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SYNTHESIS AND INVESTIGATION OF THERMOLUMINESCENCE PROPERTIES OF RARE EARTH (D_y) DOPED $CaAl_4O_7$

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HALO T. NAJM
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Synthesis and investigation of thermoluminescence properties of rare earth (D_y) doped $CaAl_4O_7$

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Supervisor:
Assoc. Prof. Dr. Vural Emir KAFADAR

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ABSTRACT

SYNTHESIS AND INVESTIGATION OF THERMOLUMINESCENCE PROPERTIES OF RARE EARTH (D_Y) DOPED $CaAL_4O_7$

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M.Sc. Thesis, Engineering Physics
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In this study the thermoluminescence (TL) properties of calcium aluminate ($CaAl_4O_7$) doped with rare earth ion, Dysprosium (Dy), have been investigated in detail. $CaAl_4O_7$:D_y phosphors were synthesized by using the sol-gel method. The glow curves of the samples were evaluated by using ^{90}Sr-^{90}Y (≈ 0.04 Gy/s) beta source for different dose levels between 0.2 Gy and 864 Gy and the kinetic parameters such as activation energy (E_a), and order of kinetics (b) were calculated by using peak shape method, heating rate method, and computer glow curve deconvolution method. The results of the experiments have shown that the sample has two general order glow peaks; P1 at 125^{o}C and P2 at 160 ^{o}C. The peak at 125^{o}C has a kinetic order of b=1.5 and activation energy E_a= 0.5 eV. The fading characteristics of the sample were also studied over a period time. The samples were irradiated and stored in a darkroom at room temperature. The results have shown that, the intensity of the main glow peak (P1) of $CaAl_4O_7$: D_y at the end of the planned storage times reduced typically 51 % of its original value.

Keywords: thermoluminescence, $CaAl_4O_7$: D_y

ÖZET

NADİR TOPRAK ELEMENTİ (D_y) İLE KATKILANMIŞ $CaAl_4O_7$ SENTEZLENMESİ VE TERMOLÜMİNESANS ÖZELLİKLERİNİN İNCELENMESİ

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Yüksek Lisans Tezi, Fizik Mühendisliği
Tez Yöneticileri: Doç. Dr. Vural Emir KAFADAR
Ocak 2016
61 sayfa

Bu çalışmada nadir toprak elementi Dizprozyum (Dy) ile katkılanmış kalsiyum alüminat ($CaAl_4O_7$) fosforunun termolüminesans özellikleri detaylı olarak incelenmiştir. $CaAl_4O_7:D_y$ fosforu sol-jel metodu kullanılarak sentezlenmiştir. ^{90}Sr-^{90}Y ($\approx$ 0.04 Gy/s) beta kaynağı ile 0.2 Gy ile 864 Gy arasında değişen dozlarda ışıma eğrileri elde edilmiş ve kinetik derece, aktivasyon enerjisi gibi tuzak parametreleri, tepe şekli, ısıtma hızı, ve bilgisayarlı tepe ayrıştırma metodları kullanılarak elde edilmiştir. Yapılan deney sonuçları $CaAl_4O_7:D_y$'un iç içe geçmiş 125^oC'de ve 160^oC iki adet genel derece ışıma tepesine sahip olduğunu göstermiştir. 125^oC'deki ışıma tepesine ait kinetik derece b=1.5 ve aktivasyon enerjisi E_a=0.5 eV olarak hesaplanmıştır. Örnek sabit bir doz oranında radyasyona maruz bırakılarak karanlık ortamda ve oda sıcaklığında bekletilerek farklı zaman süreleri için termal sönüm karakteristiği de çalışılmıştır. Termal sönüm deneyleri sonucunda P1' ait TL şiddetinde 4 haftalık sürenin ardından %51 oranında azalma görülmüştür.

Anahtar Kelimeler: termolüminesans, $CaAl_4O_7$: D_y

To my parents

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The physical properties of a solid can be determined by influence the defect in a material structure. A fundamental understanding of the defect structure is necessary for the characterization of the material and also for the interpretation of many physical properties. The defect structure of materials was studied by several different methods, such as electrical, thermal, optical, etc. The study of defects or impurity states can lead to a basic understanding of the nature of the defects and to a characterization of the material with its associated defects. Such a study can result not only in the identification and understanding of defects itself nevertheless also can lead to techniques which control the defects for suitable applications.

Thermoluminescence is one of the useful method for studying the cyclic processes among defects. Thermoluminescence is the emission of light from an insulator or semiconductor that takes place during the heating of a solid, following an earlier absorption of energy from radiation [1,2]. On the other hand vacancies, interstitials and dislocations influenced by impurity in materials can act as charge traps and/or luminescence centers. After irradiated the sample carriers are trapped in these traps, by increasing the temperature charge is released energy with emit wave often in the form light, emission light can be recorded as a function of temperature which is measured by a photomultiplier tube circuit, and it is called glow curve.

The glow curve has valuable information about the intrinsic defect. Analysis of the glow curves gives a value for the energy level at which the trap is situated (activation energy). Area under the curve reveals the number of recombination of electron-hole pairs which have taken place in the crystal. In 1945, Randall and Wilkins first determined the glow curve of TL dosimeter. The first ever glow curve revealed

multiple peaks and later it was acknowledged that the occurrence of single peak is very rare [3].

However, the final structure of a glow curve depends on several factors such as the host or the mixture of dosimeter compound, types of dopants, defect centers after irradiation, annealing, type of ionizing radiation and level of radiation dose [4,5]. The maximum point of the peak not only varies with the materials compositions and the heating mechanism but also greatly influenced by the intrinsic parameters such as the activation energy (E), the frequency factors (s), the heating rate (β), the radiation dose and the concentration of traps [6,7]

In general, application of thermoluminescence involved at three major area as, radiation dosimetry, age determination and geology, with developing technology, simultaneously thermoluminescence application was grown, the most important utilization area of thermoluminescence is the "radiation dosimetry", the main application areas [8];

i. Personnel Dosimetry (extremity dosimetry, whole-body dosimetry, tissue dosimetry)

ii. Environment Dosimetry (terrestrial dosimetry and space dosimetry)

iii. Clinical Dosimetry (diagnostic radiology, radiotherapy)

iv. High Dose (food sterilization, nuclear reactors, materials testing)

In human's life applications, thermoluminescence was utilized in nuclear medicine for therapy monitoring, measurement of doses in sensitive organs and areas, by internal emitter dosimetry and phantom dosimetry; in radiation monitoring for personnel and environmental monitoring, in experimental dosimetry for natural background studies, source calibrations and high energy physics studies, and in geology, or archaeological dating it used to measure the age of rocks [2,4,9,10], thermoluminescent materials used in industry, 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.

1.2 Historical Background

Luminescent phenomena have fascinated mankind since the earliest times. The first luminescent material was described as Bolognian Stone (BaS), which before this definition were used during the night, the first artificial phosphor described in Western literature dates around 1603 by an Italian alchemist, Vincenzo Cascariolo that used the natural mineral barite in an effort to create gold, but after heating the stone under reducing condition he obviously did not obtain gold, but he saw a persistent luminescent material. He found these stones near Bologna. So called Bolognian stone which became famous and become a subject of study and admiration for decades. It is not clear which dopant or dopants were actually responsible for the persistent luminescence, but the host material definitely was BaS. While not made intentionally but by chance, BaS thus is the first sulfide phosphor ever synthesized. Several names were given to the Bolognian Stone until the modern name for all solid or liquid luminescent materials become "PHOSPHOR" [8], but the word luminescence was first used by a German physicist, Eilhardt Wiedemann, in 1888.

The studies on thermoluminescence as a brunch of luminescence go back to the seventeenth century, thermoluminescence was Observed at first in 1663 when Robert Boyle noticed that a diamond glowed when held near a hot but non-luminous piece of iron [11]. Also scholars like Johann Sigismund Elsholtz, and Henry Oldenburg conducted experiments on minerals to see their radiation due to heating. George Kaspar Kirchmaier observed the phosphorus as a green stone powdered and mixed with water and glows when heated, and Nathaniel Grew, who used the name Phosphorus metallorum [12], and some other scientists that interested this concept. In eighteenth century, Dufay is the first to be acknowledged for his findings on thermoluminescence. He referred to lighting as a kind of burning. He worked on several materials (primarily chlorophane) and found out that too much heating would lead to loss of thermoluminescence of the material. Leading scientists, De Saussure and Thomas Wedgwood need to be mentioned in the thermoluminescence studied of the eighteenth century. The previous recognized of stones which have a luminesce by heating are classified in three types (1) those containing sulphur or a hepar (fois), a compound of sulphur, which burned in the free air, (2) those which absorb the light

and then emit it, like the diamond, and (3) those which do not require air and will luminesce under hot water, like dolomite and fluorspar [12].

However until the end of the nineteenth century it was not understood that must be externally applied energy and stored in the solid until it was released by applying sufficient heat energy. This information first was taken by Dewar in 1894. Dewar conducted an experiment in which he irradiated calcium sulphide at 90^{o}K and on heating it, observed the light. This experiment for studying thermoluminescence in crystals provided a general procedure that is still used. After, Canton brought Dufay's studied in a new level and discovering a new type of light by raising the temperature of phosphorus, which he referred to as the thermoluminescence of artificial phosphorus [12]. He declared that the intensity of the color of the fluorspar is an indicator for the level of thermoluminescence. Latter conducted a study on the thermoluminescence and triboluminescence that indicated lighting is a result of friction. His findings showed that it cannot find a solid relation between the patterns of two types of luminescence.

Studies on thermoluminescence continued in the nineteenth century. Researcher, Heinrich referred that almost all substances could emit light, if they are in powder form and subject to reasonable heating. Another researcher Theodor von Grotthus dealt specifically with the fluorspar, and showed similarity in emitting light between thermoluminescence material 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.

1.3 Luminescence

When radiation is incident on a material some of its energy are absorbed and re-emitted as light of a longer wavelength "Stoke's law" this process is called luminescence, or these materials and substances that are capable of emitting light, particularly in the visible range are termed "luminescent". In nature, most of the materials possess luminescent properties. The phenomenon of luminescence has been known since early times. The wavelength of the emitted light is characteristic of the luminescence substance and not of the incident radiation. Usually, most studies of

luminescence phenomena are concerned with the emission of visible light but other wavelength can be emitted, such as (ultra-violet or infra-red) [1]. Sometimes luminescence emission resulting from heat, or by chemical reactions, electrical energy, subatomic motions, and stress on a crystal. The various luminescence phenomena are named according to method of excitation energy. Such as photoluminescence, radioluminescence, cathodoluminescence, etc…. The category of luminescence and excitation method can be seen in Table 1.1.

Table 1.1 The category of luminescence and excitation method.

luminescence phenomena	**Methods of Excitation**
Bioluminescence	Biochemical reactions
Cathodoluminescence	Electron beam
Chemiluminescence	Chemical reactions
Electroluminescence	Application of an electric field
Photoluminescence	U.V. and infrared light
Piezoluminescence	Pressure (10 $tons/m^2$)
Triboluminescence	Mechanical, Frictional forces
Radioluminescence	Ionizing radiation
Sonoluminescence	Sound waves
Fluorescence	Ionizing radiation, U.V. and visible
Phosphorescence light	Ionizing radiation, U.V. and visible
Thermoluminescence	Ionizing radiation, U.V. and visible
Lyoluminescence	Ionizing radiation, U.V. and visible

The emission phenomenon of the light takes place after characteristic time (τ_c) which this parameter (τ_c) allows us to subdivide the process of luminescence into two parts phosphorescence and fluorescence.as illustrated in the Figure 1.1. The (τ_c) of fluorescence is smaller than (10^{-8}s) but phosphorescence is greater than (10^{-8}s) by this difference we can distinguish between the phosphorescence and fluorescence. Fluorescence emission is basically a spontaneous process because its (τ_c) value is smaller than (10^{-8}s), which after simultaneously absorbing the radiation immediately ceases when the radiation ceases.

Phosphorescence emission is the time interval which is starting the radiation absorption till reach to maximum intensity (t_{max}) and the (τ_c) value of the phosphorescence is greater than (10^{-8}s) and has been seen to continue for some time after removing the excitation. However, it is more complex to distinguish between phosphorescence and fluorescence when the time of delay is too short.

And the phosphorescence itself can be subdivided into two main kinds [13]. One is the short period phosphorescence ($\tau_c<10^{-4}$s) and another one is the long period phosphorescence ($\tau_c>10^{-4}$s). Another different between the fluorescence and the phosphorescence is the effect of temperature on the decay of luminescence clearly through practical viewpoint. Phosphorescence is heavily dependent on temperature, whereas the fluorescence is not dependent on temperature [1].

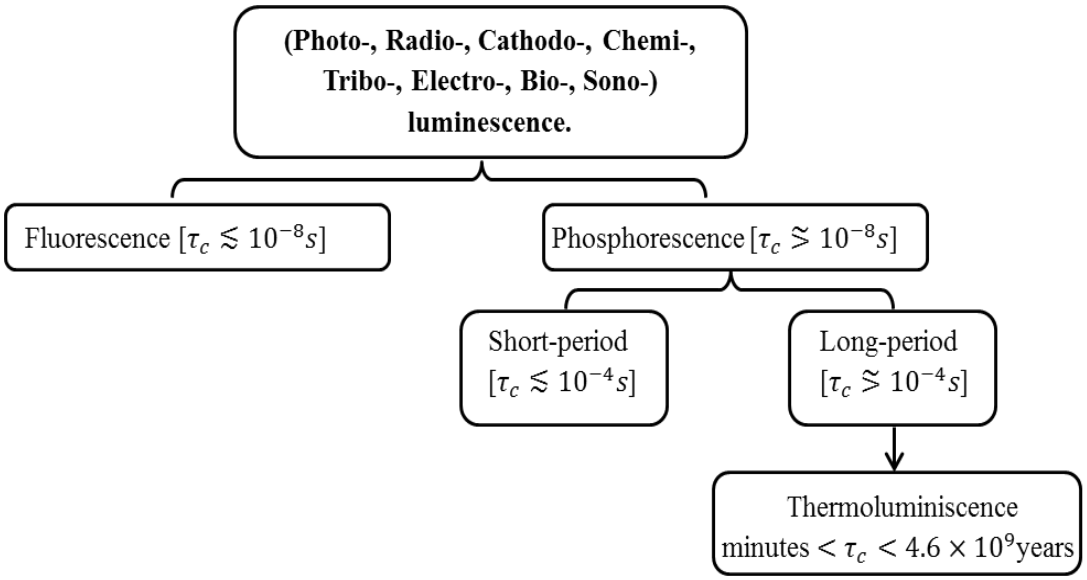

Figure 1.1 The family tree of the phenomenon of luminescence.

Luminescence phenomena are usually described by utilizing energy band theory. So it can explained the luminescence emission by transferring the energy from radiation to the electrons of the solid material, an electron after acquiring sufficient excitation energy makes a transition from the ground state (g) to the excited state (e) (transition (1) in Figure 1.2a), and when excited electrons come down to its ground state emits luminescence photon (transition (2)). If the average time between excitation and emission (life time) are less than 10^{-8}sec which is described in Figure 1.2a is called "fluorescence". And this process is independent of temperature, but some

luminescence processes cannot be described in Figure 1.2a. Instead, as shown in Figure 1.2b the diagram of the energy level is modified by the existence of a metastable level (m) in the forbidden energy gap between the excited state (e) and the ground state (g). When an electron excited from the ground state (g) to an excited state (e) may be trapped in (m) and stay in it till it is given enough energy (E) to turn to the excited state (e) and is subject to a natural transition back to the ground state (g), with subsequent light emission. Thus this trapping phenomenon results in a longer delay (seconds to years) between excitation and emission. The average time spent by the charge inside the trap at temperature (T) is given by:

$$\tau = s^{-1}\, exp^{(-\frac{E}{kT})} \tag{1.1}$$

(s) is a constant and (E) is the energy difference between the trap (m) and excited state (e) (called the trap depth); (k) is Boltzmann's constant. Thus the phosphorescence process is dependent on temperature exponentially [1]. This process of luminescence is called "phosphorescence". Energy (E) can be supplied either thermally or optically. The former is called Thermally Stimulated Luminescence (or thermo luminescence, TL) whereas the latter is named Optically Stimulated Luminescence (or OSL).

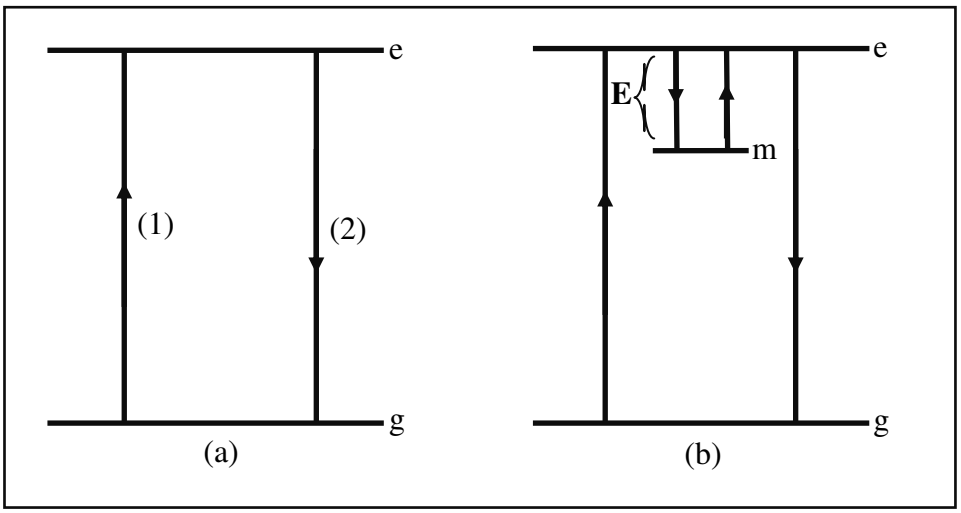

Figure 1.2 The energy level diagram of (a) fluorescence production and (b) phosphorescence production.

1.4 Thermoluminescence

The substances like insulators or semiconductors artificially or accidentally are exposed to radiation, and the radiation causes absorb energy at a given temperature, and emit this energy in the form of visible light while heating the sample. This thermally stimulated phenomenon can be called as luminescence or thermoluminescence. However, the mechanism of thermoluminescence (TL) is not simple as this explanation [8,9].

The thermoluminescence is a process differs from the light emitted spontaneously from a substance when it is heated to incandescence. Say over 200 ^{o}C (or at high temperatures) a solid substance emits (infra-red) radiation of which the intensity of it increases with increasing temperature, this process is called (thermal) or (black body radiation). To emit the light in stimulate, it needs to add some energy levels among the forbidden energy band gap, these energy levels create caused of lattice defects by insert some impurities into host lattice in thermoluminescence materials which these states are called “metastable state”. The lattice defects are the most important parameters to understand the thermoluminescence phenomenon. They occur naturally or artificially and induce electronic states in the forbidden band [14-20].

There are the three important points for the production of TL can be deduced. Firstly, the material must be an insulator or a semiconductor, metal is not useful to this process caused its structure. Secondly the luminescence emission is triggered by heating the material. Finally, the material must have at some time absorbed energy during exposure to ionizing radiation.

1.5 Thesis Outline

This thesis consists of 6 chapters arranged as following:

• Chapter 1 introduces the context and contains historical subject matter, and the other two sections devoted to description of luminescence and thermoluminescence.

• Chapter 2 is dedicated to general view of Thermoluminescence Mechanism in detail explanation, and described the output signal of process (glow curve). In the second part of this chapter, Band Theory and defect in a solid material explained, and clarified the well-known model to simplify analysis in Thermoluminescence phenomenon.

• Chapter 3 separated into two sections first, Thrmoluminescence Models which described in detail. Second, involved four methods to find out Trap Parameters.

• Chapter 4 includes the material synthesis and doping procedures, Equipment's, Radiation Source with a brief characterize of Irradiation Procedure.

• Chapter 5 presents the results on the study of the experiments stated in Chapter 4 with some determination of trap parameters. These results include the outputs from characterization analysis as well as thermoluminescence measurements.

• Chapter 6 discusses the main findings of this study and recommendations.

CHAPTER 2

THEORY OF THERMOLUMINESCENCE IN SOLIDS

2.1 Thermoluminescence Mechanism

Thermoluminescence (TL) method is a relatively complex process since it includes a trap and a luminescence center. The fundamental thermoluminescence phenomenon is given in the Figure 2.1 [8]. As can be seen from Figure 2.1, there are two bands within the system. One of them is the conduction band which is an energy band in a solid. Electrons are freely mobile in this band and they can produce a net electric current. The other is valence band which is the outermost energy band that contains electrons when a solid is in the ground state [8]. Due to radiation which is applied to thermoluminesent material, raises electrons from the valence band and trapped in some energy level in the forbidden gap near to the conduction band (electron trap) is happened. Simultaneously, resulting holes may be trapped at other energy levels that are also within the forbidden gap which are named as the “hole trap” or “recombination center” [8,9] and the light must be emitted when these trapped electrons out of the trap and come down to the lower energy level by heating the sample [2].

In sum, thermoluminescence can be described by two stages. First stage is the change of the system from equilibrium to excited state by absorption of energy from any radiation source. Then the second stage is relaxation of the system back to the equilibrium by energy release such as light with the help of thermal stimulation [9]. In this section, these stages and output of this light emission will be discussed:

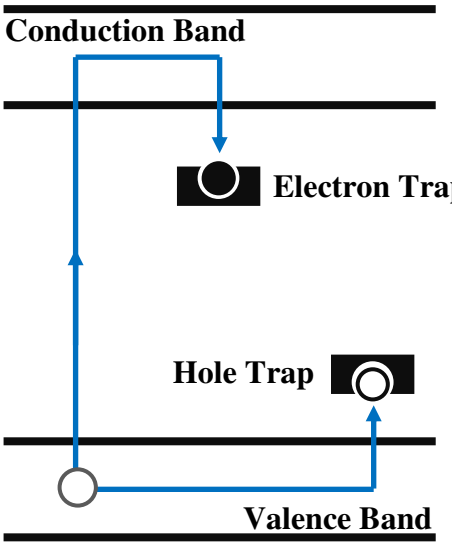

Figure 2.1 Schematic energy level diagram of a phosphor exhibiting thermo-luminescence.

2.1.1 Energy Storage

After irradiated the sample, 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 [21]. Before irradiation, materials have localized electronic energy states and after irradiation, some of these states are occupied by a non-equilibrium concentration of electrons. Therefore, these occupied states are called radiation-induced defects. According to McKeever, when investigations are taken into consideration, they show that the cause of defect creation is electronic excitation rather than non-ionizing displacement damage [9].

Energy storage caused by electronic excitation takes place by the electron-hole pair production and excitation. 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 created by pre-existing impurities or radiation induced defects, which this gap is found between conduction band and valence band. 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 [2,9,22]. In the mid gap, the electron trap is believed close to the conduction band and the hole trap is near from the valence band.

Figure 2.2 illustrates the energy storage mechanism. After irradiation, the electrons pass from valence band to conduction band and hole becomes positively charged area in the valence band. When 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 [2,9,22,23].

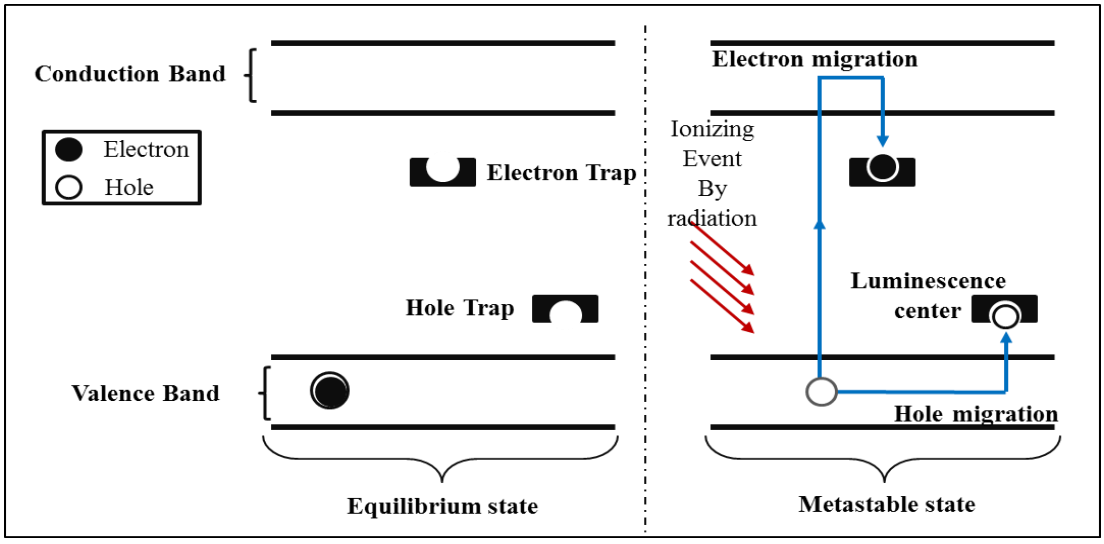

Figure 2.2 Energy-level diagram of the energy storage stage for thermoluminescence processes.

2.1.2 Energy Release

Now both types of carriers trapped in lattice imperfections in the crystalline solids. In electron trap, electrons remain for a long time when the crystals are stored at room temperature. When heat is increased, the electron trapped in the electron trap is released to conduction band. After that electron is free to re-trap 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 [2]. This process is illustrated in the Figure 2.3.

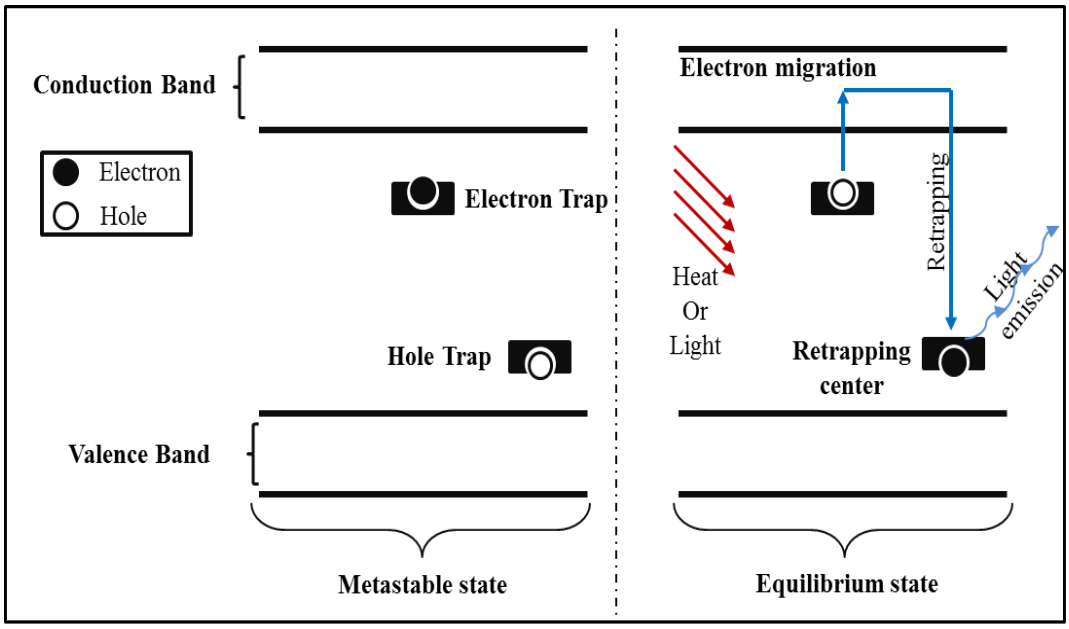

Figure 2.3 Energy-level diagram of the energy release stage for thermoluminescence processes.

2.1.3 Glow Curve

Thermoluminescence signal is expressed as a curve. This curve is called glow curve which can be defined as a graphical representation of the luminescence intensity as a function of temperature [2]. Shape of the glow curves is one or more peaks of emitted light and some of them may overlap. Generally, materials give one or more peaks on the glow curve. This depends on the host compounds, the type of impurities, radiation induced defect centers, dose and type of ionizing radiation strongly in dosimetric materials [14,24-29]. There are numerous parameters that affect the shape of the glow curve, such as dose level of the radiation, thermal treatment (annealing) of the phosphor, pre-irradiation to high doses, pre-treatment with certain chemicals. The unit of peak intensities in glow curve is an arbitrary unit. Hence, they can be used mainly in comparative manner [4,8,9]. Magnitudes and looks of the glow curves may change depending on the spectral response of the light sensitive device, different filter usage between the sample and the detector and heating rate. In addition, 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 [2]. Figure 2.4 shows some glow curve examples of some thermoluminescent materials.

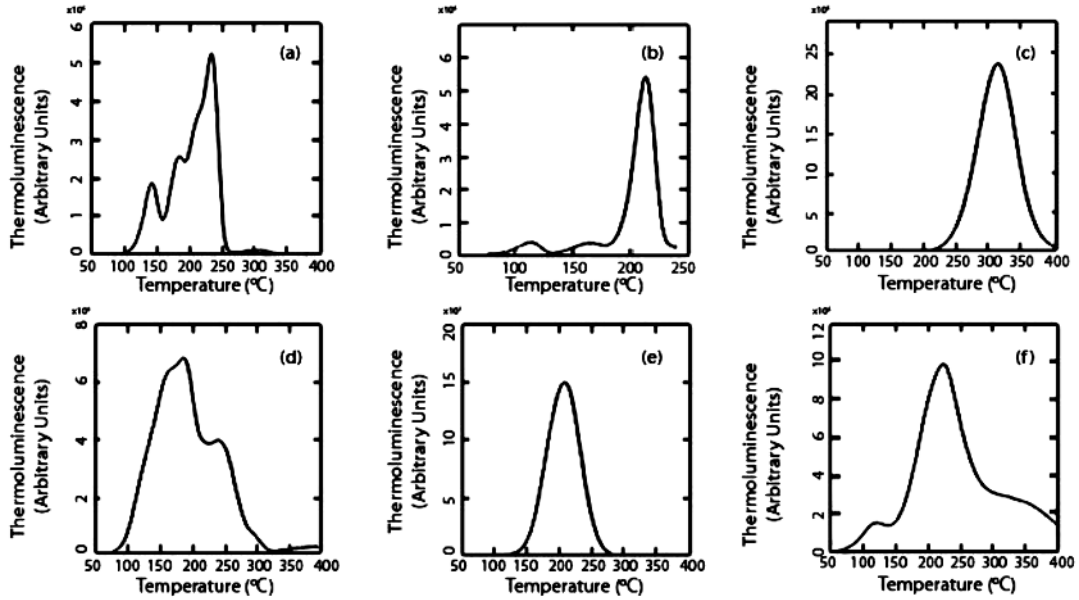

Figure 2.4 Some representative examples of glow curves of some of the main TLD materials, (a) LiF:Mg,Ti; (b) LiF:Mg,Cu,P; (c) CaF_2:Mn; (d) CaF_2:D_y; (e) AI_2O_3:C; (f) $CaSO_4$: D_y [2].

A study of these glow peaks yields information about trapping sites and recombination centres in the crystal, for example in thermoluminescence dosimetry (TLD), this curve gives information about the radiation dose to which the phosphor has been exposed. But usually the main goal of measuring and analyzing these TL glow curves is the extraction of several parameters that can be used to describe the TL process in the material. Examples of these, the activation energy E for the TL traps (also called the trap depth), the frequency factors, the order of kinetics b of the TL process, the capture cross-sections for the traps and recombination centers, and the concentrations of these traps and centers.

2.2 Band Theory of Solids

Luminescence phenomena are generally described by utilizing energy band theory. In this thesis luminescence appearing in solids during thermoluminescence processes which can be explained by the same fundamental principles as applied to

luminescence in general. Hence clarified energy band model is essential and useful in providing an understanding of processes which involve transportation of an electronic charge through the lattice [30]. Thus, in the following subsections we will first briefly look at the energy band model of solids after that we explained something about defect inside a crystal and introduce the concept of localized energy levels (traps and recombination centers). Then we will examine the position of thermoluminescence in the context of luminescence phenomena in general.

As it is clear that, every solid material contains electrons. The band theory of solids is based on a one-electron approximation. In this model it is assumed that the electron interacts with both the field of the fixed atomic cores (nuclei and inner shell electrons) and an average field a rising from the charge distribution of al1 the other outer-shell electrons.

For the perfect crystal the total crystal potential energy V($\vec{r}$) must have the periodicity of the crystal lattice. From the solution of the Schrodinger equation

$$\left(\frac{\bar{h}^2}{2m}\right)\nabla^2\Psi + [\varepsilon - V(\vec{r})]\Psi = 0 \tag{2.1}$$

which suffices for the above model, it is deduced that the electrons in solids are arranged in energy bands (closely spaced energy levels) separated by regions in energy for which no wave like electron orbitals exist. These regions are called energy gaps (band gaps or forbidden gaps). The density of occupied energy states N(E) in each band is given by

$$\mathrm{N(E)} = \mathrm{Z(E)f(E)} \tag{2.2}$$

Where Z(E) is the density of available energy states, and $f(E)$is the Fermi-Dirac distribution function for the electrons (i.e. the probability that an energy state E will be occupied in an ideal electron gas in thermal equilibrium).

$$\mathrm{f(E)} = 1/\mathrm{e\ x\ p}^{\,[\,(\mathrm{E-EF})/\mathrm{kT}\,+\,1]} \tag{2.3}$$

EF denotes the Fermi energy (i.e. the energy of the topmost filled states in the ground states).

2.3 Defects and Color Centers

Normally samples exhibit a poor thermoluminescent properties and emission of these samples are related to the concentration of imperfections. So we can say that centers of the defects and color are axis of any process of luminescence, and it is appropriate to provide these concepts here in an elementary method [31]. The concentration of imperfections can be substantially increased by the addition of small quantities of ions with another charge number which are known as doped material, also called doping agent or activator [32]. In reality all solid materials are impure and there have defects in its structure and may be classified into four categories depending on their dimensions like (point defect, linear defect, planer defect, and volume defect) as in Figure 2.5 showed and explained the type of their defects.

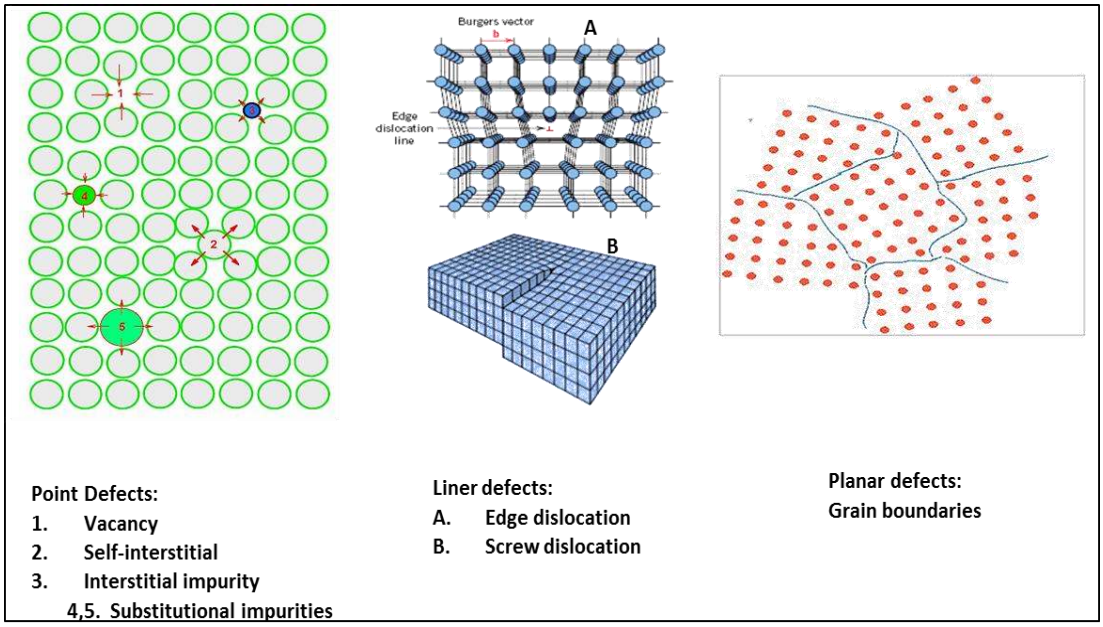

Figure 2.5 Three types of impurity defects in solid materials.

In some part of theoretical solids and especially with the effects of impurities and lattice irregularities TL is related to the band structure can be appear when ions of either signals move away from their original places these may call as centers, Consequently departure vacancy states, can be interact with holds free charge and trap, instead of ions could interstitial positions of spread and smash locally the lattice geometry ideal, lastly, can be ions impurities perturb the lattice order, because of their valances and sizes, generates differ in their neighbor, or activators are added to

a compound to perturb the relative potential energy profile of intrinsic lattice defects and also they cause new defect species. The nature and concentration of imperfection (vacant lattice sites, interstitials, and dislocations) are important factors affecting thermoluminescent properties of materials.

Creation states inside the energy gap of the host material is essential because there are the defects and impurities within them and these states may be the type of (an electron and hole). And these states which are created have the ability for light absorption from some spectrum of the visible part. The crystal is colored and, thus, described these states also as the (color centres).

From a viewpoint atomic can be defect characterized the number of charge holds and means of the signal, perhaps eventual interacts with existence of excited states, to such characterization characteristic energy for each center corresponds. Amount of energy is defined the trapped charges free when supplied to set, therefore, the center and restoring situation devastating of local order. Therefore it is virtual therefore to characterize structure in term of the valence band and conduction bands, below the conduction band at various depths are represented the defects as places lied which parted from each by forbidding gap, where free charge holds of either signal can be trapped [33].

As presented above which in an insulator all the allowed energy bands are either filled or empty. Thus there are no states immediately above the highest filled band (valence band). The nearest available state is at the bottom of the next allowed band (conduction band). The Fermi level at absolute zero is half way between, i.e. in the middle of the forbidden gap. The presence of lattice defects (impurities, radiation damage centers, vacancies, interstitials…etc.) which disturb the translational symmetry of the crystal line structure results in localized energy states which might fall within the band gap.

The localized energy states, upon capturing free charge carriers may act a straps or as recombination centers, Figure2.6. Differentiation between traps and recombination centers is based upon the relative probabilities of thermal release and recombination. The probability of thermal excitation from a localized state at a given temperature T is given by:

$$p = s \exp^{(-\frac{\Delta E}{KT})} \tag{2.4}$$

where ΔE is the energy depth, or trap depth (i.e. energy difference between the localized state and the bottom of the conduction band for the electron centers, or the top of the valence band for the hole centers); k is Boltzmann's constant, and s is a constant (This last constant will be discussed more in the next subsection) It can easily be seen From equation (2.4) that for the localized states with small ΔE the probability for the release of the charge carrier is higher than the ones with large ΔE. Thus, the localized states with small ΔE are more likely to act as traps than recombination centers. Based upon this one could locate the traps toward the bottom of the conduction and towards the top of the valence band, whereas the recombination centers will be located near the middle of the band gap. However, it should be noted that a trap at one temperature may act as a recombination center at lower temperature and vice versa. There might also exist a delocalized level of the energy depth D for which the relative probabilities of trapping and recombination are equal.

Such a level designates a demarcation between the traps and the recombination centers. In other words localized states with E<0 would act as a trap where as if E>D it would be are combination center, Figure 2.6.

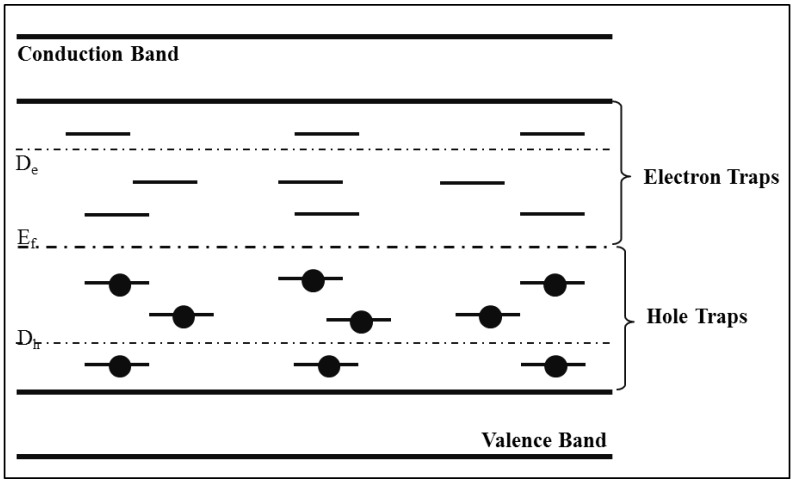

Figure 2.6 Energy levels in an insulator in equilibrium at absolute zero.

It should be mentioned that discrimination between traps and recombination centers is not solely depend in to the trap depth (ΔE). For a given concentration of trapped

charge, the probability of the recombination is governed by the value of the capture cross-section (the value of capture cross-section depends upon the potential distribution in the region of the defect). The recombination probability has the following form

$$A = v\sigma \tag{2.5}$$

where v is the carrier thermal velocity ($\alpha T^{1/2}$) and σ is the capture cross-section.

2.3.1 One-Trap and One-Recombination Model

The theory of energy band for solid materials interprets the properties of the observed thermoluminescence (TL), as we explained before. Most electrons are residing in the valence band in an ideal (semiconductor or insulator) crystalline, and the second highest band is Conduction band, which it is empty but can be occupied by electrons, and they have a gap between them which it is forbidden to occupied by electrons and called forbidden band gap with energy (Eg). However, whenever there are impurities inside the lattice, or if there are structural defects happens in a crystal, these defects caused create some bands in forbidden band gap which carriers can be filled in, the number of bands is different and may be in some sample have a lot of bands but in this model simply it assumed that (TL) sample just have two levels, one of them is located at the bottom of (C.B) and the other is located on the upper part of (V.B) as illustrated in Figure 2.7, The electron trap is denoted by (T) and it is located on the highest level above the Fermi level (E_f) and it is empty in the state of equilibrium, i.e. before exposure to the radiation and the (electrons and holes) creation. The second one is hole trap and denoted by (R) that can operate as a (center of recombination) [34], and each of them has a specific potential energy.

The absorption of radiant energy with ($h\gamma > Eg$) results in ionization of valence electrons, and produce both of (electrons) and (holes) which in this process free holes in the valence band (V.B.) and free electrons in the conduction band (C.B.) is produced, this is a transition (a) in the below Figure [34].

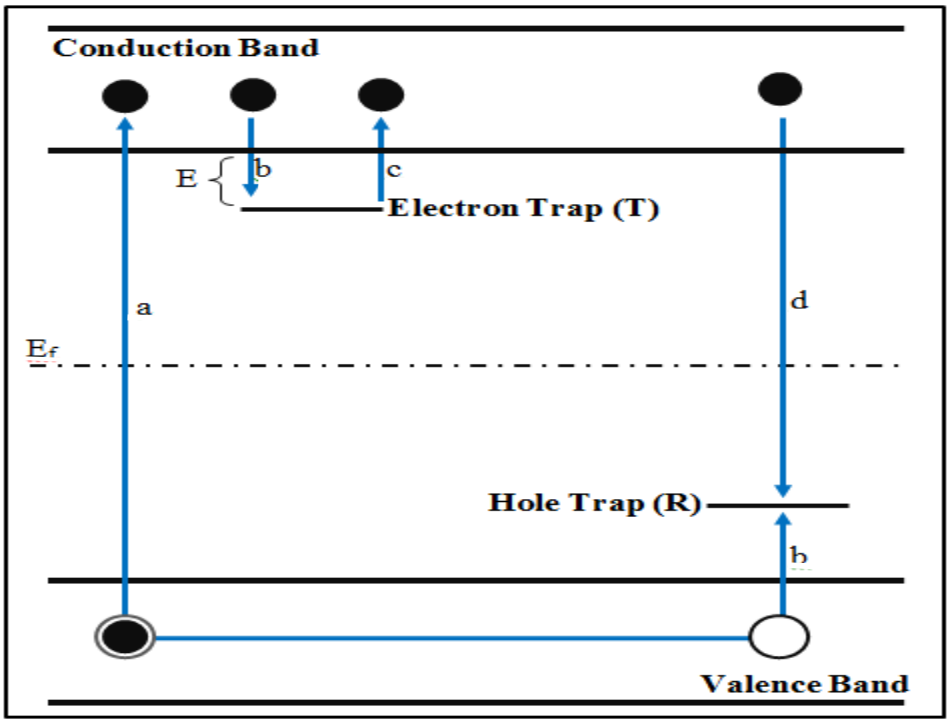

Figure 2.7 Energy band model showing the electronic transitions in a thermoluminescence material according to a simple (two-level) model, (a)is the generating electrons and holes, (b)is the trapping of electron and hole, (c)electron release due to thermal stimulation, (d)is a recombine-ation. Solid circles are electrons, open circles are holes, (E_f) is the Fermi level.

And after some times the free charge carriers (electrons and holes) recombine with each other or become trapped. In the situation of direct recombination an amount of energy will be released that might raise luminescent center. And electrons from the conduction band return to the ground with the emission of light, this process is happened in ($<10^{-8}$) and it is called (radioluminescence). Second possibility is trapped the holes in (R) and trapped the electrons in (T) transition (b) in Figure 2.7. The Arrhenius equation described the probability per unit time (p) for releasing an electron from the trap:

$$p = s \exp^{[-\frac{E}{KT}]} \qquad (2.6)$$

Where s is the frequency factor which values are in order of the lattice vibration frequency, and it is constant in the simple model, E is the trap depth or activation energy, or the energy which is necessary to release an electron from the trap to the conduction band, k is the Boltzmann's constant = 8.617×10^{-5} eV/K, and T is the absolute temperature.

The trapped electrons stay in the trap for a long time if the trap depth is much bigger than (kT_o), where (T_o) is the temperature of irradiation, caused of exposure to the radiation will exist and populated a lot of electrons in electron trap, due to the creation and annihilation the (electrons and holes) in pairs. So must be exist an equal amount of holes at the level (R), because the normal equilibrium Fermi level (E_f) is located above the level (R) and below the level (T) and it means this situation is in non-equilibrium, the reaction path is always open for returning to the state of the equilibrium, but because the perturbation from equilibrium was performed during exposure to the ionizing radiation at low temperature in comparison with (E/k), and the rate of relaxation that quantified by the equation (2.6) is small. Therefore, the non-equilibrium state is metastable and will exist for indefinite period and may change by the rate parameters E and s.

This system can be come back to equilibrium state by increasing the temperature of the thermoluminescence substances to higher than (T_o). Hence, the probability of detrapping also increase and the electrons will be released from the trap to the (C.B), transition (c). The electrons moved freely inside the conduction band until recombine with the (holes) at the recombination center (R). This recombination centre is a luminescent centre in the simple model, because is the place to recombine both of (electron and hole) after come back from the higher excited states to the ground state with emission light, i.e. thermoluminescence, this process is showed in transition(d).

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

$$I(t) = -\frac{dm}{dt} \tag{2.7}$$

In here for simplification we have two assumption, each recombination produces a photon, and all produced photons are detected.

The rate of recombination is proportional to the concentration of free electrons in the conduction band (n_c) and the hole concentration (m).

$$I(t) = -\frac{dm}{dt} = n_c m A_m \tag{2.8a}$$

(A_m) is the constant which indicated 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 the thermal release minus the rate of the retrapping

$$-\frac{dn}{dt} = np - n_c(N - n)A_n \tag{2.8b}$$

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

$$\frac{dn_c}{dt} = np - n_c(N - n)A_n - n_c m A_m \tag{2.8c}$$

Both of equations (2.8a) and (2.8c) described the traffic of the charge carrier during the process of releasing the trapped electron from a single-electron trap and recombination in a single centre. In the same way for thermoluminescence (TL) produced by the holes release, the rate equations are same to the equation (2.8). The basis of a lot of analyzes for the thermoluminescence (TL) phenomena are formed by these equations. There is no a general analytical solution and these equations must be solved by some simplifying assumptions for developing an analytical expression. This assumption is named a quasi-equilibrium assumption by Chen and McKeever [2]. And from this assumption which say that "the free electron concentration in the conduction band is quasi stationary" and this assumption is an important assumption at any time.

$$\left|\frac{dn_c}{dt}\right| \ll \left|\frac{dn}{dt}\right| \ , \qquad \left|\frac{dn_c}{dt}\right| \ll \left|\frac{dm}{dt}\right| \tag{2.9}$$

It is clear that after irradiation the trapped electrons and the trapped holes are produced in pairs and charge neutrality dictates, therefore

$$n_c + n = m \tag{2.10}$$

For ($n_c \approx 0$) it means that ($n \approx m$) and,

$$I(t) = -\frac{dm}{dt} \approx -\frac{dn}{dt} \tag{2.11}$$

When (dn_c/dt) is approximately equal to zero, and from equations (2.8a) and (2.8b) we can get:

$$I(t) = \frac{mA_m ns\ \exp^{\left[-\frac{E}{KT}\right]}}{(N-n)A_n + mA_m} \tag{2.12}$$

CHAPTER 3

MODELS AND ANALYSIS OF THERMOLUMINESCENCE

3.1 Thermoluminescence Models

Analytically, we can't solve the equation (2.12) without simplifying assumptions, hence in this section we will discuss some assumptions for solving this equation in detail, these assumptions include three part that named first-order kinetics, second-order kinetics, and general-order kinetics.

3.1.1 1st Order Kinetics

Randall and Wilkins [3,35] assumed neglected retrapping ((N-n)Ar) during the heating stage i.e. they assumed ($mA_m \gg (N-n)A_n$) and by applying this assumption, equation (2.12) becomes:

$$I(t) = -\frac{d_n}{d_t} = sn\exp^{\left(-\frac{E}{kT}\right)} \tag{3.1}$$

The above differential equation describe movement of carriers inside the lattice as a first-order process, for constant temperature also probability is constant ($p = \exp^{\left(-\frac{E}{kT}\right)}$), and can be determine intensity by integration of equation (3.1).

$$I(t) = I_0\exp^{(-tp)} \tag{3.2}$$

Where I_0 is the initial intensity at initial time. If temperature change with time, also intensity is vary and the solution of equation (3.1) becomes:

$$I(t) = -\left(\frac{dn}{dt}\right) = n_0 s\exp^{\left\{-\frac{E}{kT_{(t)}}\right\}} \times \exp^{\left\{-s\int_0^t \exp^{\left\{-\frac{E}{kT(t)}\right\}}dt\right\}} \tag{3.3}$$

Where n_0 is the total number of trapped electrons at time $t = 0$, usually TL is observed as temperature is raised as a linear function of time according to

$$T(t) = T_0 + \beta t \tag{3.4}$$

Where, (β) is the constant heating rate and (T_0) is the temperature at the time ($t = 0$). Then, the intensity I(T) as a function of temperature becomes as;

$$I(T) = -\frac{1}{\beta}\left(\frac{dn}{dt}\right) = n_0 \frac{s}{\beta} \exp^{\left\{-\frac{E}{kT}\right\}} \times \exp^{\left\{-\frac{s}{\beta}\int_{T_0}^{T} \exp^{\left\{-\frac{E}{kT}\right\}} dT\right\}} \tag{3.5}$$

Equation (3.5) is a famous (Randall–Wilkins) expression in first-order single glow peak, but the integral on the right-hand side is not elementary in the case of linear heating. But Chen showed that how the integral can be approximated by asymptotic series evaluated [36]. In practical applications it is suitable for describing the glow peak in terms of the parameters which are easy to solve experimentally, Kitis et al [37] showed that the equation (3.4) can be very accurately approximated by:

$$I(T) = I_m \exp^{\left[1+\frac{E}{kT}\frac{T-T_m}{T_m} - \frac{T^2}{T_m^2} \exp^{\left\{\frac{E}{kT}\frac{T-T_m}{T_m}\right\}}\left(1-\frac{2kT}{E}\right) - \frac{2kT_m}{E}\right]} \tag{3.6}$$

The properties of Randall–Wilkins equation (3.5) showed in Figure 3.1, this figure include some graphical curve which it is come from an example in this article [38]. When luminescence take place at first, by increases temperature, intensity also increases till reach the maximum point after this point intensity decreases (increases intensity means recombination between electrons and holes are growth, and depletion of charge carriers effected to decrease of intensity), hence the shape of intensity look like a peak shape.

The difference of intensity I(t) can be observed in the Figure 3.1a, (n_0) varies from (n_0=0.25m^{-3}) to(n_0=2m^{-3}) while (E=1eV, s=1.0×$10^{12}$$s^{-1}$ and β=1K/s) are remaining constant. It can be noted that the maximum temperature (T_m) fixed at all of peaks. This is a characteristic of all first-order TL curves, to found maximum temperature it can take ($\frac{dI}{dt} = 0$) (or, somewhat easier($\frac{d \ln I(T)}{dt} = 0$)), from this condition one gets:

$$\left(\frac{\beta E}{kT_m^2}\right) = s \exp^{\left\{-\frac{E}{kT_m}\right\}} \tag{3.7}$$

(n_0) does not appear from equation (3.7) it means that (T_m) is independent of n_0. But in Figure 3.1a, can be seen that each point of the curve is proportional to n_0, also $n_0$is an important parameter in application of dosimetry, and it is easy to find out that the n_0 is equal to the area under the glow peak.

$$\int_0^{\infty} I(t)dt = -\int_0^{\infty} \frac{dn}{dt}dt = -\int_{n_0}^{n_\infty} dn = n_0 - n_\infty \qquad (3.8a)$$

(n_∞) is zero for ($t \to \infty$). The maximum intensity for a first-order kinetics have derived by [39]

$$I_m = n_0 \frac{\beta E}{kT_m^2} \exp^{(-\frac{E}{kT_m}\ \exp^{\frac{E}{kT_m}})E_2(x)} \qquad (3.8b)$$

Where $E_2(x)$ is the exponential integral of second-order, and from this equation appear that the peak height is not only proportional to n_0, also it is proportional to β.

In Figure 3.1b activation energy (E) changes from (0.8eV) to (1.2eV), when activation energy increases, the peak shifts to higher temperatures with decrease of I_m and increase width, but area does not change (because n_0 is constant). This shift happen because charge carriers needed more energy (temperature) to release to the state if traps are deeper (E is bigger). In Figure 3.1c the same changes can be seen but in the opposite way by change frequency factor (s), when a trapping center has a high value of (s) mean that charge carriers can be free in a lower temperature(so needs few energy) and this is clearly appear in a first peak. Also in Figure 3.1d shows effect of the heating rate(β) on the shape of glow curves as it is illustrates by change (β)from (0.5 to 2K/s) the peak shifts to higher temperature with decrease the high and increase in width.

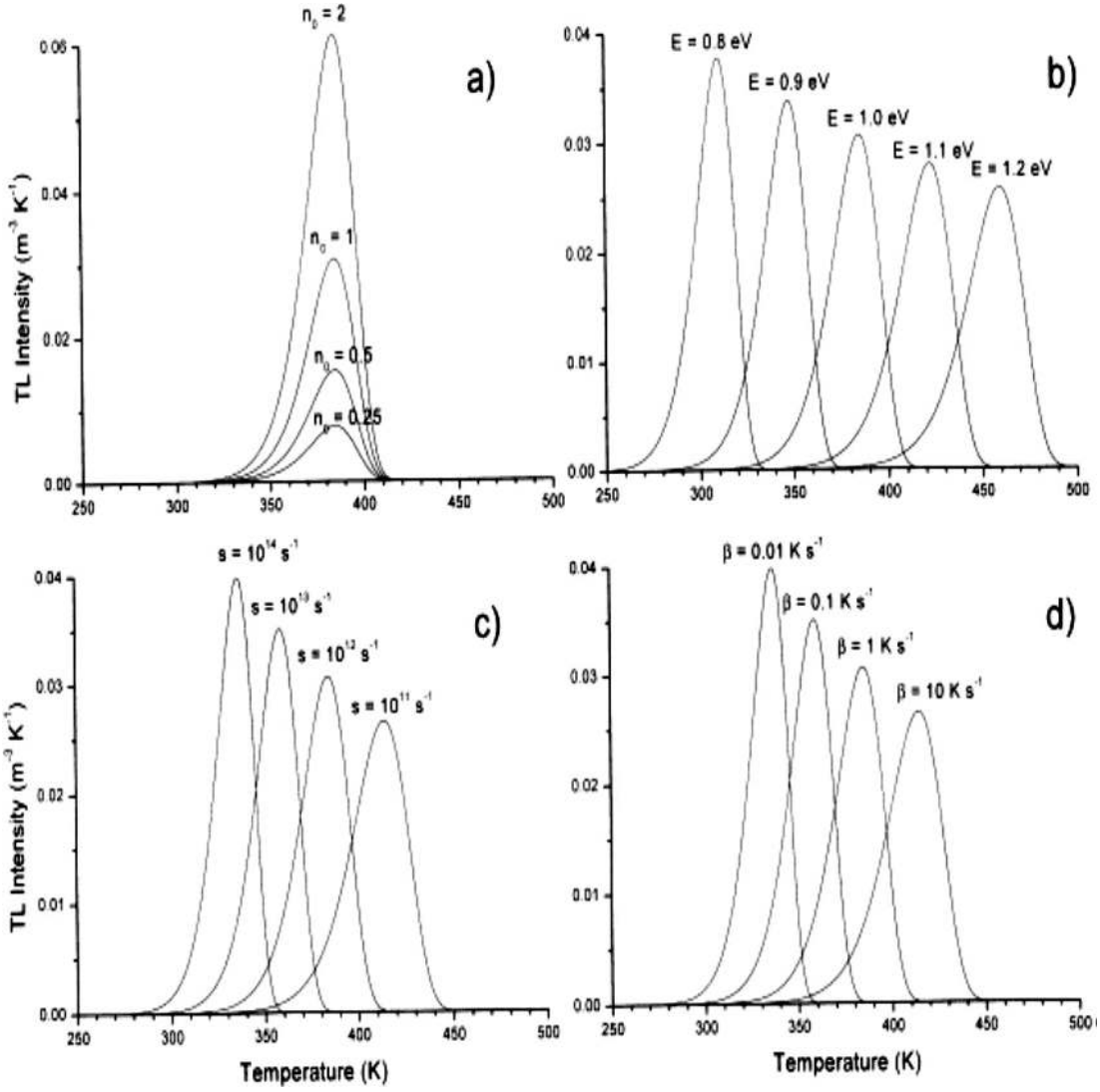

Figure 3.1 Properties of the Randall and Wilkins first-order thermoluminrscence (TL) equation, showing variation with; (a) the trapped charge carriers concentration after irradiation (n_o), (b) activation energy (E), (c) the escape frequency (s), and (d) the heating rate (β). parameter values: (n_o=1 m^{-3}) (E=1 eV) (s=1×10^{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) [38].

3.1.2 2nd Order Kinetics

The possibility which retrapping dominates was considered by Garlick and Gibson [40] ($mA_m << (N-n)A_n$). Also they suppose that the trap is far from the saturation, i.e. ($N \ll n$) and($n = m$). By these assumptions, the equation (2.12) becomes.

$$I(t) = -\frac{dn}{dt} = s\frac{A_m}{NA_n} n^2 \exp\left\{-\frac{E}{kT}\right\} \quad (3.9)$$

From the equation (3.9), it is clear that the (dn/dt) is proportional to (n^2) and that means a second-order reaction, and by the additional some assumptions, as the probability of recombination and retrapping are equal$(A_m = A_n)$, with a constant temperature, and after some mathematical equation the above equation becomes[38]:

$$I(T) = \frac{n_0^2}{N}\frac{s}{\beta}\ \exp^{\{-\frac{E}{kT}\}}\ \left[1 + \frac{n_0 s}{N\beta}\ \int_{T_0}^{T} \exp^{\{-\frac{E}{k\acute{T}}\}} d\acute{T}\right]^{-2} \tag{3.10}$$

This equation is the (Garlick–Gibson) thermoluminescence (TL) equation for the second-order kinetics. As it can be seen in Figure 3.2a, the shape of these glow curves are nearly symmetric, but the part in the end of the curve in high temperature is slightly wider than the part in low temperature. This wide curve caused of in second-order reaction considered that concentrations of released electrons are retrapped before they recombine and make a delay in the emission of luminescence and this emission is spread out over a broader temperature range. The initial concentration (n_0) is a multiplicative constant in the case of first-order but in here furthermore it affected on the shape of curves in different dose levels. And can be seen in Figure 3.2a, $T_m$is changed by varied (n_0), It can be derived that the temperature shift [41].

$$T_1 - T_2 \approx T_1 T_2 \left(\frac{k}{E}\right) \ln f \tag{3.11}$$

(T_1) is the temperature of maximum intensity at a specific dose and (T_2) is the temperature of maximum intensity at (f) times higher dose. From the above equation (3.11) it follows further that for a given increase of the dose the shallower the trap.

Figures (3.2b, c, and d) describes the variation in position and size of a second - order peak as a function of (E), (s/N), and (β) respectively. As in the case of the first-order kinetics, the area under the curve is proportional to the initial concentration (n_0) but the peak height is no longer directly proportional to the peak area, despite deviation is small.

Although similarity between both of first and second-order to find the trap depth is that can be use 'initial rise method' which the term dominating the temperature dependence in the initial rise is $(\exp^{-E/kT})$.

Garlick–Gibson thermoluminescence (TL) equation for second-order kinetics like first-order kinetics can be approximately written in terms of maximum intensity (I_m) and maximum temperature (T_m) [37].

$$I(T) = 4I_m \exp^{\left[\frac{E}{kT}\frac{T-T_m}{T_m}\right]} \times \left[\frac{T^2}{T_m^2}\left(1-\frac{2kT}{E}\right)\times \exp^{\left\{\frac{E}{kT}\frac{T-T_m}{T_m}\right\}} + 1 + \frac{2kT_m}{E}\right]^{-2} \quad (3.12)$$

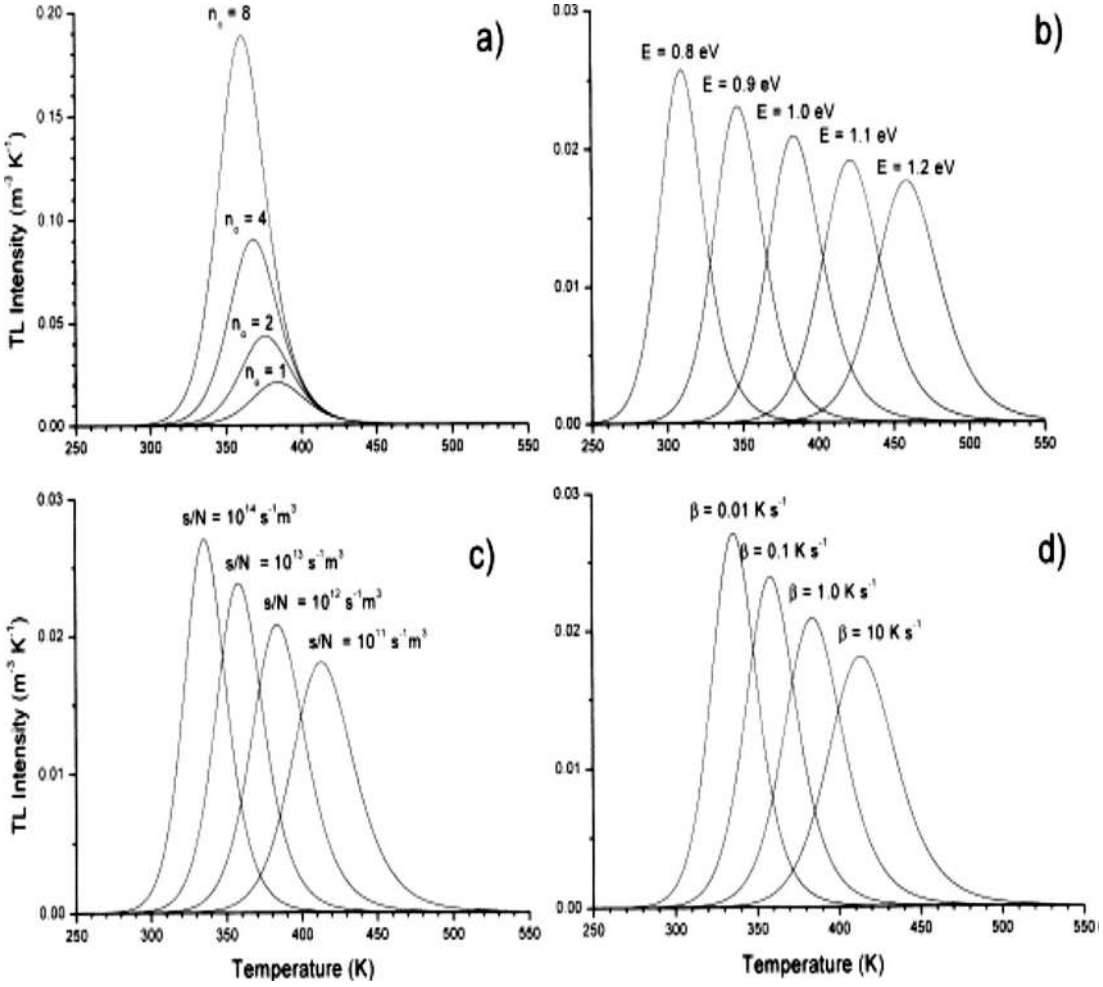

Figure 3.2 Properties of Garlick–Gibson second-order TL equation, showing variation with: (a) the trapped charge carrier concentration (n_o) after irradiation; (b) activation energy (E), (c) (s/N), and (d), the heating rate (β). parameter values: (n_o=1 m^{-3}) (E=1eV) (s/N=1×10^{12} s^{-1} m^3), of which one parameter is varied while the others are kept constant, and (β =1 K/s) for (a, b, and c) [38].

3.1.3 General-Order Kinetics

In sections (3.1.1, and 3.1.2) the first and the second-order reaction of the (TL) equation have been derived by using some simplifying assumptions. However, in reality thermoluminescence peak will fit neither the first-order nor the second-order kinetics, because experimentally do not hold these simplifying assumptions. May and Partridge [42] used an empirical expression in the case of (general-order kinetics), and this is

$$I(t) = -\frac{dn}{dt} = n^{b}\, ś\, \exp^{-\frac{E}{kT}} \tag{3.13}$$

Where the dimension of (s') is ($m^{3(b-1)}\, s^{-1}$) and (b) is defined as the parameter of the general-order and is not necessary (1) or (2). Integration of equation (3.13) for ($b \neq 1$) yields:

$$I(T) = \frac{s''}{\beta}\, n_0\, \exp^{\{-\frac{E}{kT}\}} \left[1 + (b-1)\frac{s''}{\beta} \times \int_{T_0}^{T} \exp^{\{-\frac{E}{kT}\}} dT\right]^{\frac{-b}{b-1}} \tag{3.14}$$

Where ($s'' = s'\, n_0{}^{(b-1)}$) in unit (s^{-1}), equation (3.14) includes the case of second-order, if ($b = 2$) and changes to the first-order equation when ($b = 1$), according equation (3.13) (s') has a dimension and changed with respect to the order (b). So in this case can be dealt as the first-order when ($b \rightarrow 1$) and go to the second-order when ($b \rightarrow 2$), look at Figure 3.3.

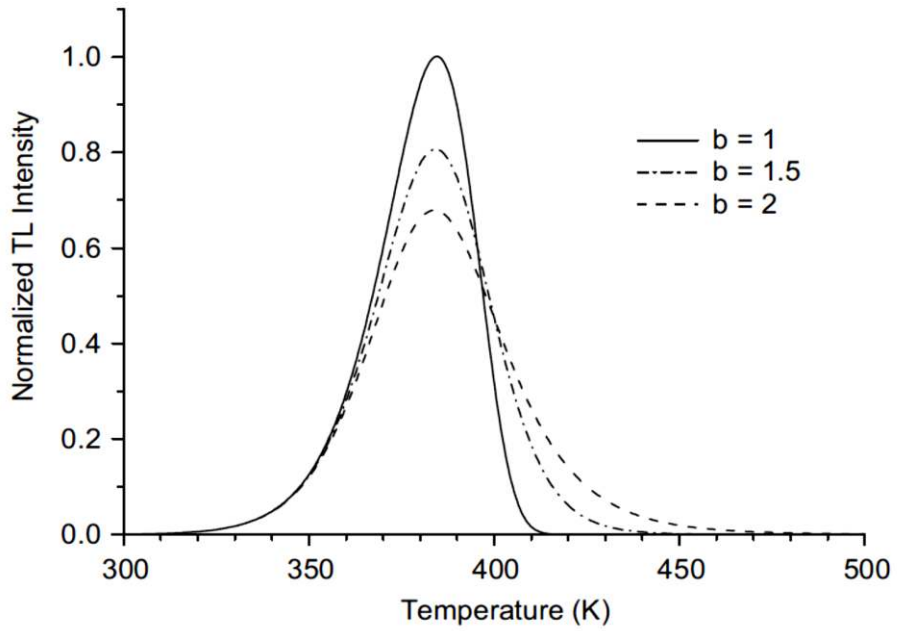

Figure 3.3 Comparison of first-order (b=1), second-order (b=2), and intermediate-order (b=1.5).

The temperature shift represented as:

$$T_1 - T_2 \approx T_1 T_2 \left(\frac{k(b-1)}{E}\right) \ln f \qquad (3.15)$$

(T_1) is the temperature of maximum intensity at a specific dose and (T_2) is the temperature of maximum intensity at (f) times higher dose. And for the general-order equation can be written in terms of (I_m) and (T_m), that has been derived [43].

3.2 Trap Parameters Determination Methods

It is important for knowing parameters of thermoluminescence, generally it have four parameters, the first two parameters which are the main physical parameters (activation energy E and frequency factor s) and named as the trapping parameters, and are fixed by the properties of the trapping center. The last two parameters can be determined experimentally by select a certain dose (n_0) and as well as through the reading of the signal at a certain heating rate (β). Determination of trapping parameters was an importance topic in half a century. In this chapter it will be briefly discussed some methods to find out trap parameters. There are different ways to

assess the trapping parameters from the glow curves [3,44-47]. When one glow peak is highly isolated from the other glow peaks, the experimental methods like (Initial Rise Method (IR), Variable Heating Rates Method (VHR), Three Points Method (TPM), Isothermally Decay Method (ID), and Peak Shape Method (PSM)) are appropriate ways for determining these parameters. In the case of overlapping peaks there are basically two methods to get these parameters. First, is the Partial Thermal Cleaning Method and the second, is the Computer Glow Curve Deconvolution Method (CGCD) program. In most cases, it cannot be used the partial thermal cleaning way for isolating the interest peak completely without making any perturbation on it. Therefore, (CGCD) program become so popular way to assess the trapping parameters from thermoluminescence glow curves in recent years [48].

3.2.1 Initial Rise Method (IR)

This method (IRM) is the most generally applicable way and also the simplest way to assess the activation energy (E) of a single peak thermoluminescence (TL). Firstly it stems from the recognition by Garlick and Gibson that is in the initial rise part in thermoluminescence curve the intensity is dominated and changed exponentially with temperature by:

$$I(T) = C\ exp^{\left(-\frac{E}{kt}\right)} \tag{3.16}$$

(C) is the constant which includes all the dependencies on the other parameters and occupancies, (k) is the Boltzmann`s constant, temperature(T), and $(E)$is the activation energy.

A straight line is obtained by drawing $ln(I)$ against $(1/T)$, with slope equal to $(-E/k)$Therefore, that it is easy to assess the activation energy (E) without any information about frequency factor as shown in the next equation.

$$E = -\frac{kd(lnI)}{d\left(\frac{1}{T}\right)} \tag{3.17}$$

The main condition to use this method is that the glow peak is well defined and clearly separated from the other peaks, but most time glow peaks is overlapped with

each other, and to overcome this problem several methods is devised to separate glow peaks, for instance the most popular technique to do it is called "thermal cleaning" technique, also un important requirement in analysis (E) is that (n)remains approximately constant.

The activation energy (E) was got from the above equation, and then we can get frequency factor (s) form this equation

$$\frac{\beta E}{kT_m} = s\, exp^{(-\frac{E}{kT})} \tag{3.18}$$

Where β is the heating rate, and (T_m) is the temperature at maximum intensity.

3.2.2 Heating Rate Method (HR)

Various heating rate is another important method to determine activation energy, the shape of peak (or maximum temperature) will be different when heating the sample at two various heating rates(β_1) and (β_2). It can be written the above equation (3.18) for each heating rate and dividing the equation for $(\beta_1 and\ T_{m1})$ by the equation for $(\beta_2 and\ T_{m2})$ and rearranging, one obtains an obvious equation to calculate the activation energy (E)

$$E = k\frac{T_{m1}T_{m2}}{T_{m1} - T_{m2}}\ ln\left[\left(\frac{\beta_1}{\beta_2}\right)\left(\frac{T_{m2}}{T_{m1}}\right)^2\right] \tag{3.19}$$

The basic feature of this method is that it only needs to take data at a peak maximum (T_m, I_m) which, in case of a large peak surrounded by smaller satellites, can be sensibly accurately determined 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 (IRM). However, to determine (E) of smaller peaks it have some difficult technique, also it have some other process to find out(T_m, I_m).

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

$$ln\left(\frac{T_m^2}{\beta}\right) = \left(\frac{E}{k}\right)\left(\frac{1}{T_m}\right) + canstant \tag{3.20}$$

By plotting $ln(T_m^2/\beta)$against $(1/T)$ is obtained a straight line with slope equal to (E/k). Hence it is possible to evaluate (E). In addition, and extrapolating to $(1/Tm = 0)$, 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. 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 $(1/Tm)$, whose slope is equal to (E/k).

3.2.3 Peak Shape Method (PS)

To determine values of [kinetics order(b), activation energy(E), and frequency factor(s)] from the peak shape it needs to know something like $(\mu_g, \delta, \tau, \omega, and\ T_m)$, following Halperin and Braner[48] we can define a geometry factor(or shape parameter) $\mu_g = \delta/\omega$ and as shown in Figure 3.4 particularly it have three points $(T_m, T_1, and\ T_2)$ $T_m$is the temperature at maximum peak(or maximum intensity), $T_1, and T_2$ are both of low side and high-side temperature at half of maximum intensity, with full width at half-maximum $(\omega = T_2 - T_1)$, half width on the high temperature side of the maximum $(\delta = T_2 - T_m)$, and half width on the low-temperature side of the maximum $(\tau = T_m - T_1)$. At first order of kinetics (b) can be founded by means of shape parameters. Chen [46] found that (μ_g) is sensitive to changes kinetics order (b) not to (E) and (s), it has been shown that the ranges of (μ_g) vary from (0.42) for pure first-order glow peaks which (b=1) to (b=2) for pure second-order glow peaks (μ_g =0.52) in case of linear heating.

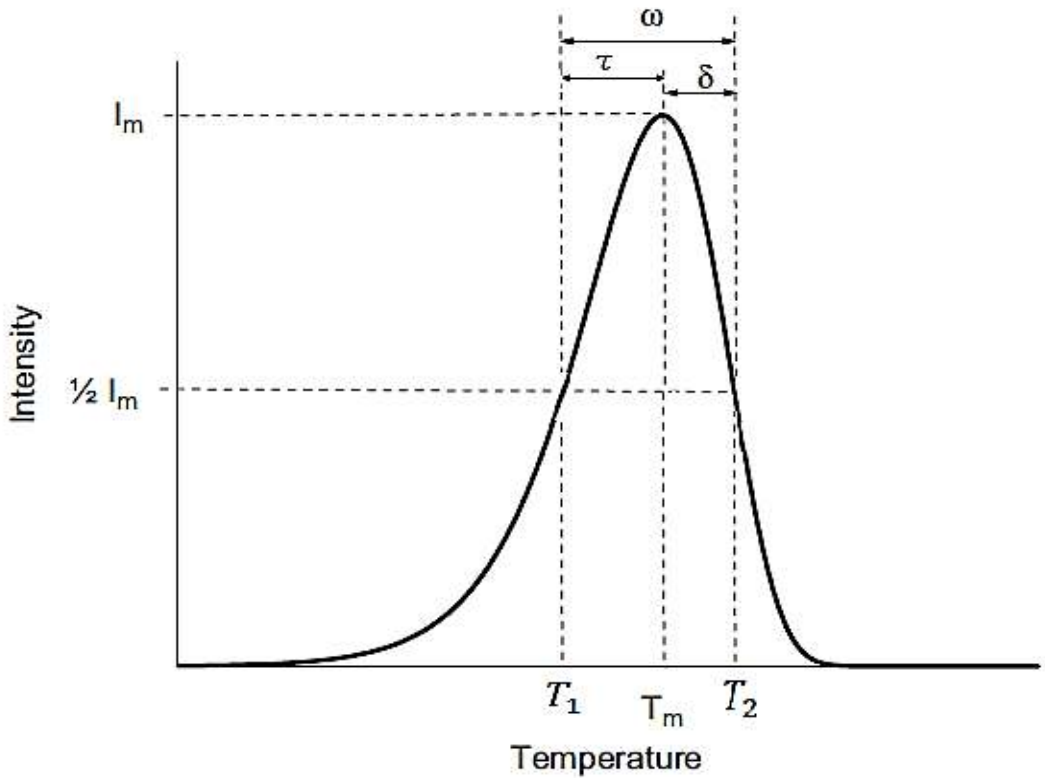

Figure 3.4 Normalised glow peak and shows characteristics of a single glow peak with define the peak shape parameters.

The first peak shape method has been developed by Grossweiner [46], later Chen modified Halperin and Braner's equations [48] to calculate activation energy (E);

$$E_\tau = \left[1.51 + 3\left(\mu_g - 0.42\right)\right]\frac{kT_m^2}{\tau} - \left[1.58 + 4.2\left(\mu_g - 0.42\right)\right]2kT_m$$

$$E_\delta = \left[0.976 + 7.3\left(\mu_g - 0.42\right)\right]\frac{kT_m^2}{\delta} \qquad (3.21)$$

$$E_\omega = \left[2.52 + 10.2\left(\mu_g - 0.42\right)\right]\frac{kT_m^2}{\omega} - 2kT_m$$

After estimate both of activation energy and the kinetic order, using the following expressions to find frequency factor(s), it must be noted that this parameter called as pre-exponential factor in the general order kinetic, can be determined for first and general order kinetics respectively.

$$s = \frac{\beta E}{kT_m^2} \exp^{\left[\frac{E}{kT_m}\right]}$$

$$s = \frac{\beta E}{kT_m^2}\left[\exp^{(-\frac{E}{kT_m})(1+\frac{(b-1)\,2kT_m}{E})}\right]^{\frac{b}{b-1}} \quad (3.22)$$

Gartia, Singh & Mazumdar modify Chen's equation to determine activation energy which it is more accurate. According to this method can be use any three points of a peak, this equation requires the prior knowledge of the kinetics order,

$$E_a = \frac{(C_0 + C_1 + C_2 b^2)}{|T_x - T_y|} + (D_0 + D_1 b + D_2 b^2) kT_m \quad (3.23)$$

Where $|T_x - T_y| = \tau, \delta, \omega$, for each of $E_\tau, E_\delta, and E_\omega$ respectively.

These above coefficients ($C_0, C_1, C_2, D_0, D_1, and D_2$) are showed in table (3.1) which used in the range of kinetic order (b=0.7 to 2.5) and for x=1/2, 2/3, and4/3.

Table 3.1 Numerical values of the coefficients comparing in equation (3.23).

Ratio	Parameter	C_0	C_1	C_2	D_0	D_1	D_2
1/2	τ	1.019	0.504	-0.066	-1.059	-1.217	0.109
	δ	0.105	0.926	-0.048	0.154	-0.205	-0.128
	ω	1.124	1.427	-0.113	-0.902	-0.346	-0.061
2/3	τ	0.684	0.426	-0.055	-0.720	-1.21	0.098
	δ	0.146	0.683	-0.048	0.184	-0.432	-0.094
	ω	0.830	1.108	-0.103	-0.529	-0.607	-0.029
4/5	τ	0.449	0.342	-0.043	-0.0480	-1.184	0.085
	δ	0.153	0.487	-0.041	0.180	-0.606	-0.062
	ω	0.602	0.829	-0.084	-0.293	-0.777	-0.006

3.2.4 CGCD Method

Computer glow curve deconvolution (CGCD) method is one of the most important ways to derive values of parameters E, s, and b these methods of computerized curve fitting it is more accurate in values with apparent success in use. The procedure is began, by find out the approximate positions of the most prominent peaks in the glow-curve and estimate each values of E, s, and b by using one of the analytical method and a theoretical curve is computed by using the general-order equation for b ≠ 1, or the first-order equation for b=1.

The computed curve is compared with the actual experimental curve and estimated a root mean square (RMS) deviation between them. The next action are changing E, s, and b values until a minimum value of the RMS deviation is obtained. This method can be used in largely overlapping peak's glow curve without acting to heat treatment therefore it is useful and better than experimental methods. It utilized two different models in a computer program. First, the glow curve is approached to the first-order thermoluminescence (TL) kinetic by using below expression,

$$I(T) = n_0 s\, exp^{\left(-\frac{E}{kT}\right)}\, exp^{\left[\left(-\frac{s\,kT^2}{\beta\ E} exp^{\left(-\frac{E}{kT}\right)}\right)*(0.9920-1.620\frac{kT}{E_a})\right]} \tag{3.24}$$

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

$$I(T) = n_0 s\, exp^{\left(-\frac{E}{kT}\right)}\ \left[1+\left(-\frac{(b-1)s}{\beta}\frac{kT^2}{E} exp^{\left(-\frac{E}{kT}\right)}\right)*(0.9920 - 1.620\frac{kT}{E_a})\right]^{\frac{b}{b-1}} \tag{3.25}$$

Where all of $(n_0, s, E, k, T, \beta, and\ b)$are annotated previously. Summation of overall peaks and contribution of background can lead to composite glow curve formula as described below:

$$I(T) = \sum_{i=1}^{n} I_i(T) + a + b\ exp^{(T)} \tag{3.26}$$

Where $I(T)$ is the fitted total glow curve, (a) allows for the electronic noise contribution of the planchet and dosimeters infrared to the background. Starting from the equation (3.26), the procedure of the least square minimization and also the figure of Merit (FOM) was used for judging the fitting results on whether they are good or not. Like,

$$FOM = \sum_{i=1}^{n} \frac{|N_i(T) - I(T)|}{A} = \sum_{i=1}^{n} \frac{|\Delta N_i|}{A} \tag{3.27}$$

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 [8], It can be said that if the (FOM) values are between (0.0%) and (2.5%) the fit is good, and for (2.5 %) and (3.5%) the fit is fair, and if greater than (3.5%) the fit is bad. To have a graphic representation of the agreement between the experimental and fitted glow curves, the computer program also plots the function,

$$X(T) = \frac{N_i(T) - I_i(T)}{\sqrt{I_i(T)}} \tag{3.28}$$

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

CHAPTER 4

EXPERIMENTAL PROCEDURE

The materials, equipments and experimental procedures utilized in this work are described below.

4.1 Experimental Procedure and Equipments

The samples were irradiated at room temperature with beta rays from a calibrated ^{90}Sr-^{90}Y source. The activity of β-source is about 100 mCi. It is calibrated by manufacturer on March, 10, 1994. The recommended working life-time is about 15 years. Stronium–90 emits high energy beta particles from their daughter products (^{90}Sr β-0.546 MeV together with ^{90}Y β-2.27 MeV). Beta radiation is absorbed by air, so its intensity declines with distance much more rapidly than inverse square law calculations would indicate.

The maximum range of Y–90 beta particles in air is approximately 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 for fine grains on aluminium, or 3.3 Gy/min=0.055 Gy/sec for 100 m quartz on stainless still. The irradiation equipment is an additional part of the 9010 Optical Dating System which is purchased from Little More Scientific Engineering, UK [49]. The irradiated samples were read out with a Harshaw QS 3500 manual type reader that is interfaced to a PC where the TL signals were studied and analyzed. It economically provides high reliability. The basic block diagram of reader is shown in Figure 4.1. A standard clear glass filter was always installed 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 TLD Shell software that runs on the PC. All data storage, instrument control, and operator inputs are performed on the PC. Signal acquisition and conditioning are performed in the reader. In this way, each glow curve can be analyzed using a best-fit computer program based on a

Marquardt algorithm minimisation procedure, associated to first-order and general-order kinetic expressions. The program resolves the individual peaks present in the curve, giving the best values for the different peak parameters. 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 that produces adjustable linearly ramped temperatures from 1 ^{o}C to 50 ^{o}C per second accurate to within ± 1 ^{o}C to 600 ^{o}C in the standard reader.

The Time Temperature Profile (TTP) is user defined in three segments: Preheat, Acquire, and Anneal, each with independent times (Pre-read anneal: adjustable 0 to 1000 sec, Linear ramp: adjustable from 1 ^{o}C to 50 ^{o}C per second, Post-read anneal: 0 to 1000 sec) and temperature (Pre-read anneal:room temperature to 200 ^{o}C, Post-read anneal: up to 400 ^{o}C). The typical time temperature profile is shown in Figure 4.2. To improve the accuracy of low-exposure readings and to extend planchet life, the 3500 provides for nitrogen to flow around the planchet. By eliminating oxygen in the planchet area, the nitrogen flow eliminates the unwanted oxygen-induced TL signal. Nitrogen is also routed through the photo-multiplier tube (PMT) chamber to eliminate moisture caused by condensation.

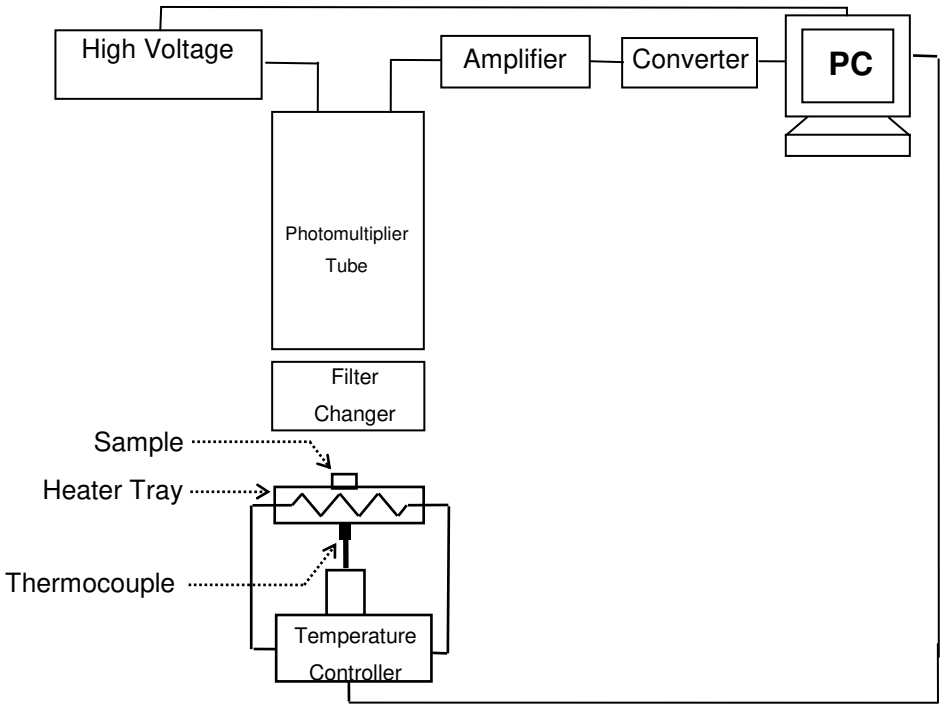

Figure 4.1 Basic block diagram of TL reader. [49]

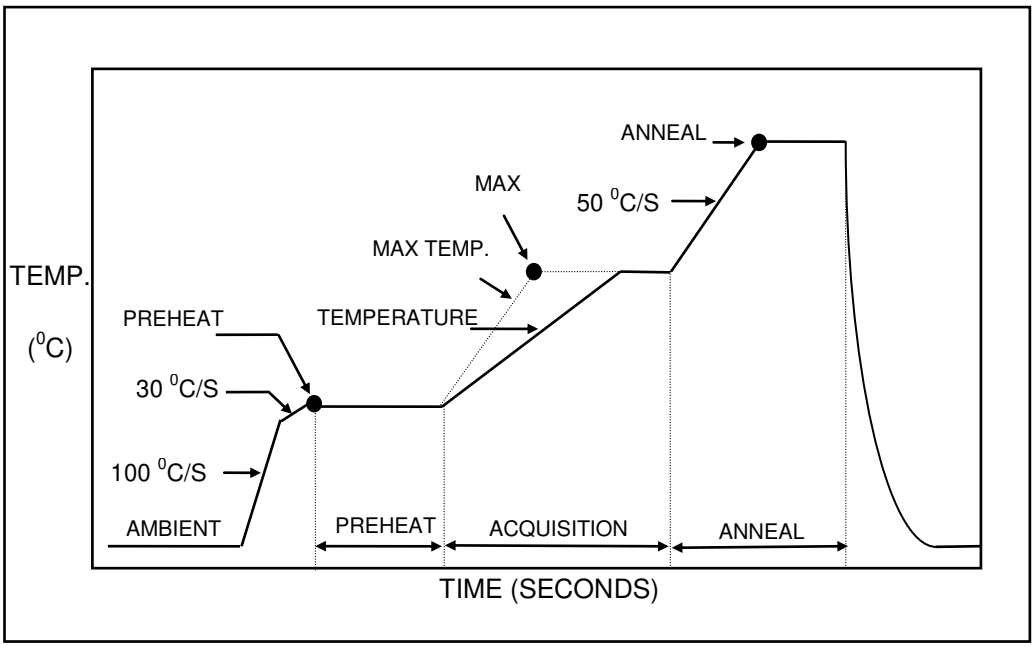

Figure 4.2 Typical time temperature profile (TTP). [49]

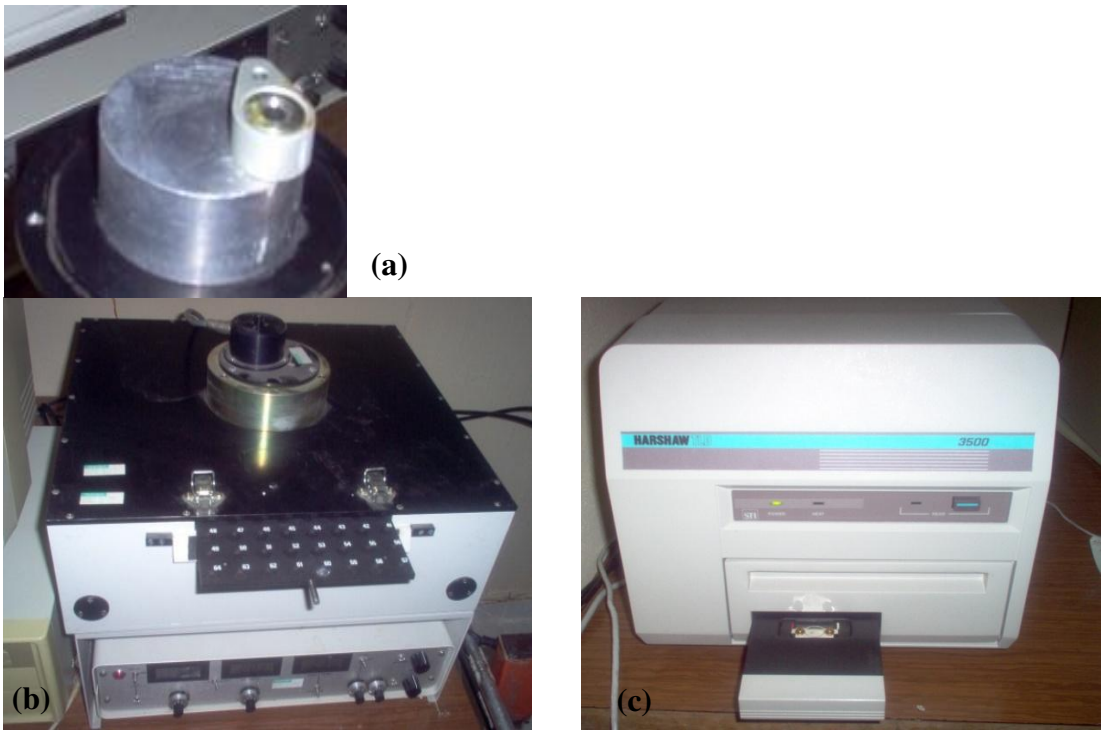

Figure 4.3 Experimental equipments (a) ^{90}Sr-^{90}Y β-source (b) 9010 Optical Dating System (c) Harshaw TLD System 3500.

4.2 Synthesis of Dysprosium doped Calcium Aluminates ($CaAl_4O_7$:D_y)

The raw materials including $Al(OH)_3$, $CaCO_3$, Dy_2O_3 were purchased from Merck and used as received without further purification. Calcium Aluminates ($CaAl_4O_7$) have been prepared by the sol-gel method. Stochiometric quantities of the starting materials, $CaCO_3$ and $Al(OH)_3$, were weighed separately and dissolved into citric acid and ethylene. The mixture was stirred and heated in order to evaporate extra water until a viscous gel resulted. The hot gel was transferred into a platinum crucible and then was put into electrical furnace and heated at 140 ºC for 2 hour in air atmosphere. The mixture was annealed at 250 ^oC for 2 h and ground in an agate mortar. The polymeric gel partially decomposes at this temperature. After grinding the solid mixture was annealed at 1400 ^oC for 16 h. The concentration of D_y-ions doped into $CaAl_4O_7$ is 2 % by wt. 10 mg sample was used in each measurement. The samples were irradiated at room temperature with a newly calibrated ^{90}Sr-^{90}Y beta source. The glow curves were obtained by using a Harshaw QS 3500 Manual type TL reader interfaced to a PC where the TL signals were analyzed. Glow curve readout was carried out on a platinum planchet at a linear heating rate of 1 ^oC/s up to 400 ^oC.

CHAPTER 5

EXPERIMENTAL RESULTS

Alkaline earth aluminates are important host materials that prepared and studied by several researchers for luminescence applications [50]. Calcium Aluminate crystals exist in monoclinic as well as orthorhombic structures [51]. Many researchers have studied Calcium Aluminate as an important compound and can be used as luminescent host, and it has several reports which dealing with the luminescence studies about $SrAl_2O_4$, $BaAl_2O_4$ and $MgAl_2O_4$ in the literature [52]. However, there are few reports that dealing with $CaAl_4O_7$ as a TL material. In this study we have investigated, it deals with the thermoluminescence properties of Calcium Aluminate doped with Dysprosium, and determined the trapping parameters by using different techniques.

In this study, first of all the structure of $CaAl_4O_7:D_y^{3+}$ was characterized by X-ray powder diffraction (XRD), in the range of diffraction angle $20^o \leq 2\Theta \leq 70^o$ using a 0.021^o with 40 kV at 40 mA, CuKα (1.54A^o) radiation using a Rigaku RadB diffractometer. The X-ray diffraction patterns (XRD) of the $CaAl_4O_7:D_y^{3+}$ (synthesized at 1100 ^{o}C) are shown in Figure 5.1 The pattern indexed as a major phase $CaAl_4O_7$ (JCPDF No.: 72-0767) has monoclinic crystal system with Pmmm space group and unit cell parameters of (a=12.87, b=8.880, c=5.440) A°; $\alpha = \gamma = 90^o$ $\beta = 106.75^o$

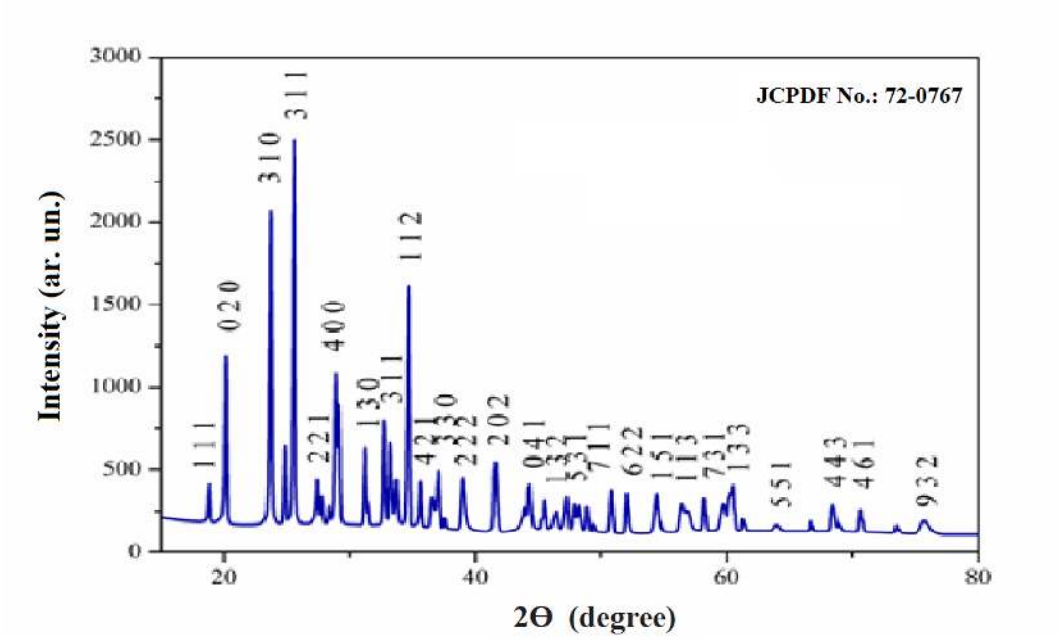

Figure 5.1 The XRD patterns of the $CaAl_4O_7:D_y^{3+}$ phosphor.

The surface morphology of $CaAl_4O_7:D_y^{3+}$ phosphor synthesized using sol-gel technique was observed through SEM image analysis and these micrographs are given in Figure 5.2 SEM micrographs with 50000X magnification indicate that average grain size in the obtained $CaAl_4O_7:D_y^{3+}$ phosphor are in the range from 230 to 650 nm and microstructures of the phosphors consisted of regular fine grains.

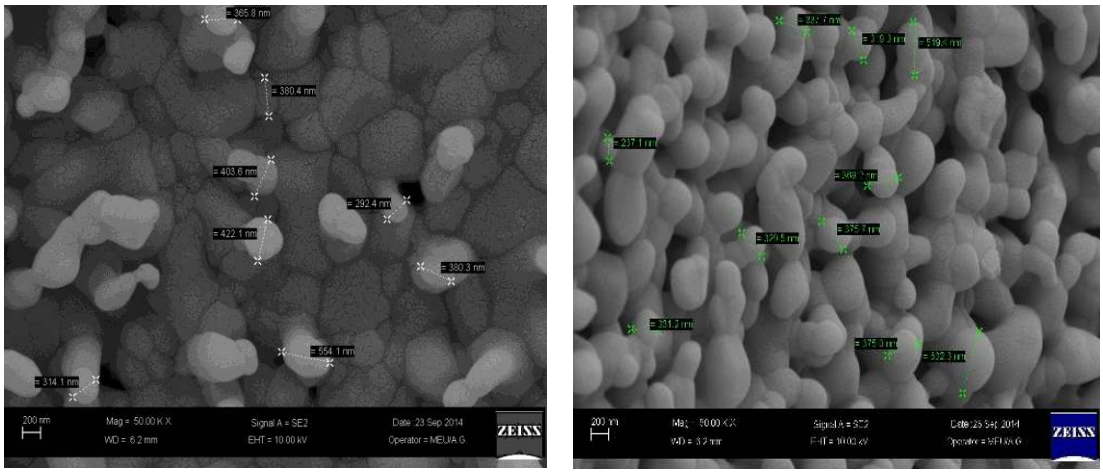

Figure 5.2 SEM micrographs of $CaAl_4O_7:D_y^{3+}$ phosphor

Also in this study the dose response behaviour of ($CaAl_4O_7$:D_y) has been investigated, in each time 10mg of the sample was irradiated at room temperature by β-ray source, between (0.2Gy to 864 Gy) to check the dose dependency influence on the peak positions. Note that (this sample that used in TL measurements were in powder form), and some of the selected glow curves after different dose levels are shown in Figures 5.3 to 5.6. Generally experimental examinations showed that there are not great changes in the position of peak temperatures, just may have a few shift in temperature degree with increasing dose level, in the other word the glow peak temperature gradually shifted to the high temperature sides with increasing dose levels. Each peak reaches the maximum intensity at nearly (≈125 ^{o}C to 160 ^{o}C) for different dose level, also in these figures displayed increase or decrease of height peak with respect to change dose.

As clarified in section (3.2) for single glow curve it has several experimental techniques such as (initial rise (IR), various heating rates (VHR) and peak shape (PS)) methods for evaluating trapping parameters. In this study, Peak Shape Method, Variable Heating Rate Method, along with the Deconvolution Method has been utilized to evaluate trapping parameters of the main dosimetric peak of D_y-doped $CaAl_4O_7$. In this part we utilized peak shape method for calculating the trapping parameters. Earlier studies have demonstrated that the activation energy evaluation and the frequency factor mostly rely on the kinetic order (b) knowledge and the glow peaks correct number in the glow curve [53]. Hence, firstly to find out kinetic order to (144Gy), we utilized (maximum temperature, T_1, and T_2) as explained in section (3.2.3), and determined, which nearly equal to (1.5) means in the range of general-kinetic order, after that activation energy and frequency factor were determined by using Chen Peak Shape Method equation (3.21), Mazumdar Peak Shape Method equation (3.23), and all of values are illustrated in Table 5.1

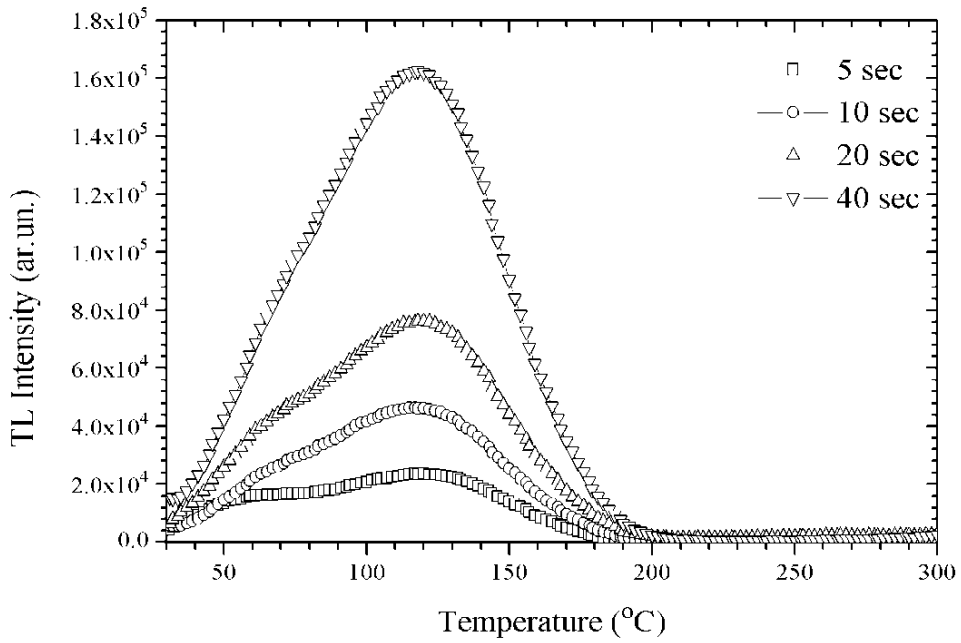

Figure 5.3 Glow curves of $CaAl_4O_7:D_y$ measured after different exposed dose levels (0.2, 0.4, 0.8, and 1.6) Gy with (β=1°C/s).

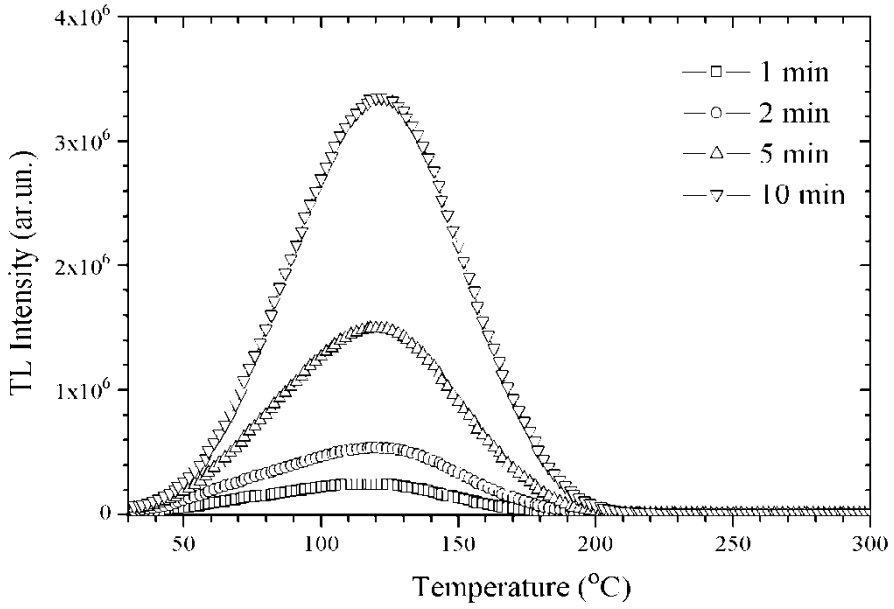

Figure 5.4 Glow curves of $CaAl_4O_7:D_y$ measured after different exposed dose levels (2.4, 4.8, 12, and 24) Gy with (β=1°C/s).

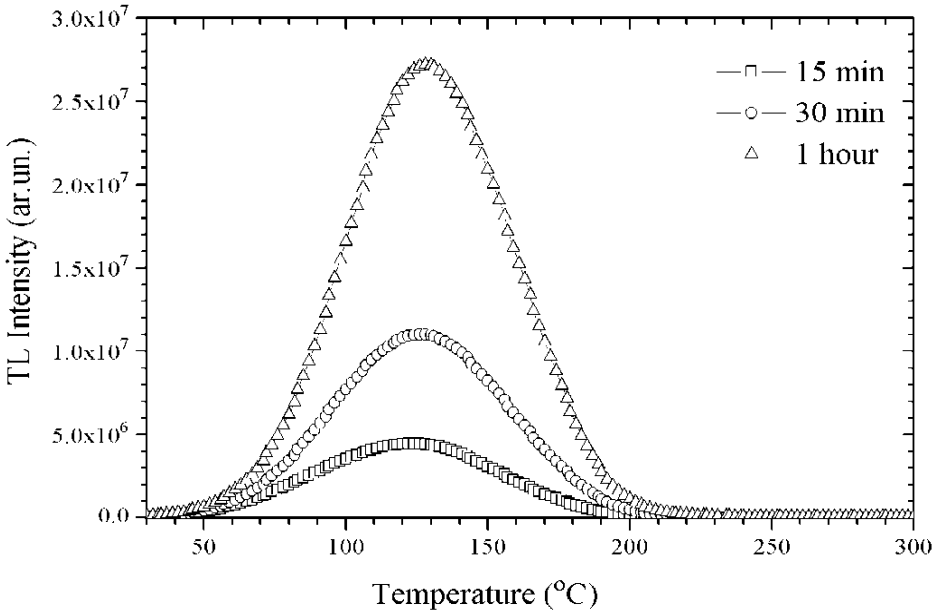

Figure 5.5 Glow curves of $CaAl_4O_7:D_y$ measured after different exposed dose levels (36, 72, and 144) Gy with (β=1°C/s).

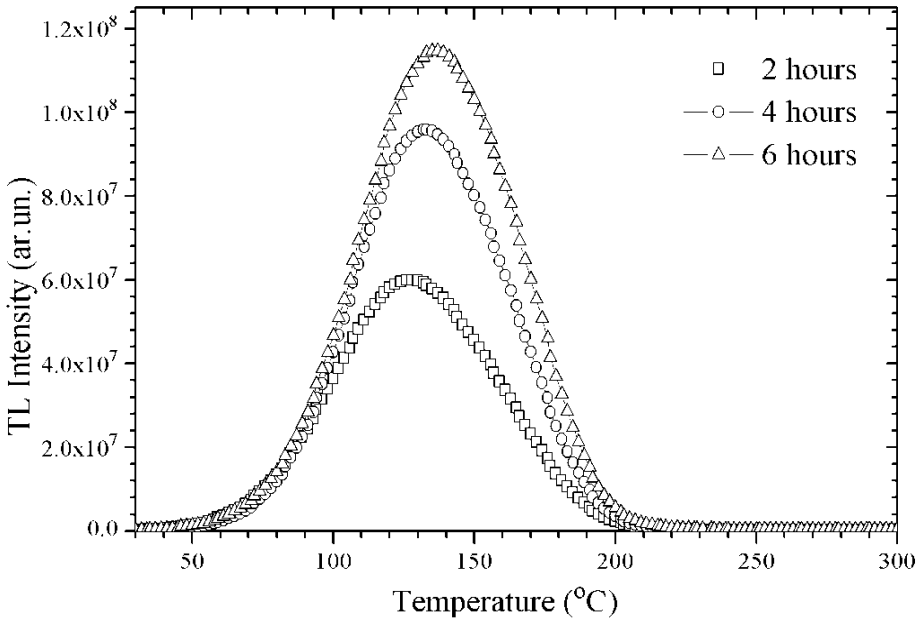

Figure 5.6 Glow curves of $CaAl_4O_7:D_y$ measured after different exposed dose levels (288, 576, and 864) Gy with (β=1°C/s).

Another process in this study is to understand the effect of linear heating rates on the glow curve features of $CaAl_4O_7:D_y$. In this section the dose response behaviour of $CaAl_4O_7:D_y$ has been investigated at different linear heating rates between 1°C to 10°C. Samples were irradiated with β-ray with a ^{90}Sr-^{90}Y source (36Gy), glow curves were recorded for different heating rates of (1, 2, 3, 5, 7, and10)^{o}C/s, and it is shown in both of Figures 5.7 and 5.8. From these figures, it can be understand the effect of different linear heating rates were applied to the sample, thermoluminiscence glow peak shifts to higher temperatures with increasing heating rate, and the width of peak increases with decreasing in maximum intensity, as expected in theory. The decreasing luminescence intensity of glow peaks 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 because of the increased non-radiative transition probability [54].

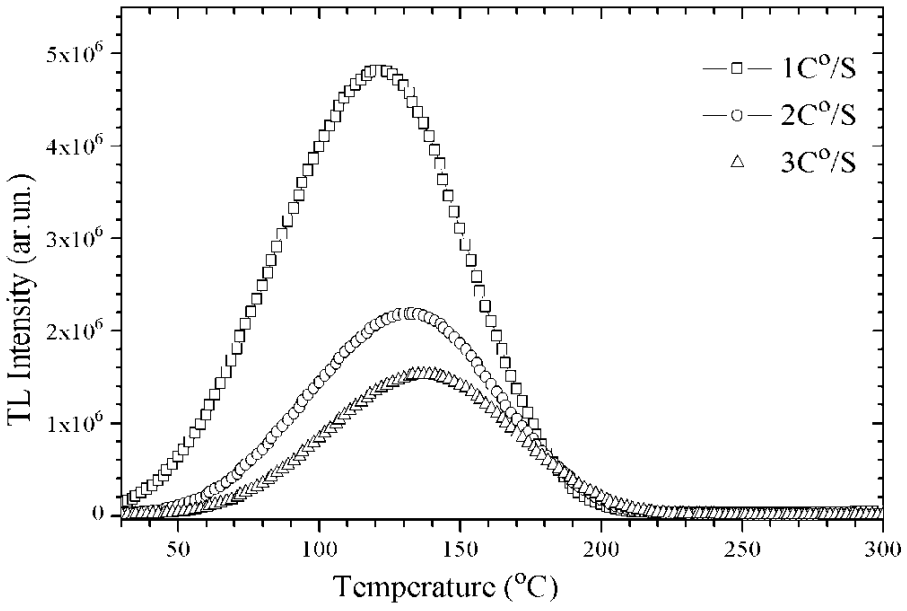

Figure 5.7 Some of the selected glow curves of $CaAl_4O_7:D_y$, measured at different heating rates for (1, 2, and 3) ^{o}C/s after β irradiation of 36Gy.

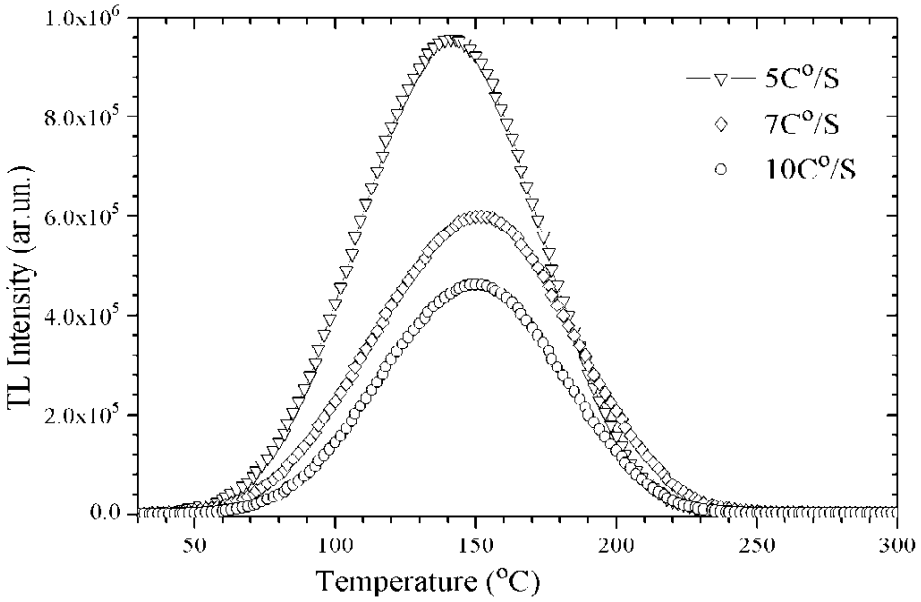

Figure 5.8 Some of the selected glow curves of $CaAl_4O_7:D_y$, measured at different heating rates for (5, 7, and10)°C/s after β irradiation of 36Gy.

Heating Rate Method (HR) is another important technique for calculating the trapping parameters particularly in this study to determine activation energy. The main features of this technique is that just needed data from the tip of the peak, for single peak can be easily found the magnitude of (I_m, T_m) from the glow curve, till it is same for a large peak which surrounded by smaller satellites. In this method by plotting $\ln(T_m^2/\beta)$ versus $(1/T_m)$could offer a straight line with slope (E/k) and by substituting Boltzmann constant should get the magnitude of (E) as showed in Figure 5.9, from the slope and the magnitude of (k), it was calculated that E=0.49eV, as shown in Table 5.1.

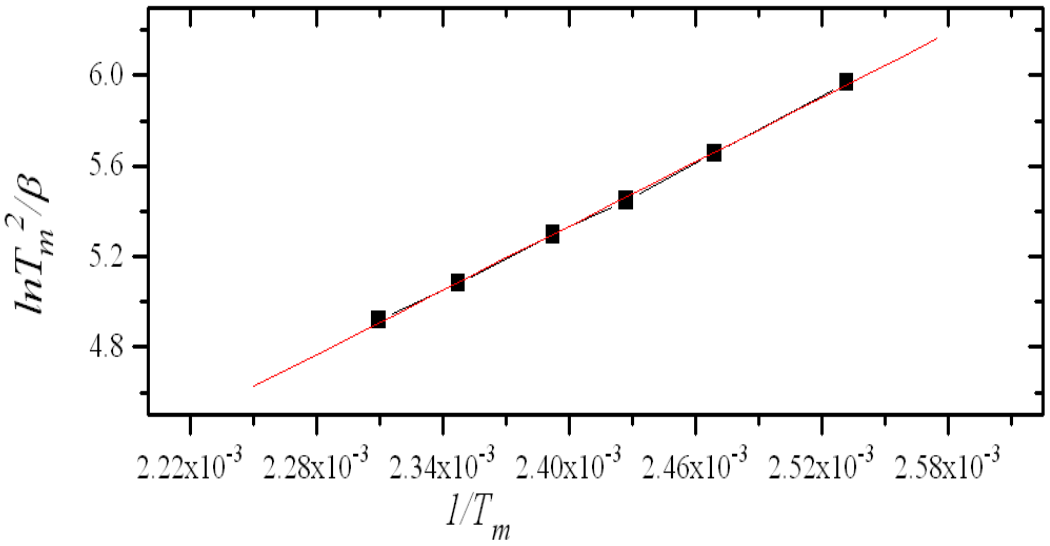

Figure 5.9 A plot of $\ln(T_m^2/\beta)$ versus $(1/T_m)$.

The stability of the stored signal at normal temperatures is an important factor in many applications such as (archeological, geological dating, personal and environmental dosimetry…etc.), any appreciable decay in the stored signal at room temperature will cancel the relationship between TL emitted and the radiations exposure that may have been delivered at some considerable time before readout. The reduction or loss in radiation induced signal in the sample as a function of time is called fading, in this phenomenon in which there is unintentional loss of the latent information, many things are causes of the process of fading, temperature is the main one, light...etc. In the thermal fading, the traps that present lower entrapment energy will fade faster than the more energetic ones, due to their higher probability of transition, belongs to this reason it must be keep samples in room temperature to avoid make errors in read out data.

For this experiment, (10mg) of the material ($CaAl_4O_7:D_y$) was irradiated up to 72Gy and it was stored in dark place at room temperature over a period of four weeks, Figure 5.10 shows the variation of TL response and decrease in TL peak intensity during four weeks. And results clearly showed in Figure 5.11 that the main glow peak at the end of the planned storage times reduced typically to 51 % of its original value.

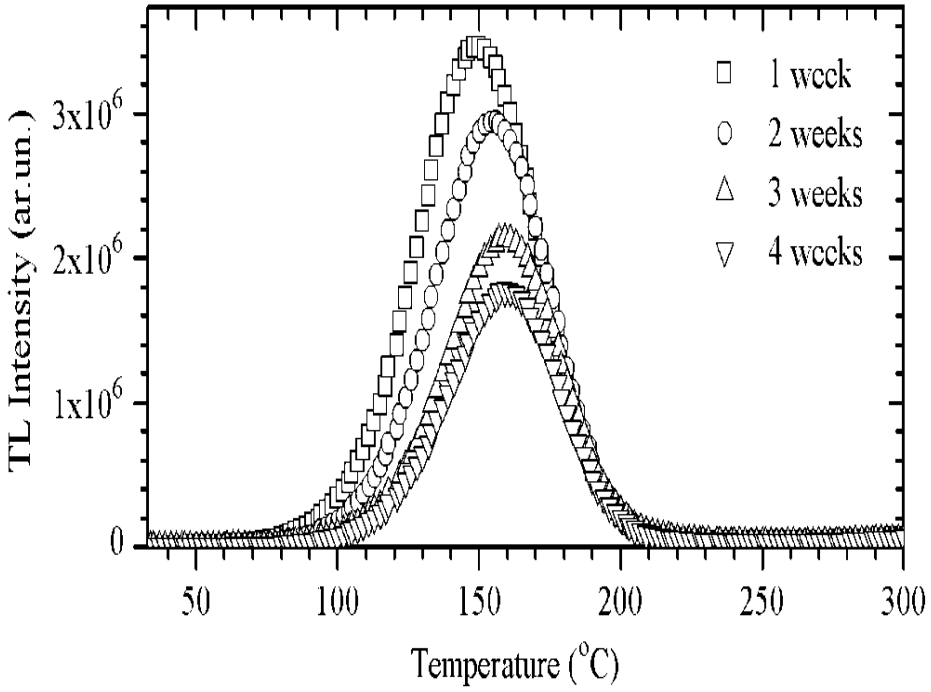

Figure 5.10 A set of TL glow curves for ($CaAl_4O_7:D_y$) recorded after various storage periods at room temperature in the dark room. Read out all glow curves at 1°C/s after exposing to an irradiation of 72Gy.

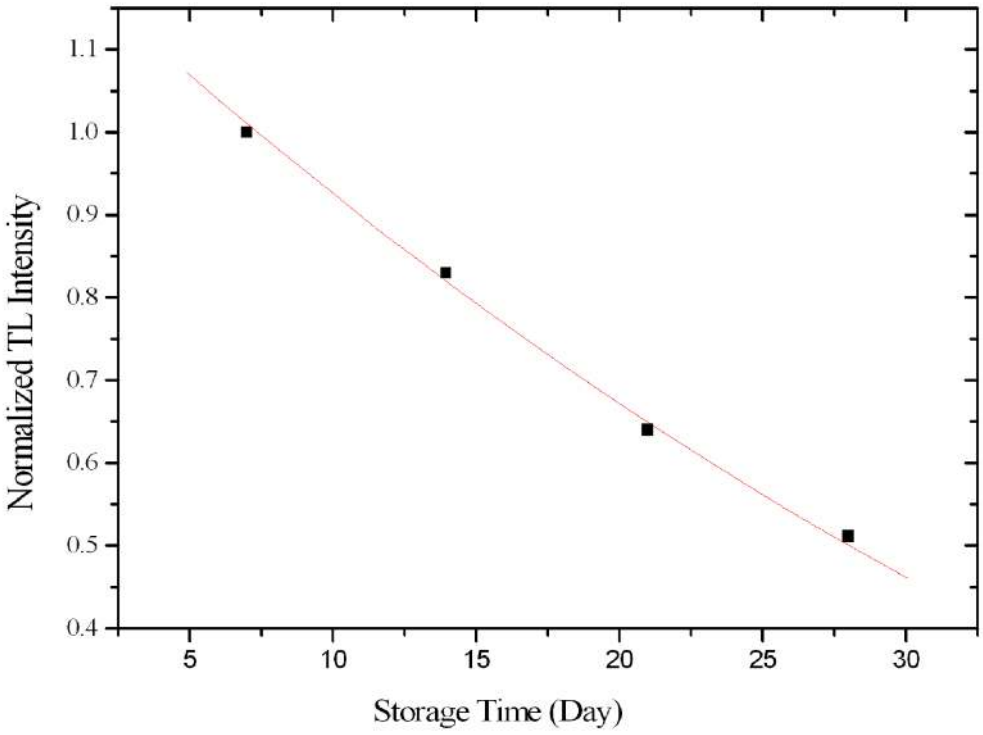

Figure 5.11 Normalized TL intensity of main glow peak after different storage times at room temperature (β=1°C/s and D=72Gy).

To analysis of the glow curve and determination of each trap parameters were also have computer glow curve deconvolution (CGCD) technique which this technique in the last two decades was very favorable for evaluating the trapping parameters. It has extensive superiority with high resolution and accuracy when it is compared to the experimental methods because of the coincident evolution of trapping parameters of all peaks without additional thermal treatments and experimental repetitions, and in this technique all the data points can be used for one of the glow curves instead of a few points only through the operations of the appropriate curve. So if added one other data point to utilize in the analysis, it is clear that the possibility for right decision of the trapping parameters also increases. Nevertheless, 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 the analysis of the complex glow curves by CGCD method, it is very important to decide correctly how many glow peaks there are in the glow curve and which of them have first or general-kinetics to obtain results. Especially, the advantages of the CGCD method may be undermined in complex TL glow curves, and useful application of CGCD technique is the decomposition of a composite TL glow curve into its individual glow peaks which is widely used since 1978 [55], note that obtained result from this method is dependent upon the input parameters which were used in the deconvolution program.

It is so important to decide properly in the complex glow curve analyses by the method of CGCD how many glow peaks exist in this glow curve and which of them have kinetics of the (first or general-order) to get real results. As a result, 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. Maybe weakening the features of the method of CGCD in particular in complex TL glow curves. 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. As a result, for the same glow curve may be have many possible sets of kinetic parameters. The utilized CGCD program, which is built on the least square

minimization procedure, was developed at the Reactor Institute at Delft, IRI-CIMAT Report include results of these models in detail [56].

In some cases, when used various 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 parameter value 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, at first should be determined the number of glow peaks and their kinetic orders in the glow curve of $CaAl_4O_7:D_y$. In this study it was noted that the structure of the glow curve of this model is described well by one first-order and one general-order glow peak .Because, the kinetic parameter results are also relying heavily on the input parameters like the individual peak site. Finally the parameters can be estimated when the values of result is the best overall fit to the features of the certain high priority of the thermoluminescence (TL) results. From CGCD fitting results of high dose, it indicated that our peak is consisted of two peaks as shown in the Figure 5.12 and values of (Ea and s) in Table 5.1, also this method was applied of low dose which it is shown in Figure 5.13, but in here it explain that our peaks is consisted of three peaks.

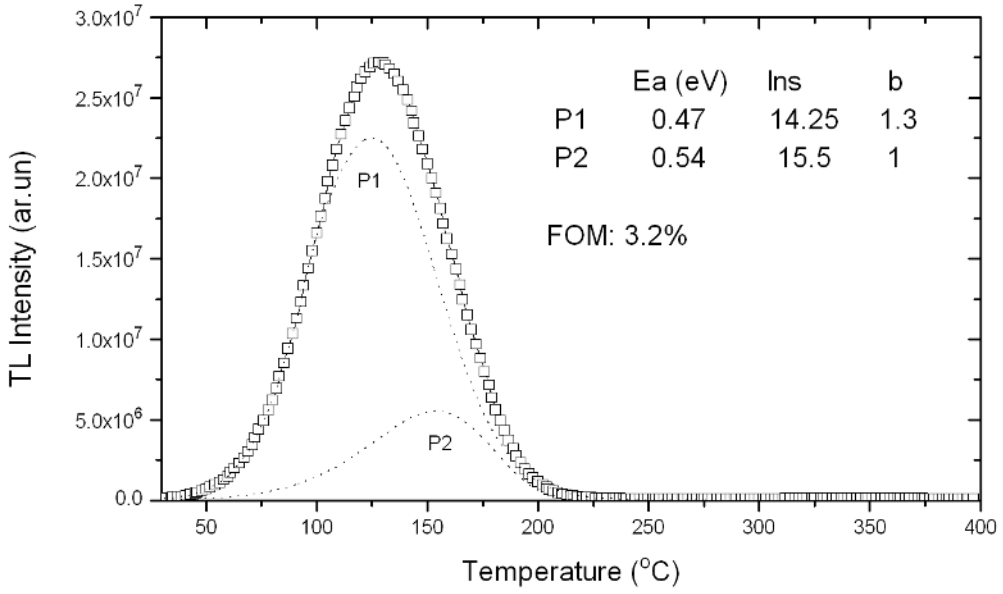

Figure 5.12 CGCD analyzed of glow curves of $CaAl_4O_7:D_y$ measured after 144Gy irradiation by β source at room temperature, with values of trap parameters.

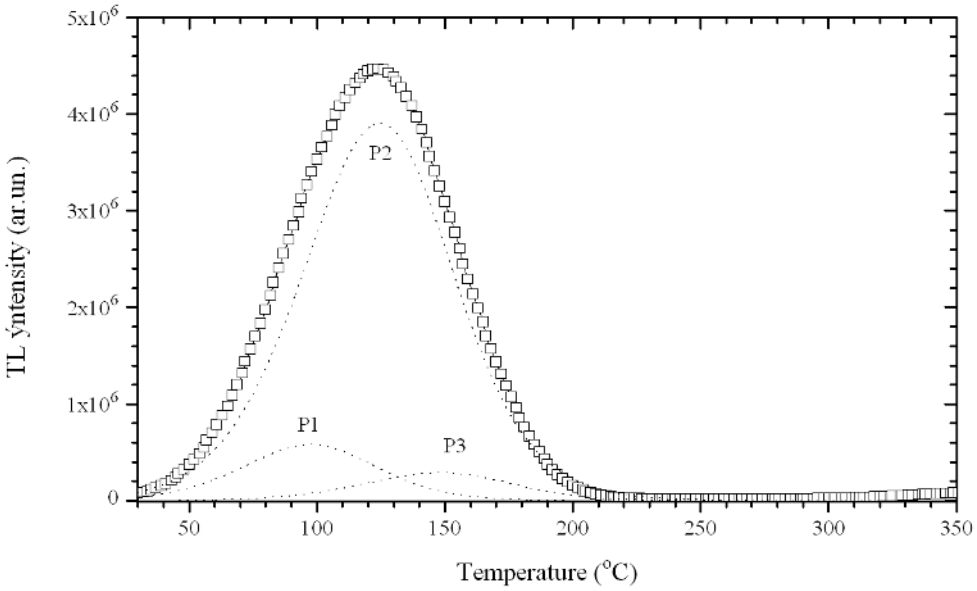

Figure 5.13 CGCD analyzed of glow curves of $CaAl_4O_7:D_y$ measured after 36Gy irradiation by β source at room temperature.

Table 5.1 The values of the trapping parameters of CaAl4O7:Dy determined by Chen's PS, Mazumdar PS, VHR and CGCD methods.

	Chen P.S.			**Mazumdar P.S.**			**H.Rate**	**CGCD for P1**
	E_τ	E_δ	E_ω	1/2 ratio	2/3 ratio	4/5 ratio		
E (eV)	0.53	0.51	0.52	0.48	0.475	0.485	0.49	0.47
b	1.5	1.5	1.5	1.5	1.4	1.35	1.5	1.3
lns (s^{-1})	13.78	13.78	13.78	14.05	14.05	14.05	14.15	14.25

CHAPTER 6

CONCLUSION

The main purpose of our study is to synthesize and investigate the thermoluminescence properties of Calcium Aluminate ($CaAl_4O_7$) doped with D_y. In order to understand the properties of a thermoluminescent material the kinetic parameters of the different glow peaks such as the order of kinetics (b), the activation energy (Ea) and frequency factor (s) of the traps must be determined. Therefore the order of kinetics (b), activation energy (E_a) and the frequency factor (s) associated with the thermoluminescent glow peak of this material were evaluated by using different experimental techniques such as, Variable Heating Rate Method (VHR), Peak Shape Method (PS), and Computerized Glow Curve Deconvolution Method (CGCD).

In this study we tried to explore the dose dependence characteristics of the glow curves of Calcium Aluminate ($CaAl_4O_7$:D_y) using the additive dose (AD) experiments. The samples were irradiated at different dose levels between 0.2 Gy to 864 Gy at a linear heating rate of $1^oC/s$ to check the dose dependence. The experimental results indicated for the glow curve of D_y-doped $CaAl_4O_7$ after beta-irradiation between 0.2 Gy and 864 Gy in the temperature range from room temperature to 400 ^oC is the superposition of at least two glow peaks. When the dose level is increased the peak temperatures of the glow peaks are nearly constant within the experimental as illustrated in figures 5.3 to 5.6. Different techniques such as peak shape methods (Chen's and Mazumdar), variable heating rate (VHR), and computer glow curve deconvoluation methods have been applied to evaluate the kinetic parameters *b*, *E*, and *s*. The results of the Chen's Peak Shape method give values of kinetic parameters in average for P1; *b*=1.5, *Ea*=0.5 eV, *lns*=13.78. Apart from the Chen's peak shape method, we also used Mazumdar peak shape method and we get *b*=1.4, *Ea*=0.48 eV, *lns*=14.05. as seen from figures 5.7 and 5.8, the peak temperatures of all peaks are shifted slightly to higher temperatures

and the integrated peak area of the curves decreases as the heating rate increases as expected in theory. The results of the heating rate method are b=1.5, $E\approx$ 0.49eV. As mentioned before this study has been supported with analyzing the measured glow curves by CGCD program. It is very popular method to evaluate the absorbed dose and trapping parameters of glow peaks from the glow curves. Because during the curve fitting procedure whole curve points are utilized in the analysis, rather than just a few points on the glow curve, Figure 5.12 was shown the results of CGCD fitting of irradiated sample with (high dose) 144Gy on the assumption of two peaks with summarizes values of kinetic parameter values for each of the peaks. And TL Glow Curve Analyzer software with Figure of Merite (FOM) values 3.2%. The values evaluated with CGCD method for P1 are b=1.3, Ea=0.47 eV, lns=14.25. all these values can be seen in detail in Table 5.1, and the result of low dose experiment of CGCD also shown in Figure 5.13.

For the storage time experiment $CaAl_4O_7$:D_y sample was exposed to 72 Gy dose each time and left fading. The storage time experiments were performed for different time periods from 1 week to 4 weeks. The measured glow curves of $CaAl_4O_7$:D_y at the end of the planned storage periods are shown in figure 5.10 and 5.11. as seen from this figures, the intensity of the main glow peak (P1) of $CaAl_4O_7$: D_y at the end of the planned storage times reduced typically 51 % of its original value.

The results of the experiments have proved that $CaAl_4O_7$: D_y is a good candidate for TL dosimetry studies and it is recommended to investigate the thermoluminescence properties of calcium aluminates doped with other rare-earth ions.

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