UNIVERSITY OF GAZİANTEP

GRADUATE SCHOOL OF

NATURAL & APPLIED SCIENCES

INVESTIGATION OF DOSIMETRIC AND THERMOLUMINESCENCE PROPERTIES OF $Li_2B_4O_7$: Mn (TLD-800) CRYSTALS

**M.Sc. THESIS
IN
PHYSIC ENGINEERING**

BY

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JANUARY 2013

Investigation of Dosimetric and Thermoluminescence Properties of Li$_2$B$_4$O$_7$:Mn (TLD- 800)

M.Sc. Thesis

in

Engineering Physic

University of Gaziantep

Supervisor

Asist.Prof.Dr. Vural Emir KAFADAR

by

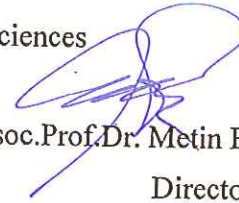**Hikmat Ramadhan Hajee ZEBARİ**

January 2013

REPUBLIC OF TURKEY
UNIVERSITY OF GAZİANTEP
GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES
ENGINEERING PHYSICS

Name of the thesis: Investigation of Dosimetric and Thermoluminescence Properties of $Li_2B_4O_7$:Mn (TLD- 800)

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Exam date: 17/01/2013

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ABSTRACT

INVESTIGATION OF DOSIMETRIC AND THERMOLUMINESCENCE PROPERTIES OF $Li_2B_4O_7$: Mn (TLD-800) CRYSTALS

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M.Sc. in Engineering Physics

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January 2013

58 pages

The dosimetric characteristics of any TL material mainly depend on the sensitivity, energy response and the kinetic parameters quantitatively describing the trapping emitting centers responsible for the TL emission. Thus, a reliable dosimetric study of a thermoluminescent material should be based on a good knowledge of its kinetic parameters. Evaluation of kinetic parameters, i.e. the activation energy E_a of the traps involved in the TL emission, the kinetic order b, and the frequency factor s, associated with the glow peaks. $Li_2B_4O_7$: Mn is a well-known TLD material with an excellent tissue equivalence of human. It is used in practice for personnel dose monitoring in various branches. It is known commercially under the trademark TLD-800. In the given study, the additive dose (AD), variable heating rate (VHR), peak shape (PS), three point method (TPM), and computerized glow deconvolution (CGCD) methods were used to determine the kinetic parameters glow peaks of $Li_2B_4O_7$: Mn. The results of the analysis have shown that TLD-800 has a general order glow peak of E_a=0.58 eV at 170 ^{o}C.

Key Words: Thermoluminescence, kinetic parameters, $Li_2B_4O_7$: Mn.

ÖZ

$Li_2B_4O_7$: Mn (TLD-800) KRİSTALLERİNİN DOZİMETRİK VE TERMOLUMİNESANS ÖZELLİKLERİNİN İNCELENMESİ

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Ocak 2013
58 sayfa

Dozimetrik bir malzemenin termoluminesans özellikleri, temelde malzemenin doz hassasiyetine, enerji cevabına ve termoluminesans ışıldama eğrilerini oluşturan tuzak parametresi değerlerine bağlıdır. Güvenilir bir dosimetrik çalışma için bu tuzak parametrelerinin, kinetik derecesi b, aktivasyon enerjisi E_a ve frekans faktörü s'in belirlenmesi oldukça önemlidir. $Li_2B_4O_7$: Mn kristali doku eşdeğerine sahip bir TLD materyaldir ve kişisel dozun ölçümü gibi pek çok alanda TLD-800 ticari koduyla kullanılmaktadır. Bu çalışmada değişken doz, farklı ısıtma hızları, tepe şekli, üç nokta ve bilgisayarlı ışıma eğrisi ayrıştırma yöntemleri kullanılarak $Li_2B_4O_7$: Mn kristalinin tuzak parametre değerleri hesaplanmıştır. Analiz sonuçları TLD-800 kristalinin 170 ^{o}C'de genel dereceden, 0.58 eV enerjiye sahip bir ışıldama tepesine sahip olduğunu göstermiştir.

Anahtar kelimeler: Termoluminesans, tuzak parametreleri, $Li_2B_4O_7$: Mn.

To my parents , my family (wife & children) , to my Supervisor: Asist. Prof. Dr. Vural Emir KAFADAR and to all humanity .

ACKNOWLEDGEMENT

Foremost, I would like to express my sincere gratitude to my supervisor Assist. Prof Dr. Vural Emir KAFADAR for the continuous support of my M.Sc. Study and research, for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my M.Sc. Study. His wide knowledge and his logical way of thinking have been of great value for me. His understanding, encouraging and personal guidance have provided a good basis for the present thesis.

I owe my most sincere gratitude to Assist. Prof. Dr. R.Güler YILDIRIM. Her extensive discussions around my work and interesting explorations in operations have been very helpful in this study.

I warmly thank Assist. Prof. Dr. Hüseyin TOKTAMIŞ for his valuable advice and friendly help.

I would like to thank my family and my parent. Since giving birth to me in the first place and supporting me spiritually throughout my life.

I would like to pay high regards to my wife, my children. They have lost a lot due to my research abroad. Without their encouragement and understanding it would have been impossible for me to finish this work. My special gratitude is due to my brothers, my sisters and their families for their loving support.

LIST OF CONTENTS

CONTENTS	PAGE

LIST OF TABLES

LIST OF FIGURES

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CHAPTER 1

INTRODUCTION

1.1 What is thermoluminescence

The substances like insulators or semiconductors absorb energy while irradiated at a given temperature, and give off this energy in the form of light while heating the sample.This thermally stimulated phenomenon can be called as luminescence or thermoluminescence. This thermally stimulated light contains information about the trap structure of the TL material and its previous exposure to the ionizing radiations. The thermoluminescence is a process differs from the light emitted spontaneously from a substance when it is heated to incandescence. Say over 200 °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). And the thermoluminescence is produced when irradiates the sample with radiation and electrons with high energy are trapped within the sample, and the phenomena of the thermoluminescence (TL) can be noted in semiconductors and insulators which features the electrons in defect positions in the stability circumstance. The light must be emitted when these trapped electrons out of the trap and come down to the lower energy level through the potential barrier by heating the material [1].

There are three basic components necessary for the production of TL. First, these materials must have a luminescence properties in order to produce (TL) like semiconductors and an insulators , but metals don't have this property. Second, the materials absorbing energy at some time when the ionizing radiation falls on them. Third , the light is coming out of the materials (luminescence emission) when heating these materials [2]. The thermoluminescence (TL) material absorbs (stored) some energy during exposure to ionizing radiation, and when heating this material will release the energy which is absorbed as a visible light. In fact that

thermoluminescence (TL) does not point to thermal excitation, but to another way which is named as a thermal stimulation of luminescence in a sample which is excited in a various way .This means a thermoluminescence (TL) material should be exposed again to the ionizing radiation like; (alpha, beta, gamma and X-rays or UV-rays or when it undergoes certain chemical reactions or mechanical stress) in order to produce light again because a (TL) substances by reheating and simply cooling cannot emit light again. The storage capacity of a thermoluminescence materials makes them suited for the dosimetric applications. When one is irradiated a (TL) material some of this irradiation energy will be used to transfer the electrons to inside the traps. By raising the temperature of the (TL) material this energy which was stored in the form of the (trapped electrons) was released and converted to the luminescence. It can be obtained a lot of information about the process of the trap and liberation of electrons from (TL) spectrum. And that, after stopping the radiation source, the thermal stimulation of luminescence is monitored under a condition of steadily rising temperature [2].

The effective atomic number of the Lithium tetra borate ($Li_2B_4O_7$) is (Z_{ef} =7.3) and it is very close to human tissue (Z_{ef} =7.4) and it is therefore an appropriate material for (TL) dosimetry [3]. $Li_2B_4O_7$:Mn phosphor was the first material which was presented in radiation dosimetric from the lithium tetraborate [4]. But it gives low thermoluminescence sensitivity, and partly caused the emission in the (600nm) region of the spectrum, which is still far from an exemplary wavelength zone for most commercial photomultipliers (approximately 400 nm). There are a various ways to prepare these thermoluminescence materials which have subsequently been developed , but various thermoluminescence characteristics comes from different activators [5]. The first application of the (TL) phenomena which has been known for a long time for dosimetric purposes was from Daniel et al [6]. And since that time it has been implementing many of the research on understanding and improving the characteristic of materials, as well as the development of new thermoluminescence materials. In these days, the thermoluminescence dosimetric (TLD) technique solidifies in many areas like (personnel, environmental and clinical) dosimetry. The thermoluminescence dosimetric (TLD) is based on materials that emit light while being heated after exposure to ionizing radiation. Impurities in the thermo luminescence material (TL) are the reason of the existence of local energy

levels in the prohibited energy band gap and these are decisive in the thermoluminescence process. As a way of detecting the presence of these defect levels, the sensitivity of the thermoluminescence (TL) is unparalleled. Townsend and Kelly [7]. The major attributes required to make a good material thermoluminescence (TLD dosimeter) nominees are; the broad separator in which the intensity of the luminescence is linearly proportional to the absorbed dose. In most of the substances, the super linearity and saturation (decay) for the intensity of the thermoluminescence at large doses is limits the linear interval .And the linear dose dependence determined the benefit range [8].

- Lower accreditation of the TL response to the energy to the incident radiation. If required, it can rely on the energy partially offset metal filters.
- A high sensitivity, it is mean that the high thermoluminescence (TL) signals per unit these doses which are absorbed. And it is important to use this high sensitivity in medical dosimetric and personal,and also in environmental radiation monitoring.
- A few fading, it means that the capability to store information of the dosimetric for a long time.
- The TL curve is simple (one isolated peak). If they have several peaks, the dosimeter heating protocol is not easy (complicated).
- The spectrum of the luminescence must be commensurate with the uttermost spectral sensitivity of the photomultiplier.
- The thermoluminescence dosimetric material must be chemically inert, strong mechanically, and radiation resistant.

Thermoluminescence (TL) is the light emitted from thermal stimulation process after absorbing energy from the previous radiation. A curve is obtained (glow curve) during the readout by using a linear time-temperature heating profile after detection a thermoluminescence emission and plotting as a function of the time. The glow curve can be analyzed by introducing the parameter which is called the (order of kinetics) from an experimental method. The trapped electrons have two types of opportunities to jump to the down after they are jumping up by thermal energy to the conduction band. First is the process of the re-trapping or return to the same type of traps and second, is electrons recombine with holes accompanied by emission of the

thermoluminescence light. When neglects the probability of the re-trapping process, therefore, the peak shape of the glow curve will be narrow because of the fast recombination process which is interpreted by Randall and Wilkins [9]. And the wide peak of the curve has interpreted by Garlick and Gibson when the re-trapping dominates and the recombination electrons with holes are suppressed [10]. The two explanations which are described above are termed the (first order kinetics) and the (second order kinetics), respectively . The general order kinetics are entered between these two kinds to provide a continuance from separate two kinds of kinetics interpreted by May and Partridge [11].

The characteristics of the dosimetric for thermoluminescence materials rely mainly on the kinetic parameters which describe quantitatively the trapping-emitting centers and are responsible for thermoluminescence emission. To determine the kinetic parameters and therefore active region of research and different techniques placed to derive the parameters of the glow curve. The glow curves from several various natural quartz samples are recorded by David and colleagues and affirmed that it was hard to compare thermoluminescence (TL) which were published from the various samples due to controversies in pre-irradiation treatment, heating rates, way of manufacture, and content of impurities, etc. [12]. Therefore, the objective of this study is to identify the kinetic parameters, dose-response and the stability of thermoluminescence (TL) peaks of the ($Li_2B_4O_7$) specimens.

There are different ways to evaluate the kinetic parameters of the thermoluminescence (TL) glow curves [1]. When highly isolated one of the glow peaks of the other glow peaks, the empirical ways like. Variable heating rates (VHR), initial rise (IR) and peak shape (PS) ways are appropriate in determining the kinetic parameters. The several overlapping peaks exists in the glow curve of the ($Li_2B_4O_7$) as in most thermoluminescence materials. When glow curve consists of more than one glow peak, and to get these parameters there are basically two ways. First, each individual thermoluminescence (TL) peak insulated from other peaks by using the partial thermal annealing treatment. Second, complete glow curve analysis is made by using deconvolution [13]. There are some difficulties in the first way without losing the intensity because of the problems in isolating the peak of interest.The main attractive property of the deconvolution technique is the

4

simultaneous determination of the kinetic parameters of each peak without thermal treatment. The disadvantages of the deconvolution way over classical ways in certain instances, and especially the structure of the glow curve are too complex.

1.1.1 Luminescence

The material can be absorbed and re-emitting some of its energy in the light of a longer wavelength when the radiation falling on it (Stoke's law) and this process is called luminescence. Luminescent material can be characterized from the wavelength of the light emitted but it is cannot be characterized from the incident radiation. Usually the phenomenon of luminescence in most studies is attached with the emission of the visible light but other wavelengths like (ultra-violet or infra-red) may be emitted [2]. After absorbing radiation the emission of the light takes place a characteristic time (τ_c) and this parameter (τ_c) allows us to subdivide the process of luminescence as illustrated in the figure 1.1. The (τ_c) of fluorescence is smaller than (10^{-8}s) and (τ_c) of 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), and happens simultaneously during absorbing the radiation and 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 [14]. One is the short period phosphorescence ($\tau_c < 10^{-4}$s) and another one is the long period phosphorescence ($\tau_c > 10^{-4}$s). The only way to distinguish between the fluorescence and the phosphorescence is the study of 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 [2].
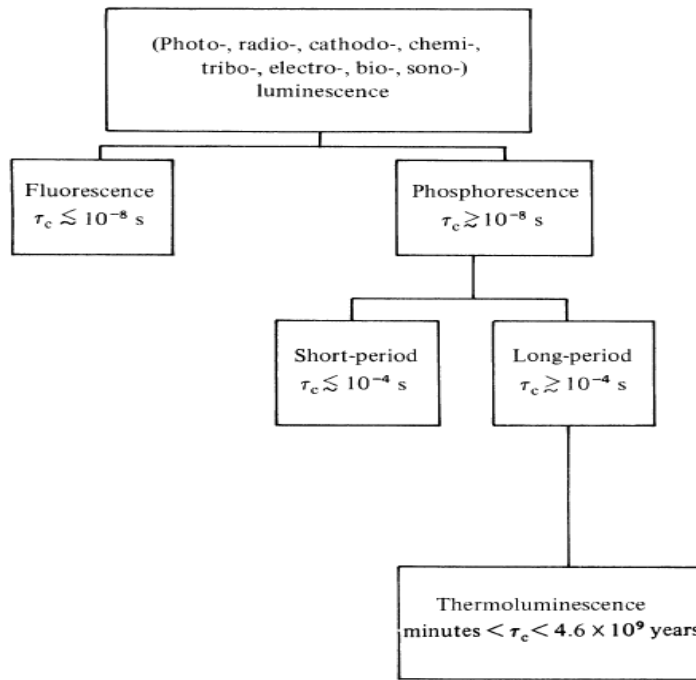
Figure 1.1 The "family tree" of the phenomenon of luminescence, the different between fluorescence and phosphorescence is due to the delay (τ_c) between emission and excitation.
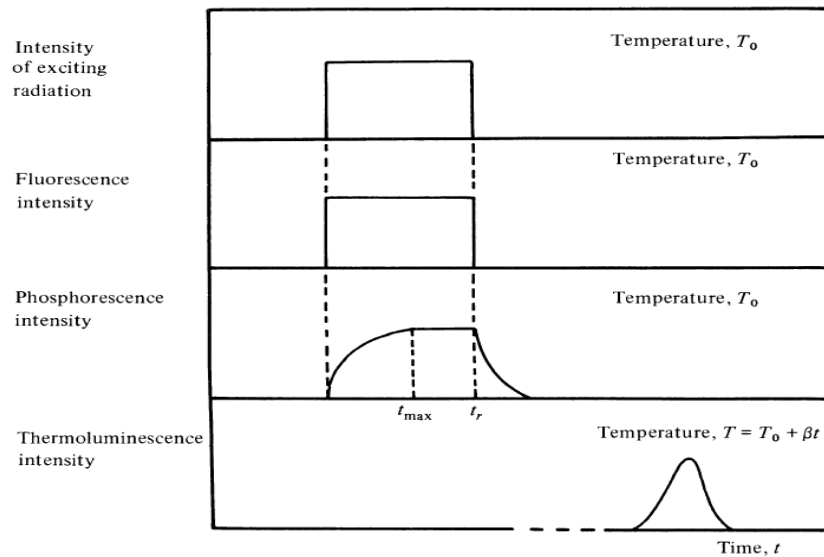
Figure 1.2 The relationship between absorption of radiation and the emission of phosphorescence, fluorescence and thermoluminescence. (T_0) is the temperature at which irradiation happens; (β) is the heating rate, (t_r) is the time of starting the decay of phosphorescence after ending irradiation time.

6

It can also be explained the luminescence emission by transferring the energy from radiation to the electrons of the solid material, (transition (i) in figure 1.3 a) means exciting the electron from the ground state (g) to an excited state (e), and when this an excited electrons come down to its ground state emits luminescence photon (transition (ii)). Thus, for fluorescence the delay between transition (i) and (ii) is ($<10^{-8}$). And this process is independent of temperature.

Chen[6] has presented the first interpretation of temperature dependent phosphorescence. In the figure (1.3b) 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 the delay observed in phosphorescence complies with the time which is spends the electrons in the trap (m). From the arguments of thermodynamic it may demonstrate that the mean time (τ) that the electron spends in the trap at temperature (T) is found by :

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

(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 [2].
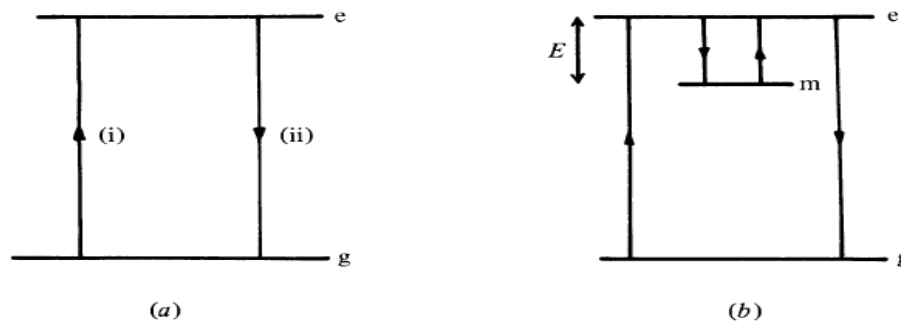
Figure 1.3 The energy transitions involved the fluorescence production (*a*) and phosphorescence production (*b*) [2].

1.2 Requirements of a suitable TL material

A thermoluminescence (TL) phosphor which is used to measure the dose and it should combine the several properties , as a consequence, only reduce the choice to few inorganic compounds. A (TLD) phosphor has some properties which are more desirable and these properties are [15]:

First, high concentration of the (electron) traps or (hole) traps and a highly efficient of light emission associated with the process of recombination. Second, Adequate store stabilization of the (electron) trap or (hole) trap to not cause any unwanted fading even during long storage of the ambient temperatures or a slightly increasing temperature (desert or tropical climates) or , the studies of the implantation of biomedical , temperature of the body . And this must be applied to the opposite end of the climate inside (the Arctic Circle) where the temperatures are low. Third, when the detector system (photomultiplier and filter combination) is responding well. The spectrum of the emission of the thermoluminescence (TL) light has least possibilities interfere with incandescence (infrared) emission of the hot phosphor and its surroundings areas . Forth , the distribution of the trap which does not complicate the procedure of evaluation because of the existence additional fading (low temperature or high temperature) peaks (that is maybe hard to anneal) and due to the process of the re-trapping, etc. And must be completely annealing the phosphor during the procedure of readout, without changes its sensitivity and reading of the background or (linearity).

The fifth , The temperature of the main peak (Tm) located between (180 ^{0}C and (250 ^{0}C). Increasingly ,at the higher temperature the infrared emission from the hot model and the model holder interferes with the low dose measurement. The spectrum wavelength between about (300 nm) and (500 nm) are the most desirable only if sensitive system used specifically for UV. Sixth, the resistance against the environmental troublesome potential factors likes (humidity, gases, light, common fumes and organic solvent). If this is not possible, sealed the detector into a bulb of glass permanently. Seventh, the phosphor must be cheaper and easier for working with "one-way" dosimeter, and it must be non-toxic and does not deteriorate during storage for a long time. It is possible to use a small model only , taking into account if there are no spurious effects like (Tribo- or chemiluminescence, oxygen effects,

etc.) and may be useful if can be prepared the material easily with the properties of reproducible in a naturally equipped laboratory of chemical . Eighth, for most applications, the desirable features, the low photon energy dependence of response in the extending range are depending on the particular use, a (high) or (low) thermal neutron sensitivity or a specific (LET) response can be the desirable properties.

1.3 Advantages of TL phosphors in personal dosimetry

The several advantages are found in (TL) systems for personal dosimetry [17]:

1) The devices to detect a thermoluminescence (TL) (TL detectors) are abundant in the form of powder or solid in a broad range of volume.
2) Practically, the thermoluminescence (TL) materials do not depend on the rate of dose and on the angle of incident radiation.
3) Thermoluminescence detectors are appropriate for postal service .
4) That it is possible to have a re-evaluation of the absorbed dose of irradiation of UV and readings of a high temperature peak (PTTL).
5) The minimum of detection is about (0.2) mGy ;
6) Some materials (TL) have a near tissue -equivalent configuration (LiF, $Li_2B_4O_7$, MgB_4O_7, BeO) which cancels the need to get energy debugging;
7) A large monitoring services are evaluated from automated /computerized.

1.4 General features of thermoluminescence

Luminescence of many solid materials is unlisted in the category of either (Luminescence) or (Thermoluminescence) , but represents a various phenomenon when rises their temperature to incandescence. Luminescence in solids can be occurred mainly by (ultra-violet radiation, γ or X radiation , energetic electrons , nucleons and pions , and as well as from an electric field). And also can shine solids by some of the chemical and biological processes. Emissions largely depends on the distinctive attributes of impurity atom, which works as an activator. When the

exciting radiation stopped , some of the materials have the ability to emit light in the range of (visible) or (near visible) this phenomena is called luminescence. A period of continuation of this afterglow can be too short is about (10^{-8} to 10^{-7}s). But in many instances there may be an extra element of the afterglow which continued for much longer . This element is called phosphorescence , typically established from the role attributed to metastable states of activator in the host material [17].

1.5 Defects and color centers

The 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 [18]. The point defects are between these simple defects that are found in the structure of the crystal and which are easily able to mathematically formulate. Creation states inside the energy gap of the host material 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). The names of different phenomena of the luminescence are given , as illustrated in the table 1.1 which reflects the kind of radiation that are used for emission excitation. The lists which are described in the below table are (the phenomena of luminescence and excitation method) [19].

1.6 Thermoluminescence Applications

The significant progress has been made in the thermoluminescence application technique for practical purposes during the past twenty years or so. And the application which is developed very widely , however indicates to its use in radiation dosimetry which spans areas of health physics and biomedical science, radiation protection and control. And the equally impressive growth of the TL technique is reflected in its applications in dating of archaeological and geological [20-21]. The recent thermoluminescence application is related to the date of the sand dunes, which have the effects in their movement study and some of the other sides of the desert environment [30]. Interesting, but it is not developed sufficiently, the applications which have been mentioned in the science of forensic which means the

characterization of suspicious materials and determine the forged objects which are susceptible for thermoluminescence (TL) investigations.); in industry (study of burnt concrete of fire – damaged buildings and of industrial pollutants) and, via the TSC mechanism, in solid state ionography [22].

Table 1. Describes the phenomena of luminescence and excitation method [19].

THERMOLUMINESCENCE 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 Phosphorescence light Thermoluminescence Lyoluminescence	Ionizing radiation, U.V. and visible

CHAPTER 2

THERMOLUMINESCENCE THEORY

2.1 Basic concepts of thermoluminescence (TL) in solids

Daniel et al [23] was the first person who used the applications of the thermoluminescence (TL) phenomenon for the purposes of dosimetry. In spite of that phenomena of TL have been known for a long time in order to develop new thermoluminescence materials, it has been implemented a lot of researches to understand and improve the characteristics of the materials. In these days, a TLD is the dosimetric technique which is established well with applications in the domains like (personnel, environmental and clinical dosimetry). Thermoluminescence dosimetry (TLD) is based on that material which emits light while they are heated, after exposure these materials, to ionizing radiation. The energy levels which are existing among the forbidden energy band gap, due to the impurities existence in the thermoluminescence materials and these are the crucial reason for the process of thermoluminescence. And as a way of detecting that the thermoluminescence (TL) sensitivity is unparalleled, during presence these defect levels. Townsend and Kelly [7]. Appreciate that the technology is able to detect at least (10^9) levels of defects in the model. In order to put this number in the proper perspective, the important thing that should be realized that the purity of the model is (6) orders of high magnitude. On the one hand , the high sensitivity allowed to identify a very low radiation dose, but it handicaps us to investigate the relation between the defects involved in this process and luminescence in the other hand. And for the various types of dosimeter the sensitivity of thermoluminescent   material will be various. A process of relaxation of emitting light during the thermal stimulation is thermoluminescence. The traps are generated in (dosimetric) by high energy radiation . Appears on the thermoluminescence (TL) curve a series of peaks, and these attributable to trap levels which is featured by a different activation energies.

The theoretical description of the thermoluminescence (TL) usually assumes standard traps spatial distribution and centers of recombination [1]. The thermoluminescent dosimetry has been studied by many investigators during the past ten years [24-25] .When the matter absorbs ionizing radiation, and eventually most of these energy which is absorbed goes into heat, and the chemical bonds are broken just by dissipation a small part of this energy. So small part of the energy in some materials are stored in metastable energy states such as (phosphorus). If the material is heated, and later can be restored some of this energy as visible photons .The releasing of the visible photons by thermal means is the luminescence (TL) [26-27]. Some of the phosphors have very good dosimetric characteristics and now widely used for radiation monitoring and dosimetry. In the thermoluminescent dosimetry, the effects upon the glow curve of thermal annealing are quite important.

The below figure (2.1) explains the phenomena of thermal excitation of luminescence which is said that when a thermoluminescence material absorbs some of that energy which is stored during the period of exposure this material to ionizing radiation . When it is heated , released this energy which is stored as a visible light. In fact that the thermal excitation does not represent thermoluminescence (TL), but TL refers to the stimulation of luminescence in a model that is excited in a various method. In order to produce or (emit) light again from thermoluminescence material must be reheating this material and re-exposed to the ionizing radiation. The capacity of the storage energy of a thermoluminescence material makes it suitable for applications of dosimetric [28].
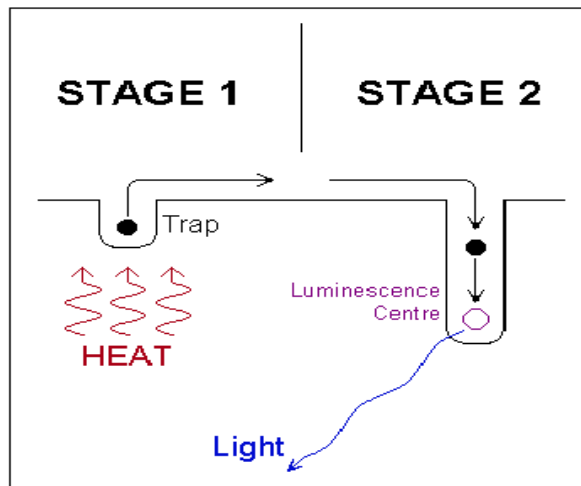
Figure 2.1 The phenomena of thermal excitation of luminescence.

2.2 The one trap – one centre model

The theory of energy band for solid materials interprets the properties of the observed thermoluminescence (TL). Most electrons are residing in the valence band in an ideal (semiconductor or insulator) crystalline. Conduction band is the second highest band, which can be occupied by electrons, and the other band which has existed between these two bands is the forbidden band gap. And (E_g) is the difference of energy between the (V.B) and the (C.B). However, whenever there are impurities inside the lattice, or if there are structural defects happens in a crystal, in this state the electrons have the possibility of owning energies that are prohibited in an ideal crystal. In a simple (TL) model assumes 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 (2.2). The potential of the trap of the electron is (T) and it is located on the highest level and over the (E_f) and it is hollow in the state of equilibrium, i.e, before exposure to the radiation and the (electrons and holes) creation. The potential hole trap (R) is the other level that can operate as a (center of recombination) [6].

The radiant energy absorption (hγ >Eg) is result of ionizing the valence electrons, and produces the energetic (electrons) and (holes) which will, after the process of thermalization , and produces free holes in the valence band (V.B.) and free electrons in the conduction band (C.B.) ,this is a transition (a) in the below figure. 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 freed that might raise luminescent center [6].
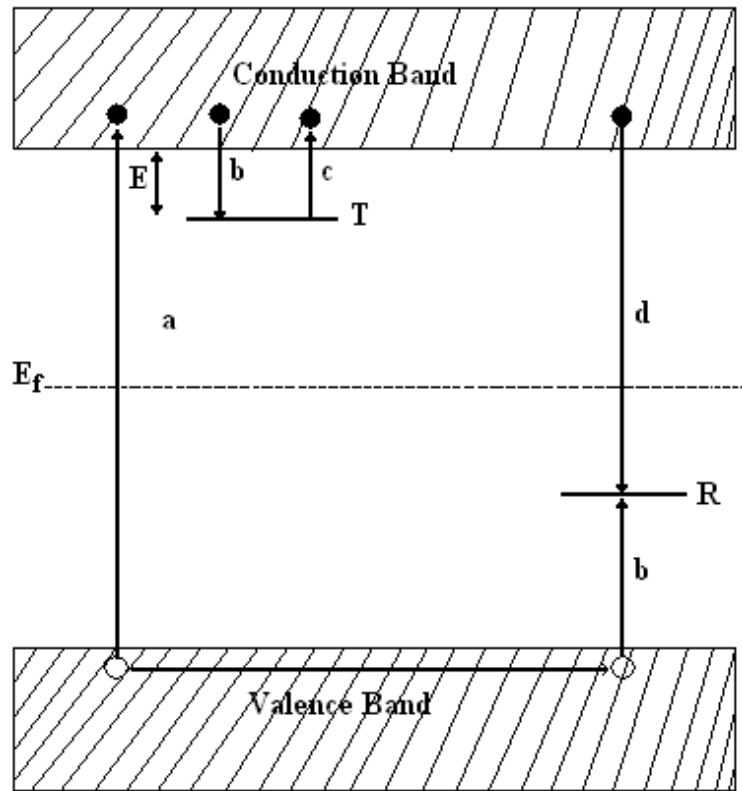
Figure 2.2 The electronic transitions in a thermoluminescence material are shown from the energy band model according to a simple (two-level) model, and (a) is the generating electrons and holes; (b) is the trapping of electron and hole ; (c) is the release of electrons because of thermal stimulation; (d) is a recombination . (●) are electrons, (○) are holes. And the level (T) is a trap of electrons, and the level (R) is a centre of recombination, (E_f) is the Fermi level.

Under the light emission, the center of luminescence relaxes, i.e, returns to the ground state. And with that, trapped a specific percentage of the charge carriers, in the materials (semiconductor and insulator). Trapped the holes in (R) and the electrons are trapped at (T) these are transition (b) as shows in the figure. The Arrhenius equation describes the probability per unit time (p) for releasing an electron from the trap :

$$p = s\,exp\{-E/kT\} \qquad\qquad (2.1)$$

15

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

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

The equilibrium can come back quickly by increasing the heat level of the thermoluminescence substances higher than (T_0). And by this the detrapping probability will increase and now the electrons going out (or freed) from the trap and move to the (C.B). Moves the electrons from the conduction band of the substance until recombine with the (holes) at the recombination center (R). This centre of recombination is a luminescent centre in the simple model, where the (electron and hole) recombination go out from the centre to one of the higher excited states, and come back to the ground state after emitting light, i.e. (TL). And the thermoluminescence intensity I(t) in photons per second at any time (t) during the heating is commensurate with rate of holes and electron recombination at the centre of recombination (R). If the concentration of holes trapped at (R) is (m (m^{-3})), can be written the intensity of the thermoluminescence (TL) as the :

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

In here we suppose that a photon produces from all recombination and that are detected from each photon which were produced . The rate of recombination is proportional to the concentration of free electrons (n_c) in the conduction band and the hole concentration (m).

$$I(t) = - dm/dt = n_c m A \qquad (2.3a)$$

At the constant (A) the probability of recombination (p) expressed in units of volume per unit time which is supposed to be independent of the temperature. The change rate (-*dm/dt*) of the concentration of trapped electrons (n) is equal to the rate of the thermal release (*np*) minus the rate of the retrapping (n_c *(N-n)A_r*),

$$-dn/dt = np - n_c(N - n) \qquad (2.3b)$$

Where (*N*) are the electron traps concentration and (*A_r*) is re-trapping probability (m^3/s). Similarly average concentration of the free electrons (dn_c /dt) is equal to the thermal release rate   (*np*) minus the re-trapping rate (n_c (N-n)A_r) and the recombination rate, (n_c m A).

$$dn_c/dt = np - n_c (N - n)A_r - n_c mA \qquad (2.3c)$$

Equation (2.3a) and the equation (2.3c) described the traffic of the charge carrier during the process of releasing the trapped electron from the trap of a (single-electron) and the recombination in a (single-centre). The thermoluminescence (TL) produced by the holes release, the rate equations are same to the equation (2.3a). 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. The assumption which is called by Chen and McKeever [1]. Is a quasi equilibrium assumption. And this is due to that the concentration of free electron   is quasi stationary in the conduction band, and this assumption at any time is an important assumption;

$$|dn_c/dt| \ll |dn/dt| \quad , \quad |dn_c/dt| \ll |dm/dt| \tag{2.4}$$

This assumption produces the trapped electrons and the trapped holes in pairs during the irradiation and charge neutrality dictates therefore,

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

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

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

When (dn_c/dt) is approximately equal to zero, one can get from the equation (2.3a) and the equation(2.3b) is ;

$$I(t) = (mAns \exp\{-E/kT\})/((N - n)A_r + mA) \tag{2.7}$$

2.3 First-Order Kinetics

Analytically, we can't solve the equation (2.7), but it can be solved by adding the additional simplifying assumption . The Randall and Wilkins [9] neglected the rate of retrapping ((N-n)Ar) from equation(2.7) during the heating stage. The transport of charges which is described by this differential equation in the lattice as a process of (first-order) and the glow peaks that are calculated from this differential equation are called (the first-order glow peaks). The solution of equation (2.7) gives:

$$I(t) = -(dn/dt) = n_0 s \, exp\{-E/kT\}\exp\{-s\int_0^1 \exp\{-E/kT(t')\}dt'\} \tag{2.8}$$

In accordance with the below equation the temperature is increased as a (linear function of time) , and the total number of trapped electrons at a time (t = 0) is (n_0)

$$T(t) = T_0 \;+\; \beta t \tag{2.9}$$

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;

$$I(t) = -\frac{1}{\beta}(dn/dt)\,n_0\frac{s}{\beta}exp\{-E/kT\}\exp\{-\frac{s}{\beta}\int_{T_0}^{T}\exp\{-E/kT'\}dT'\} \quad (2.10)$$

The equation (2.10) is a famous (Randall–Wilkins) expression of the first-order for a peak of a single glow. The figure (2.3) explains the properties of the equation of the Randall–Wilkins. The difference of intensity $I(t)$ can be observed in the figure (2.3a), if (n_0) varies from (n_0=0.25 m^{-3}) till (n_0=2 m^{-3}) while (E=1 eV, s=1.0×10^{12} s^{-1} and β=1 K/s) are remaining constant.

It can be pointed that the temperature remains constant at the maximum of the peak (Tm), and this is a feature of all thermoluminescence (TL) curves of the first-order. It can be found the condition for the maximum by placing $\left(\frac{dI}{dt}\right) = 0$ (or, it is simple from $\left(\frac{d\,ln\,I(T)}{dt} = 0\right)$ we can obtain the following equation.

$$(\beta E/kT_m^2) = s\,\exp\{-E/kT_m\} \quad (2.11)$$

The (n_0) disappeared from the equation (2.11) it means that (T_m) is independent of n_0. It can be further seen in the figure (2.3 (a)) that each point of the curve is proportional to n_0. In dosimetric application the n_0 parameter is the most important one because it is proportional to the absorbed dose. Also it is easy to find out that the n_0 is equal to the area under the glow peak.

$$\int_0^\infty I(t)dt = -\int_0^\infty \frac{dn}{dt}\,dt = -\int_{n_0}^{n_\infty} dn = n_0 - n_\infty \quad (2.12)$$

When ($t\rightarrow\infty$) the (n_∞) is zero. In the figure (2.3(b)) the activation energy (E) changes from (0.8 eV) to (1.2 eV). As illustrated in the figure (2.3(b)), the peak reaches to high temperature when increases the value of the activation energy E, and this is leading to a decrease in height and increases the peak width, but the area does not change ,it is mean that n_0 is constant.

It can be also observed the same changes but in the opposite direction as seen in the figure (2.3(c)). The peak reaches to low temperature when increases the value of (s), and this leads to increases the height of the peak and reduces the width of the peak. But the figure (2.3(d)) one can be seen that when the heating rate(β) increases the peak is transferred to the higher temperature, and this is leading to a decrease in height and increases the peak width, specifically as in the case of diminishing (s).

This can be predicted when (s) and (β) shown as a ratio of (s/β) in the equation (2.10). And it is important for knowing the four parameters , the first two parameters are the major physical parameters (E) and (s) which are named as the parameters of the trapping, and determined by the properties of the trapping center. The last two parameters can be determined experimentally by identifying or selecting a particular dose (n_0) and as well as through the reading of the signal at a particular heating rate (β). Hampers showed that the assessment in equation (2.11) can be approximated the integral by the series of asymptotic due to the fact that in the integration of the linear heating case is not elementary on the right side [6]. In practical applications it is appropriate for describing the glow peak in terms of the parameters that are easily derived experimentally, it means the temperature at the maximum (Tm) and the peak intensity at the maximum (Im) . Kitis et al [29] showed that the equation.(2.11) can be very accurately approximated by:

$$I(T) = I_m \exp\left[1 + \frac{E}{kT}\frac{T - T_m}{T_m} - \frac{T^2}{T_m^2}\exp\left\{\frac{E}{kT}\frac{T - T_m}{T_m}\right\}(1 - \Delta) - \Delta_m\right] \qquad (2.13)$$

Where ($\Delta = \frac{2kT}{E}$) and ($\Delta_m = \frac{2kT_m}{E}$) . Newly,Pagonis et al [30], have showed that the first-order (TL) curve is described accurately by Weibull distribution function and these expressions may be appropriate for the purposes of peak fitting.
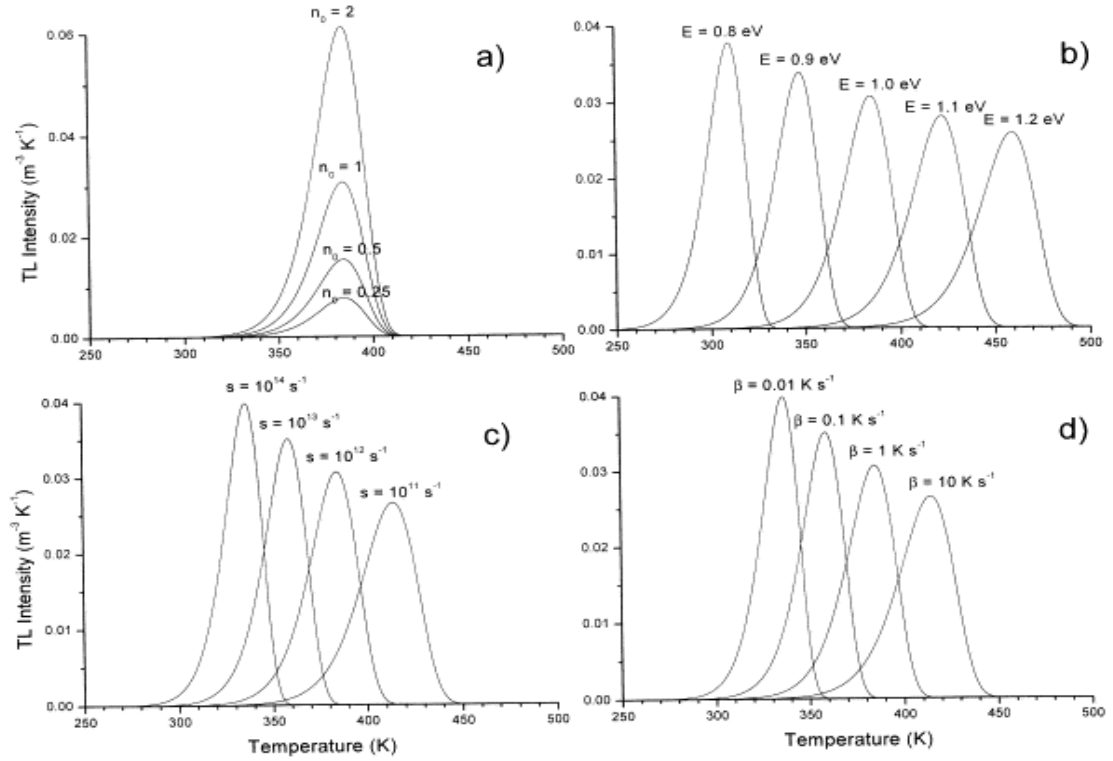
Figure 2.3 The properties of the Randall and Wilkins first-order thermoluminrscence (TL) equation, figure (a) explains the variation with the trapped charge carriers concentration after irradiation (n_0) ; figure (b) shows the difference with the energy of activation (E); (c) shows the difference with the escape frequency (s); figure (d) explains the difference with the heating rate (β). The values of the parameter: (n_0=1 m^{-3}) , (E=1 eV) ; (s=1×10^{12} s^{-1}) , (β=1 K/s) the other parameters are remaining constant when varied one parameter.

2.4 Second-Order Kinetics

The possibility in which the retrapping dominates was considered by Garlick and Gibson[10]. It means that (mA<<(N-n)Ar). They suppose that the trap is far from the saturation, i.e. (N>>n) and (n=m). By these assumptions, the equation (2.6) becomes .

$$I(t) = -\frac{dn}{dt} = s\frac{A}{NA_r} n^2 \exp\{-\frac{E}{kT}\} \qquad (2.14)$$

From the equation (2.14), it is clear that the the (dn/dt) is proportional to (n^2) and that means the reaction of a (second-order) ,and by the additional assumption when

21

the probability of recombination (A) is equal to the probability of retrapping (A_r), the integration of the equation (2.14) becomes ,

$$I(T) = \frac{n_0^2}{N} \frac{s}{\beta} \exp\left\{ -\frac{E}{kT} \right\} \left[1 + \frac{n_0 s}{N\beta} \int_{T_0}^{T} \exp\left\{ -\frac{E}{kT'} \right\} dT' \right]^{-2} \tag{2.15}$$

The above equation (2.15) is the equation of the (Garlick–Gibson) thermoluminescence (TL) for the kinetics of the second-order. The major characteristic of this curve is that it is approximately symmetric, the part of the half of the high temperature is slightly wider than the part of the half of the low temperature of the curve. And this can be understood from the fact consideration that in a second-order reaction the great concentrations of releasing electrons are retrapped before they recombine, and this method has led to a delay in the emission of luminescence and this emission is spread out over the range of broader temperature. The initial concentration (n_0) shows here not just as a (multiplicative constant) as in the case of first-order, the variation in different dose levels is the reason of changing the whole curve shape. This is explained in the figure (2.4 (a)). It is considered that (T_m) decreases when increases the (n_0). The temperature shift can be derived [29] and approximated by the following equation;

$$T_1 - T_2 \approx T_1 T_2 (\frac{k}{E}) \ln f \tag{2.16}$$

(T_1) is the temperature of the maximum intensity at a specific dose and (T_2) is the temperature of the maximum intensity at (f) times higher dose. And the parameter values in the figure (2.4(a)) the shift is (25 K). When (E=1 eV), (T_1=400 K) and the absorbed dose is increased by a factor (1000), that is simple to know experimentally, and can be expected a temperature shift of (77 K). From the above equation (2.16) it follows further that for a given increase of the dose the shallower the trap, it is mean

by increasing the activation energy (E) the peak will shift to the small peak , as shown in the figure (2.4(b)). This figure describes the difference in position and size of a second - order peak as a function of (E). In the figure (2.4(c)) (s) is a function of the (s/N), and in the figure (2.4(d)) as a function of the heating rate (β). 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 the small deviation.

It can be noted that, in the (first-order case), the term dominating the temperature dependence in the initial rise is (exp(-E/kT)).
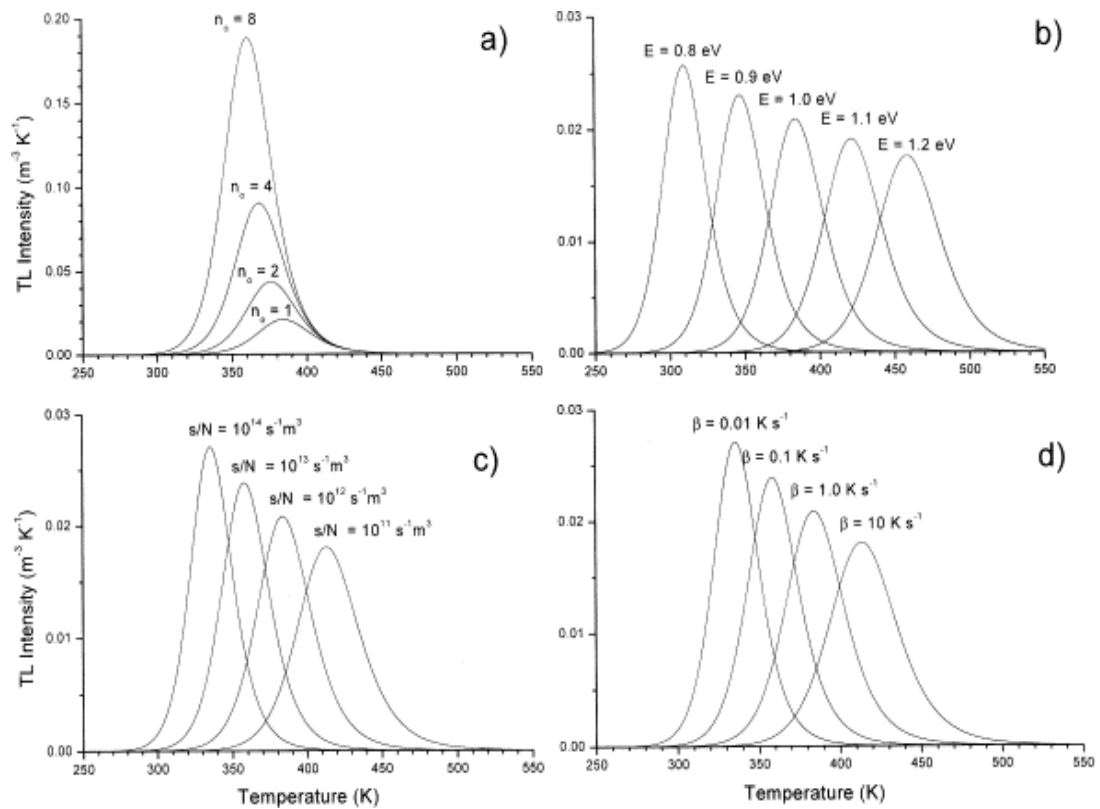
Figure 2.4 The properties of (Garlick–Gibson) second-order equation of the thermoluminescence (TL), showing: (a) Difference with the trapped charge carrier concentration (n_0), after irradiation; (b) The difference with the activation energy (E); (c), the difference with (s/N); (d), the difference with (β),the heating rate. and the values of the parameter are : (n_0=1 m^{-3}), (E=1 eV) , (s/N=1×10^{12} s^{-1} m^3), (β=1 K/s). The other parameters remain constant when varied one parameter.

Also can be applied here the initial rise way' for determination of the trap depth and for the kinetics of the (second-order) the shape of the glow peak, the equation (2.15)

can be approximated with a function written in terms of intensity of the maximum peak (I_m) and the temperature of the maximum peak (T_m) [10].

$$I(T) = 4I_m \exp\left(\frac{E}{kT}\frac{T-T_m}{T_m}\right) \times \left[\frac{T^2}{T_m^2}(1-\Delta)\exp\left\{\frac{E}{kT}\frac{T-T_m}{T_m}\right\} + 1 + \Delta_m\right]^{-2} \tag{2.17}$$

Where ($\Delta = \frac{2kT}{E}$) and ($\Delta_m = \frac{2kT_m}{E}$)

2.5 General-Order Kinetics

The forms of the (first-order) and the (second-order) of the equation of the thermoluminescence (TL) have been derived by using the specific, simplifying assumptions. However, the peak of the thermoluminescence (TL) will commensurate neither kinetics of the first-order nor the kinetics of the second-order at the time which are do not hold these simplifying assumptions. May and Partridge [11] used in the case of (general-order kinetics) an experimental expression for the kinetics of the general-order (TL), and this is.

$$I(t) = -\frac{dn}{dt} = n^b s' e^{-\frac{E}{kT}} \tag{2.18}$$

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 the equation (2.18) for ($b \neq 1$) yields :

$$I(T) = \frac{s''}{\beta} n_0 \exp\left\{-\frac{E}{kT}\right\}\left[1 + (b-1)\frac{s''}{\beta}\int_{T_0}^{T}\exp\left\{-\frac{E}{kT'}\right\}dT'\right]^{-b/(b-1)} \tag{2.19}$$

Where ($s'' = s' n_0^{b-1}$) is in unit (s^{-1}). The equation.(2.19) includes the case of second-order ($b=2$) and changes to the equation.(2.10) when ($b \rightarrow 1$). In accordance with the equation (2.18) the (s') dimension must be ($m^{3(b-1)}$ s^{-1}). This means that changing the dimension with the order (b) making it difficult to interpret physically. However, the case of the general-order is useful for intermediate cases can be dealt with and it

24

running smoothly to the first-order when ($b \rightarrow 1$) and to the second-order when ($b \rightarrow 2$), look the figure 2.5.
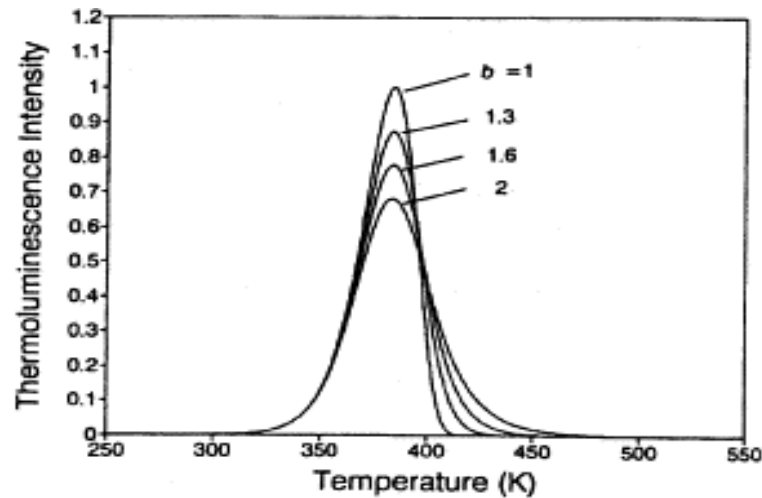
Figure 2.5 The differences between the first-order which is (b=1) TL peaks, second-order (b=2) TL peaks and intermediate-order (b=1.3 and 1.6) TL peaks, with (E=1 eV), (s=1×10^{12} s^{-1}), (n_0=N=1 m^{-3}) and (β=1 K/s) [22].

2.6 Advanced models

The model of the one trap-one center explains all the properties of the thermoluminescence (TL) phenomenon and interprets the behavior of the shape of the glow peak in accordance with the difference of the dose and heating rate (β). And thus, there are no existing thermoluminescence (TL) substances known that minutely is described by the simple model. It does not mean that this model has no significance. But in opposite it has helped us to interpret a lot of features that can be considered like the variations of the one trap–one centre model. All the advanced models are discussed in the textbook of the (Chen and McKeever) in detail [1]. Here, it is very briefly mentioned only some models in order to get an idea of the complexity of this phenomenon in the real thermoluminescence (TL) substance. Generally, it will appear more than one single electron trap of real thermoluminescence material and it is not to be active all the traps in the range of temperature in which the sample is heated. The trap, that can be filled with electrons during radiation is called the thermally disconnected the trap but the sample which has a trap depth much greater than an active trap such that when the sample is heated only electrons trapped in the active trap (AT) and release the shallow trap (ST) (figure.(2.6(a)). Electrons that are trapped in the deeper levels are not affected, and

25

thus, this deep electron trap was shown in the figure (2.6(a)). It is said that (DET) is disconnected thermally. But its presence has an impact on the trapping filling and ultimately on the glow peak shape. [31].

Suppose that the trapped electrons is released during the heating, while the holes trapped are snapping in the recombination center. And thus, can be changed this status after the release of an electrons and holes at the same time from their traps and at the same period of temperature, and in thermally will release the holes from the same centers and operating as sites of recombination of the thermally freed electrons and vice versa, look the figure (2.6 (b)). The equation (2.2) is invalid in this case. And should be formulated new differential equations. The analysis of this complicated kinetic sample detects a (TL) glow curve that reserves the simple Randall–Wilkins (equation (2.11)) or Garlick–Gibson (equation (2.16)) shape, depending on the selected values of the parameters. However, the (E) and (s) values used in the equation (2.11) and equation (2.16).
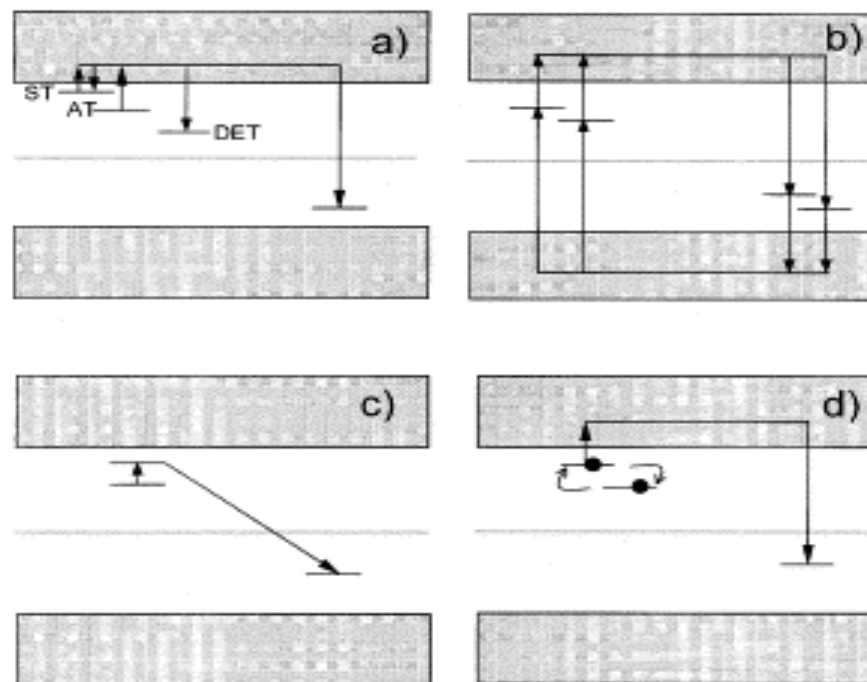

Figure 2.6 Advanced models describing the thermally stimulated release of trapped charged carriers including: (a) Where (ST) is a shallow trap , (DET) is a deep electron trap and (AT) is an active trap; (b) two centres of recombination and two active traps; (c) is a localized transition ; (d) explains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

For getting this model a suitable on this complex kinetics require additional explanation. And there is another process that could be occur is a process of recombination without transition of an electron into the (C.B) (see figure (2.6 (c)). When allow a transition of an electron into the center of recombination, the electron is thermally stimulated into an excited state. And this means that trap is near the center .

The probability of transition may deeply depend on the distance between the two centers. It can be derived an expression for the intensity of the (TL) by a certain assumptions [31]. Finally, we can remind the possibility that the defect is not stable but is participating with another defect interaction, the figure (2.6 (d)) while the concentration of the trapped electron is stable at low temperature the result may be that the depth of the trap will change. And the electrons are participating in two processes at higher temperature : firstly, is the escape of electrons to the (C.B), secondly, is the reaction of the defect [32].

2.7 Trapping Parameter Determination Methods

There are different ways to assess the parameters of the trapping from the glow curves. And the determination of these trapping parameters from (TL) glow curves it was a topic of importance for half a century [9,31-34]. When one glow peak is highly isolated from the other glow peaks, the experimental methods like the (initial rise (IR), variable heating rates (VHR), isothermally decay(ID), and peak shape methods (PSM)) methods 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 (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 [35].

Assessment of (E) from the peak shape using parameters such as (T_m), full width at half-maximum ($\omega = T_2 - T_1$), the half width of the high temperature side of the

maximum ($\delta = T_2 - T_m$) , the half width of the low-temperature side of the maximum ($\tau = T_m - T_1$) and ($\mu_g = \delta/\omega$) called the shape parameter. The kinetics order (b) can be appreciated by means of shape parameters. Chen [33], and found that (μ_g) is insensitive to changes in (E) and (s) , but it changes with the kinetics order (b) . It has been shown that the ranges of (μ_g) vary from (0.42) for (b=1) to (0.52) for (b=2) in case of linear heating.

2.7.1 Peak Shape (PS) Method

The first peak shape method has been developed by Chen [33], later Halperin and Braner's adjusted the equations [35] to calculate the values of (E);

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

$$E_\delta = \left[0.976 + 7.3(\mu_g - 0.42)\right]\frac{kT_m^2}{\delta} \tag{2.20}$$

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

After selecting the activation energy and the kinetic order , using the following expressions (s) frequency factor, it must be observed that this parameter   called as pre-exponential factor in the general order kinetic, can be appreciated for first and general order kinetics respectively.

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

$$s = \frac{\beta E}{kT_m^2}\left[\exp(-\frac{E}{kT_m})(1 + (b-1)\frac{2kT_m}{E})\right]^{\frac{b}{b-1}} \tag{2.22}$$

2.7.2   CGCD Method

Deconvolution computer glow curve (CGCD) method has the features of the experimental ways in that they can be used in largely interlaced-peak glow curves

Without the need for heat treatment. And it is one of the most important ways for determining the trapping parameters of the thermoluminescence (TL) glow curves.

The application of the glow-curve deconvolution (CGD) technique for a composite thermoluminescence (TL) glow curve analysis into its individual glow peaks was very popular during the past two decades. And suggested many of functions that describe a single glow peak, which were analyzed and summarized minutely by Bos et al [36] and Kitis et al [29] proposed approximative functions for the Randall-Wilkins [9] expression of the first order of a single glow peak under linear heating condition. In addition, their approximative functions yield minute values of the activation energy within (3%) of the correct values was shown by Kitis et al [29].

They were utilized two different models in a computer program. First, the glow curve is approached to the first-order thermoluminescence (TL) kinetic by using the below expression,

$$I(T) = n_0 s \ \exp(-\frac{E}{kT}) \exp\left[(-\frac{s}{\beta}\frac{kT^2}{E}\exp(-\frac{E}{kT}) * (0.9920 - 1.620\frac{kT}{E_a})\right] \qquad (2.23)$$

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

$$I(T) = n_0 s \ \exp(-\frac{E}{kT})\left[1 + (-\frac{(b-1)s}{\beta}\frac{kT^2}{E}\exp(-\frac{E}{kT}) * (0.9920 - 1.620\frac{kT}{E_a})\right]^{\frac{b}{b-1}} \qquad (2.24)$$

Where (n_0 (m^{-3})) is the trapped electron concentration at ($t = 0$), (E (eV)) is the activation energy, (s (s^{-1})) is the frequency factor for (first-order) and the pre-exponential factor for the (general-order), (k (eVK^{-1})) is the Boltzmann's constant, (T (K)) is the absolute temperature, (β (^{0}Cs^{-1})) is the heating rate and (b) is the kinetic order. Summation of overall peaks and contribution of background can lead to composite glow curve formula as described below :

$$I(T) = \sum_{i=1}^{n} I_i(T) + a + b\exp(T) \tag{2.25}$$

Where I(T) is the fitted total glow curve, (*a*) allows for the contribution of the electronic noise to the contribution of the planchet and dosimeters infrared to the background. Starting from the equation (2.25), 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,

$$FOM = \sum_{i=1}^{n} \frac{|N_i(T) - I(T)|}{A} = \sum_{i=1}^{n} \frac{|\Delta N_i|}{A} \tag{2.26}$$

Where ($N_i(T)$) is the i-th experimental points (total n=200 data points), ($I(T)$) is the i-th fitted points, and (*A*) is the integrated area of the fitted glow curve.
In many experiments [36].

It can be said that if the the (FOM) values are between (0.0%) and (2.5%) the fit is good, if the (FOM) values between (2.5 %) and (3.5%) the fit is fair, and if the (FOM) values is 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,

$$X(T) = \frac{N_i(T) - I_i(T)}{\sqrt{I_i(T)}} \tag{2.27}$$

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

2.7.3 Initial Rise Method (IRM)

The method of the initial rise (IRM) is the most generally applicable way and also the simplest way to assess the energy of the activation (E) of a single peak of the thermoluminescence (TL). The fundamental hypothesis underlying this way is that at the end of low temperature peak, each relating occupancies of the states, the trap, the

center of recombination and, sometimes, can be considered other interactive states as being almost constant, thus:

$$I(T) = C\exp(-E/kT) \qquad (2.28)$$

where the intensity as a function of temperature is *I(T)*, the constant which includes all the dependencies on the other parameters and occupancies is *(C)*, the energy of the activation *(E)* in (eV), the Boltzmann`s constant is *(k)* in (eV/K^{-1}) and the temperature in (K) is *(T)*.

A linear plot is obtained with slope equal to *(–E/k)* by drawing *ln(I)* against *(1/T)*. Therefore, that it is easy to assess the activation energy *(E)* without frequency factor knowledge as shown in the equation below.

$$E = -kd(\ln(I))/d(1/T) \qquad (2.29)$$

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

$$\frac{\beta E}{kT_m} = s\exp(-\frac{E}{kT}) \qquad (2.30)$$

where the *(β, E , k , T)* is the heating rate , activation energy , Boltzmann constant , absolute temperature , respectively. And *(T_m)* is the maximum intensity temperature. But can be used this way only in those cases when a peak is glow clearly defined and clearly separated from other peaks.

2.7.4 Heating Rate Method (HRM)

Various heating rates are another important method to determine (E), and the peak temperatures will be different when heating the sample at two various heating rates *(β_1)* and *(β_2)*. It can be written the above equation (2.30) for each heating rates and dividing the equation for *(β_1 and T_{m1})* by the equation for *(β_2 and T_{m2})* and reordering, one obtains an obvious equation to calculate the activation energy (E)

$$E = k \frac{T_{m1}T_{m2}}{T_{m1} - T_{m2}} \ln[(\frac{\beta_1}{\beta_2})(\frac{T_{m2}}{T_{m1}})^2] \qquad (2.31)$$

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

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

$$\ln(\frac{T_m^2}{\beta}) = (\frac{E}{k})(\frac{1}{Tm}) + cons\tan t \qquad (2.32)$$

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

2.7.5   Three Points Method (TPM)

Recently,   the method of the three point analysis was improved by Rasheedy [37] to separate a composite thermoluminescence (TL) glow curve into its individual components of glow peaks and for assessing the parameters of the trap of these peaks. In accordance with this way, the kinetic order (b) can be obtained from this equation,

$$b = \frac{T_y[T_x - T_z]\ln(y) - T_z[T_x - T_y]\ln(z)}{T_y[T_x - T_z]\ln[A_x / A_y] - T_z[T_x - T_y]\ln[A_x / A_z]} \qquad (2.33)$$

Where (A_x) is the area under the glow peak from the temperatures $(T_x$ to $T_f)$, (A_y) is the area under the glow peak of the temperatures $(T_y$ to $T_f)$, and (A_z) is the area under the glow peak of the temperatures $(T_z$ to $T_f)$. As they are shown in the figure (2.7). The value of (y) can be obtained from ($y=(I_x/I_y)$) and (z) value can be obtained from $(z=(I_x/I_z))$.

The featured point in this equation is that any combination of the three data points in the thermoluminescence glow curve could result the order of kinetics (b) of the glow peak. And after that, activation energy (E (eV)), then frequency factor (s (s^{-1})) and the concentration of trapped charge carriers after irradiation (n$_0$ (cm^{-3})) of this peak are determined, successively.

The activation energy (E_a) can be found either by

$$E_a = \{\ln y - b\ln[A_x / A_y]\}\{\frac{kT_xT_y}{T_x - T_y}\} \qquad (2.34)$$

or by

$$E_a = \{\ln z - b\ln[A_x / A_z]\}\{\frac{kT_xT_z}{T_x - T_z}\} \qquad (2.35)$$

And also, the frequency factor (s) in the first-order case is found by

$$s = (\beta E_a / kT_m^2)exp(E_a / kT_m), \qquad (2.36)$$
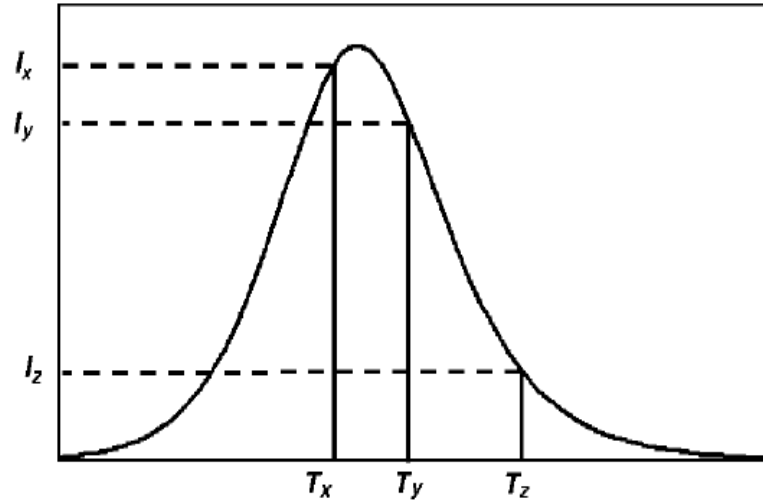
Figure 2.7 An isolated thermoluminescence (TL) glow peak. The parameters *Ix, Iy, Iz, Tx, Ty,* and *Tz* are as defined in the text [37].

However, the pre-exponential factor (s'') in the case of general-order glow peaks is given by:

$$s'' = \frac{\beta E_a \, exp(\, E \, / \, kT_m \,)}{[\, bkT_m^{\,2} \,] - (\, b - 1\,)E_a \Phi \, exp(\, E_a \, / \, kT_m \,)}, \tag{2.37}$$

Where

$$\Phi = \int_{T_o}^{T_m} exp(\, -E_a \, / \, kT' \,)dT' \tag{2.38}$$

And in the end, the relative value of (n_o) is given by

$$n_0 = \frac{I_m \, exp(\, E_a \, / \, kT_m \,)}{s''}\left[\frac{bkT_m^{\,2}s''}{\beta E_a \, exp(\, kT_m \,)}\right]^{\frac{b}{b-1}} \tag{2.39}$$

34

CHAPTER 3

EXPERIMENTAL PROCEDURE

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

3.1 Lithium borates

The material that performed in this study was $Li_2B_4O_7$: Mn (TLD-800) from Thermo Electron Corporation. The dimensions of this sample are (3.2 x 3.2 x 0.89 mm^3), with a mean mass of (0.220g). Thermoluminescence dosimeters (TLD) like manganese activated lithium borate have attracted a significant attention due to their low atomic number, which is an approach to tissue equivalence, simple glow curve and low cost. Lithium borate has been utilized as a practical radiation dosimeter [38]. Most of the earlier publications pertain to the use of lithium borate with (0.1 wt%) of manganese impurity in medical applications, while in this work, lithium borate with (0.3 wt%) impurity of manganese has been prepared for applications of high-dose (1-30 kGy) [39].

Thermoluminescence dosimetry with borates has been of interest for some 15 years and has been stimulated by a number of factors. The most obvious is that materials such as $Li_2B_4O_7$ or MgB_4O_7 have a near tissue – equivalence and therefore, it is worth considering for the properties of their TL. In fact that the dosimeters of the lithium borate are overridden to LiF in tissue equivalence terms. The borates are relatively stable chemical compound and reply without serious problems for trying for doping them with thermoluminescence sensitisers like the rare earths , ions of copper or manganese [40]. This was followed by rapid cooling to the temperature of the room. The resultant glassy material was then crystallized by subsequent heating at 650 ^{0}C Dopants can be added at the melt stage, for example in the form of $CuCL_2$ [40]. Manganese impurities also stimulate a TL response but in the earlier work this

was thought to be less effective for TLDs ; however, the problem was primarily that the Mn impurities cause TL emission in the green to the orange part of the spectrum , whereas the Cu shifts the emission to the UV/blue region at 368 nm where conventional TL dosimetry photomultiplier tubes are sensitive .

This wavelength shift offered a twenty fold signal advantage for the PM tube used by Takenaga et al [39]. Doping with rare earths and Mn ions was performed by Rzyski and Morato [41], by melting additions which resulted in a glass sample . These authors further added some 0.25% of silica to reduce the problem of the hygroscopic response and the use of silica , is now a standard procedure for inhibiting attack with moisture in the borates . T_m doped material has also been prepared. Sintered pellets have been prepared [42], by heating just below the melting point . Lithium borate is prone to reactions with humid air and sensitivity decreases of 10 to 25% within a few months of sample preparation have been recorded if exposed to high humidity conditions. The tetragonal crystal structure of $Li_2B_4O_7$ is complex [43] with a boron −oxygen network throughout the crystal along with interstitial alkali metal ions. The crystal structure is illustrated in figure 3.1.

A typical glow curve for $Li_2B_4O_7$:Mn consists of an ostensibly single peak centered at 185 ^{0}C when heated at 10 ^{0}C.s^{-1} , but the glow peak position has been reported to move to (Mn) impurity level [43] .The emission spectrum of thermoluminescence dosimeter (TLD-800) is demonstrated that in the case of (Mn) acting as a recombination center , the emission spectrum shows orange emission. For rare earth doped material the emission spectra are characteristic of the rare earth ions [44] as expected and as with the calcium sulphate, the more intense signals arise with (D_y) and (T_m) impurities , although (T_b) may also be effective . The addition of copper dopant has been particularly popular because of the match of emission spectra to the optimum wavelengths for PM tubes. Earlier data showed that the performance was sensitive to the origin of the starting materials ; that is the TL was suppressed in some case by trace impurities , and that the glassy form of lithium borate is a factor of three less intense than the crystallized material [45].
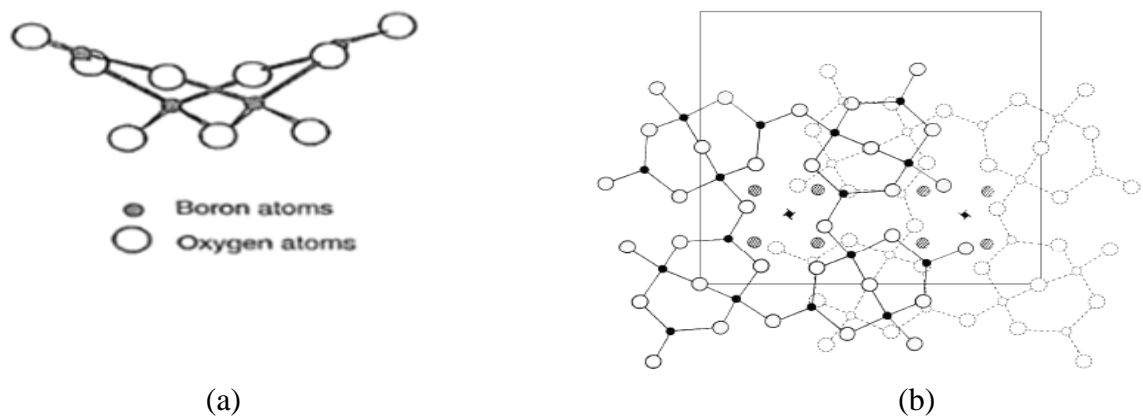
<p style="text-align:center">(a)   (b)</p>

Figure 3.1 (a) The basic structural unit of borate lattice , and (b) a projection of the cell along the c axis . Impurity ions , such as copper , may be linked to oxygen vacancy sites if included as Cu2+ , or introduce lattice distortion if in a single charged state [44].

The current preparation uses an optimal copper doping of (0.1 mol%) in a material sintered at 800 ^{0}C [46]. However, as there is evidence that the lithium borate compound includes several phases it is not surprising that there are problems of reproducibility between samples.

Activation energy analysis of the glow peaks [44] does not give cleanly defined values for the peaks .Instead, each broad peak may be interpreted in terms of a range of closely overlapping components, or perhaps a distribution of states. Such a range of trapping levels may be considered in terms of the lithium borate network which is a complex framework formed from the lithium and boron oxyde. Figure 3.1 offers a view of the basic structural unit together with a projection view of atomic sites for a copper doped lithium borate example. Suggestions include placement of both Cu$^+$ and Cu^{2+} ion [44]. This leads to a mixture of BO$_4$ tetrahedra a BO$_3$ triangles .The addition of copper is possible at several sites and the minor differences in local distortions can consequently allow a range of TL activation energies and vibrational frequencies . The overall form of the glow curve is relatively stable up to (~100 Gy) but for higher doses the peaks shift to lower temperatures and include more components . The attempted analysis in terms of activation energies by Srivastava and Supe [42], was not clear cut and instead they interpret their glow curve data in terms of a range of trap depths ranging from (0.9 to 1.73) eV . These do not come in

a simple pattern with increasing temperature but those near (80 -130)^{0}C are near (1.05 eV), those from (150-250 ^{0}C) near (1.6 eV), falling to (1.1 eV) for peak components near (310-360 ^{0}C).

Very little information is available in the literature concerning the mechanism of TL production in lithium borate. In rare earth doped material one can speculate on the formation of divalent species caused by the trapping of electrons during irradiation, followed by recombination of holes and subsequent emission of light characteristic of the rare earth ion. However, such a simplistic view is probably not warranted considering the complex nature of the lattice and the possibility of energy transfer processes similar to those described for $CaSO_4$. In Cu-doped materials the role of the copper in the TL can be followed by ESR measurements where the TL is associated with the capture of holes at Cu^0 sites to give excited Cu^+ ions which relax with emission of (360 nm) light [47].

The preparation of $Li_2B_4O_7$: Mn is relatively straight forward [44]. A mixture of (32.5 g) of lithium carbonate and (108.96 g) of boric acid is prepared. The mixture is added to a (5 ml) aqueous solution of (75 mg) $MnCl_2.4H_2O$ which is heated at 100 ^{0}C for 12 h. The product is placed in a platinum crucible, heated up to 950 ^{0}C and then rapidly cooled. The crystalline mass thus obtained is ground and graded between 75 and 175 µm. Silica, 0.25% by weight, can be added to reduce the influence of humidity on the lithium borate , which is very hygroscopic. The material can either be sintered at 900 ^{0}C to prepare solid detectors or diffused into a plastic carrier such as teflon or silicon rubber. For the establishment of the dosimetric characteristics, this thermoluminescent dosimeter was irradiated with ^{90}Sr-^{90}Y β-source, The thermoluminescence detectors were irradiated in the dose interval of (0.1) Gy to (100 Gy).

3.2 Experimental Procedure and Equipments

Before next irradiation, the samples were first annealed to wipe any remaining information and then cool rapidly in the air at (75 ^{o}C/min) to the temperature of the room. For this reason $Li_2B_4O_7$: Mn (TLD-800) samples were annealed at (300 ± 1

^{o}C) for thirty minutes. All the annealing treatments were implemented with specially designed oven of microprocessor- controlled electrical which is able to control the temperature within (± 1.0 ^{o}C). The samples were irradiated at room temperature with beta rays from a calibrated ^{90}Sr-^{90}Y source. The β-source activity is about (100 mCi). It is calibrated by the manufacturer on March, 10, 1994. The recommended working lifetime is about fifteen years. Strontium–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 reduced with distance much More quickly than inverse square law calculations would indicate.

The maximum range of Y–90 beta particles in air is approximately 9 meters. The typical strength of a 100 mCi Sr–90 β-source installed in a 9010 Optical Dating System is 2.64 Gy/minute=0.0438 Gy/Sec for fine grains of aluminium, or 3,3 Gy/min=0.055 Gy/Sec for 100 m quartz on stainless steel. The equipment of irradiation is an additional part of the 9010 Optical Dating System which is purchased from Little More Scientific Engineering, UK [48] . The irradiated samples were read out by a reader of Harshaw QS 3500 manual type that is connected to a PC where studied and analyzed the signals of thermoluminescence. It economically provides high reliability. The basic block diagram of reader is illustrated obviously in the figure 3.2. It always has been installed the standard filter of clear glass in the reader between the planchet and photomultiplier tube to eliminate the emitted infrared lights from the reader plus samples. All functions are divided between the reader and the specialized software Shell of the TLD that are running on the computer. All data storage, instrument control, and operator inputs are performed on the PC. Signal acquisition and conditioning are performed in the reader. As such, and can be analyzed each glow curve by using a best-fit computer program depends on a procedure of a Marquardt algorithm minimization, related to expressions of the first-order and general-order kinetics. The individual peaks present in the curve are resolved by the program , giving the best values for the parameters of different peak . The instrument includes a sample change drawer for inserting and removing the TLD elements. The reader uses contact heating with a closed loop feedback system which produces adjustable linearly lifted temperatures from 1 ^{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). Figure 3.3 shows the profile of the typical time temperature. For improving the low-exposure reading accuracy and to extend planchet life, the 3500 provides for nitrogen to flow around the planchet . Through the elimination of oxygen in the salinity, flow of nitrogen eliminates unwanted TL signal caused by the oxygen. Nitrogen is also directed through the photo-multiplier tube (PMT) chamber to eliminate moisture caused by condensation.
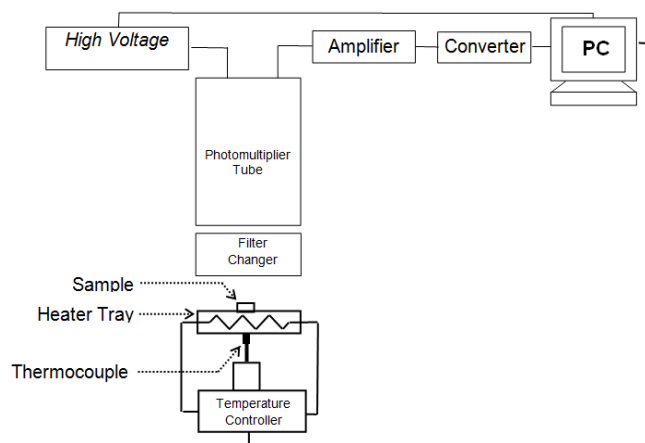

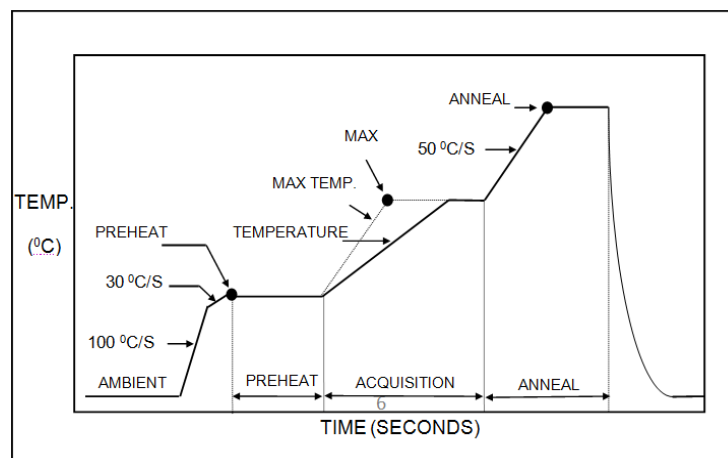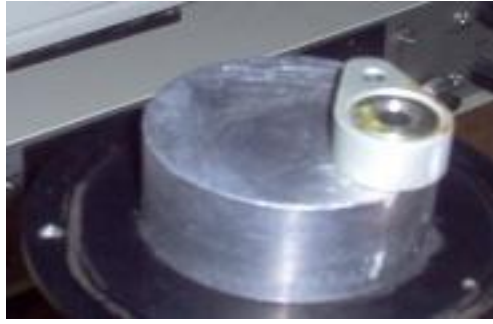Figure 3.2 Basic block diagram of TL reader [48].

Figure 3.3 Typical time temperature profile (TTP) [48].

(a)

(b)

(c)

Figure 3.4 Experimental equipments (a) ^{90}Sr-^{90}Y β-source (b) 9010 Optical Dating System (c) Harshaw TLD System 3500.

CHAPTER 4

EXPERIMENTAL RESULTS

Thermoluminescence (TL) is a useful and sensible method to record radiation information in insulators and it is extensively used in various fields such as; radiation dosimetry and archaeological dating, also to examine the crystalline defects and recently in the sensing of phase transitions [2]. The thermoluminescence (TL) event has been studied for ages. It has been done a great deal of study to get a better understanding and enhance the properties of the substances and also to grow a new thermoluminescence material. At the our present time, (TLD) is an established dosimetric way with measured dose used in areas like (personnel, clinical and environmental dosimetry). TLD relies on materials which give off light while they are heated. The localized energy levels inside the forbidden energy band gap are generated by putting the impurities in the thermoluminescence (TL) material [6].

Thermoluminescence dosimetry studies with borate compounds has been of issue for some 25 years and has been excited by a number of aspects. The most apparent is that materials such as $Li_2B_4O_7$ or MgB_4O_7 have a close tissue equivalence and are thus worth think about for their TL properties. Surely the lithium borate dosimeters are distinguished from LiF in terms of tissue equivalence. The borate compounds are rather steady chemical compound and react without serious problems when trying to dope them with TL activators like the rare earths, copper or manganese ions. The outcome materials now exhibit some desired properties for TL in terms of high sensitivity , linearity and storage and many of the before difficulties of fading , light

sensitivity and poor humidity manners have been avoided. $Li_2B_4O_7$ was mentioned as a TLD as early as 1967 by Schulman et al [49].

Thermoluminescence dosimeters such as the manganese activated lithium borate have drawn an extensive concern because of their low atomic number, near to tissue equivalence, simple glow curve and low cost.

Manganese impurities also excite a TL response but in the earlier works this was thought to be less useful for TLD s; however, the problem was mainly caused by the Mn impurities emitting TL in the green to the orange part of the spectrum , nevertheless the Cu shifts the emission to the UV/blue region at 368 nm where common TL dosimetry photomultiplier tubes are sensitive . This wavelength shift offered a twentyfold signal advantage for the PM tube used by Takenaga et al [39].

Lithium tetraborate is a supporting material for nonlinear optics and piezoelectric devices. These applications imply expansive studies of $Li_2B_4O_7$ single crystals [2]. However, this material is also crucial for an older application: when doped with impurities such as Cu, Mn, or Eu, it is known to be desirable to produce thermoluminescent detectors (TLD) of ionizing radiation. The tissue equivalence is one of the most crucial features of the thermoluminescence dosimeter materials in the area of medical physics. Owing to their near tissue equivalence Z_{eff} =7.42, less expensive, and easy manipulation process, thermoluminescence (TL) studies with lithium tetraborate compounds are especially suitable for utilizations in dosimetry, in particular clinical applications and radiation therapy [2].

Mainly features of dosimetric of any thermoluminescence dosimeter rely on the sensitivity, energy response and the trapping parameters which quantitatively describes the trapping–emitting centers principal for the thermoluminescence emission. Therefore, a dependable dosimetric research of a thermoluminescent material need to be depend on a virtue knowledge of its kinetic parameters. For example, the coincident approximation of the dose rate and the time elapsed since exposure are intimately related to the position of the trapping levels within the band gap, and therefore it is essential to have a virtue knowledge of these parameters. There are particular techniques to appraise the trapping parameters from TL glow

curves. If isolates a glow peak highly from the other ones, the experimental techniques such as (initial rise (IR), various heating rates (VHR) and peak shape (PS)) methods are proper techniques for evaluating them. As a consequence, in this study, the additive dose (AD), variable heating rate, peak shape ,three point methods (TPM) along with the deconvolution method have been utilized to evaluate trapping parameters of the main dosimetric peak, called P3, of Mn-doped $Li_2B_4O_7$ (TLD-800).

Earlier studies have demonstrated that the activation energy evaluation and the factor of frequency mostly relies on the former kinetic order (b) knowledge and the glow peaks correct number in the glow curve [50]. According to the TL theory [29], supposed to alter the glow peak temperatures solely with the heating rate for $b=1$. Thus, for a constant heating rate, the peak temperature should not be affected by other experimental parameters and should be quite constant in the extent of the experimental precariousness. Nevertheless, for $b \neq 1$ and below the trap saturation points $\{n_o$ (concentration of trapped electrons) $< N_t$ (concentration of traps)$\}$, it is commonly received that the peak temperatures are altered to the low-temperature side with increasing dose levels. Hence, to form an estimation about the glow peak numbers of and kinetic orders (b) of all separate glow peaks in the glow curve structure of c-doped $Li_2B_4O_7$, the additive dose method was first employed in this study.

The $Li_2B_4O_7$:Mn (TLD-800) crystals were irradiated at several doses between ≈ 2.4 and ≈ 7 kGy to check the dose dependency influence on the peak positions. Some of the chosen glow curves after various dose levels can be seen in Figure 4.1. Experimental examinations have proved exactly that there are not great changes in the glow peak temperature of Mn-doped $Li_2B_4O_7$ with increasing dose level. And this figure shows that, the peak temperature positions of P3 are in the experimental imprecision ± 2 ^{o}C for all the doses. Clearly explains this result that the main glow peak, P3, and also all of the TLD-800 glow peaks should have first-order kinetics.. After the additive dose experiments the measured glow curves were as well as utilized for calculating the trapping parameters of the peak shape method. This technique relies on the shape and full width of a single glow peak at half maximum (FWHM $= T_2–T_1$) and calculated the E_a values by the improved PS method of Chen [40]. Due to this way, readily, the shape parameter (geometric factor) (μ_g) evaluate

the b of a single peak, $\{\mu_g = (T_2–T_m)/(T_2–T_1)\}$ and μ_g changes to the kinetics order b from (≈ 0.42 to ≈ 0.52) where these two limits compatible with kinetics of first- and second-order, respectively.The kinetic parameters have also identified by using Gartia, Singh & Mazumdar peak shape method in addition to Chen's peak shape method [33] which needs the previous information of the kinetics order.

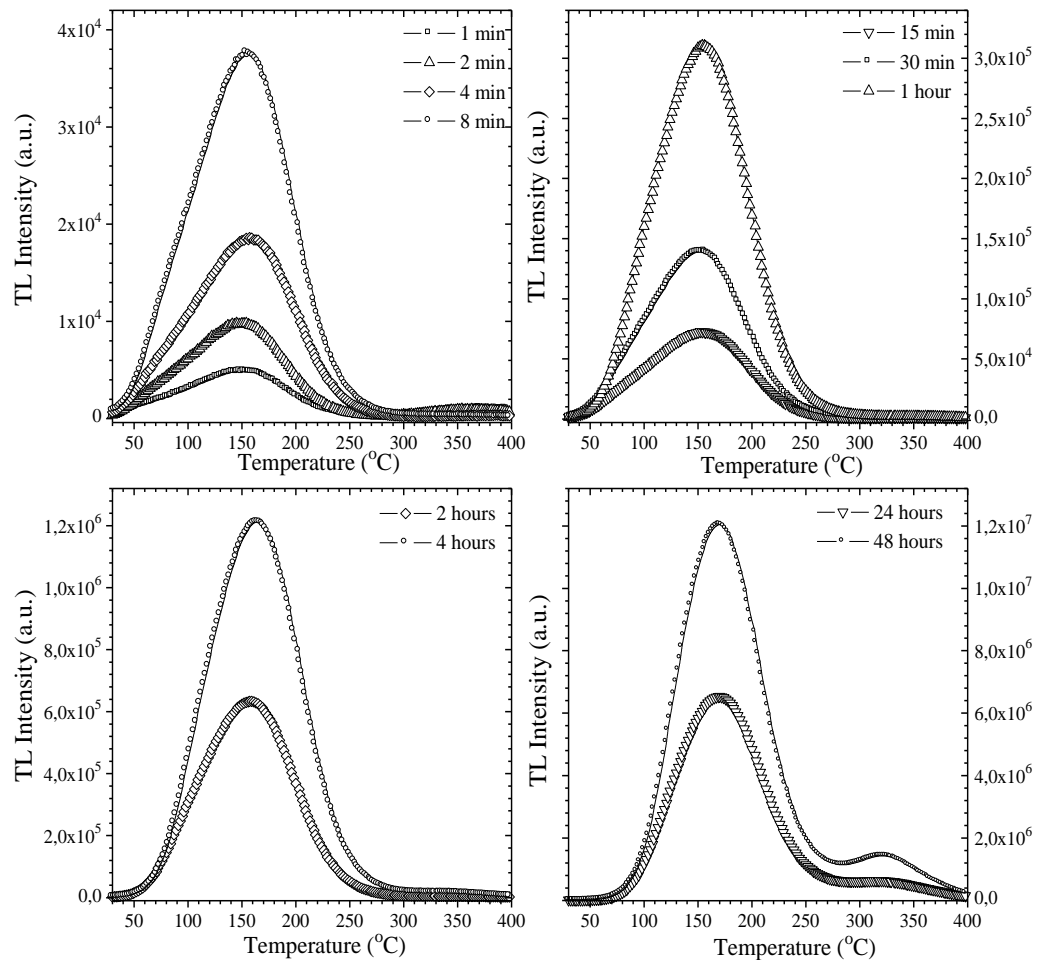Figure 4.1 The glow curve of Mn-doped $Li_2B_4O_7$ (TLD-800) measured after different radiation exposed dose levels (β =1 ^{o}C/s).

The trapping parameters of TLD-800 crystal were also calculated by the Rasheedy's [40] three point method (TPM) by using the equation (2.35) to calculate the kinetic parameters; 15% of the maximum intensity of main dosimetric peak (P3) at temperature 170 ^{o}C was used.

Some other technique which is used for calculating the trapping parameters in this thesis is the way of the various heating rates (VHR). This technique depends on an attitude change of temperature (T_m) at the maximum intensity point (I_m) to higher temperatures as increases the heating rate. In the lack of an activation energies distribution, a drawing of $\ln(T_m^2 / \beta)$ against $1/(kT_m)$ could offer a straight line of rise E_a/k and objection ln (sk/E_a). The foremost features of this technique are that the needed information must be taken at the high end of the peak. It can be correctly found the (I_m, T_m) from the glow curve, if there is a large peak surrounded by smaller satellites. And applied the different linear heating rates in this method between (1 $^oCs^{-1}$ and 20 $^oCs^{-1}$). And can be seen some of the measured glow curves after these heating rates in figure (4.2). This figure shows that the temperature of the peak maximum increases by increasing of the heating rate, but in addition to that there is a small decrease in each of the intensities of the glow peaks. The decreasing luminescence intensity of glow peaks of $Li_2B_4O_7$: Mn phosphor as a function of the increasing heating rate is an event frequently observed in the practice of TSL. It has been recommended that it is because the effect of thermal quenching which reduces the effectiveness of the luminescence when increases temperature because of the increased non-radiative transition probability [43]. The   result of the trapping parameters calculated from the slopes and intercepts are given in the table 4.1.
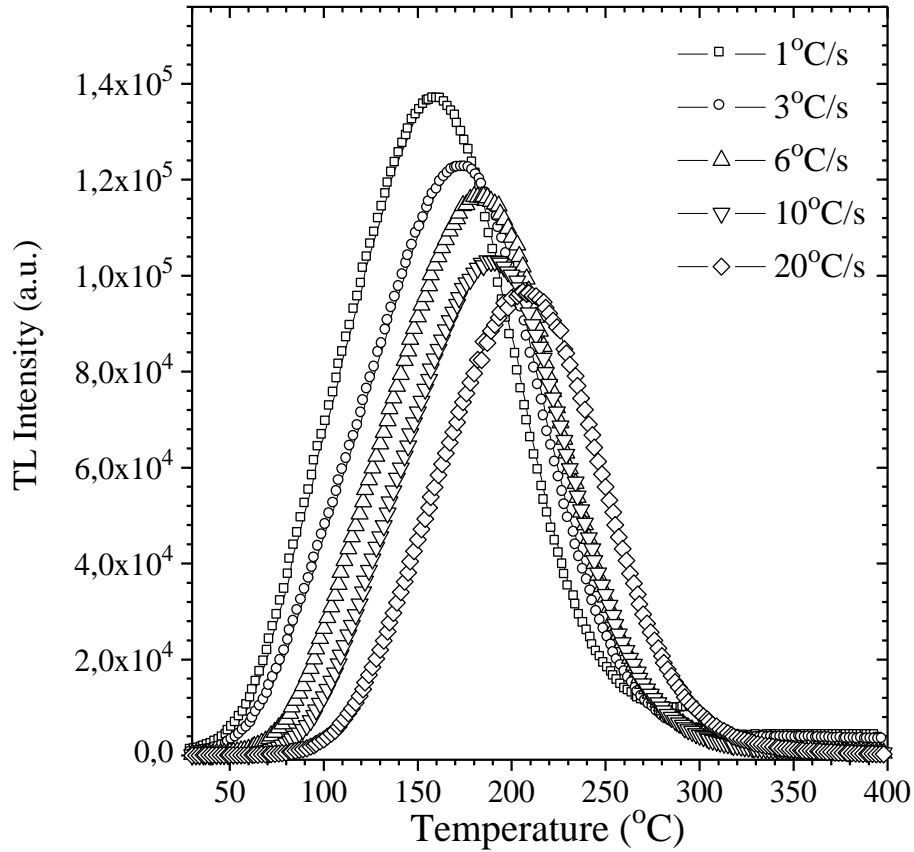
Figure 4.2 Some of the selected glow curves of Mn-doped $Li_2B_4O_7$ (TLD-800) measured at different heating rates for (1, 3, 6, 10 and 20 $^oC/s$). Measured all the glow curves after β irradiation of 72 Gy.

The analysis of the glow curve was also done by using the computer glow curve deconvolution (CGCD) technique. For the last two decades this technique has become very favorable for evaluating the trapping parameters [40]. It has extensive superiority 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. Also, in this technique can be used all the data points for one of the glow curves instead of a few points only through the operations of the appropriate curve. If increase one of them the number of data points utilized in the analysis, it is clear that the possibility for right decision of the trapping parameters also increases.

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. 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 the computer glow curve deconvolution, look to be unsure. May be 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, applies many sets of kinetic parameters could be designated to the same glow curve. The utilized program of the CGCD , that depend on the procedure of the least square minimization , was developed at the Reactor Institute at Delft, The Netherlands. An IRI-CIMAT Report gave the detailed results of these models [51].

The fit goodness for each measured glow curve was tested by using the figure of merit (FOM) [1]. Depends on many studies. It can be interpreted that, the fit is good, if the (FOM) values are among the range of (0.0% and 2.5%), but is fairly fit, if the values of (FOM) are between (2.5% and 3.5%), and the fit is bad if the value of (FOM) greater than (3.5%). It is so important to decide properly in the complex glow curve analyses by the method of CGCD the number of glow peaks exist in the glow curve and which of them have kinetics of the (first or general-order) to get real results.

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 values do not reflect their correct values when suppose that an incorrect number of the glow peaks in the glow curve even if obtain the best-fits. Therefore, first one should be determine the number of glow peaks and their kinetic orders in the glow curve of $Li_2B_4O_7$: Mn. In this study it was noted that the structure of the glow curve of this model is described well by three general-order glow peaks. Because, the kinetic parameter results are also relying heavily on the input parameters like the individual peak site. The parameters finally so selected were the values that resulted the best overall fit to the features of the certain high priority of the thermoluminescence (TL) results. The CGCD fitting results on the

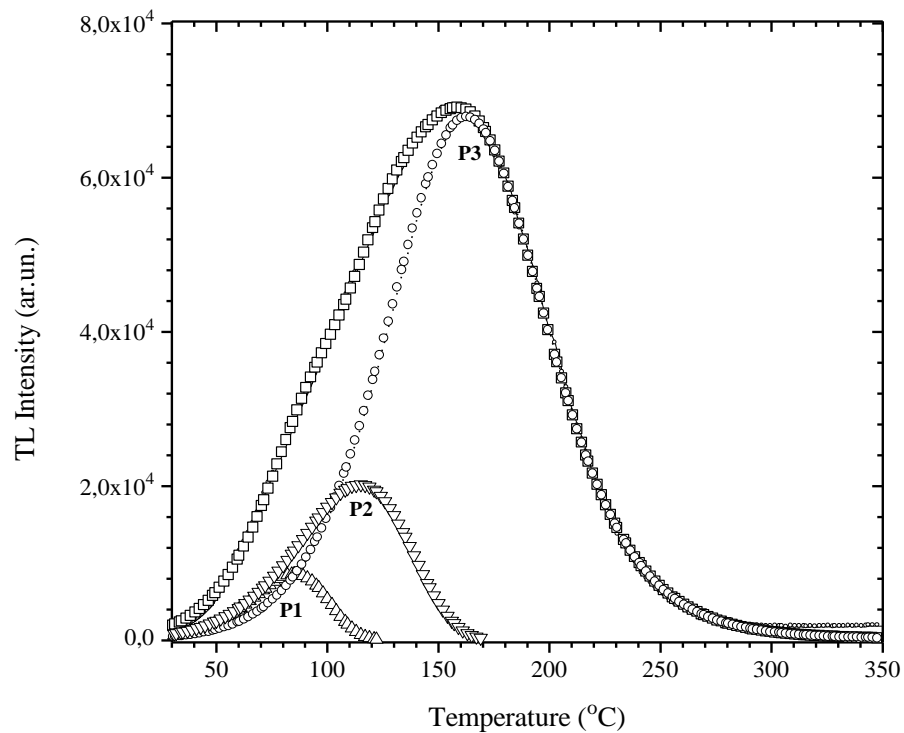assumption of three peaks are shown in the figure 4.1 and the table 4.1 summarizes the values of (E_a and s).

Figure 4.3 The CGCD analyzed glow curves of $Li_2B_4O_7$: Mn measured after 72 Gy irradiation by beta ray at room temperature.

We have also studied in this thesis the storage time effect on the intensity of the glow peaks of $Li_2B_4O_7$: Mn. For this experiment, the material was annealed at 300 ± 1 ^oC for 30 min and irradiated up to 36 Gy. The storage time experiments were performed for different time periods. The figure (4.4) shows the measured glow curves at the end of the scheduled storage periods. Also as shown from the figure 4.5 that the main glow peak (P3) of TLD-800 at the end of the scheduled storage times reduced typically 50 % of its original value.
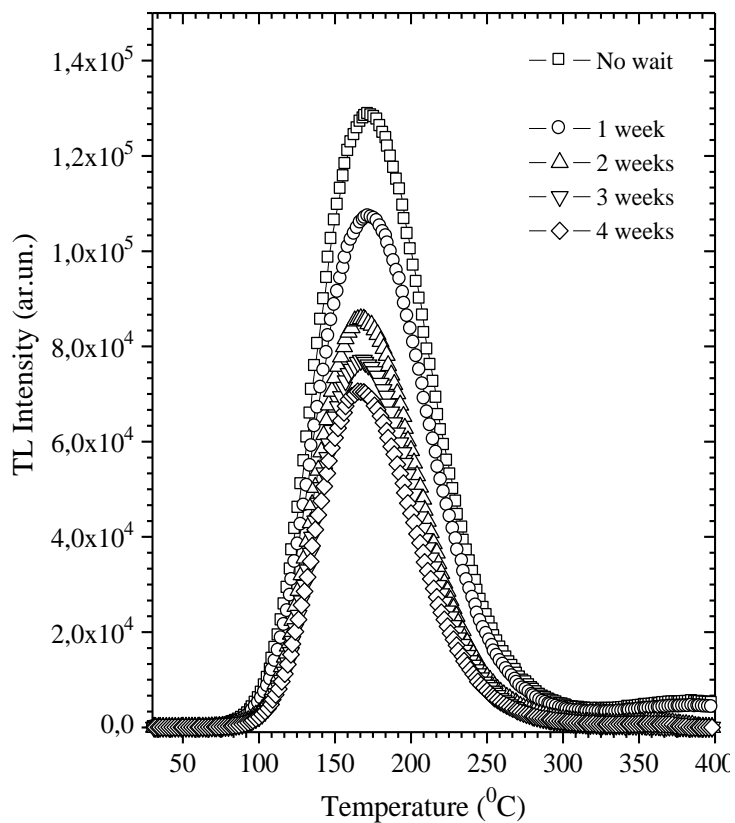
Figure 4.4 A set of TL glow curves for Li2B4O7: Mn crystal measured after various storage periods at room temperature. Read out all glow curves at 1 ^{o}C/s after exposing to an irradiation of 36 Gy.
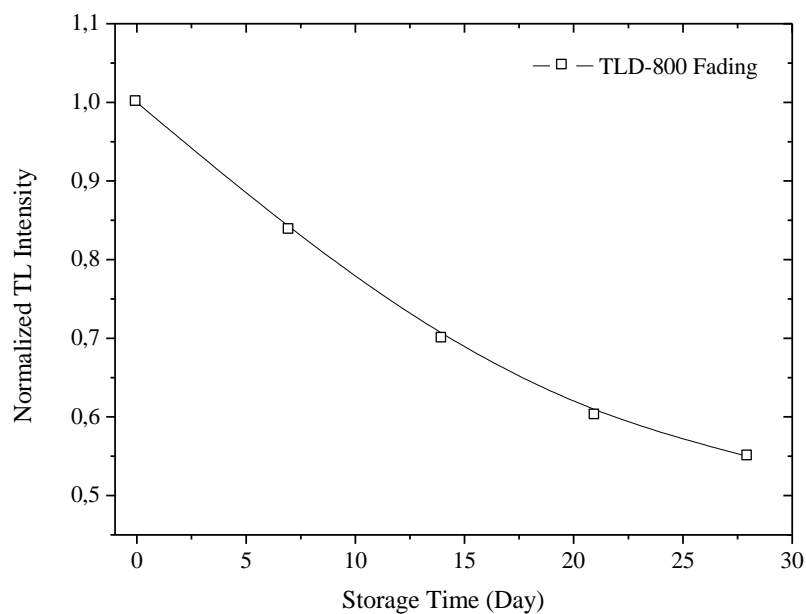
Figure 4.5 Normalized TL intensity of main glow peak (P3) of TLD-800 after different storage times at room temperature. (β=1 ^{o}C / s and D=36 Gy).

Table 4.1   The values of the trapping parameters of TL peaks of $Li_2B_4O_7$: Mn determined by Chen's PS, Mazumdar PS, TPM, VHR and CGCD methods.

P3	MazumdarP.S.			Chen P.S.					
	1/2 ratio	2/3 ratio	4/5 ratio	E_τ	E_δ	E_ω	**CGCD**	**TPM**	**H.Rate**
E (eV)	0.57	0.54	0.58	0.54	0.6	0.57	0.55	0.54	0.63
b	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.55	1.6
lns(s^{-1})	12	12	12	12	12	12	12	13	12.5

CHAPTER 5

CONCLUSION

This thesis was planned to evaluate the trapping parameters called the kinetic order (b), activation energy (E_a) and the attempt to escape frequency factor (s) of Mn doped $Li_2B_4O_7$ (TLD-800) by using various techniques such as Chen's peak shape (PS) method, various heating rates (VHR) method, Rasheedy's three points (TP) technique and computer glow curve deconvolution (CGCD) method. Also the fading characterisitcs of the glow curves of TLD-800 has been investigated at different time periods.

In order to explore the dose dependence characterisitcs of the glow curves of TLD-800, first of all additive dose (AD) experiments were employed. After the thermal treatment at 400 ^oC for 30 minutes, the TLD-800 crystals were irradiated at different dose levels between 7.2 Gy and 288 Gy at a linear heating rate of 1 $^oC/s$. As it is illustrated in figure 4.1. When the dose level is increased the peak temperatures of the glow peaks are nearly constant within the experimental errors. According to the thermoluminesecence theory, the peak temperatures don't change when the dose level is increased at a constant linear heating rate in the case of the kinetic order of 1. The results of the additive dose experiment were also used for the other experimental techniques. One of the experimental techniques to obtain the trapping parameters from the glow curves is the peak shape method. In this thesis, a peak shape method of Chen has been utilized to calculate the kinetic parameters. According to the this method, the value of the symmetry factor $\{\mu_g = (T_2–T_m)/(T_2–T_1)\}$ was found to be 0.48 which corresponds to the general order kinetics. After Chen's peak shape method, Mazumdar's peak shape method was applied by taking the 1/2, 3/4 and 4/5 of the maximum intesity of the glow peak. The results of this method has shown that $Li_2B_4O_7$ (TLD-800) has a general order glow peak at 170 ^oC and having activation energy of nearly 0.58 eV.

After the peak shape methods variable heating rate method was employed to find the trapping parameters. This technique relies on the shift position of the peak temperature (T_m) at the maximum point of intensity (I_m) to higher temperatures as the heating rate is increased. The results of the VHR method have shown that the main glow peak of TLD-800, called P3, has activation energy of 0.63 eV.

To evaluate the kinetic parameters also Rasheedy's three points technique was also used taking the 15% of the maximum intensity of main dosimetric peak (P3) and the calculated values for the kinetic order, frequency factor and activation energy are; 1.55, 4.5×10^5 s^{-1} and 0.54 eV respectively. After these methods, the computer glow curve deconvolution method was used which is a powerful technique over the experimental method. Because in this method all of the data points can be used instead of taking just a few points from the glow curve. The initial parameters of this method selected were the values that yielded the best overall fit to the designated high priority features of the TL results. Figure 4.3 shows the results of CGCD fitting on the assumption of three general order peaks and table 4.1 summarizes the value of the kinetic parameters calculated by all of the methods. As seen from this table the values are in agreement with each other.

For the storage time experiment TLD-800 sample was annealed at 400 ± 1 $^{\circ}$C for 30 minutes than, 36 Gy dose exposed each time and left fading. The storage time experiments were performed for different time periods from 1 to 4 weeks for dark fading. The obtained glow curves of $Li_2B_4O_7$ at the end of the different storage periods are shown in figures 4.4 and 4.5. As seen from these figures, the main glow peak (P3) of TLD-800 at the end of the planned storage times reduced typically 50 % of its original value.

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