



THERMOLUMINESCENCE BEHAVIOR of  $Y_2SiO_5 : Ce^{3+}$   
PHOSPHOR IN VIEW OF SECOND ORDER KINETICS.

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This Masters thesis has been submitted for examination with my approval as university advisor.

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## Abstract

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This work covers Thermoluminescence(TL) behavior of  $Y_2SiO_5 : Ce^{3+}$  phosphor in second order kinetic. Theoretically show that  $TL$  intensity verses temperature with important  $TL$  kinetic parameters . To investigate the thermoluminescence behavior  $Y_2SiO_5 : Ce^{3+}$  phosphor in second order kinetics properties by using one trap and one recombination model (*OTOR*). According to prefer  $Y_2SiO_5 : Ce^{3+}$  phosphor in second order equation (Garlick Gibson). We have get different characteristics of glow peak curves, the values of kinetics parameters are changed then as follows. Firstly the activation energy changes the glow curve can be goes from minimum to the maximum of temperature, because of when we used the large activation energy to use more charges moves from valance band to conduction band, if lower activation it has large glow curves but the larger activation the small glow peak curves. Next the  $TL$  intensity peak shifts slightly to higher temperature a glow curve peak maximum with change (increase) heating rate. These glow curves shift . Thidly a glow curve peak maximum with change in concentration of electron the glow curves verses to the concentration of electron increases, and the height of the thermoluminescence peak changes to the high temperature and intensity of thermoluminescence also increases these glow curves unique from experimental glow curves . Finally a glow curve peak maximum with increases in frequency factor and,

## LIST OF FIGURES

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increases the frequency to need small amount of energy needed trigger the charge therefore glow curve shift to from maximum to lower temperature ,and intensity of thermoluminescence also decreases. Therefore studying luminescence properties for possible applications such as long lasting phosphorescence and display devices.

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## Introduction

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### 1.1 Background of the study

Luminescence is a collective term for different phenomena where a substance emits light without being strongly heated, i.e., the emission is not simple thermal radiation [1]. This definition is also reflected by the term "cold light". Luminescence can be categorized into fluorescence or phosphorescence. Fluorescence is light emission caused by irradiation with light (normally visible or ultraviolet light) and typically occurring within nanoseconds to milliseconds after irradiation [1-3]. It involves the excitation of electrons into states with a higher energy, from which radioactive decay is possible. Typically, the emitted wavelengths are longer than the excitation wavelengths; otherwise up-conversion fluorescence will occur. Phosphorescence is a light emission that can occur over much longer times (sometimes hours) after irradiation [1-3]. It involves storage of energy in a meta state and its release through relatively slow (often thermally activated) processes. In other words, phosphorescence is a radiation transition, in which the absorbed energy undergoes intersystem crossing into a state with a different spin multiplicity [4]. The lifetime of

phosphorescence is usually from  $10^{-4}$ - $10^{-2}$  s, much longer than that of fluorescence [4]. Luminescence is, in some ways, the inverse process to absorption. Absorption of photons of appropriate frequency causes an atomic system shift to the excited states. This atomic system can return to the ground state by spontaneous emission of photons. This de-excitation process is called luminescence. However, the absorption of light is only one of the multiple mechanisms by which a system can be excited. In a general sense, luminescence is the emission of light from a system that is excited by some form of energy [1-4]. The origin of the luminescence from a phosphor is the host material or the dopants or both of them. A dopant, which is also called an activator, is an impurity ion which is incorporated in to the host lattice to form a luminescent center. This luminescence center absorbs energy and gives off luminescence when excited. In luminescence process, the emission spectrum shifts to a lower energies relative to the absorption spectrum. This shift is called Stoke's shift. To obtain it is also possible luminescence at photon energies higher than the absorbed photon energy. This is called anti-Stokes or up-conversion luminescence and it occurs for multilevel systems. Thermoluminescence (*TL*) is the thermally stimulated emission of light from a semiconductor or insulator following the previous absorption of energy from radiation [1-3]. The word phosphor refers to a luminescent material synthesized for the purpose of practical applications which converts absorbed energy into visible light [4-9]. Because of their excellent chemical stability, high luminescence efficiency and flexible emission colors with different activators, inorganic compounds doped with rare earth elements form an important class of phosphors [10,11]. These phosphors have versatile applications,

for example, in cathode ray tubes, photodiodes, lamps and x-ray detectors, bio-detectors, in lamp industries, color display, radiation etc [12-16]. Rare earth activated yttrium silicate phosphor host material displays some exciting practical applications such as long lasting phosphorescence, lasers, X-ray imaging, plasma display panels (PDP), flat panel displays (FPD) and environmental monitoring and have recently attracted much attention [17-19].  $Y_2SiO_5$  can exist in x1-monoclinic or x2-monoclinic phases depending on the synthesis temperature. A high temperature synthesis leads to x2-type whereas a low temperature synthesis forms the x1-type [20]. Therefore, in this work, the excitation of electrons radiation on the  $TL$  properties of  $Y_2SiO_5 : Ce^{3+}$  commercial phosphor is reported.

## 1.2 Statement of the problem

In general, the excitation of electrons caused absorption of energy from external source such as radiation. The rare earth ions most commonly used for the application as phosphors are called lanthanide ions. Experimentally the properties  $Y_2SiO_5 : Ce^{3+}$  was studied by different researcher and generated different glow curve using first, second and general order kinetics. But the  $TL$  properties of this phosphor is not studied theoretically to the best of our knowledge. Activation energy, linear heating rate and the initial concentration of electron on  $TL$  glow curve therefore, in this work we determine the properties, the effect glow curves of  $Y_2SiO_5 : Ce^{3+}$  commercial phosphor. Finally to study affect frequency factor on  $TL$  on glow curves of  $Y_2SiO_5 : Ce^{3+}$  phosphor.

### 1.3 Basic Research Questions

What is the effect of activation energy on  $TL$  glow curves of  $Y_2SiO_5 : Ce^{3+}$  phosphor ?

How does linear heating rate affect the concentration of electron trap ?

How do the concentration of electron  $n_0$  in trap effect the properties of the  $TL$  glow curve of  $Y_2SiO_5 : Ce^{3+}$  phosphor ?

what is the effect of frequency factor on the  $TL$  glow curves of  $Y_2SiO_5 : Ce^{3+}$  ?

### 1.4 General objectives

To study the thermoluminescence behavior of  $Y_2SiO_5 : Ce^{3+}$ , phosphor in view of second order kinetics.

### 1.5 Specific objectives

The specific objective of this study is: To determine the effect of activation energies on  $TL$  glow curves of  $Y_2SiO_5 : Ce^{3+}$

To study linear heating rate effect on the concentration of electrons in the traps.

To concentration of electron  $n_0$  in trap on  $TL$  glow curves of  $Y_2SiO_5 : Ce^{3+}$  phosphor.

To determine the effect of frequency factor on the  $TL$  glow curves of  $Y_2SiO_5 : Ce^{3+}$

## 1.6 The scope of the study

A part from given condensed concept and definitions of the kinds of luminescence in the introduction part , it is much difficult to deal with all theoretical approaches, properties so, we confine ourselves to only one kinds of thermoluminescence behavior of  $Y_2SiO_5 : Ce^{3+}$  phosphor in the view of second order kinetics.//

## 1.7 The limitation of the study

This study requires many things our study excluding only thermoluminescence behavior  $Y_2SiO_5 : Ce^{3+}$  phosphor in view of second order kinetics, due to time constraint, lack of pre knowledge of application used and adequate research knowledge.

## 1.8 The significance of the study

Thermoluminescence ( $TL$ ) is a well establish technique widely used in dosimetric and dating application among various phosphor material this study was compare experimental results of  $Y_2SiO_5 : Ce^{3+}$  phosphor by varying activation energy, heating rate, concentration trapped electrons and frequency factor of  $Y_2SiO_5 : Ce^{3+}$  in view of second order kinetics . Interesting to theoretically we compare with experimentally results and also see how vary with temperature and size in which the  $TL$  glow curves are generated, to determine the properties of the  $TL$  glow curve  $Y_2SiO_5 : Ce^{3+}$  phosphor, determine heating rate affect the concentration of electron



traps finally to determine the activation energy and effect of frequency factor on  $TL$  glow curves of  $Y_2SiO_5 : Ce^{3+}$  phosphor.

## 1.9 Outlines of the thesis

This study was organized as follows: In Chapter 1, we have discussed some background concepts of Luminescence and Thermoluminescence including the statement of the problem, research question, objectives and significance of the study, scope of the study and limitation of the study. In Chapter 2, we review the theoretical concept of thermoluminescence, type of thermoluminescence, the kinetic parameter, concept kinetics, model of  $TSL$  and application of thermoluminescence. In Chapter 3, material and methodology . In Chapter 4 result and discussion of the glow curve of thermally stimulated luminescence of  $Y_2SiO_5 : Ce^{3+}$  phosphor, and finally in chapter 5, we draw some summary and conclusions .

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## REVIEW RELATED LITERATURE

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### 2.1 Introduction

The first scientifically recorded observation of thermoluminescence was made in 1963 by Robert Boyle who reported to the Royal Society of London on October 28, 1963, the observation of a 'glimmering light' from diamond [33]. Boyle also stimulated the luminescence emission by more conventional means by using the heat from a hot iron, from friction and from a candle, though the phenomenon did not find proper interpretation for about three quarters of a century. The first clear observation of this observation was provided by Du Fay, who showed that this kind of emission was in fact delayed phosphorescence [34]. In 1676, Eschalot observed a similar effect from the mineral fluorspar and thought that the heat itself was being directly converted to light [35]. Oldenburg (1676), referring to the thermoluminescence of a phosphor called 'phosphorus smaragdinus', wrote that the material received its light 'from the fire itself' [36] and most of the other observations at the time supported this or similar views. Though he provided possibly the first clear evidence later that thermoluminescence was nothing more than delayed

phosphorescence [37], Du Fay (1726) thought that the luminescence was due to 'a sulphur' which actually burned on heating [38]. He performed experiments on natural quartz and showed that the thermoluminescence could be reactivated by irradiating the sample. Henri Becquerel [39-40] detected the occurrence of delayed phosphorescence in certain phosphorescent samples toward the end of nineteenth century. Moreover, in 1821, Calloud, a chemist from Annecy in France, discovered that heating sulphate of Quinine produced an intense blue luminescence between  $100^{\circ}$  and  $180^{\circ}C$  and his work was also reported by Deribere in 1936 [41]. However, the exact time when the word thermoluminescence was first used in the published literature is not known. This may be because of the fact that most of the early observations focuses on natural thermoluminescence and experimental works concerning this phenomenon was not common. But probably the first careful investigation of experimentally radiation-induced thermoluminescence was reported by Wiedemann and Schmidt in 1895 after their study of wide variety of synthetically produced phosphors [42-43]. This type of thermoluminescence was called 'artificial'. However, in 1898, Trowbridge and Burbank proved that thermoluminescence from natural specimens could be regenerated in the laboratory by heating fluorites then re-exciting thermoluminescence by exposing the specimen to radiation [44]. The discovery of x-rays accelerated the work on  $TL$  as they played a major role in re-exciting this phenomenon by using as external radiation.  $TL$  measurements in the form of glow curves were perhaps carried out for the first time in Przibram's laboratory during 1925-1930 [45]. His co-author Urbach reported the  $TL$  of alkali halides and attempted to explain them theoretically [46]. The theoretical basis for the  $TL$

glow peak was given for the first time by Randall and Wilkins [47] and a modification of this theory was given by Garlick and Gibson [48]. In order to understand how thermoluminescence ( $TL$ ) can be used to study luminescent materials, a theoretical background of the phenomenon is indispensable. The following discussion borrows heavily from references [5-9]. The basic effect leading to the production of  $TL$  is the trapping of charge carriers, i.e., electrons and holes, produced during exposure to an external source at defect sites in the material. An example of the second category is a lattice vacancy caused by a higher valence impurity ion at the position of a lattice ion. A trivalent cation impurity in a divalent lattice, for example, would induce the formation of a cation vacancy in the lattice to maintain charge neutrality. Cationic vacancies are potential sites for trapping holes. There are many other types of defects that can act as electron or hole trapping centers. Revealing the nature of those defects is part of the research of luminescent materials. Heating of the material causes the release of the trapped charge carriers and the recombination of electrons and holes at a luminescent center. The release of some of the stored energy excites the center and relaxation may lead to the emission of light. The nature of the luminescent center can be revealed by measuring the emission spectrum which is in many cases characteristic for a specific element. We note that not every recombination event leads to luminescence. If, for example, there is not enough energy available to excite the center, the recombination will be non-radiative. The process leading to recombination includes, in many cases, the transition of charge carriers through the conduction or valence band, but localized transitions may also take place. The theory of  $TSL$  consists of solving the relevant sets of coupled dif-

ferential equations, describing the charge transfer. In the following, we discuss the simplest model. This model shows all the characteristics of the *TSL* phenomenon.

## 2.2 Simple Model of Thermoluminescence (TL)

. The simplest model to explain *TL* is the One Trapping center One Recombination (*OTOR*) model (Figure 2.1 ). Absorption of radiant energy with energy greater than the band gap results in the ionization of valence electrons, producing energetic electrons and holes which will, after thermalization, produce free electrons in the conduction band and free holes in the valence band. A certain percentage of the freed charge carriers will be trapped: the electrons at *Tr* and the holes at *R* (transitions b). There is a certain probability that the charge carriers escape from these traps due to thermal stimulation. The probability per unit time of release of an electron from the trap, *p*, is assumed to be described by the Arrhenius equation.

$$p = S \exp\left(\frac{-E}{kT}\right) \quad (2.1)$$

The pre-exponential factor *s* is called the frequency factor or attempt-to-escape factor. In the simple model, the factor *s* is considered as a constant (not temperature dependent) with a value in the order of the lattice vibration frequency, namely  $10^{12}$  -  $10^{14} \text{ s}^{-1}$ .

. For explanation of *E* and *E<sub>f</sub>* see text from the trap into the conduction (see Figure 3.1 ). The other symbols have their usual meaning; *k* = Boltzmann's constant =  $8.617 \times 10^{-5} \text{ eV/K}$ , and *T* is the absolute temperature. The quantities *E* and *s* are

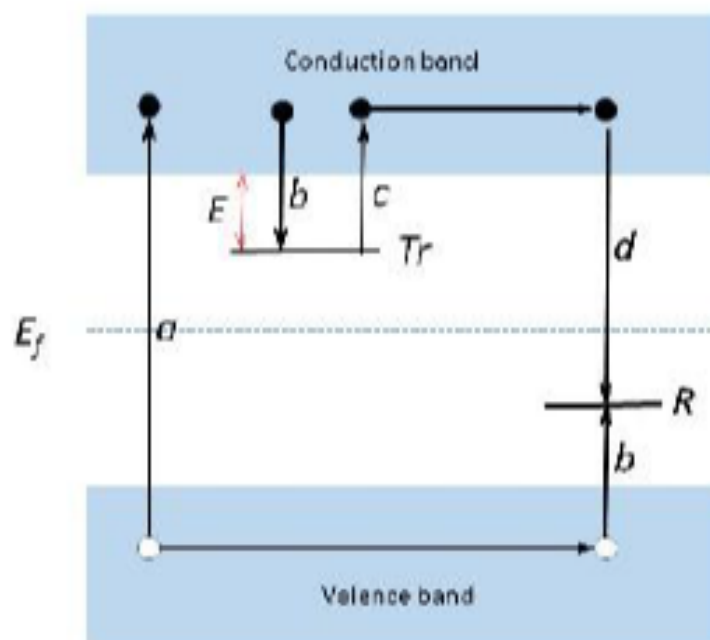


Figure 2.1: A simplified model of the thermoluminescence mechanism: During the excitation stage (a) electrons and holes are produced which are trapped (b) in trapping,  $T_r$ , and Recombination centers,  $R$ . During the heating stage (c) electrons are released to the conduction band and move through the Conduction band until they encounter a hole in a recombination center (d). The recombination energy will excite the center and relaxation of the excited center will produce the luminescence

called the trap parameters. Their values determine whether the electron will escape at a certain temperature  $T$ . If the trap depth  $E \gg kT_0$ , with  $T_0$  representing the temperature at irradiation, then any electron that becomes trapped will remain so for a long period of time, so that even after exposure to the radiation, there will exist a substantial population of trapped electrons. Furthermore, because the free electrons and holes are created and annihilated in pairs, there must be an equal population of trapped holes at level  $R$ . Because the normal equilibrium Fermi level  $E_f$  is situated below level  $T_r$  and above level  $R$ , these populations of trapped electrons and holes represent a non-equilibrium state. The return to equilibrium can be speeded up by raising the temperature of the *TL* material above  $T_0$ . This will increase the probability of detrapping and the trapped electrons will now be released from the trap into the conduction band. The charge carrier migrates through the conduction band of the material until it undergoes recombination at recombination center  $R$ . The model proposed by *RW* for *TL* intensity was modified by Garkick and Gibson (*GG*) [48] using the same *OTOR* model. The assumption made by *GG* was that an electron which is detrapped in to the conduction band from the trap centers after absorption of thermal energy may either recombine with a hole trapped at recombination center to produce luminescence or may be retrapped by any of the vacant traps. However, in *RW* model, retrapping is ignored and the detrapped electrons are assumed to recombine directly with the trapped holes emitting light. Using the probability coefficients for retrapping and recombination  $A$  and  $A_r$  respectively, the recombination and retrapping terms, respectively are proportional to  $A_r n$  and  $A(N - n)$ , where  $N$  is the total number of the traps and  $n$  is

the number of available recombination centers at any time. In the *EOTOR* model  $n$  is also equal to the number of filled traps, so that the charge neutrality condition is maintained. The recombining fraction  $\eta = \frac{n}{N}$  of this combined probability of transitions for any excited carrier, then

$$\eta = \frac{A_r n}{A_r n + A(N - n)}. \quad (2.2)$$

Garlick and Gibson (*GG*) assume that the excited charge carrier has no particular preference for recombination or rewrapping which means  $A_r = A$ . Therefore, in contrast to the *RW* model in which the value  $\eta$  is equal to 1, the value of  $\eta$  in *GG* model becomes  $\eta = n/N$ . One can see that the *TL* intensity  $I(T)$  previously given by (referee) would be modified by a factor equal to  $n/N$ . Thus, in *GG* model,

$$I(T) = -\frac{dT}{dt} = \frac{n}{N} n s \exp\left(-\frac{EKT}{N}\right) = \frac{n^2}{N} s \exp\left(-\frac{EKT}{N}\right). \quad (2.3)$$

Since the TL intensity  $I(T)$  is proportional to  $n^2$  in *GG* model, it is called second order kinetics and discussed in detail in the next section. Again assuming linear heating rate  $\beta = \frac{dT}{dt}$  and integrating yields the value of  $n$  at any temperature  $T$  as,

$$n(T) = \frac{n_0}{1 + \frac{1}{N} \frac{s}{\beta} n_0 \int_{T_0}^T \exp\left(-\frac{E}{KT}\right) dT}. \quad (2.4)$$

Plugging this equation in one can get the following equation for glow curve [2]

$$I(T) = n_0^2 \frac{s}{N} \exp\left(-\frac{E}{KT}\right) \left[1 + \frac{n_0 s}{\beta N} \int_{T_0}^T \exp\left(-\frac{E}{KT}\right) dT\right]^{-2}. \quad (2.5)$$

It is worth to mention that, if  $n \ll N$  (low dose sample) so that  $AN$  becomes much greater than  $A_r n$ , second order kinetics can be obtained in *OTOR* model even if  $A_r \neq A$ . Under this condition,  $\eta = \frac{A_r n}{AN}$  and in (2.3),  $n/N$  gets replaced by  $\frac{A_r n}{AN}$  and in



(2.3),  $\frac{s}{N}$  gets replaced by  $\frac{sA_r}{AN}$ . Thus,

$$I(T) = n_0^2 \frac{sA_r}{NA} \exp\left(\frac{-E}{KT}\right) \left[1 + \frac{n_0 s A_r}{\beta \beta N A} \int_{T_0}^T \exp\left(\frac{-E}{KT}\right)\right]^{-2} \quad (2.6)$$

Therefore, it should be noted that in the case of  $A_r \neq A$ , the second order kinetics is obeyed only in low dose samples  $n \ll N$ , whereas it is valid at all doses for the case when  $A_r = A$ . The characteristics of the glow curves computed from *GG* model (equation (2.4)).

### 2.3 Energy band model of luminescence

The band theory of energy levels in solids provides a generalized description of the luminescence process (McKeever, 1985; Yacobi and Holt, 1990; Gucsik, 2009;). According to band theory, materials are classified into three categories based on the energy separation between the valence band (*VB*) and the conduction band (*CB*). At equilibrium conditions and  $T = 0K$ , the valence band is fully occupied by electrons while the conduction band is empty. Insulators are characterized by a large energy gap (e.g.,  $8 eV$  and for  $Y_2SiO_5$   $7.4 eV$ ) where additional energy states can be created by the presence of defects a condition that is essential for the production of luminescence in many luminescent materials. Luminescence is also produced in semiconductors having a relative small energy gap (e.g.,  $1eV$ ) but it is absent in metals where the two bands are not separated. In the following discussion, the various events involved in the luminescence production are treated from the scope of electron,  $e^-$ , transitions (i.e., luminescence is explained assuming that electrons are the mobile species), but similar consideration can be developed for the participation of

holes,  $h^+$  (i.e., removal of electrons from atomic positions results in formation of holes). The processes (i.e., absorption, charge transfer, and luminescent emission) described below in and

are also those likely to result in  $TL$  emission. In a perfect insulating or semiconducting crystalline material the gap between the  $VB$  and the  $CB$  (i.e., forbidden gap) will contain no electronic states. Excitation of the crystal, for example, by ionizing radiation, excites valence band electrons to the conduction band from where they can fall back to the valence band and recombine directly with the holes created upon removal of the electrons (Figure 2.2-transition 1). The band-to-band recombination of electrons and holes results in emission of luminescence (i.e., also known as excitant emission) with energy approximately equal to the energy gap (McKeever, 1985; Yacobi, 1990; and Holt, 1990; Gucsik, 2009). Generally, inter band transitions are most associated with fluorescence emission and have low probability to occur (McKeever, 1985). In the real world, perfect crystals do not exist. Any natural or man-made material possesses several types of crystal imperfections or defects as a result of inhomogeneities in chemical composition, mixture of chemical phases, and manufacturing conditions. Imperfections such as distorted surfaces due, for example, to mechanical treatments, displaced or missing atoms, and impurities introduce into the forbidden gap localized meta stable states which are responsible for the short- and long-period phosphorescence phenomena (Leverenz, 1968; Holt

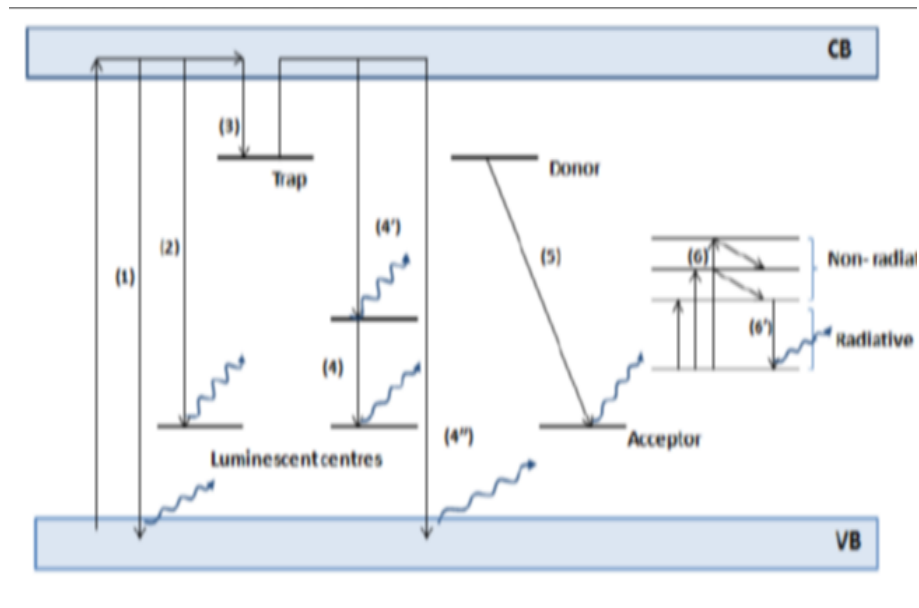


Figure 2.2: Schematic representation of the energy level diagram illustrating the absorption, charge transfer, and luminescent emission processes between the valence band ( $VB$ ), the conduction band ( $CB$ ), and the various localized states of a phosphor. Labels indicate: (1) band-to-band electron hole recombination, (2) fluorescence emission by direct transition of electrons from the conduction band to the recombination centre, (3) electron trapping, (4) recombination of trapped electrons excited into the conduction band with holes located at a luminescent centre via a direct transition, (4') recombination of trapped electrons excited into the conduction band with holes located at a luminescent centre via the excited state of the luminescent centre, (4'') recombination of trapped electrons excited into the conduction band with holes in the valence band, (5) direct donor-acceptor pair recombination, (6) electron excitation from the ground to any of the excited states of a luminescent centre, and (6) radiative return of excited electron back to the ground state of a luminescent center.

and Yacobi , 1990). A distinction between traps and luminescent recombination centers is usually made to specify if a certain defect plays the role of electron (or hole) trap or the level to which trapped charges are transported to recombine and emit luminescence. Energy states created by the presence of foreign elements (i.e., impurities) can also be found in the space between the two bands. These are either known as donor states if they contribute electrons to the conduction band or acceptor states if they contribute holes to the valence band. Usually, they appear occupied by charges prior to excitation (Yacobi and Holt, 1990). With the introduction of the additional localized meta stable levels several promptly and stimulated radiative transitions can take place as illustrated in Figure 2.2. Following absorption of energy sufficient to cause band gap ionization, electrons are released from the valence band leaving behind positively charged holes. Once in the conduction band, these electrons can either make a direct transition to a luminescent centre giving rise to fluorescence emission (2) or occupy an electron trap (3). Trapped electrons can then be raised by stimulation back to the conduction band from where they can finally recombine at a luminescence centre via a direct transition (4) or via the excited state of the luminescent centre (4), or otherwise recombine with a hole in the valence band (4). Another possibility (5) is that of direct electron-hole or donor acceptor pair recombination (McKeever, 1985; Yacobi and Holt, 1990 ; Gucsik, 2009). The recombination processes 2, 4 and 5 may all give rise to photon emission of the same wavelength, if they happen to originate in the same luminescent centre. In such cases, the charge transfer mechanism that has preceded can possibly be identified by conductivity measurements if the conduction band is involved in the emission

process or by studying the behavior of the peak of the spectral emission as a function of the excitation intensity. For instance, donor-acceptor pair recombination is characterized by a shift of the position of the peak emission as the intensity of the excitation source varies (Yacobi and Holt, 1990). Another radiative transition where neither the conduction band nor the valence band are involved is shown as 6 in Figure 2.2. Here, electrons that reside in the ground state of the luminescent centre are excited to any of the available excited states of the centre (Gucsik, 2009). The return to the ground state may happen in two stages involving both processes where energy is dissipated by phonons (i.e., non-radiative emission) and radiative emissions when the upper excited level has been reached (6) or only radiative emissions if excitation has raised electrons to the first excited state (6). Very often, these luminescent centers are related to impurity ions (e.g.,  $Ce^{3+}$  in  $Y_2SiO_5$ ) providing a means to recognise them by the detection of the characteristic wavelength of the emission. Besides the three fundamental processes of energy absorption, transfer, and energy conversion there are additional mechanisms by which luminescence may be delayed or quenched. Retrapping of stimulated charges back into the same or into other traps is very likely to occur causing a delay in the light emission or reduction if there is not sufficient energy for further stimulation. Non-radiative mechanisms, such as multiple phonon emission, Auger effects, and recombination at the electronic states found at the surface are mainly associated with nonradioactive transitions resulting in reduced luminescence efficiency. Elevated sample temperature conditions, particularly during stimulation, are known to enhance the non-radiative processes. Thermal quenching, in which the luminescence yield decreases with

increasing temperature is attributed to the increased probability for radiation less transitions (McKeever, 1985; Yacobi and Holt, 1990).

## 2.4 Types of Luminescence

According to the type of radiation used to excite the emission, can be classified in to different types.

### 2.4.1 Thermoluminescence

Thermoluminescence ( $TL$ ), which is also called radiation induced thermally stimulated luminescence or simply thermally stimulated luminescence (TSL), is the thermally stimulated emission of light following the previous absorption of energy from radiation [1, 3, 12]. The primary causes for the induction of  $TL$  in a given material are the ionization radiations such as x-rays, gamma rays rays, UV light etc, to which the sample is pre-exposed. However, the application of heat stimulates the release of the stored energy in the sample due to pre-exposure to the ionizing radiations which in turn produces luminescence. Therefore, heat has only a secondary role in the process of  $TL$ .

### 2.4.2 Photoluminescence

As discussed above, an electron in a semiconductor or insulator is excited to a higher energy quantum state upon absorption of external energy from electromagnetic radiation. If the electron returns (relaxes) to a lower energy quantum state by radiating a photon, the process is called photoluminescence ( $PL$ ) [7-8]. In other words, photoluminescence is the process in which a substance absorbs photons and radiates photons back out. Quantum mechanically, this can be described as an excitation to a higher energy state and then a return to a lower energy state accompanied by the emission of photon. The period between absorption and emission is typically extremely short, in the order of 10 nanoseconds. The  $PL$  intensity depends on the measurement temperature and the energy of the exciting light (known as photoluminescence excitation or  $PLE$  spectrum).

### 2.4.3 Cathode luminescence

Cathode luminescence ( $CL$ ) occurs due to the emission of light during electron irradiation [13-15]. In the beginning of the last century it was observed that invisible cathode rays produced by electrical discharges in the evacuated tubes, produced light when they struck the glass walls of the tube. The modern name for cathode rays is electrons and this type of luminescence has retained the name  $CL$ . This is a very useful form of luminescence. Beams of electrons are used for many purposes. The electron microscope employs beams of electrons to produce high reso-

lution images of small specimens. In some cases, the beam produces *CL* from the specimen. This is particularly useful for the study of minerals in rocks where the presence of transition metal trace elements can cause the mineral to give off a distinctive color light.

#### **2.4.4 Electroluminescence**

When a material emits electromagnetic radiation as a result of the application of an electric field, the process is called electroluminescence (*EL*) [9-10]. The photon emitted results from radiative recombination of electrons and holes created in the phosphor by the voltage between the two electrodes. One of the electrodes is transparent to the wavelength of the light emitted by the device. In other words, electroluminescence is the efficient generation of light in a non-metallic solid or gas by an applied electric field or plasma. Another type of electroluminescence is that produced by some crystals when an electric current passes through them. In this case the current or electrons excites electrons that occupy energy levels involved with chemical bonds inside the crystal. When the excited electrons decay back to their ground state, they emit visible light. Both organic and inorganic light emitting diodes (*LEDs*), operating on a different principle, has now become a widely used application of electroluminescence [10-12].



### 2.4.5 Triboluminescence

Triboluminescence is the emission of light on applying an external mechanical energy inducing stress. It could be excited by cutting, cleaving, grinding, rubbing, and compressing or by impulsive deformation of solids. Because of this it can also be called electroluminescence. B. V. Bukvetskii et al, described the phenomenon of triboluminescence as the glow resulting from crystal destruction or friction [21] and stated its importance in the process of converting mechanical energy in to light energy. It has been observed that all piezoelectric crystals exhibit triboluminescence and it is sometimes called piezoluminescence. The spectra of triboluminescence light are similar to those of photoluminescence in many substances. The excitation is due to electrification of the cleavages and cracks. Chandra [22] has summarized the mechanism of this emission in different substances.

### 2.4.6 Radioluminescence(Scintillation)

Radioluminescence is produced by ionizing radiation [23, 24]. Some polymers contain organic molecules which emit visible light when exposed to such radiations as x-rays, gamma rays, or cosmic rays. It is also called scintillation because it is used as a technique to detect individual light pulses generated by the incidence of each x or gamma ray photon or a nuclear particle [23]. Such light pulses are called scintillations, since like a spark they are very short-lived. The intensity of the scintillation (light pulse) is directly proportional to the incident gamma ray photon energy when

it is totally absorbed. The measurement of the pulse intensity, therefore, provides the means for knowing the gamma ray energy. The mechanism of light emission in radioluminescence and electroluminescence is the same because in both the cases it is the electrons, incident primarily from cathode rays or the secondary electrons produced after the first interaction of the incident x-ray photon or nuclear particle, which cause the excitation of the luminescent species in the bulk sample.

### 2.4.7 Ionoluminescence

Another interesting method of producing luminescence is the visible light produced when fast ions collide with organic, in-organics compounds. This is called ionoluminescence and it can also be defined as a phenomenon of non-thermal light emission induced by high energy accelerated particles or ion beams [25, 26]. An early application of ionoluminescence was to luminous clock dials. These relied upon a rather hazardous method of making light that involved radioactivity. A radioactive material, such as radium, was mixed with a material that displays luminescence, such as zinc sulphide. As the radium decays, it emits alpha particles and other radiation. This excites electrons in the luminescent material to give off light. This is very handy, since the light persists indefinitely, limited only by the half-life of the radium isotope used,  $^{226}\text{Ra}$ , which is 1600 years. However, the manufacturing process for such watch dials gave radiation exposure, mainly internal exposure- to workers involved in this work in 1920 s and 1930 s.

### 2.4.8 Chemiluminescence

Chemiluminescence is produced as a result of a chemical reaction usually involving an oxidation reduction process [16-17]. The most common mechanism for such an emission is the conservation of chemical energy, released in a highly exothermic reaction, in to light energy in the visible region. In some chemical reactions energy can be transferred to electrons in the chemical bonds. As these electrons decay down to lower excited states, they emit light. Some of these reactions proceed slowly, so the light can be emitted for a considerable time. This is known as chemiluminescence. This is distinct from more vigorous chemical reactions where so much heat is released that the chemicals actually catch fire or otherwise glow red hot (incandescence). However the process of chemiluminescence remains to be not fully understood. Lyoluminescence, which is the phenomenon of light emission during the dissolution of previously irradiated solids in suitable solvents is a type of chemiluminescence [18].

### 2.4.9 Bioluminescence

Electronic excited states of the biomolecules can be produced due to biochemical reactions inside the cells of the living organisms such as fire flies, glow-worms, some bacteria, fungi and many sea creatures (such as planktons) both near surface and at great depths and interesting luminescence phenomena can be observed from these living beings [19-20]. The chemical reactions are the enzymic oxidations. For exam-

ple, the oxidation of luciferin in the presence of enzyme luciferase is responsible for occurrence of bioluminescence [20]. Other living organism such as sea crustacean and the luminous bacteria also give a glow, even though the chemical nature of the luciferin in each of these is said to be quite different from each other.

## 2.5 Characteristic luminescence

Characteristic luminescence occurs by doping the host lattice with either transition ( $3d$ ) or rare-earth ( $4f$ ) metal ions (impurities) that substitute for host lattice cations. An electron gets excited to a higher energy level in the atom itself. Rare earth ions from  $Ce^{3+}$  (atomic number of 58) to  $Yb^{3+}$  (70) have partially filled  $4f$  orbitals with energy levels characteristic to each ion and show a variety of luminescent properties around the visible region. Many of these ions can be used as luminescent ions in phosphors. There are 15 rare earth materials and the lanthanides are those rare earths with the atomic numbers between 57 ( $La$ ) and 71 ( $Lu$ ). The  $4f$  electronic energy levels of lanthanide ions are characteristic of each ion. The levels are not affected much by the environment because  $4f$  electrons are shielded from external electric fields by the outer  $5s^2$  and  $5p^6$  electrons. This is in strong contrast with transition metal ions, whose  $3d$  electrons, located in an outer orbit, are heavily affected by the environmental or crystal electric field [27]. Typical phosphors used in  $CRTs$  and  $FEDs$  consist of a host matrix doped with activators such as the rare earths ( $4f$ ) and the transition metals ( $3d$ ) [28]. Among the various types of luminescence discussed above, attention is given to thermoluminescence phenomenon in this study.

This is owing to its wide applications in various disciplines of science. However, before discussing some of its wide applications, it is useful to discuss mechanism of thermoluminescence and the role of defect centers in a given specimen.

## 2.6 Defect centers and mechanism of thermoluminescence

As discussed above,  $TL$  is a two step process involving excitation by exposure to ionizing radiations and thermal stimulation. Irradiation of a sample causes transitions of electrons between the valence band and the conduction and creating free electrons in the conduction band and free holes in the valence band. Though some electrons and holes undergo recombination almost instantaneously during irradiation, some still diffuse in the lattice and trapped in the defect centers. These imperfections in the crystal, associated with impurities and(or lattice defects may create new localized energy levels in the forbidden band gap whose positions depend on the nature of the imperfections(defects and the host lattice [1]. Some of these defects are capable to trap an electron or a hole. Therefore the centers are referred to as electron or hole traps and after trapping an electron or hole the new defects are called trapped electron or trapped hole centers, respectively. In other words, the presence of certain types of defects in the regular structure of a  $TL$  material which should be capable of capturing electrons or holes during exposure to ionizing radiations is very important for the induction of  $TL$  in the concerned material. This means that  $TL$  is very sensitive to the ,presence of defects or impurities in a given sample. Furthermore, the captured electrons(holes should be retained in the defect centers (also called  $TL$  centers) until the sample is heated to an appropriate

temperature to read the  $TL$ . The term "center" is used to designate these structures since they are present as an isolated entities and are not part of the regular lattice, which is a continuous repetition of the unit cell of a crystalline material. There is also another type of defect which is associated with impurities, for example, ions of transition elements. This is usually the main cause of a characteristic color from certain minerals and the color is due to absorption bands caused by electronic transitions between energy levels in the band gap. The wave functions of the transition ions (*in particular 4f-ions*) are highly localized. As mentioned above, the energy levels in the band gap depend on the nature of the imperfection, lattice defect or impurity and can in principle be located at any energy position varying from just below the bottom of the conduction band to just above the top of the valence band. Due to their high mobility, free electrons and holes produced by ionizing radiation can migrate in the crystal until they are trapped by different trap centers such as impurities, luminescent centers and other imperfections in the crystal. A trap is characterized by the energy  $E$  that a trapped electron (or hole) must acquire from lattice vibrations to escape to the conduction band (or valence band). A necessary condition for a mineral to be a suitable luminescent material for  $TL$  dating is that the relevant traps are deep, i.e. not easily emptied. This implies that the energy of the trapped electron should be located sufficiently far from the bottom of the conduction band. Similarly, the energy of the trapped hole should be located sufficiently far from the top of the valence band. In  $TL$ , during the heating stage, different kinds of transitions of electrons and holes can take place during the detrapping process from their respective trap centers so that luminescence can occur. These transition

options, which may or may not involve the delocalized bands, are discussed below.

## 2.7 Transitions involving delocalized bands

The alteration in occupancy of the various localized energy states, which can be implemented by electronic transitions from one energy state to another, is an essential feature of all luminescence processes. For both electrons and holes, several kinds of transitions are possible and some are shown in the Figure 2.3 Because of irradiation, a valence electron from a host atom is excited in to the conduction band in which state it has enough energy to move freely through the lattice (transition (a)).

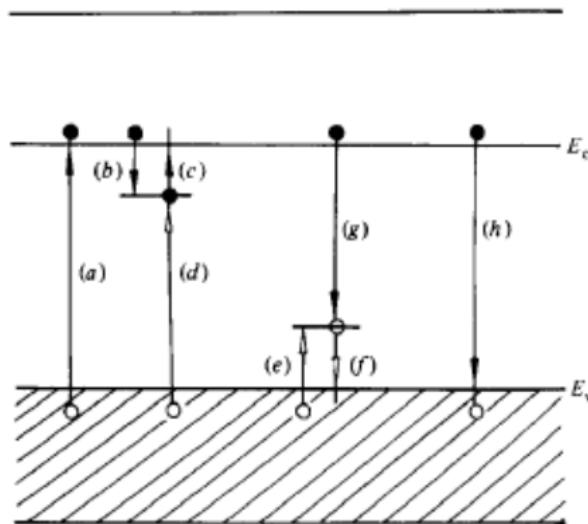


Figure 2.3: Common electronic transitions in crystalline semi conductors and insulators

Thus, this transition corresponds to the process of ionization and is a result of the absorption of energy from an external source. Since for every free electron in the conduction band a free hole is left behind in the valence band, the process of ionization results in the creation of free electron-hole pairs which may wander through the crystal until they become localized at defect(trap)centers. This is shown as the trapping of electrons (transitions  $(b)$ ) and holes (transition  $(e)$ ). However, through thermal excitation, the localized electrons and holes may be released from their traps (transitions  $(c)$  and  $(f)$ ) to become free and move through the crystal. The free electrons and holes have also an option to undergo recombination with a charge carrier of opposite sign at recombination centers. This can take place either directly (transition  $(h)$ ), or indirectly by recombining with a previously trapped carrier (transitions  $(d)$  and  $(g)$ ). If either of these recombination mechanisms is accompanied by the emission of light (i.e., it is radiative) then luminescence results.

## 2.8 Transitions not involving delocalized bands

Transitions not involving delocalized bands Unlike the above discussion, which is strictly valid for transitions involving the delocalized bands, electron and hole transitions can occur directly between centre in many materials without the carriers being raised into the conduction and valence bands.

Transitions of this type are important in luminescence processes (including thermoluminescence) of many luminescent materials (phosphors). Figure 2.4 depicts a typi-



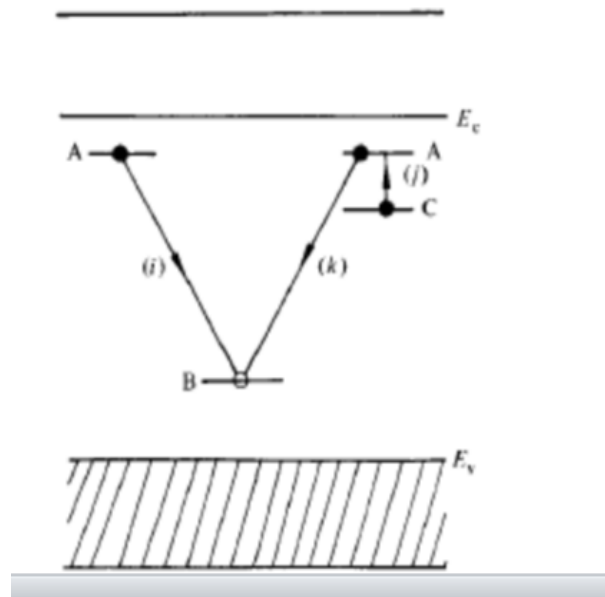


Figure 2.4: Electron transitions in a semiconductor or insulator not involving the delocalized band

cal center-to-center transition of electrons that can take place. In this figure, though only electron transitions are represented for simplicity, similar transitions also occur for holes. Transition (i) shows recombination of an electron trapped at level A with the hole trapped at level B.

This type of recombination commonly happens if energy levels A and B are within the same atom. Good examples of substances which exhibit this kind of recombination are rare earth. This is one of the earliest classical examples of this kind of recombination. Moreover, luminescence can also be induced when dopants are incorporated into the lattice of different host materials and this luminescence is primarily a characteristic of the particular rare earth used, and not of the host material [29]. The incomplete  $4f$  shell in the rare earth ions results in a large num-

ber of well-defined luminescence emission lines caused by transitions between the wide range of low-lying energy levels. The  $4f$  electrons are effectively shielded from their surroundings by the  $5s^2$  and  $5p^6$  shells. This means that the  $4f$  states are not perturbed by the surrounding host ions and therefore the spectra of the emissions remain essentially invariant in most host lattices. Rare-earth-doped materials are becoming popular as luminescent phosphors because of the fact that the transitions within the dopants are normally radiative. If levels  $A$  and  $B$  in Figure 2.4, are not within the same atom, a transition of type (i) can still take place by tunneling. This is commonly true if the defects responsible for the levels are situated close to each other few lattice constants apart in the host lattice. This type of recombination is reported in a variety of organic and inorganic materials [30-32]. An alternative possibility is that an electron has to be elevated to a higher energy level before recombination with a trapped hole can take place. Thus, in Figure 2.4, an electron at level  $C$  has to be raised to  $A$  (transition (2)) before recombination (transition(3)) take place. The fact that electron transitions of this sort do not involve excitation into the conduction band has a consequence that there will not be any accompanying conductivity phenomena, while transitions involving delocalized bands (Figure 2.4) will be associated with changes in conductivity.

## 2.9 The concept of kinetic order

The term order of kinetics or kinetic order in  $TL$  theory has been taken from chemistry. When the rate of a chemical reaction is directly proportional to the change in the concentration of only one of the reactant, it is called mono molecular kinetics

or first order kinetics. If the rate of chemical reaction is directly proportional to the change in the concentration of both the reactants, it is called bi-molecular kinetics or second order kinetics [11]. Some early investigators of  $TL$  phenomena said that 'if the probability of retrapping before recombination is non-zero, we have second-order kinetics'. For  $OTOR$  case in  $GG$  model, when  $A_r = A$  and the concentration  $h$  of recombination center is equal to the concentration  $n$  of electrons in traps (so that the over-all charge neutrality condition is satisfied), it becomes a case of second order kinetics. Under the condition  $A_r = A$ , the 'reaction' rate between the released charges from the traps and the recombination center becomes equal to  $n^2$  (as shown in equation (2.9) which means we have kinetic order equal to 2

## 2.10 Application of thermoluminescence

The modernization and development in the instrumentation; and better understanding of  $TL$  have helped the professionals to solve their problems in many fields. The present understanding of  $TL$  has explored its very high application potential in various fields. Some of the fields are discussed below.

### 2.10.1 Archaeology

The technique of  $TL$ , which is usually done by collecting the  $TL$  output from quartz grain collected from pottery or brick, is highly important in dating ancient pottery samples [49, 50]. The  $TL$  output from the specimen is mostly attributed to  $TL$  sensitive mineral inclusions (mostly quartz) in the host clay matrix of the pottery fired in the kiln some time in the long past. That event is considered to be the starting of the

'*TL* clock' for archaeological dating [51]. Whatever *TL* has been stored earlier in the mineral inclusion due to internal and external irradiations over the geological times is considered to be erased during the kiln firing. The presence of internal irradiation from radioactive elements such as Uranium, Thorium and Potassium contents in the clay and external radiations makes the pottery start building up *TL* after the onset of the '*TL* clock' (the kiln firing). The archaeological age of the specimen can also be evaluated from the following relation [1, 51].

$$Age = \frac{Accumulated\ dose}{Annual\ dose} \quad (2.7)$$

### 2.10.2 Defects in solids

*TL* is very sensitive to traces of impurities or defects within the host material of a given sample and experiments on *TL* yields useful information on the properties of the various types of defect present within an insulator or semiconductor [1, 52, 53]. This includes the position of the defect within the energy gap and sometimes the type of defect itself. There are early reports on the effect of impurities on the *TL* properties of various materials [54-56]. In general the impurities give rise to the localized energy levels within the forbidden energy gap and that these are crucial to the *TL* process. For the purpose of detecting the presence properties of these defect levels, the analysis of *TL* glow curves is important. In addition to defect levels produced by external means such as irradiation or doping, there are also those due to defects, such as lattice vacancies and interstitial inherently present in the material. The presence of this type of imperfection is also crucial to the *TL* process in many materials.

### 2.10.3 Radiation dosimetry

*TL* has an interesting application in the field of radiation dosimetry [50-57]. It is clear that the absorption of radiation increases the level of *TL* observed from a given sample by filling the localized energy levels with trapped electrons while the absorption of heat from the environment tends to reduce the numbers of trapped electrons by detrapping them. Therefore, the intensity of *TL* from the sample is the result of a competition between trap filling by radiation and trap emptying by thermal excitation. Since many materials display an intensity of *TL* which is proportional to the amount of radiation absorbed [52], *TL* may be used as a means of radiation dosimetry. The first proper application of *TL* to dosimetry was in 1953 when *LiF* was used to measure radiation following an atomic weapon test [1]. The eligibility of *LiF* for radiation dosimetry is mainly because of its high sensitivity and it was used as small pellets to measure internal radiation doses received by cancer patients treated with radioactive isotopes [58]. The procedure was that the patients were made to swallow small *LiF* pellets which were recovered after passage through the digestive system. Then, the accumulated dose received by the patients was obtained by measuring the *TL* from the pellets and comparing it with that produced in similar crystals which had been irradiated with a known dose of radiation.

### 2.10.4 Geology

The  $TL$  technique is also important in dating geological specimens [50, 59].  $TL$  would start building up in a geological specimen from the time of its crystallization and would normally continue throughout its existence due to the radioactivity present within the minerals and in the surrounding materials till it saturates. By using a material with a negligible radioactivity in it, for example: quartz [59], the accumulated  $TL$  mostly represents the environmental dose rate at a place from where the geological specimen was collected. Accumulation of  $TL$  can be affected by natural light especially its ultraviolet component. In geology the sun light bleaching is considered to be the basis for dating the geological event. The exposure of sand grains to sun light during their weathering and transport through wind and water results in bleaching of their geological  $TL$ . This bleaching is effective enough to reduce  $TL$  level to a negligible value. These bleached sand particles, once embedded in a sand dune or beach, get shielded from further exposure to sunlight. This helps particles to acquire more  $TL$  due to radiations exposure from their new environment within the sand dune. Therefore, the age of a given geological sample (since its first exposure to sunlight) can also be estimated [1, 59].

### 2.10.5 Forensic sciences

The study in forensic sciences mainly focuses on evolving and standardizing methods to compare evidentiary materials with similar materials of known origin, which are invariably available only in minute quantities and are required to be analyzed

nondestructively for evidence purposes. An attractive technique can be offered by the method of *TL* [50] to some selected materials that are commonly encountered in the criminal cases (glass, soil, safe insulation materials etc) [60]. This can be used as evidence i.e., when the *TL* characteristics do not match it, one can say with certainty that a particular sample does not come from a known source. In addition to the above mentioned disciplines, the method of *TL* is also important in the fields of quality control in industry for controlling the quality of many glass, ceramics, and semiconductor products; biology and biochemistry for studying the properties (involving different chemical reactions) or contents of proteins, leaves etc [53, 61]. Moreover, *TL* has also interesting applications in space science, thermostimulated luminescence (*TSL*) photography, radiation physics, petroleum exploration [50], etc.

## **2.11 Structural and electronic properties of some selected phosphors**

### **2.11.1 definition of phosphors**

The word phosphor was invented in the early 17th century and its meaning remains unchanged till today. Early alchemists found a heavy crystalline stone with a gloss at the foot of a volcano, and fired it in a charcoal oven intending to convert it to a noble metal. They found that the sintered stone emitted red light in the dark after expo-

sure to sunlight rather than being converted in to metal. After this discovery, similar findings were reported from many places in Europe, and these light-emitting stones were named phosphors [23]. This word means "light bearer" in Greek. In other words, a phosphor emits energy from an excited electron as a light. In general, the excitation of electron is caused by absorption of energy from an external source such as another electron, a photon, or an electric field. Phosphors have wide applications in today's science and technology. The applications of phosphors can be classified as light sources represented by fluorescent lamps, display devices represented by cathode-ray tubes, detector systems represented by x-ray screens and scintillators, and other simple applications such as luminous paint with long persistent phosphorescence [24]. Therefore, designing a phosphor for a particular application requires the understanding of the properties of the constituents of the phosphor. In addition to the host material (insulator or semiconductor), inorganic phosphors consist of impurities (dopants or activators) purposely incorporated in small amounts in to the host [25]. The luminescence emission from a given phosphor depends on many factors. In general, a phosphor with high luminescence efficiency is characterized by properties such as low phonon energy, high optical damage threshold, high quantum efficiency, stability, etc. In this research work, interesting silicate phosphors have been investigated for possible applications in display medium and  $TL$  dosimetry. These phosphors are  $Ce^{3+}$  doped  $Y_2SiO_5$  and are discussed in detail in the following sections



## 2.12 Properties of $Y_2SiO_5 : Ce^{3+}$ phosphor

The structure of  $Y_2SiO_5$  contains isolated  $SiO_4$  tetrahedral and non silicon-bonded oxygen. Two different monoclinic structures have been found, a low temperature phase ( $X1$ ) and high temperature phase ( $X2$ ). The  $X1$  phase has the space group  $P21/c$ , whereas the space group  $B2/c$  is assigned to the  $X2$  phase. Both  $X1$  and  $X2$  phases have two different  $Y^{(3+)}$  sites, the coordination numbers of which are 7 and 9 for the  $X1$  phase and 6 and 7 for the  $X2$  phase [39-42]. During the preparation method of  $Y_2SiO_5 : Ce$ , the activator  $Ce^{(3+)}$  (radius of 0.106 nm) can easily substitute  $Y^{(3+)}$  (radius of 0.093 nm) thus also resulting in the two different crystallographic sites. The notation  $A1$  and  $A2$  are given to the two sites in the  $X1$  - phase with coordination number ( $CN$ ) of 9 and 7.  $B1$  and  $B2$  are denoted to the  $X2$  - phase with  $CN$  of 6 and 7 [39].  $A1$  with the  $CN$  of 9 means that there are 8 oxygen atoms bonded to yttrium and silicon and only one that is bonded to only yttrium and  $CN$  of 7 means that 4 oxygen atoms are bonded to yttrium and silicon and 3 are bonded to yttrium only. Both  $B1$  and  $B2$  have two oxygen atoms that are only bonded to yttrium [39].  $Y_2SiO_5$  has a wide band gap of about 7.4 eV (insulator) so doping it with an activator such as  $Ce$  creates an energy level structure inside the wide band gap.

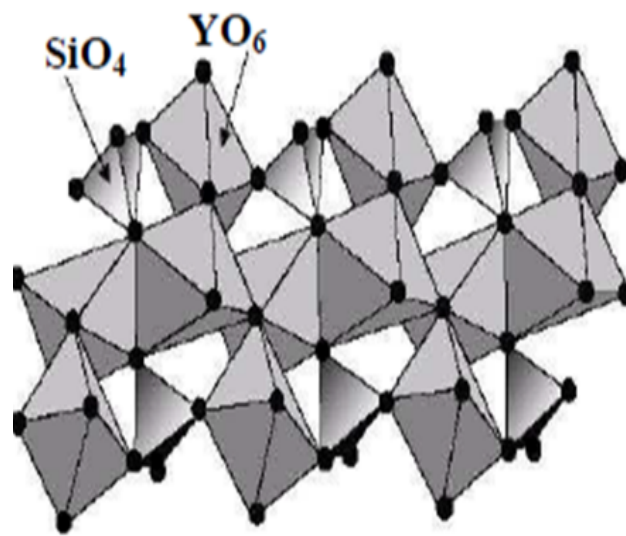


Figure 2.5: The complicated monoclinic crystal structure of  $Y_2SiO_5$  is formed from the  $SiO_4$  and  $(YO_6)$  (tetra and octahedron) structure

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## Materials and Methodology

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### 3.1 Materials

An intensive survey of literature from published articles book, journals, thesis and dissertation were carried out based on the title of the research.

### 3.2 Methodology

### 3.3 Analytical

In this thesis one of the method or approach used to solve the problem is analytical method therefore for numerical approach to thermoluminescence we uses and write MATHEMATICA software for behavior of  $Y_2SiO_5 : Ce^{3+}$  phosphor in view of second order kinetics would have been used..

### 3.4 Graphical

The optical properties of thermoluminescent behavior of  $Y_2SiO_5 : Ce^{3+}$  phosphor in view of second order kinetics. Therefore during this studying different glow curve generated but the unique one theoretically on concentration of electron traps different from experimental glow curves.

## 4

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### Result and discussion

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#### 4.1 The effect of activation energy on thermoluminescence ( $TL$ ) or $TSL$ glow curves of $Y_2SiO_5 : Ce^{3+}$

It is the energy,  $E$ , expressed in ( $eV$ ), assigned to a level within the forbidden band gap between the conduction band ( $CB$ ) and the valence band ( $VB$ ) of a crystal. This energy is also called trap depth. The properties of activation energy  $E = 0.2 eV$ ,  $0.21 eV$ , and  $0.22 eV$ , of  $Y_2SiO_5 : Ce^{3+}$  can be given in the graphs below.

A plot of thermoluminescence intensity versus temperature, we get glow curves at different activation energies. Therefore, we see from the deeper the traps the glow peak temperature shifts to the higher temperature which corresponds with the thought that the deeper the trap, the more energy is needed to release the charge carrier. These show the luminescence is spread out over a wider temperature interval, resulting in a broader glow peak. When activation energy increases, the intensity of the thermoluminescence decreases, therefore trapping electrons more energy produces on the high activation energy and less energy is produced on the least activation energy and also the glow curve can go from minimum to the maximum of the temperature.

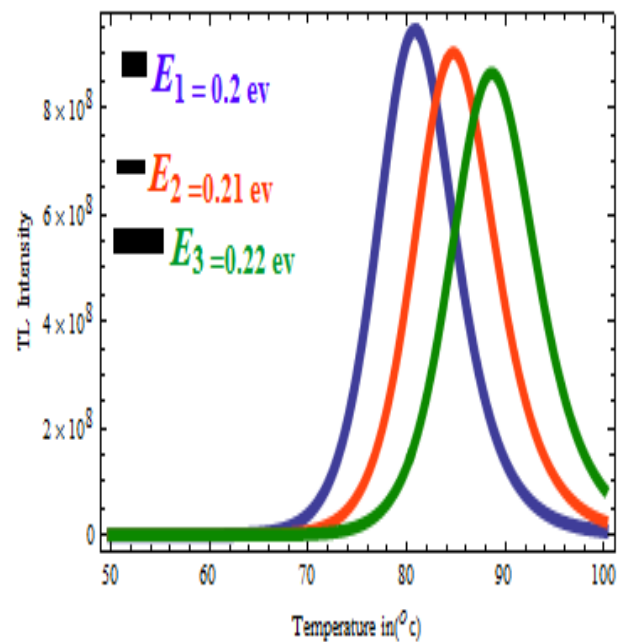


Figure 4.1: Thermoluminescence ( $TL$ ) glow curve peaks depending on different activation energy  $E = 0.2 eV$ ,  $0.21 eV$ , and,  $0.22 eV$  and constant dose of electron, frequency factor and linearly heating rate by using Garlick and Gibson glow curves

In luminescence process, the emission spectrum shift to a lower energies relative to the absorption spectrum because of these the peak height increase decrease activation energy.

## 4.2 Effect of Linear heating rate on Thermoluminescence $TL$ glow curves of $Y_2SiO_5 : Ce^{3+}$

Heating rate  $\beta$  is an important parameter for the determination of the various kinetic parameters of  $TL$  glow curves. In literature it has been reported that the glow peak height decreases [23] or increases [24-25] with increasing heating rate. When the linear heating rate  $\beta$  changes, the temperature  $T_m$  of the maximum  $TL$  intensity of the peak also changes: faster heating rates produce a shift in temperature toward higher values of  $T_M$ . Depending on the given data the theoretical values of thermoluminescence  $TL$  glow curves measured with different heating rates  $TL$  versus Temperature  $T$ , and known heating rates  $\beta_1 = 0.1 K s^{-1}$ ,  $\beta_2 = 0.2 K s^{-1}$ , and  $\beta_3 = 0.25 K s^{-1}$ . It is known that this  $TL$  peak follows second-order kinetics. In addition to the above discussion at constant concentration of electron  $n_0$ , activation energy  $E$  and frequency factor  $s$ . A glow Curve peak maximum with change (increase) in  $\beta$  a glow curves for  $\beta_1 = 0.1$ ,  $\beta_2 = 0.2$ , and  $\beta_3 = 0.25 K s^{-1}$  and  $T_M$  the same as to  $\beta$ . The heating rate ( $\beta$ ) increases, the glow peaks shift to higher temperatures, and the height of the thermoluminescence  $TL$  peak changes and intensity of Thermoluminescence ( $TL$ ) also increase. This all effect is shown below figure. An important experimental parameter in the study of thermoluminescence ( $TL$ ) is the heating rate, usually constant, denoted by  $\beta (K s^{-1})$ . In practically all known cases, the  $TL$  glow peak shifts to higher temperature with increasing heating rate.

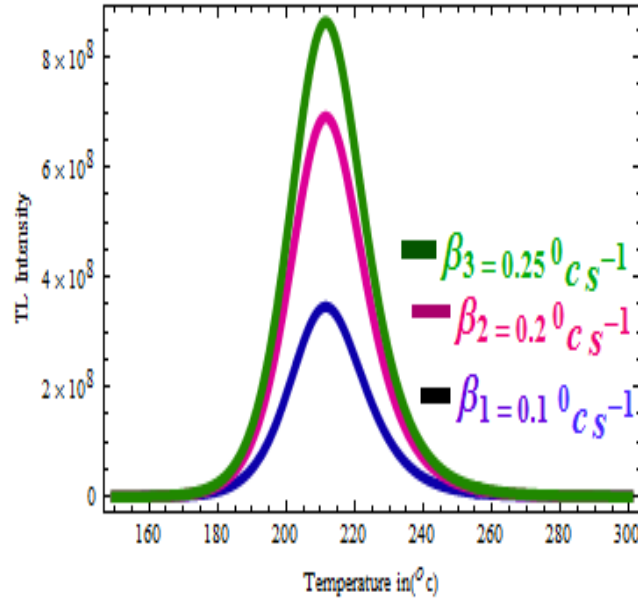


Figure 4.2: Thermoluminescence  $TL$  glow peaks of different linear heating rate  $\beta_1 = 0.1$ ,  $\beta_2 = 0.2$ , and  $\beta_3 = 0.25 K s^{-1}$  as a constant activation energy ( $E$ ), concentration of electron ( $n_0$ ) and frequency factor ( $s$ )

### 4.3 The variation of concentration of electron $n_0$

. // In trap thermoluminescence  $TL$  glow peaks calculated with the equation 3.4as , and different values of the concentration of electron  $n_{01} = 10^{10} cm^{-3}$ ,  $n_{02} = 10^{10.1} cm^{-3}$ ,  $n_{03} = 10^{10.2} cm^{-3}$  ,  $s = 10^{12} s^{-1}$  ,,  $\beta = 1 K s^{-1}$  and ( $E$ ) = 0.5 (eV) . Figure 4.3 shows the graph of concentration of electron at constant frequency factor  $s$  , activation energy  $E$  and linear heating rate ( $\beta$ ) a glow curve peak maximum with change in concentration of electron  $n_0$  a glow curves .  $n_1 = 10^{10} cm^{-3}$ ,  $n_2 = 10^{10.1} cm^{-3}$ ,  $n_3 = 10^{10.2} cm^{-3}$ ,



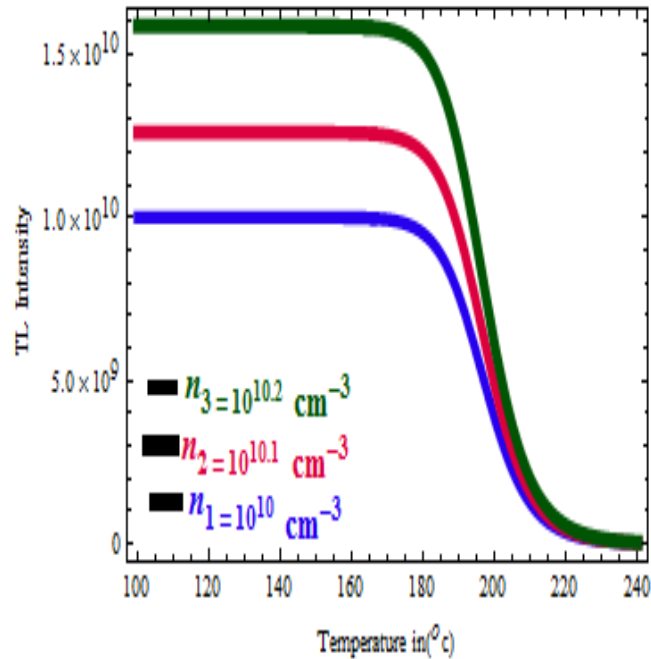


Figure 4.3: Thermoluminescence  $TL$  glow peaks of different concentration of electron calculated with the equation (4.3) as at constant activation energy ( $E$ ), frequency factor  $s$  and linearly heating rate  $e(\beta)$

$T_M$  versus to the concentration of electron  $n_0$  increases, therefore the graph shows of glow curve peak characteristics, namely the peak temperature  $T_M$  and the peak shape remain unchanged when the initial filled concentration  $n_0$  of the traps is changed. This means that the peak characteristics are independent of radiation dose given to the sample. However, the intensity (the area as well as the height of the peak) increases in direct proportion to  $n_0$  for given  $E$ ,  $s$  and  $\beta$ . This means that the intensity is directly proportional to dose given to a sample, assuming that the

trap filling is directly proportional to the dose. These characteristics are unique to second order kinetics and are of even importance in the application of  $TL$  in radiation dosimetry as well as in kinetics analysis of the glow curves.

#### 4.4 The effect of frequency factor on thermoluminescence ( $TL$ ) glow curves of $Y_2SiO_5 : Ce^{3+}$

As discussed above, the untrapping of an electron from a trap of depth ( $E$ ) under thermal stimulation involves two steps: first, the electron is elevated to an energy level ( $E$ ) above the ground state of the trap by the thermal agitation. The fraction of the trapped electron population that can achieve energy nearly equal to the trap depth ( $E$ ) above the ground state of the trap Boltzmann function, Figure 4.4 shows the graph of frequency factor at constant concentration of electron  $n_0$ , activation energy ( $E$ ) and linear heating rate ( $\beta$ ). A glow curve peak maximum with change in  $s$  a glow curves for ( $s$ ),  $s_1=10^{12}$ ,  $s_2=10^{12.1}$ , and  $s_3=10^{12.2}$ ,  $S^{-1}$ ,  $T_M$  versus  $s$  the frequency factor increases, the glow peaks shift to lowest temperatures or temperature is decrease, and the height of the thermoluminescence ( $TL$ ) peak changes to the lowest temperature (decrease) and intensity of Thermoluminescence ( $TL$ ) also decrease. Because of to need small amount of energy trap the charge carrier.

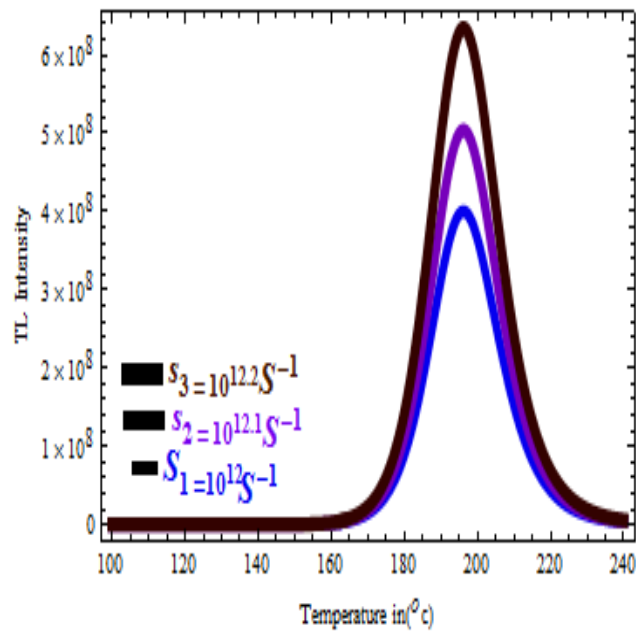


Figure 4.4: Thermoluminescence (TL) glow curve peak maximum with change in  $S$  a glow curves for  $s_1 = 10^{12}$ ,  $s_2 = 10^{12.1}$ , and  $s_3 = 10^{12.2}$ ,  $s^{-1}$ ,  $T_M$  versus  $S$  the frequency factor increases, the glow peaks shift to  $T$  lowest temperatures

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## Summary and Conclusion

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### 5.1 summary

The luminescence phenomena are controlled by structural defects; the nature and concentration of which depend on the sample and growth variables. Of the different types of defects, oxygen vacancies are considered the most important constituents for the production of luminescence in *yittriumsilicate* materials. A complex processes participate in the production of luminescence in anion deficient  $y_2sio_5$  materials more is known about their combination sites as revealed by the characteristic wavelengths of the luminescence emissions than about the trapping states. These are lattice point defects may be found naturally in the crystal structure (non-stoichiometry effect) but primarily are related to the growth and fabrication conditions and the presence impurities.  $y_2sio_5 : Ce^{3+}$  single crystals that are specifically produced for applications in dosimetry contain high concentrations of oxygen vacancies arising from the combined effect of high temperature treatment and *cerium* doping. The emission of electrons or hole generated from two-level model top to bottom or bottom to top. It was additionally discussed that the production of lumi-

nescence may also be affected by the arrangement of the different phases within a crystal .

## 5.2 Conclusion

This thesis we have deal with thermoluminescence behavior  $Y_2SiO_5 : Ce^{3+}$  phosphor in second order kinetics. Explaining different possible behaviors of  $TL$  glow curves with the factors influencing glow curve during the process of luminescence emission are activation energy, Linear heating , initial concentration of trap electrons and also frequency factor. In Figure 4.1, the shape of the so-called glow peak according to above Equation is shown for different values of the trap depth  $E = 0.2 eV$ ,  $0.21 eV$  and  $0.22 eV$  while the other parameters are kept constant. We see that for deeper traps the glow peak temperature shifts to a higher temperature which corresponds with the thought that the deeper the trap, the more energy needed to release the charge carrier; and also the luminescence is spread out over a wider temperature interval resulting in a broader glow peak. Figure 4.3 shows the graph of concentration of electron at constant frequency factor  $s$  , activation energy  $E$  and linear heating rate ( $\beta$ ) a glow curve peak maximum with change in concentration of electron  $n_0$  a glow curves .  $n_1 = 10^{10} cm^{-3}$ ,  $n_2 = 10^{10.1} cm^{-3}$ ,  $n_3 = 10^{10.2} cm^{-3}$ ,  $T_M$  versus to the concentration of electron  $n_0$  increases, therefore the graph shows of glow curve peak characteristics, namely the peak temperature  $T_M$  and the peak shape remain unchanged when the initial filled concentration  $n_0$  of the traps is changed. This means that the peak characteristics are independent of radiation dose given to the sample. However, the intensity (the area as well as the height of the peak) in-

creases in direct proportion to  $n_0$  for given  $E$ ,  $s$  and  $\beta$ . This means that the intensity is directly proportional to dose given to a sample, assuming that the trap filling is directly proportional to the dose. These characteristics are unique to second order kinetics and are of even importance in the application of  $TL$  in radiation dosimetry as well as in kinetics analysis of the glow curves. Figure 4.4 shows the graph of frequency factor at constant concentration of electron  $n_0$ , activation energy ( $E$ ) and linear heating rate ( $\beta$ ). A glow curve peak maximum with change in  $s$  a glow curves for ( $s$ ),  $s_1 = 10^{12}$ ,  $s_2 = 10^{12.1}$ , and  $s_3 = 10^{12.2}$ ,  $S^{-1}$ ,  $T_M$  versus  $s$  the frequency factor increases, the glow peaks shift to lowest temperatures or temperature is decrease, and the height of the thermoluminescence ( $TL$ ) peak changes to the lowest temperature (decrease) and intensity of Thermoluminescence ( $TL$ ) also decrease. Because of to need small amount of energy trap the charge carrier. Since it show that to need small amount of energy trigger the charge carrier. Therefore we obtained from experimental values and also I would compression with theoretically values then our value approach to the experimental glow peak curves. From our results we conclude that the shapes of ( $TL$ ) curves depend strongly on the activation energy, heating rate, initial traps charge concentration of electrons and also frequency factor. We also showed that the values of those all parameters determined our basic research questions used.

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