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INVESTIGATION OF DOSIMETRIC AND THERMOLUMINESCENCE PROPERTIES OF $CaSO_4$:Dy (TLD 900) CRYSTALS

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Asist.Prof.Dr. Rabia Güler YILDIRIM

by

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ABSTRACT

INVESTIGATION OF DOSIMETRIC AND THERMOLUMINESCENCE PROPERTIES OF $CaSO_4$:Dy (TLD 900) CRYSTALS

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M.Sc. in Engineering Physics

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The dosimetric characteristics of any TL material mainly depend on the sensitivity, energy response and the kinetic parameters quantitatively describing the trapping emitting centers responsible for the TL emission. Thus, a reliable dosimetric study of a thermoluminescent material should be based on a good knowledge of its kinetic parameters. Evaluation of kinetic parameters, i.e. the activation energy E_a of the traps involved in the TL emission, the kinetic order b, and the frequency factor s, associated with the glow peaks. $CaSO_4$:Dy (TLD 900) 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-900. 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 $CaSO_4$:Dy (TLD- 900) . The results of the analysis have shown that TLD-900 has a first order glow peak of E_a=0.68 eV at 225 ^oC.

Key Words: Thermoluminescence, kinetic parameters, $CaSO_4$:Dy (TLD 900)

ÖZ

$CaSO_4$:Dy (TLD-900) KRİSTALİNİN DOZİMETRİK VE TERMOLUMİNESANS ÖZELLİKLERİNİN İNCELENMESİ

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Dozimetrik bir malzemenin termoluminesans özellikleri, temelde malzemenin doz hassasiyetine, enerji cevabına ve termoluminesans ışıldama eğrilerini oluşturan tuzak parametresi değerlerine bağlıdır. Güvenilir bir dozimetrik çalışma için bu tuzak parametrelerinin, kinetik derecesi b, aktivasyon enerjisi E_a ve frekans faktörü s'in belirlenmesi oldukça önemlidir. $CaSO_4$:Dy (TLD-900) kristali doku eşdeğerine sahip bir TLD materyaldir ve kişisel dozun ölçümü gibi pek çok alanda TLD-900 ticari koduyla kullanılmaktadır. Bu çalışmada değişken doz, farklı ısıtma hızları, tepe şekli, üç nokta ve bilgisayarlı ışıma eğrisi ayrıştırma yöntemleri kullanılarak kristalinin $CaSO_4$:Dy (TLD-900) tuzak parametre değerleri hesaplanmıştır. Analiz sonuçları TLD-900 kristalinin 225 ^{0}C'de birinci dereceden, 0.68 eV enerjiye sahip bir ışıldama tepesine sahip olduğunu göstermiştir.

Anahtar kelimeler: Termoluminesans, tuzak parametreleri, $CaSO_4$:Dy (TLD-900)

To my parents , to my Supervisor: Asist. Prof. Dr. Rabia Güler YILDIRIM and Asist. Prof. Dr. Vural Emir KAFADAR to all humanity

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CHAPTER 1

INTRODUCTION

1.1 LUMINESCENCE

Luminescence is the emission of light by a substance not resulting from heat; it is thus a form of cold body radiation. It can be caused by chemical reactions, electrical energy, subatomic motions, or stress on a crystal. Luminescent material can be characterized from the wavelength of the light emitted but it cannot be characterized from the incident radiation. Generally the phenomenon of luminescence in most studies is attached with the emission of the visible light but other wavelengths may be emitted. 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. One is the short time phosphorescence ($\tau_c < 10^{-4}$s) and another one is the long time phosphorescence ($\tau_c > 10^{-4}$s). [1]

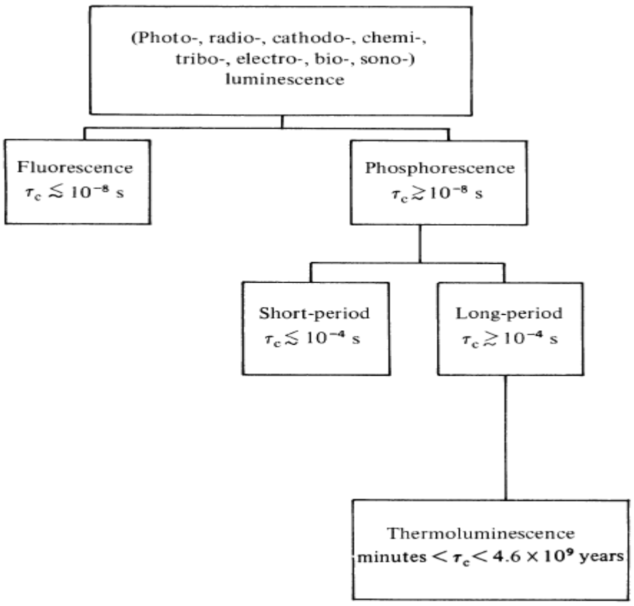
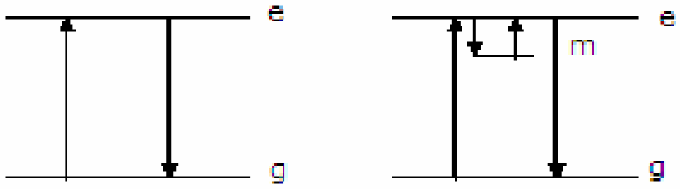


Figure: 1.1 Fluorescence and phosphorescence time table[1]

When an electron excited from the ground state (g) to an excited state (e) an electron 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), a 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 :

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

(E) is the energy difference between the trap (m), (e) is excited state, (k) is Boltzmann's constant (s) is a constant . Thus the phosphorescence process is dependent on temperature exponentially.



(a) (b)

Figure: 1.2 (a) fluorescence (b) phosphorescence[1]

Table 1.1 Describes the phenomena of luminescence and excitation method.

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

1.2 Thermoluminescence

Thermoluminescence is a luminescence phenomenon of an insulator or semiconductor which can be observed when the solid is thermally stimulated. [2] Thermoluminescence is the thermally stimulated emission of light following the prior absorption of energy from radiation. TL should not be confused with the light spontaneously emitted from a substance when it is heated to incandescence. There are the three important points for the production of TL can be deduced. Firstly, the luminescence emission is triggered by heating the material. Secondly the material must be an insulator or a semiconductor. Finally, the material must have at some time absorbed energy during exposure to ionizing radiation. When a material is exposed to ionizing radiation energy is stored in material. The stored energy is released in the form of visible light when the material is heated.

Thermoluminescence (TL) method is a relatively complex process since it includes a trap and a luminescence center. When an insulator or semiconductor is exposed to ionizing radiation at room or at low temperature, electrons are released from the conduction band to the valance band. Thus, a hole occurred in valance band. Both types of carriers become mobile in their respective bands until they recombine or until they are trapped in lattice imperfections in the crystalline solids. In trap electrons remain for a long time when the crystals are stored at room temperature. If is given sufficient energy , trapped electrons can release. These electrons may act in the crystalline solid until they recombine with suitable recombination centers that contain hole with the emission of TL light.This process is called as simply thermoluminesence.

1.3 Application Of Thermoluminesence

The phenomenon of TL has been extensively studied by many investigators. The understanding of the mechanism of occurrence of thermally stimulated emission is the important field of fundamental research. Many researchers have suggested their views for TL mechanism for pure and impurity activated materials. With expanding knowledge of solid state physics, it is a topic of research to give latest plausible mechanism of TL.However, the present understanding of TL has explored very high application potential of it in various fields. The modernization and development in the instrumentation; and better understanding of TL have helped the professional to solve their problems in many fields.

Applications of thermoluminesence ;

1) Geology
2) Archaeol1ogy
3) Forensic science
4) Solid state physics
5) Radiation physics
6)Space science
7) Radiation dosimeter
8) Medical science
9) Biology
10)Exploration Petroleum of Product from earth crust

1.4 General Thermoluminesence Properties of $CaSO_4$:Dy (TLD-900)

The interest in calcium sulphate dosimeters has an even longer history and variants of the material have been proposed and demonstrated since the late 1960s. In this case the material differs significantly from body tissue in terms of effective atomic number and so the applications will rarely include personnel monitoring as one function.

However , in other roles , such as the monitoring of background radiation from natural source the essential property of the dosimeter is its very high sensitivity. Here the $CaSO_4$:Dy , $CaSO_4$:Tm ,or some more recent versions of the dosimeter , is excellent since they have response which is some 30 times greater than TLD-100 . In all cases the dosimeters have a linear response over the range of interest for personnel monitoring and saturation and non-linearity factors do not need to be considered until > 10Gy. $CaSO_4$ is called as TLD-900.[3]

Calcium sulphate doped with dysprosium or thulium is excellent thermoluminescent phosphors for dosimetry of ionizing radiations due to their high sensitivity, wide dose range (from 10^{-6} to 1 Gy), relatively simple trap structure, good chemical, thermal and physical stability and ease of preparation. At present, they are among the most sensitive thermoluminescence (TL) dosimeter [materials so that their application to the measurement of small doses (environment, space dosimetry, radiation dosimetry at nuclear power plants, TL-dating, and so on) is extensive. [4] $CaSO_4$ suitable anneal temperature is between 400 ^{0}C to 700 ^{0} C

CHAPTER 2

THEORY OF THERMOLLUMINESCENCE IN SOLID

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. 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 identifying 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 are featured by different activation energies.

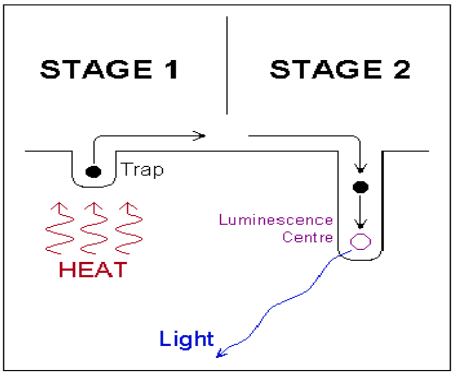


Figure 2.1 The phenomena of thermal excitation of luminescence.

According to 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.

2.1 The one trap-one recombination centre model

An explanation of the observed TL properties can be obtained from the energy band theory of solids. In an ideal crystalline semiconductor or insulator most of the electrons reside in the valence band. The next highest band that the electrons can occupy is the conduction band, separated from the valence band by the so-called forbidden band gap. The energy difference between the delocalized bands is Eg. However, whenever structural defects occur in a crystal, or if there are impurities within the lattice, there is a possibility for electrons to possess energies which are forbidden in the perfect crystal. In a simple TL model two levels are assumed, one situated below the bottom of the conduction band and the other situated above the top of the valence band (see Fig. 2.2). The highest level indicated by T is situated above the equilibrium Fermi level (E_f) and thus empty in the equilibrium state, i.e. before the exposure to radiation and the creation of electrons and holes. It is therefore a potential electron trap. The other level (indicated by R) is a potential hole trap and can function as a recombination centre. The absorption of radiant energy with $h \geq E$g results in ionization of valence electrons, producing energetic electrons and holes which will, after thermalisation, produce free electrons in the conduction band and free holes in the valence band (transition a). The free charge carriers recombine witheach other or become trapped. In the case of direct ($<10^{-8}$s) recombination an amount of energy will be released which may excite a luminescent centre (which may coincide with the recombination centre). The luminescent centre relaxes (returns to the ground state) under the emission of light. The phenomenon of direct recombination of free electrons and holes under emission of light is called adioluminescence. However, in semiconductors and insulators a certain percentage of the charge carriers is trapped: the electrons at T and the holes at R (transition b) .

The probability per unit time of release of an electron from the trap is assumed to be described by the Arrhenius equation;

$$p = sexp\left(-\frac{E}{kT}\right) \qquad (2.1)$$

where p is the probability per unit time. S is called the. frequency factor or attempt-to-escape factor. E *is* called the trap depth or activation energy. K is Boltzmann's constant = 8.617×10^{-5} eV/K, and T the absolute temperature. If the trap depth $E >> k\ T_0$, with T_0 the temperature at irradiation . [2]

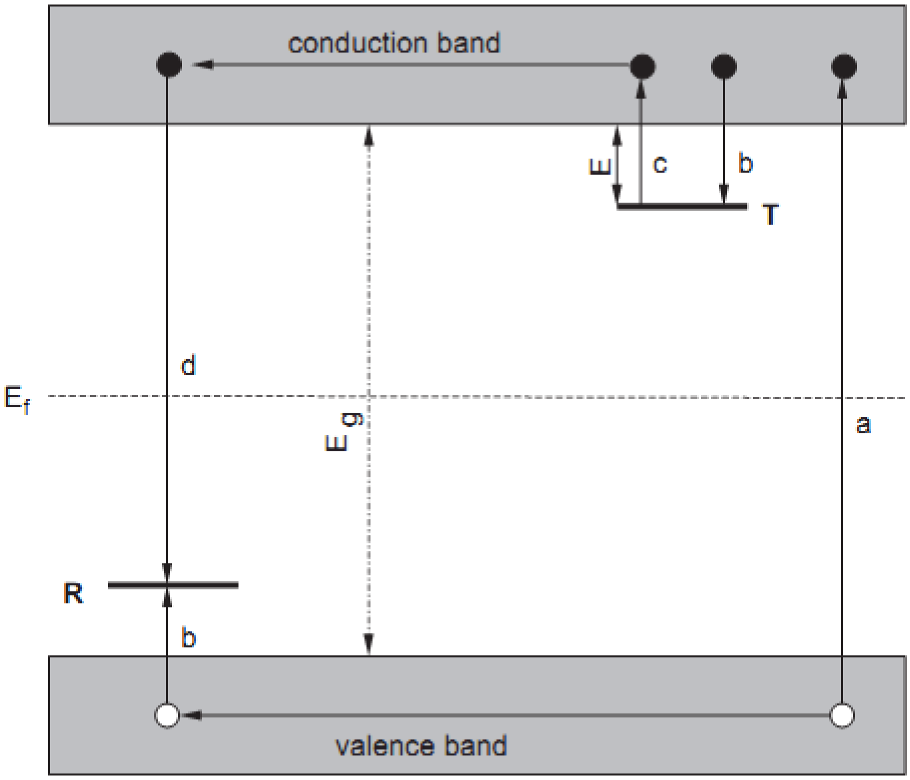


Fig: 2.2. Energy band model showing the electronic transitions in a TL material according to a simple two-level model: (a) generation of electrons and holes; (b) electron and hole trapping; (c) electron release due to thermal stimulation; (d) recombination. Solid circles are electrons, open circles are holes. Level T is an electron trap, level R is a recombination centre, E_f is Fermi level, Eg is the energy band gap. R is a recombination centre. [2]

If the concentration of holes trapped at (R) is (m (m^{-3})), can be written the intensity of the thermoluminescence (TL) as the

$$I(t) = -\,dm/dt \qquad (2.2)$$

we suppose that a photon produces from all recombination in here 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).

$$I(t) = -dm/dt = n_c \, m \, A \tag{2.3}$$

A is constant. P is the probability of recombination. 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 ($n_c (N\text{-}n)A_r$),

$$-dn/dt = np - n_c(N - n) \tag{2.4}$$

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 $(N\text{-}n)A_r$) and the recombination rate, (n_c m A).

$$dn_c/dt = np - n_c\,(N - n)A_r - n_c mA \tag{2.5}$$

The assumption which is called by Chen and McKeever. This assumption at any time

$$\left|\frac{dn_c}{dt}\right| \ll \left|\frac{dn}{dt}\right|, \left|\frac{dn_c}{dt}\right| \ll \left|\frac{dm}{dt}\right| \tag{2.6}$$

is an important assumption;

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

$$n_c + n = m \tag{2.7}$$

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

$$I(t) = -\,dm/dt \approx -dn/dt \tag{2.8}$$

When (dn_c/dt) is approximately equal to zero, one can get from the equation (2.3) and the equation(2.4) is ;

$$I(t) = (mAns \exp\{-E/kT\})/((N - n)A_r + mA) \tag{2.9}$$

2.2 First-Order Kinetics

The most simplified mathematical model which describes the above process was first given by Randall and Wilkins (1945 a,b) [9]. Consider a material containing defects which give rise to a single electron trap level, having trap depth or activation energy E containing n electrons at time r and at temperature T (in Kelvin). The energy distribution of electrons within the trap will be described by Boltzmann distribution, and hence the probability p of release of an electron from the trap is given by the Arrhenius equation,

$$p = s\,exp\left(-\frac{E}{kT}\right) \tag{2.10}$$

Where, k is Boltzmann's constant and s is a frequency factor or attempt to escape factor having value in the order of the lattice vibration frequency, namely 10^{12}-1014s^{-1}. The rate of release of electrons from the trap is

$$-\frac{dn}{dt} = nsexp\left\{-\frac{E}{kT(t)}\right\} \tag{2.11}$$

Randall and Wilkins assumed that all electrons released from traps undergo TSL transitions, i.e., there is no retrapping. This leads to the concept that the rate of release is proportional to the trapped charge concentration, and thus termed a "first-order" reaction. The intensity of the TSL glow, I(t) depends on the rate of release of electrons from traps and their rate of arrival at luminescence centers:

$$I(t) = -C(dn/dt) = Cnsexp(-E/kT) \tag{2.12}$$

where C is a constant related to luminescence efficiency.

$$\beta = dT/dt \tag{2.13}$$

Equation (2.11) becomes,

$$(dn/dT) = -(1/\beta)\ ns\ exp\ (-E/kT) \tag{2.14}$$

On integration, we get

$$\ln\left(\frac{n}{n_0}\right) = -\int\left(\frac{1}{\beta}\right) sexp\left(\frac{E}{kT}\right) dT \tag{2.15}$$

where n_0 is the number of electrons present in the trap at time t_0 and temperature T_0. Finally, substituting for n in equation (2.12),

$$n\frac{s}{\beta}exp\left\{-\frac{E}{kT}\right\} \times exp\left\{-\frac{s}{\beta}\int_{To}^{T} exp\left\{-\frac{E}{kT}\right\} dT\right\} \tag{2.16}$$

This is the expression for the glow intensity I from electrons trap at a single trapping level E. It is a Randall and Wilkins expression for first order (monomolecular) kinetics. The plot of I against T is termed as glow curve. The glow curve has a characteristics asymmetric shape being wider on the low temperature side than on the high temperature side. The condition of maximum intensity can be found by differentiating equation (2.16) with respect to T and equating the derivative to zero (i.e. (dI/dT) T=Tm = 0) which yields,

$$\frac{\beta E}{kT_m^2} = s\ exp\left\{-\frac{E}{kT_m}\right\} \tag{2.17}$$

where Tm is glow peak temperature. From equation (2.10) and (2.17) it is concluded that greater the value of E and smaller the value of s, the greater is the thermal stability of the trapped electrons and hence the higher is the temperature of the glow peak.

2.3 Second Order Kinetics

A modification of this view was presented by Garlick and Gibson (1948) [22], who used this same one-trap, one-recombination center model but who included the concept of significant retrapping of the released charges. This leads to the rate of the reaction being proportional to the square of the rapped charge concentration, and thus, we have a “second-order” reaction. Here we have

$$\frac{dn}{dt} = -n^2 s' exp\left(-\frac{E}{kT}\right) \tag{2.18}$$

where, s` = s/N, and N is the total concentration of available electron traps. This leads to the Garlick-Gibson equation for TSL under second-order kinetics,

$$I(T) = \frac{n_0^2\, s' exp\left[-\frac{E}{kT}\right]}{\left[1 + \frac{n_0 s'}{\beta} \int_{T_0}^{T} exp\left(-\frac{E}{kT}\right) dT\right]^2} \tag{2.19}$$

The main feature of these equations is that the glow is nearly symmetric, with the high temperature half of the curve slightly broader than the low temperature half. This can be understood from the consideration of the fact that in the second order reaction , significant concentrations of released electrons are retrapped before they recombine in this way giving rise to a delay in the TSL and spreading out of the emission over a wider temperature range.

2.4 General Order Kinetics

The Randall-Wilkins and Garlick-Gibson forms of TSL equation have been derived with the use of specific assumptions concerning the relative values of the retrapping and recombination probabilities. However, when these simplifying assumptions do not hold, the TSL peak will fit neither first- nor the second order kinetics. May and Partridge (1964) gave the following empirical expression for general order TSL kinetics[9]

$$I(t) = -\frac{dn}{dt} = n^b s' exp\left(-\frac{E}{kT}\right) \quad (2.20)$$

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

$$I(T) = \frac{s''}{\beta} n_0 exp\left\{-\frac{E}{kT}\right\}\left[1 + (b-1)\frac{s''}{\beta}\int_{T_0}^{T} exp\left\{-\frac{E}{kT'}\right\} dT'\right]^{-b/(b-1)} \quad (2.21)$$

Where, s`` = s`n$_0$ $^{b-1}$ with units s$^{-1}$. The above equation includes the second- order case (b=2) and reduces to equation (2.16) when b= 1. It should be noted that the dimensions of s` is m $^{3(b-1)}$s^{-1} which means that the dimension changes with the order of kinetics b. Thus, it is difficult to interpret s` physically.

The theoretical mechanism discussed above is related only to electrons trapped at a single trapping level. In real phosphors many different trapping levels will be present, each one due to a particular lattice defect or complex of defects. Each trapping level will give rise to an associated glow peak maximum, which may or may not be resolved during readout. The area and peak height of each glow peak depends on number of associated electron traps present. This in turn depends on the number of lattice defects and, for real phosphors, on the type and amount of impurity atoms present, as well as on the thermal history and treatment of the material.

2.5 Methods For Thermoluminescence

In this thesis is used four methods . Using methods are peak shape method , CGCD method , heating rate method and three point method.

2.5.1 Three Point Method

Recently, the method of the three point analysis was improved by Rasheedy [10] 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,

$$b = \frac{T_y[T_x - T_z]\ln(y) - T_z[T_x - T_y]\ln(z)}{T_y[T_x - T_z]\ln[A_x / A_y] - T_z[T_x - T_y]\ln[A_x / A_z]} \tag{2.22}$$

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 (2.3). 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

$$E_a = \{\ln y - b\ln[A_x / A_y]\}\{\frac{kT_xT_y}{T_x - T_y}\} \tag{2.23}$$

or by

$$E_a = \{ln\, z - b\, ln[\, A_x \,/\, A_z\,]\}\{\, \frac{kT_xT_z}{T_x - T_z}\, \} \tag{2.24}$$

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

$$s = (\beta E_a / kT_m{}^2)exp(E_a / kT_m), \tag{2.25}$$

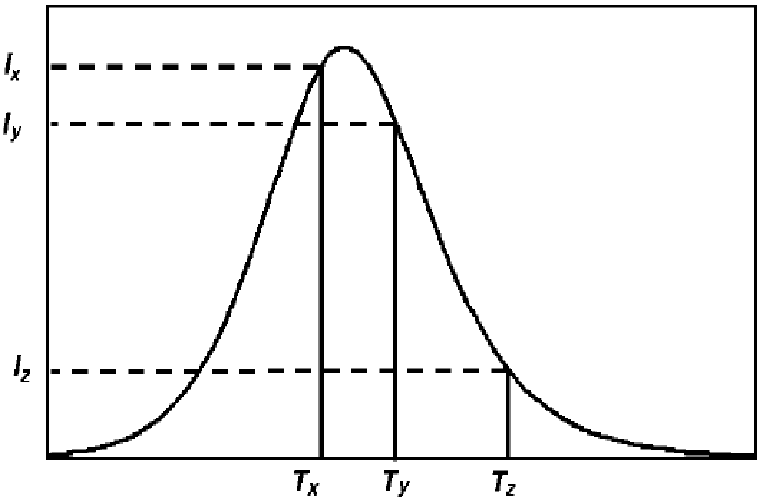


Figure 2.3 An isolated thermoluminescence (TL) glow peak. The parameters *Ix*, *Iy*, *Iz*, *Tx*, *Ty*, and *Tz* are as defined in the text [10].

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

$$s'' = \frac{\beta E_a \, exp(\, E / kT_m \,)}{[\, bkT_m^{\;2} \,] - (\, b-1)E_a \Phi \, exp(\, E_a / kT_m \,)}, \tag{2.26}$$

Where

$$\Phi = \int_{T_o}^{T_m} exp(\, -E_a / kT' \,)dT' \tag{2.27}$$

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

$$n_0 = \frac{I_m \, exp(\, E_a / kT_m \,)}{s''} \left[\frac{bkT_m^{\;2} s''}{\beta E_a \, exp(\, kT_m \,)} \right]^{\frac{b}{b-1}} \tag{2.28}$$

2.5.2 Peak Shape Method

Peak shape method has been developed by Chen [6], after Halperin and Braner’s adjusted the equations [11] to calculate the values of (E);

$$
\begin{aligned}
E_\tau &= \left[1.51+3(\mu_g-0.42)\right]\frac{kT_m^2}{\tau}-\left[1.58+4.2(\mu_g-0.42)\right]2kT_m \\
E_\delta &= \left[0.976+7.3(\mu_g-0.42)\right]\frac{kT_m^2}{\delta} \qquad (2.29) \\
E_\omega &= \left[2.52+10.2(\mu_g-0.42)\right]\frac{kT_m^2}{\omega}-2kT_m
\end{aligned}
$$

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.

$$
\begin{aligned}
s &= \frac{\beta E}{kT_m^2}\ \exp\left[\frac{E}{kT_m}\right] \\
s &= \frac{\beta E}{kT_m^2}\left[\exp\left(-\frac{E}{kT_m}\right)(1+(b-1)\frac{2kT_m}{E})\right]^{\frac{b}{b-1}}
\end{aligned}
\qquad (2.30)
$$

2.5.3 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 [12] and Kitis et al [13] proposed approximate functions for the Randall-Wilkins [9] expression of the first order of a single glow peak under linear heating condition. In addition, their approximate functions yield minute values of the activation energy within (3%) of the correct values was shown by Kitis et al [13].

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,

$$I(T) = n_0 s \exp(-\frac{E}{kT}) \exp\left[(-\frac{s}{\beta}\frac{kT^2}{E} \exp(-\frac{E}{kT}) * (0.9920 - 1.620\frac{kT}{E_a}) \right] \qquad (2.31)$$

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

$$I(T) = n_0 s \ \ \exp(-\frac{E}{kT}) \left[1 + (-\frac{(b-1)s}{\beta}\frac{kT^2}{E} \exp(-\frac{E}{kT}) * (0.9920 - 1.620\frac{kT}{E_a}) \right]^{\frac{b}{b-1}} \qquad (2.32)$$

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 ($^0Cs^{-1}$)) 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 :

$$I(T) = \sum_{i=1}^{n} I_i(T) + a + b\exp(T) \qquad (2.33)$$

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 (2.33), 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,

$$FOM = \sum_{i=1}^{n} \frac{|N_i(T) - I(T)|}{A} = \sum_{i=1}^{n} \frac{|\Delta N_i|}{A} \qquad (2.34)$$

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 [12].

It can be said that if 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,

$$X(T) = \frac{N_i(T) - I_i(T)}{\sqrt{I_i(T)}} \qquad (2.35)$$

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

2.5.4 Heating Rate Method

Various heating rates are another important method to determine (E), and the peak temperatures will be different when heating the sample at two various heating rates (β_1) and (β_2). It can be written the above equation (2.36) 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)

$$E = k\frac{T_{m1}T_{m2}}{T_{m1} - T_{m2}}\ln[(\frac{\beta_1}{\beta_2})(\frac{T_{m2}}{T_{m1}})^2] \qquad (2.36)$$

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.

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

$$\ln(\frac{T_m{}^2}{\beta}) = (\frac{E}{k})(\frac{1}{Tm}) + cons\tan t \qquad (2.37)$$

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).

CHAPTER 3

EXPERİMENTAL PROCEDURE

3.1 Experimental Procedure and Equipments

The material that was performed in this study was $CaSO_4$: Dy (TLD 900) from Thermo Electron Corporation. The dimensions of this sample are (1.8 x 1.8 x 0.35 mm^3) . Before next irradiation, the samples were first annealed to wipe any remaining information and then cool rapidly in the air at (75 ^oC/min) to the temperature of the room. For this reason $CaSO_4$: Dy (TLD 900) samples were annealed at (400 ± 1 ^oC) 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 ^oC). 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[20].

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 aluminum, 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 [9] . 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. [21]

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).

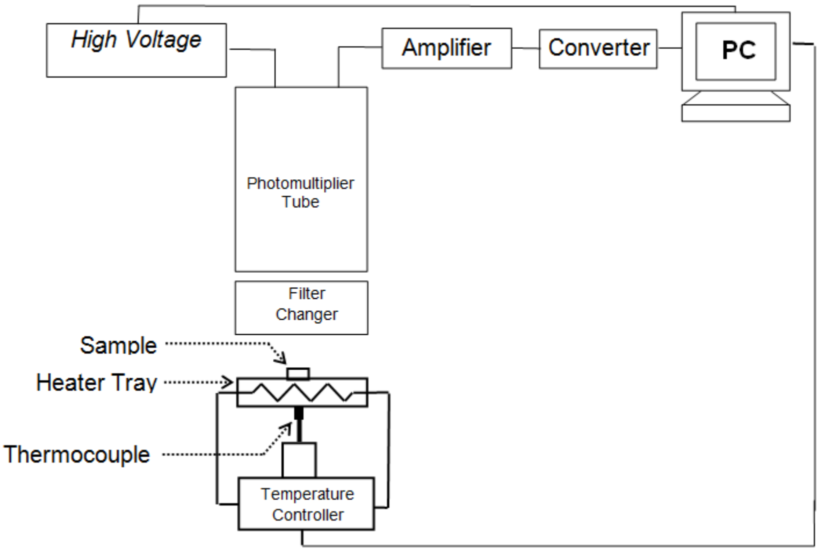


Figure 3.1 Basic block diagram of TL reader [9].

(a)

(b)

(c)

Figure 3.2 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 [1]. The thermoluminescence (TL) event has been studied for ages. It has been done a great deal of study to get a better understanding and enhance the properties of the substances and also to grow a new thermoluminescence material. At the 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 [5].

The $CaSO_4$:Dy (TLD-900) crystals were irradiated at several doses between ≈0,04Gy and ≈3,5 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 Dy-doped with in $CaSO_4$ rising dose level The result of the additive dose experiments the measured glow curves were also utilized for calculating the trapping parameters for 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 [8]. Due to this way, readily, the shape parameter (μ_g) evaluate the b of a single peak, {$\mu_g = (T_2 - Tm)/(T_2 - T_1)$} 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[23] peak shape method in addition to Chen's peak shape method [6] which needs the previous information of the kinetics order.

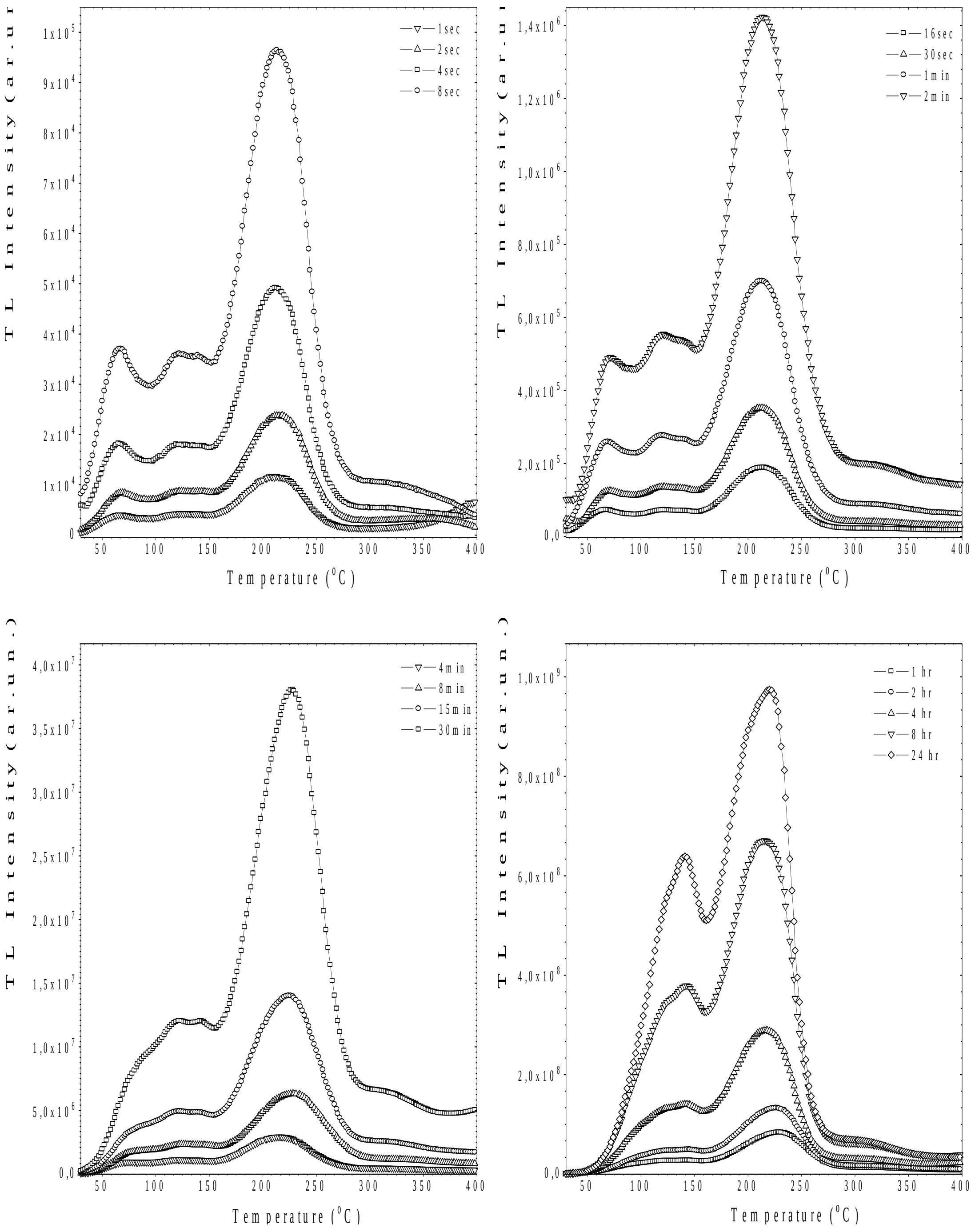


Figure:4.1 The glow curve of Dy-doped CaSO$_4$ (TLD-900) measured after different radiation exposed dose levels (β=1 ^{o}C/s).(1min. ≈ 2.4Gy)

The trapping parameters of TLD-900 crystal were also calculated by the Rasheedy's [8] three point method (TPM) by using the equation (2.24) to calculate the kinetic parameters.

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 $^{o}Cs^{-1}$ and 30 $^{o}Cs^{-1}$). 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 $CaSO_4$: Dy 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 [7]. The result of the trapping parameters calculated from the slopes and intercepts are given in the table 4.1.

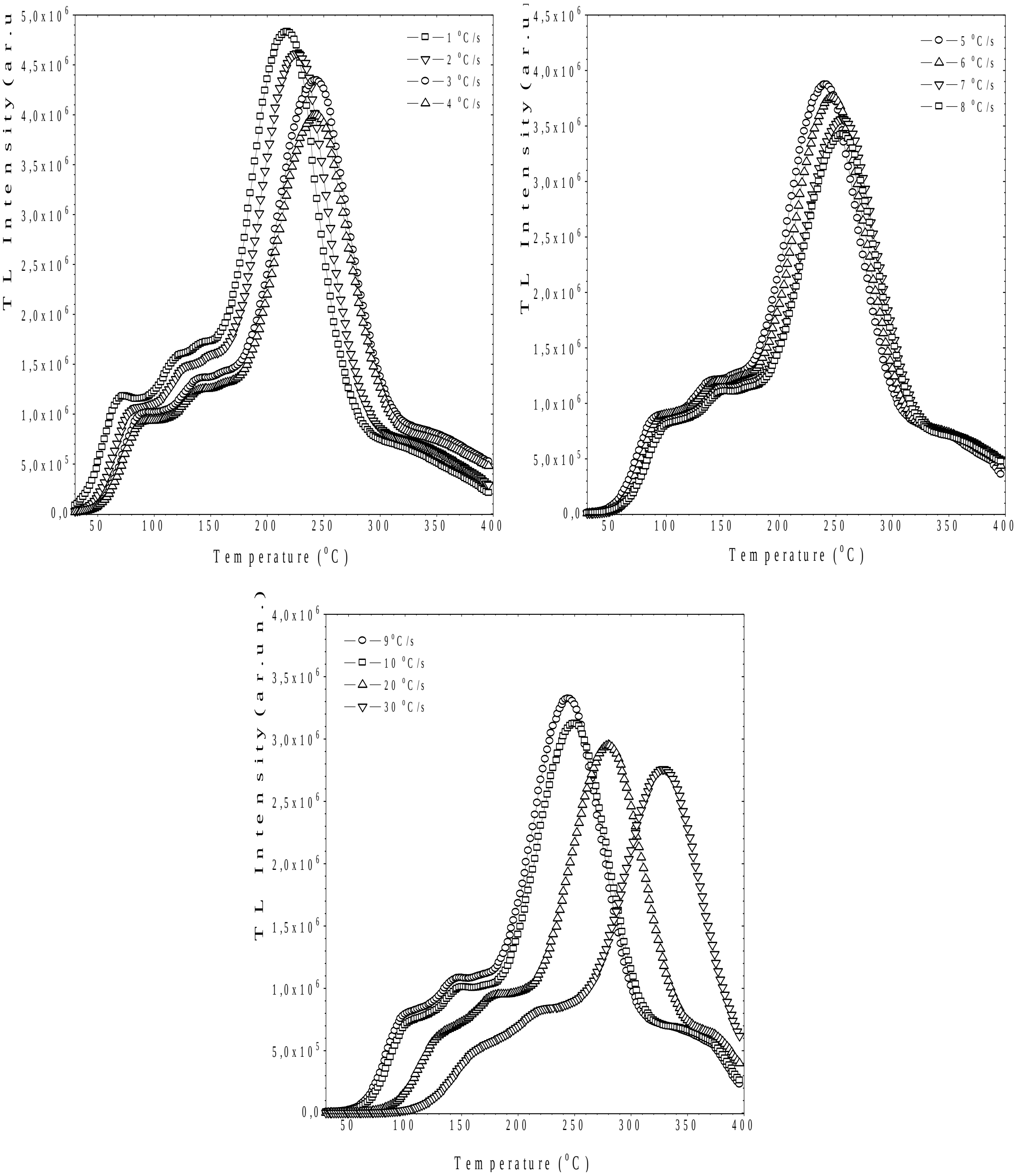


Figure 4.2 Some of the selected glow curves of Dy-doped $CaSO_4$ (TLD-900) measured at different heating rates for (1,2, 3,4,5,6,7,8,9,10,20, 30 °C/s).

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 [8]. 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, this technique can be used for 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. [15]

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[19]. 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 [14].

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. [16]

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 $CaSO_4$:Dy. 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[17] . 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).

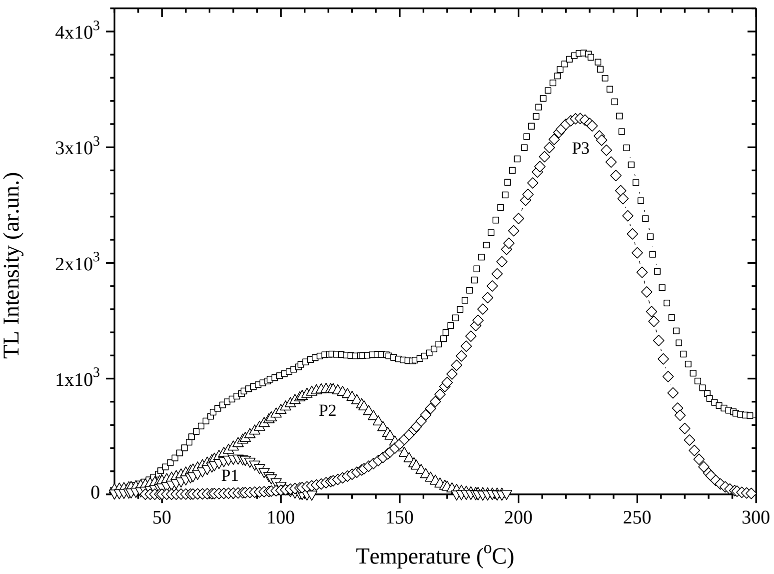


Figure 4.3 The CGCD analyzed glow curves of $CaSO_4$:Dy measured after 72 Gy irradiation by beta ray at room temperature.

We have also studied in this thesis the storage time effect on the intensity of the glow peaks of $CaSO_4$:Dy. For this experiment, the material was annealed at 400 ± 1 °C for 30 min and irradiated up to 12 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. [18] The main glow peak (P3) of TLD-900 at the end of the scheduled storage times reduced typically 15.7 % of its original value. According to the result of fading experiment reduced 7% end of first week , 11.2% end of second week , 15.7% end of third week and 26.8% end of fourth week.

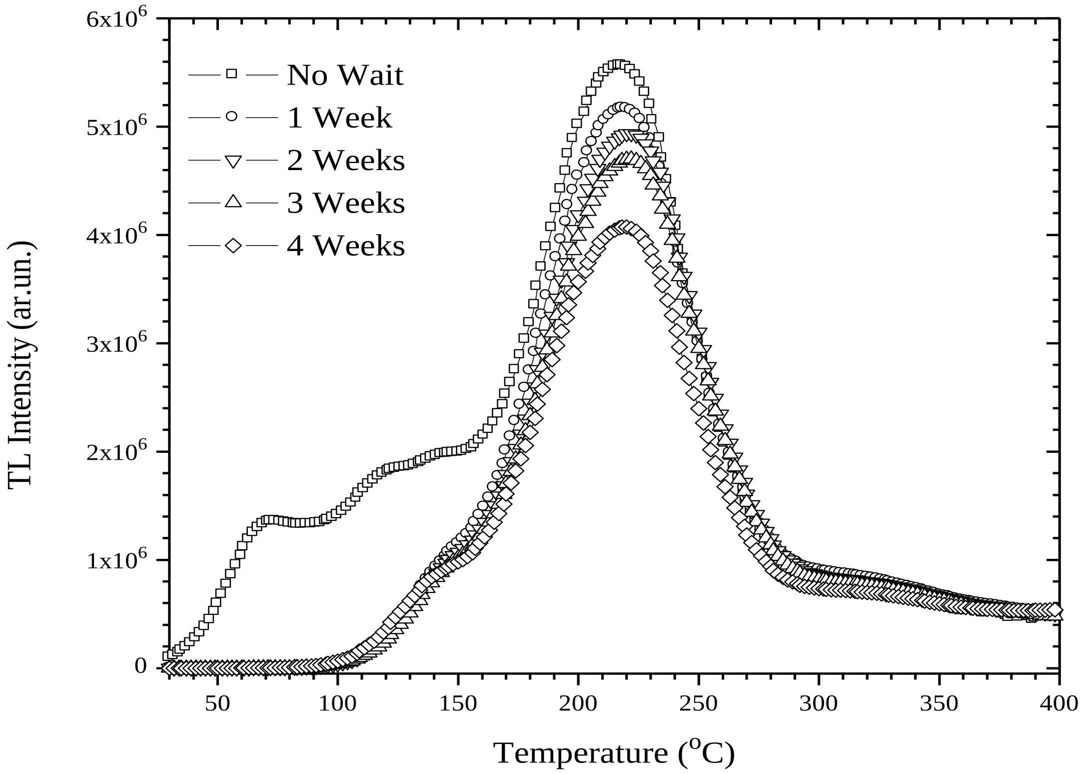


Figure 4.4 A set of TL glow curves for $CaSO_4$:Dy crystal measured after various storage periods at room temperature. Read out all glow curves at 1 °C/s after exposing to an irradiation of 12 Gy.

Table 4.1 The values of the trapping parameters of TL peaks of $CaSO_4$:Dy determined by Chen's PS, Mazumdar PS, TPM, VHR and CGCD methods.

TLD 900 **Tm= 225°C**	**Mazumdar P.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)	0.68	0.66	0.69	0.69	0.71	0.68	0.68	0.67	0.69
b	1	1	1	1	1	1	1	1	1
lns(s^{-1})	16.7	16.7	16.7	17	17	17	17.5	17.4	17.5

In this study have been used T_m= 225 ^{0}C due to maxsimum intesity of main dosimetric peak (P3) and parameters have been calculated.

CHAPTER 5

CONCLUSION

In this thesis was studied the trapping parameters called the kinetic order (*b*), activation energy (E_a) and the attempt to escape frequency factor (*s*) of Dy doped $CaSO_4$ (TLD-900) by using different 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. Furthermore, the fading characteristics of the glow curves of TLD-900 has been investigated at different time periods.

In order to explore the dose dependence characteristics of the glow curves of TLD-900, first of all additive dose (AD) experiments were employed. After the thermal treatment at 400 ^oC for 30 minutes, the TLD-900 crystals were irradiated at different dose levels between 0.04 Gy and 3.5 kGy 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 thermoluminesence 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 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 first order kinetics. After Chen's peak shape method, Mazumdar's peak shape method was applied by taking the 1/2, 3/4 and 4/5 of the maximum intensity of the glow peak. The results of this method has shown that has a first order $CaSO_4$ (TLD-900) glow peak at 225 ^oC and having activation energy of nearly 0.68 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.

To evaluate the kinetic parameters also Rasheedy's three points technique was also used the maximum intensity of main dosimetric peak 225^{o}C and the calculated values for the kinetic order, frequency factor and activation energy are; 1, 83x10^7 s^{-1} and 0.68 eV respectively.

For the storage time experiment TLD-900 sample was annealed at 400 ± 1 ^{o}C for 30 minutes than, 0.2 kGy 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 at the $CaSO_4$ (TLD-900) end of the different storage periods are shown in Figures 4.4

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