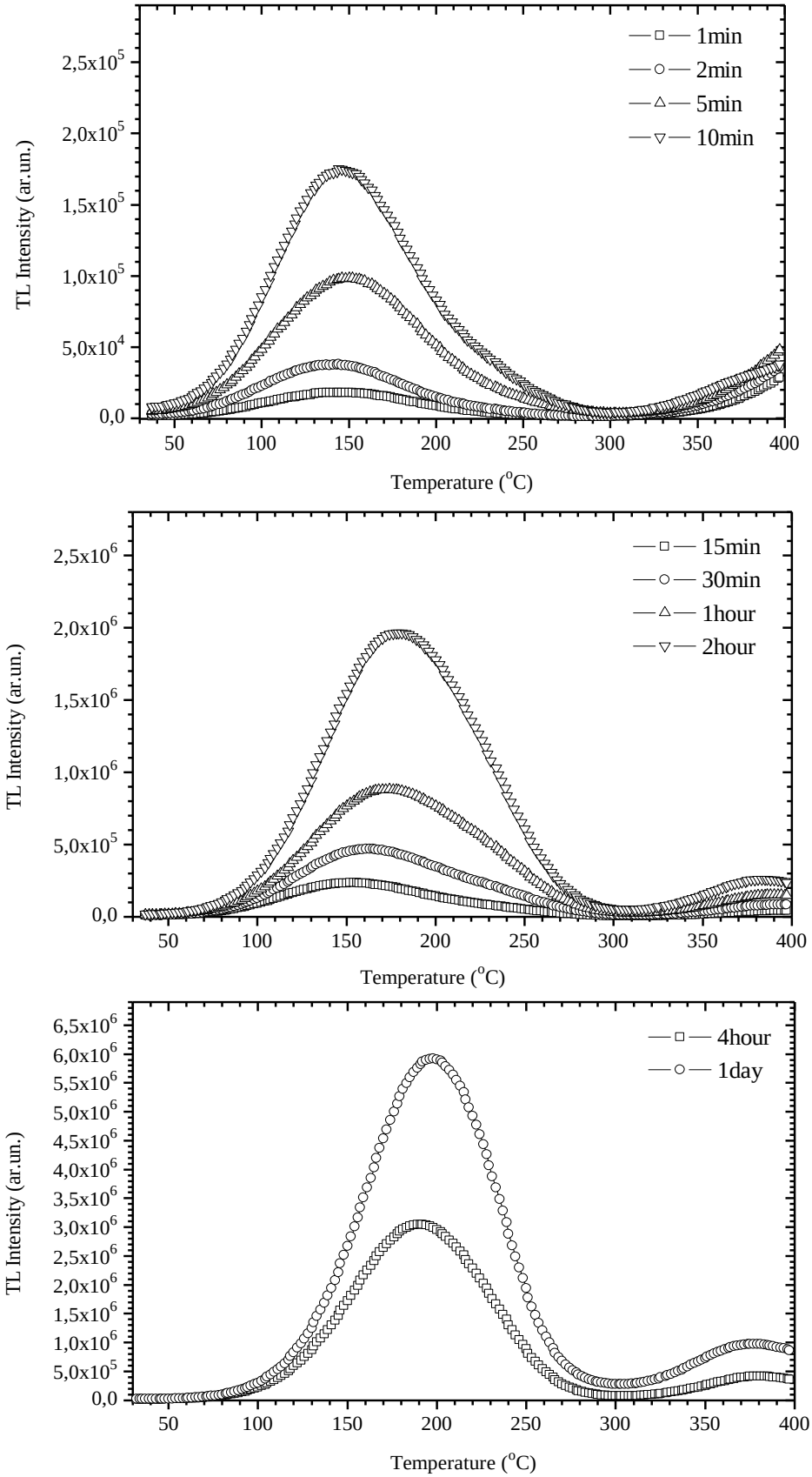
Some another technique which is used for calculating the trapping parameters in this thesis is the way of the various heating rates (VHR). This technique relies on an attitude change of temperature (T_m) at the maximum intensity point (I_m) to higher temperatures as increases the heating rate. In the lack of an activation energies distribution, a drawing ofln (T_m^2/β) against (1/ (kT_m)) could offer a straight line of rise (E_a/k) and objection ln (sk/E_a). The foremost features of this technique are that the needed information must be taken at the high end of the peak. It can be correctly found the (I_m,T_m) from the glow curve, if there is a large peak surrounded by smaller satellites. And then applied the different linear heating rates in this method between (1 ℃ $s^{-1}$and 20 ℃ s^{-1}). And some of the measured glow curves can be seen after these heating rates in figure (5.2).


TL Intensity (ar.un.)
3,0x10^5
2,5x10^5
2,0x10^5
1,5x10^5
1,0x10^5
5,0x10^4
0,0
50
100
150
200
250
300
350
400
Temperature (°C)
1min
2min
5min
10min


TL Intensity (ar.un.)
2,5x10^6
2,0x10^6
1,5x10^6
1,0x10^6
5,0x10^5
0,0
50
100
150
200
250
300
350
400
Temperature (°C)
15m
30m
1hour
2hour


TL Intensity (ar.un.)
1,0x10^7
8,0x10^6
6,0x10^6
4,0x10^6
2,0x10^6
0,0
50
100
150
200
250
300
350
400
Temperature (°C)
1day
4hour

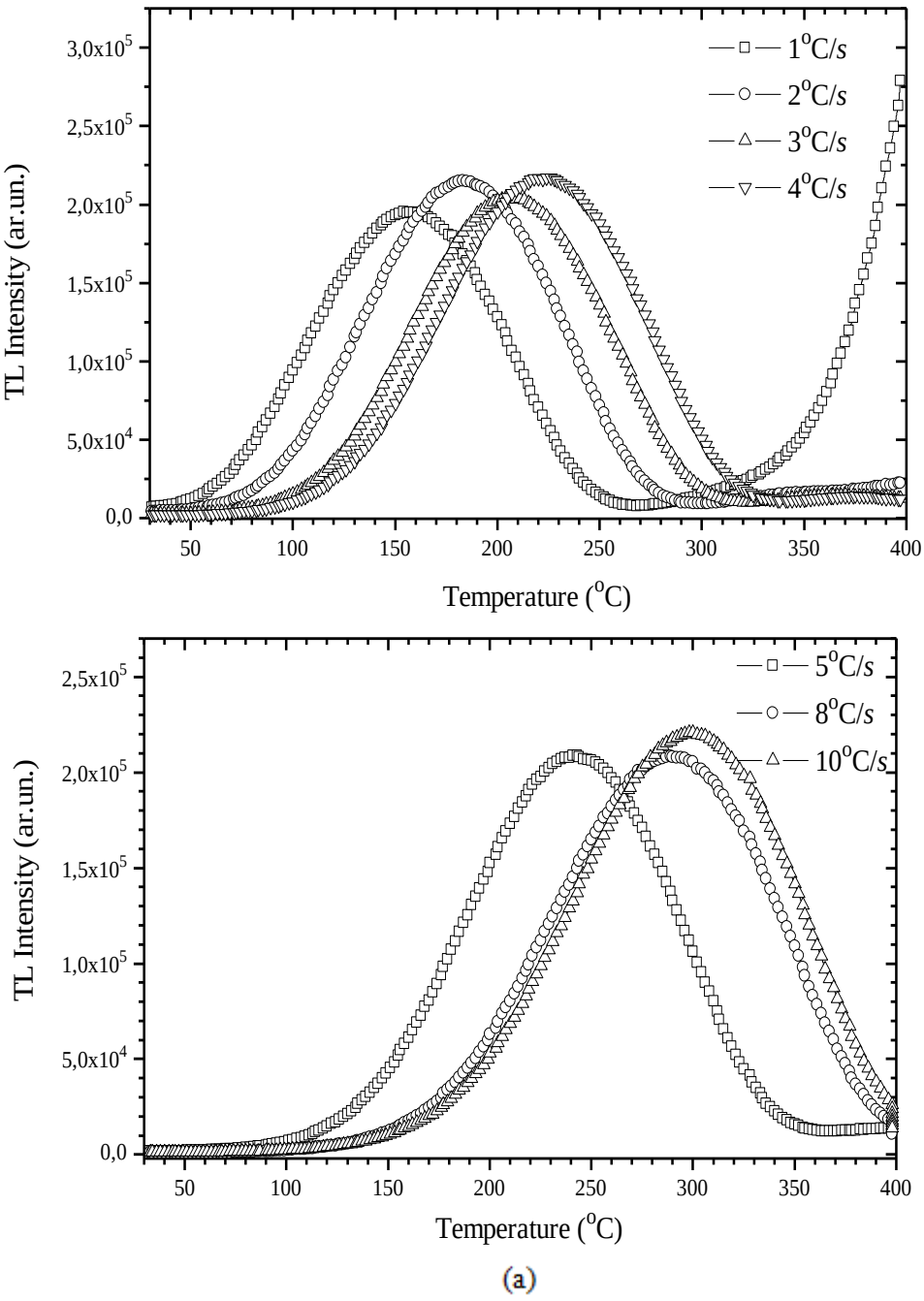
(a)



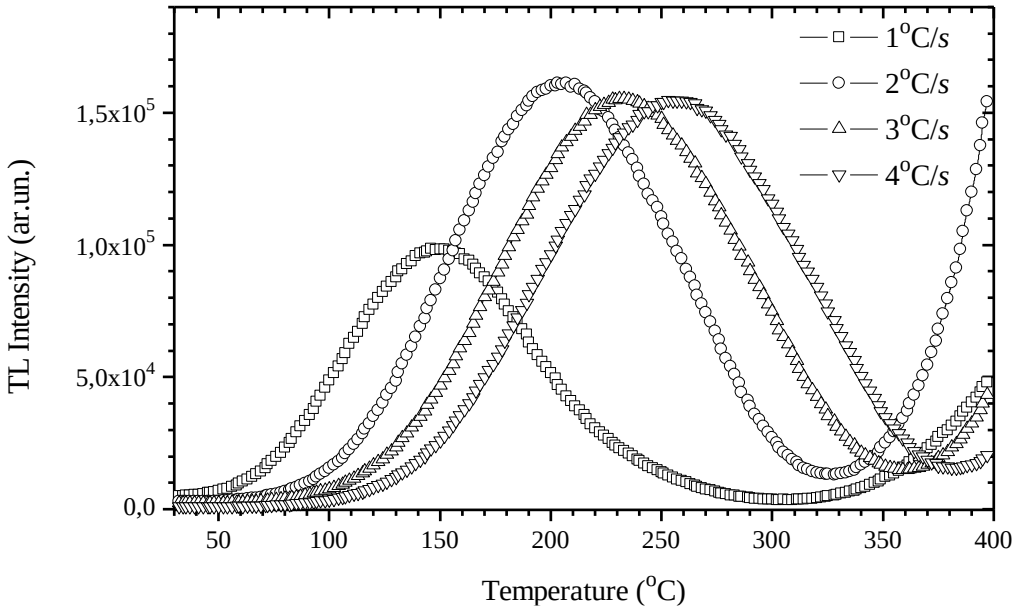
(b)

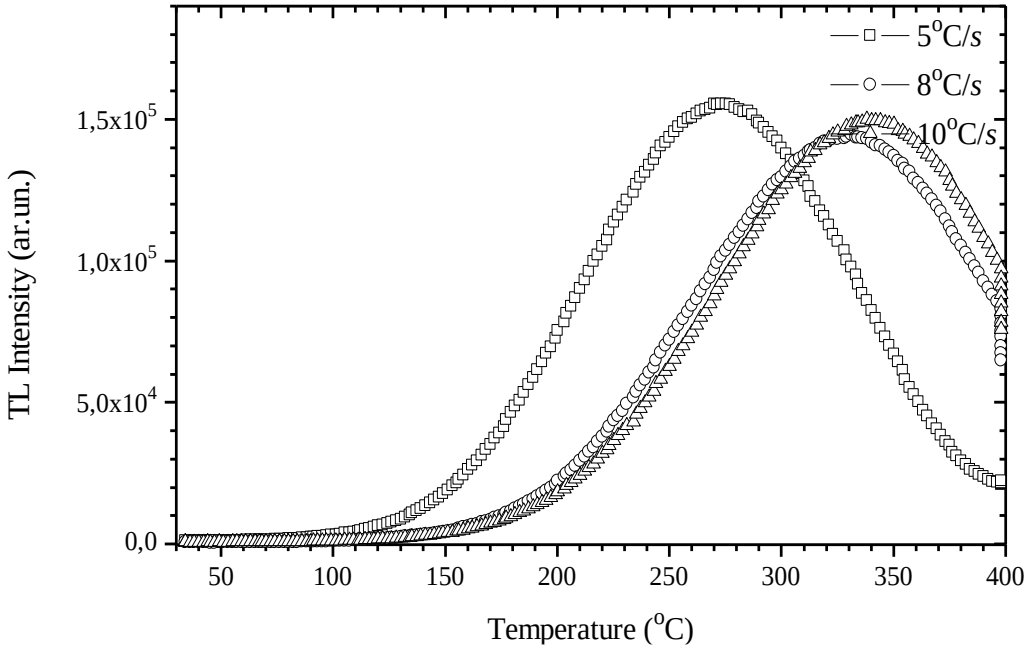
Figure 5.1The glow curve of marbles measured after different radiation exposed dose levels (β =1℃ /s). (a) White marble. (b) Pink marble.

This figure demonstrates that the temperature of the peak maximum increases by increasing of the heating rate, but in addition to that there is a small decrease in each of the intensities of the glow peaks. The decreasing luminescence intensity of glow peaks of Marbles phosphor as a function of the increasing heating rate is an event frequently observed in the practice of TSL. It has been recommended that it is because the effect of thermal quenching which reduces the effectiveness of the luminescence when increases temperature due t the increased non-radiative transition probability [42]. The result of the trapping parameters calculated from the slopes and intercepts are given in the table 5.1.



(a)





(b)

Figure 5.2 Some of the selected glow curves of Marbles measured at different heating rates for (1, 2, 3, 4, 5, 8, and 10 ℃ /s). (a) White marble. (b) Pink marble.

The analysis of the glow curve was also done by using the computer glow curve deconvolution (CGCD) technique. For the last two decades this technique has become very favorable for evaluating the trapping parameters [43]. It has extensive superiority when it is compared to the experimental methods due to the coincident evolution of trapping parameters of all peaks without additional thermal treatments and experimental repetitions. After, in this technique can be used all the data points for one

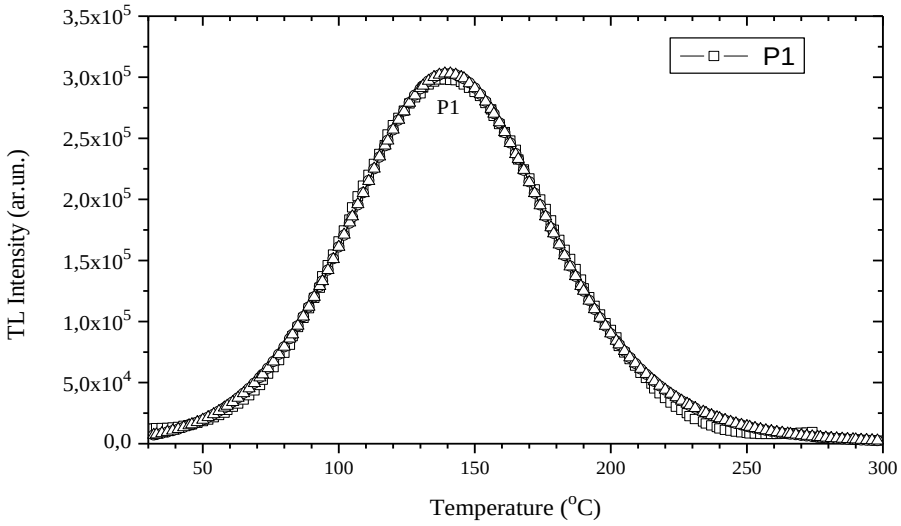
of the glow curves instead of a few points only through the operations of the appropriate curve. If increase one of them the number of data points utilized in the analysis, it is clear that the possibility for right decision of the trapping parameters also increases [44].

Although, it should be pointed that various samples, estimations and procedures of minimization may be utilized for the analysis of the glow curves in the computer glow curve deconvolution program. In short, one may be questioned about if the results of CGCD method reveal the true trapping parameters of the thermoluminescence glow peaks. On the authority of many proficient researchers, in some cases, the results that taken by the method of the computer glow curve deconvolution, look to be unsure [45]. One may obtain a local minimum of the least square function which may result erroneous trapping parameters as the computerized appropriate routine tries to determine the "best-fit" to the numerical data. In conclusion, applies many sets of kinetic parameters could be designated to the same glow curve. The utilized program of the CGCD, which rely on the procedure of the least square minimization, was developed at the Reactor Institute at Delft, The Netherlands. An IRI-CIMAT Report gave the detailed results of these models [37].

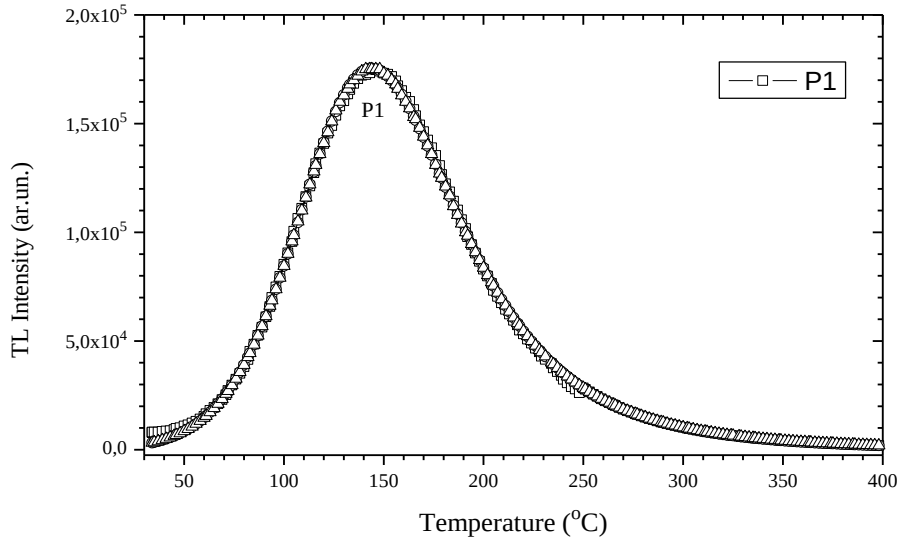
The fit goodness for each measured glow curve was tested by using the figure of merit (FOM) [3]. It can be interpreted that, the fit is good, if the (FOM) values are among the range of (0.0% and 2.5%), but is fairly fit, if the values of (FOM) are between (2.5% and 3.5%), and the fit is bad if the value of (FOM) greater than (3.5%). It is so important to decide properly in the complex glow curve analyses by the method of CGCD the number of glow peaks exists in the glow curve and which of them have kinetics of the (first-order or general-order) to get real results [46].

In some cases, when used several peak numbers in the CGCD analysis instead of real numbers of glow peaks to be in the glow curve can be obtained the best-fits. In any way, the kinetic parameters values do not reflect their correct values when suppose that an incorrect number of the glow peaks in the glow curve even if obtain the best-fits. Therefore, first one should be determine the number of glow peaks and their kinetic orders in the glow curve of Marbles. In this study it was noted that the structure of the glow curve of this model is described well by three general-order glow peaks. Because, the kinetic parameter results are also relying heavily on the input parameters like the individual peak site [47]. The parameters finally so selected were the values

that resulted to best overall fit to the features of the certain high priority of the thermoluminescence (TL) results. The CGCD fitting results on the assumption of three peaks are seen in the figure 5.1 and the table 5.1 summarizes the values of ($E_a$and s).



(a)



(b)

Figure 5.3 The CGCD analyzed glow curves of Marbles measured after 72 Gy irradiation by beta ray at room temperature. (a) White marble. (b) Pink marble.

Table 5.1 The values of the trapping parameters of TL peaks of Marbles determined by Chen's PS, Mazumdar PS, VHR and CGCD methods.(a) White marble (b) Pink marble.

(a)

P1	Mazumdar P.S.			Chen P.S.				
	1/2 ratio	2/3 ratio	4/5 ratio	E_τ	E_δ	E_ω	CGCD	VHR
E (eV)	0,52	0,54	0,56	0,498	0,555	0,524	0,498	0,505
b	2	2	2	2	2	2	2	2
lns(s^{-1})	18,5	18,3	18,6	17,5	17,8	17,4	16,92	17,05

(b)

P1	Mazumdar P.S.			Chen P.S.				
	1/2 ratio	2/3 ratio	4/5 ratio	E_τ	E_δ	E_ω	CGCD	VHR
E (eV)	0,49	0,52	0,55	0,50	0,524	0,512	0,524	0,509
b	2	2	2	2	2	2	2	2
lns(s^{-1})	17,9	18,2	18	17,8	18	17,6	17,02	16,9

CHAPTER 6

CONCLUSION

Marble is a metamorphic rock, i.e. it is formed from a sedimentary rock (limestone or dolstone) by solid-state changes in mineralogy and texture as a result of changes in temperature, pressure and the action of chemically active fluids. Different marble formations correspond to different conditions of metamorphosis, which result in different defect and trace element concentrations. We could reasonably consider the thermoluminescence properties of marble to be similar to those of calcite. However, in an attempt to ensure the validity of the method for different types of marble and to minimise possible errors, we made and will present here a full study containing glow-curve shapes, activation energies, frequency factors, response to radiation dose and experimental data concerning regenerated thermoluminescence for a number of marbles.

In this study the evaluated trapping parameters are called the kinetic order (b), activation energy (E_a) and the attempt to escape frequency factor (s) of Marbles by using several techniques such as Chen's peak shape (PS) method, several heating rates (VHR) method and computer glow curve deconvolution (CGCD) method. The fading characteristics of the glow curves of Marbles have been investigated at different time periods.

In order to explore the dose dependence characteristics of the glow curves of Marbles, first of all additive dose (AD) experiments were employed. After the thermal treatment at 400 ℃ for 30 minutes, the Marbles shown in figure 5.1. were irradiated at different dose levels between 2.4 Gy and 3.5 kGy at a linear heating rate of 1 ℃/s. When the dose level is increased the peak temperatures of the glow peaks are nearly constant within the experimental errors. According to the theory of thermoluminescence the peak temperatures do not change when the dose level is increased at a constant linear heating rate in the case of the kinetic order of 1. The results of the additive dose

experiment were also used for the other experimental techniques. One of the experimental techniques to obtain the trapping parameters from the glow curves is the peak shape method. In this thesis, peak shape (PS) method of Chen has been utilized to calculate the kinetic parameters. According to the method, the value of the symmetry factor $\{\mu_g = (T_2 - T_m)/ (T_2 - T_1)\}$ was found to be 0.51(white marble) and 0.55(pink marble) which corresponds to the first order kinetics. After Chen's peak shape method, Mazumdar's peak shape method was applied by taking the 1/2, 3/4 and 4/5 of the maximum intensity of the glow peak. The results of this method have shown that white marble has a second order glow peak at 140 ℃ and having activation energy of nearly 0.56 eV. And pink marble has a second order glow peak at 145 ℃ and having activation energy of nearly 0.55 eV.

After employing the peak shape method, the next, to find the trapping parameter was heating rate method which depends on the shift position of the peak temperature (T_m) at the maximum point of intensity (I_m) to higher temperatures as the heating rate is increased. The results of the VHR method have shown that the main glow peak of Marbles (white and pink), called P1, has activation energy of 0.505 eV and 0.509 eV respectively.

Then the computer glow curve deconvolution method was used which is a powerful technique over the experimental method. This method has the advantage over experimental methods in that they can be used in largely overlapping-peak glow curves without resorting to heat treatment. The selected initial parameters of this method were the values that yielded the best overall fit to the designated high priority features of the TL results. Figure 5.3 shows the results of CGCD fitting on the assumption of three general order peaks and table 5.1 summarizes the value of the kinetic parameters calculated by all of the methods. As seen from this table the values are in agreement with each other.

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