GENERAL ORDER KINETICS THERMOLUMINESCENCE BEHAVIOR OF ZINC OXIDE

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This is to certify that the thesis prepared by **GETACHEW MELAKU** Graduate Studies entitled "**GENERAL ORDER KINETICS THERMOLUMINESCENCE BEHAVIOR Of ZINC OXIDE** " in fulfillment of the requirements for the degree of **Master of Science** complies with the regulations of the University and meets the accepted standards with respect to originality and quality. .

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Abstract

In this thesis,the thermoluminescence glow curves of zinc oxide has been investigate theoretically in view of general order kinetics.The effects of various thermoluminescence kinetic parameters such as the activation energy(E),the frequency factor(s),the order of kinetics(b)on the properties of the glow curves and the variation of concentration of electron in the trap has been studied. As activation energy increases the glow curve shifts to higher temperatures with a decrease in the height. For higher E values or deeper traps more energy or higher temperature is needed to release the charge carriers. Therefore, similar changes can be noticed as the parameter s is varied but now in the opposite way: As frequency factor s increases the peak shifts to lower temperatures with an increase of the height and a decrease in width. A trapping center with a high frequency factor needs less energy or it needs lower temperature to free a charge carrier.

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Chapter 1

Introduction

1.1 Background of The Study

Luminescence is the emission of light by a material as a consequence of absorption of energy. A material that emits light is called luminescent material. It is a cooler and more efficient mechanism of light emission. In luminescence, the light output per unit energy input is much greater than in the case of incandescence. Luminescence is produced by the selective excitation of the atomic or molecular energy levels. Excitation takes the atom or the molecule to a higher energy state[1]. Its fall to ground state results in the emission of light, which is called luminescence. Excitation takes place usually by UV light .Based on excitation there are different types of luminescence. TL is one of a large family of luminescence. Thermoluminescence (TL) is a luminescence phenomenon of an insulator or semiconductor which can be observed when the solid is thermally stimulated. TL should not be confused with the light spontaneously emitted from a substance when it is heated to incandescence. Thermoluminescence is the thermally stimulated emission of light following the previous absorption of energy from radiation. The absorption of energy from an ionizing radiation by an insulator or semiconductor material causes the excitation of free electrons and free holes

and the subsequent trapping at defects (meta stable states). After irradiation the sample is heated such that thermal energy causes the liberation of charge carriers (say, electrons) which are then able to recombine with charge carriers of the opposite sign (thermally stimulated relaxation).In the thermoluminescence heat is not exiting agent,but it acts only as a stimulant.Light is emitted in a series of discrete maxima as the sample temperature.Each maximum in the light intensity corresponds to certain energy of trapped electron. A thermoluminescent material is the material that during exposure to ionizing radiation absorbs some energy, which is stored. The stored energy is released in the form of visible light when the material is heated. Note that TL does not refer to thermal excitation, but to stimulation of luminescence in a sample which was excited in a different way. This means that a TL material cannot emit light again by simply cooling the sample and re-heating it another time. It should first be re-exposed to ionizing radiation before it produces light again. The storage capacity of a TL material makes it in principle suitable for dosimetric applications. In general Phosphor research delivered promising results for several new applications in know days science and technology including, display medium and dosimetry. zinc oxide is nowadays becoming popular to bring in a great attention and has being studied due to its outstanding optical properties and potential applications in a variety of devices such as, LEDs , bio-sensors , UV detectors , gas sensors and nano-generator, zinc oxide present a reasonably high thermal conductivity, a good enough mechanical hardness,large exciton binding energy, a high electron mobility,high thermal conductivity,a good transparency, wide and direct band gap(3.37ev). In addition to all the aforementioned interesting properties, zinc oxide has much higher energy transfer efficiency than other semiconductor and , this makes it an interesting material for

luminescence. Although studies on the structural and optical properties of zinc oxide crystals have been made. In this work, the investigation of luminescence properties of zinc oxide phosphor is present and important TL kinetic parameters such as activation energy (E) and the frequency factor (s) was determined by using rate equation approach.

1.2 Statement of The Problem

Zinc oxide is extensively studied because of its excellent optical properties and potential applications in a wide a variety of devices. However, the theoretical investigation of the TL properties of Zinc oxide is not reported in the literature to the best of our knowledge. Therefore, in this work we focus on the theoretical study of its Thermoluminescence properties, effect of heating rate, activation energy and frequency factor of zinc oxide in view of general order kinetics.

1.3 Research Questions

- ✓ What is the effect of heating rate on the thermoluminescence glow curves of zinc oxide in view of general order kinetics?
- ✓ What is the effect of frequency factor on the thermoluminescence glow curves of zinc oxide in view of general order kinetics?
- ✓ What is the effect of activation energy on thermoluminescence glow curves of zinc oxide in view of general order kinetics ?
- ✓ What is the effect of order of kinetics on the thermoluminescence glow curves of zinc oxide in view of general order kinetics?

1.4 Objectives of The Study

1.4.1 General Objectives

The general objective of this study is :-

To investigate theoretically the thermoluminescence behavior of zinc oxide with linear heating rate in view of general order kinetics.

1.4.2 Specific Objectives

The specific objectives of this study are:

- ✓ To identify the effect of activation energy on the glow curves of zinc oxide in view of general order kinetics.
- ✓ To determine the effect of frequency factor on Thermoluminescence glow curves of zinc oxide in view of general order kinetics.
- ✓ To determine the effect of heating rate on the glow curves of zinc oxide in view of general order kinetics.
- ✓ To describe the effect of activation energy on the concentration of electrons in traps of zinc oxide in view of general order kinetics.
- ✓ To identify the effect of frequency factor on the electron concentration in traps of zinc oxide in view of general order kinetic.
- ✓ To determine the effect of heating rate on the electron concentration in traps of zinc oxide in view of general order kinetics.

✓ To investigate the effect of order of kinetics on the thermoluminescence glow curves of zinc oxide.

1.5 Scope of The Study

The scope of the study is limited to theoretically investigate the properties, effect of heating rate, on the material zinc oxide phosphor by using rate equation in view of general order kinetics.

1.6 Limitation of The Study

Due to lack of suitable apparatus that helps practical measurements, the study is depend on the theoretical calculation and the scope the study is limited to investigate the properties, effect of heating rate on zinc oxide phosphor by using rate equation in view of general order kinetics.

1.7 Thesis Outline

This study contains five chapters and organized as follows:Chapter 2 deals with the theoretical back ground on luminescence in general and the concepts,application,different model of thermoluminescence. chapter 3 the methods of analysis of thermoluminescence glow curves. The main results of the study discussed in chapters 4 and 5.

Chapter 2

Review Literature

2.1 Introduction

2.1.1 Luminescence

Luminescence is a collective term for different phenomena where a substance emits light without being strongly heated, i.e the emission is not simply thermal radiation [4]. This definition is also reflected by the term cold light. In the process of luminescence, when radiation is incident on a material some of its energy is absorbed and re-emitted as a light of a longer wavelength, a process known as Stokes law. In the process of luminescence, the wavelength of light emitted is characteristics of a luminescent substance and not on the incident radiation. The light emitted could be visible light, ultra-violet, or infrared light.This cold emission, i.e. luminescence, that does not include the emission of black body radiation involve two steps.The excitation of electronic system of a solid material to higher energy state and Subsequent emission of photons or simply light.The emission of light takes place at characteristics time τ_c

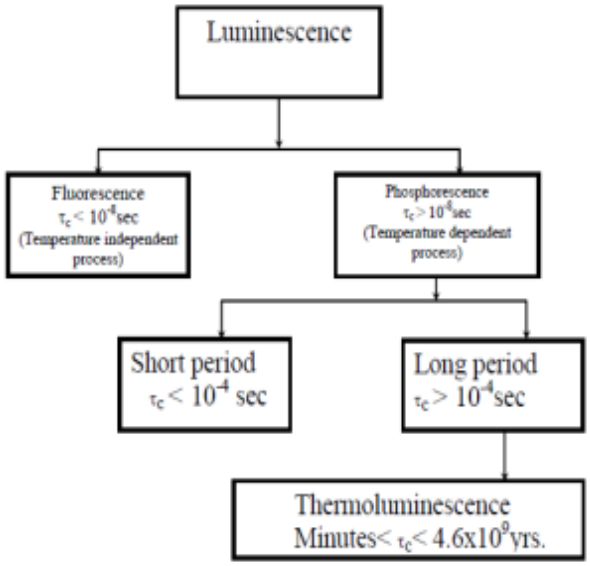

Figure 2.1: illustration of family tree of luminescence phenomena(Mckeever,1985(6))

after absorption of the radiation, this parameter allows us to sub-classify the process of luminescence into fluorescence and phosphorescence. The prefix to the term luminescence distinguishes between the modes of excitation, whilst the delay between excitation and emission τ_c fluorescence and phosphorescence. Thus, if $\tau_c < 10^{-8}$ s, then it is known as fluorescence; whereas if $\tau_c > 10^{-8}$s, then it is known as phosphorescence[9]. A large number of substances both organic and inorganic show the property of luminescence, but the principal materials used in various application of luminescence, involves inorganic solid insulating materials such as alkali and alkaline earth halides, quartz (SiO_2), phosphates, borates, and sulphate etc. Luminescence solids are usually referred to as phosphors.

2.1.2 Type of Luminescence

There are several varieties of luminescence, each named according to what the source of energy is, or what the trigger for the luminescence is, for example

- ✓ Chemiluminescence; The emission of light by the release of energy from a chemical reaction.
- ✓ Cathodluminescence; The light emission is a result of electron beam of excitation.
- ✓ Electroluminescence; Light is generated in response to applied electric field on ascertain material.
- ✓ Photoluminescence;Emission of light is the results of exciton by electron magnetic radiation(photon).
- ✓ Thermoluminescence;The luminescence activated thermally after initial irradiation by other means such as α, β, γ,x-ray.
- ✓ Radioluminescence; Light produced in a material by bombardment with ionizing radiation such as beta particles, x-ray, gamma ray.

2.1.3 General Characteristics of Luminescence

Luminescence emission may be explained by the transfer of energy from radiation to the excited state as shown in Fig. (a) (i) The emission of a luminescence photon takes place when an excited electron returns to its ground state as shown in Fig. (a) (ii) This is the process of fluorescence. In 1935, Jablonski gave the first explanation of temperature dependent phosphorescence by introducing a meta-stable level in the forbidden gap between the excited and ground states are shown in Fig (b).

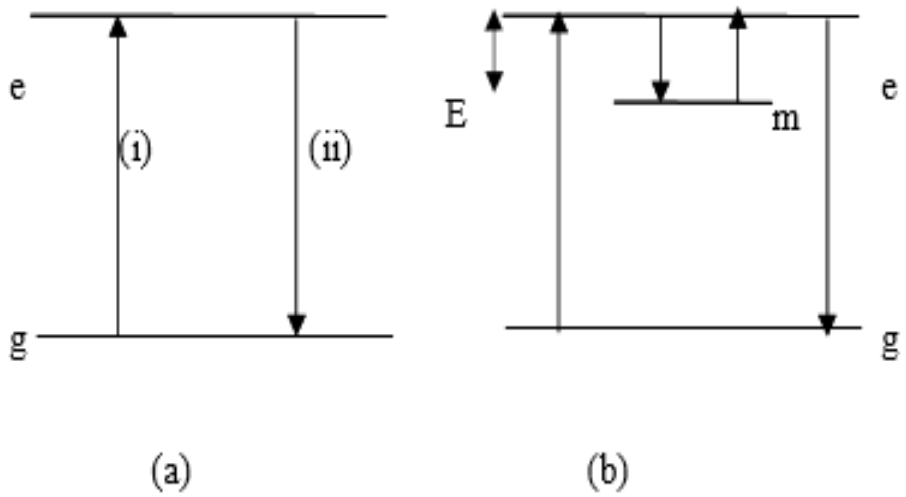

Figure 2.2: Fluorescence and phosphorescence,where e is excited state,g is ground state, m is meta-stable level and E is energy difference m and e.(mckeever,1985;Lars bØtter-Jensen 2000)

electron excited from the ground state to the excited state can be trapped in the meta-stable state until it is given enough energy to return to the ground state with emission of light[4]. Thus the delay observed in phosphorescence corresponds to the time the electron spends in the meta-stable state. The mean time spent in the trap at temperature T is given by;

$$\tau = s^{-1} e^{\frac{-E}{kT}} \tag{2.1.1}$$

2.1.4 Thermoluminescence

The term thermo luminescence, is a combination of two words -thermo, meaning heat and luminescence, meaning emission of light. Thermo luminescence also known as thermally stimulated luminescence (TLS) is the emission of light for insulator or semi

conductor which observed when the solid is thermal stimulated[6,10,12]. They are three conditions are necessary to obtain TL emission[6,12].

✓ The material must be an insulator or semiconductor.

✓ the material absorbed energy during exposure to radiation

✓ excitation of TL by exposure to ionizing radiations

2.1.5 Energy Band Model

The locations where electron and holes are caught up are called trap. A hole may be captured a location where positive charge or negative charge is excess. The binding energy of the trapped charge carriers is called the trap depth or the activation energy of the trap. A recombination center (RC) is an electron or hole trap in which the probability of recombination with an opposite sign charge carrier at the the site is greater than that of thermal excitation of the trapped carrier to its respective delocalized band [13]. Though the presence of impurities in general shifts recombination processes from direct to in direct transition it is difficult to predict the effect of individual impurities [14]. The role of an impurity as trap or recombination center dependent on the base combination of the material,the other impurities present the concentration of all impurities and oxidation will not necessarily act as recombination center in different material. Also,a recombination center that results in radiative recombination in a material produce non radiative recombination in other material [4,14]. An essential feature of all luminescence process in the change in occupance of the various localized energy sates to another,several kinds of transition are possible can some are disused below the interaction between an incident radiation and atoms luminescence material,

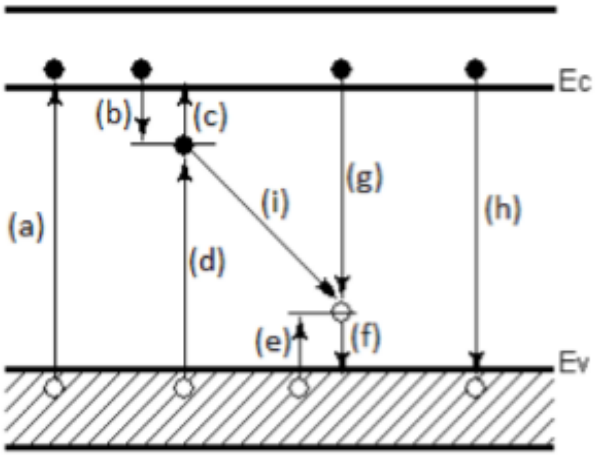

Figure 2.3: Schematic-illustration of common types of electronic transition involving the condition band E_c and valence band E_v.

may be described schematically using the energy band diagram as shown fig,In the figure,the letter denote that the following processes,(a) ionization;(b) electron(solid cirel) trapping;(c) electron release(de-trapping);(d) band-to-band recombination;(e) hole(open cirecle)Trapping;(f) hole release;(g) band-to-center recombination;(h) band to-band recombination;and(i) center-to-center recombination; respectively the primary interaction between ionizing radiation and the electronic structure atomic is the eventual formation of electron-hole pairs i.e transition (a),which can occasional become trapped as shown in transition (b) and(e), through heating these electron and holes can be stimulated in to migration.transitions(C) and(f) which can lead to electron-hole recombination. If light is emitted during the recombination process thermoluminescent occurs [6]. The are three distinct types of recombination processes are possible as shown in fig above

✓ band-to-band Transition(h)

✓ band-to-center Transition(d)and (g)

✓ center-to-center Transition (c)

band to band recombination is termed direct to electron in the conduction band recombining with hole in the the valence band(i.e an excited electron to the ground state). The band to center and center to center recombination process are termed in direct due to recombination involving localized levels that is transition from or a trap center [15].

2.1.6 Simple Models of Thermoluminescence

The simplest possible model that has been used to describe the process by which materials emitted light when heated consists of two localizes levels: an isolated electron trap and a recombination center. This approach is commonly called One-Trap-One Recombination center (OTOR) model . The simple scheme of one trap/one-center model The simple scheme of one trap/ one-center model is shown in fig consisting of two localized levels:one act as trap and other act as recombination center,filled of concentration from in trap(n),filled of concentration from in recombination center(m),recombination probability coefficient(A_{mn}),total concentration from in trap(N)and re-trapping probability coefficient(A_n). The traps are assumed to be electron traps and the recombination centers are hole traps. The traps and the recombination centers get filled up by the respective type of charge carriers following irradiation of the specimen. The electron are ejected out of the traps(de-trapped)and become free to move in the conduction band during the heating stage after absorption of enough energy.During the random motion of the electron in the conduction following irradiation and thermal release,the electron may recombine with holes trapped at recombination center(R)emitting light.Alternatively, the electrons may also fall back

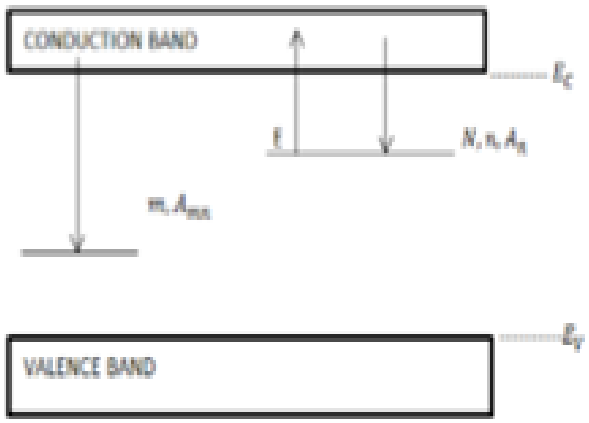

Figure 2.4: The allowed Transitions(thermal exciton, re-trapping and recombination).

into an empty trap. this is called re-trapping.Thus the transport of electron from the traps to the recombination centers to emit luminescence may be describe in terms of rate of excitation,re-trapping and recombination

$$R_{ex} = nse^{-}\frac{E}{kT} \tag{2.1.2}$$

$$R_{rex} = n_c A(N - n) \tag{2.1.3}$$

$$R_{rec} = n_c A n_h \tag{2.1.4}$$

Where , R_{ex}, R_{rex}, R_{rec}, respectively, are the excitation, ret- rapping and recombination rates, N and n, respectively, are the total and the filled concentration of the thermally active traps, n_c is the concentration of the charge carriers in the conduction band,n_h is the concentration of holes in the recombination center, E is the activation energy of the trap, which is also called the trap depth, T is the sample temperature is the Boltzmann constant, A and A_r, respectively, are the re-trapping and the radioactive recombination probability coefficients. The values of these coefficients depend

on the capture cross-sections δ and δ_r of the traps and the recombination centers, respectively, expressed as:

$$A = \delta v \tag{2.1.5}$$

$$A_r = \delta_r v \tag{2.1.6}$$

where v is the velocity electron in the conduction band. The physical scheme used in formulating any particular model of TL determines the value of n_h Since the overall charge neutrality condition should be ensured the value of n_h is the sum of all the filled traps in the sample, which means that the filled active traps n and any deeper level traps which are thermally not a ejected, at the given temperature T. The fraction η of the excited carriers which produces luminescence during heating stage is given by the following equation

$$\eta = \frac{R_{rce}}{R_{ret} + R_{rec}} \tag{2.1.7}$$

Here, η is also called the luminescence efficiency and its value strongly depends on the values of the parameters. However, the expression of η would change according to the applicable physical model since the denominator in increase depending on the existence of other possible routes of relaxation such as non-radioactive recapture in deeper level traps.Depinding on the values of the parameter the value of luminescence efficiency would be change.It there are addition routes of relaxation,for nano-radiative recapture in deeper levels Traps,these would add to denominator of the equation above the expression for luminescence efficiency would change according to the applicable physics model.

2.1.7 Expression For Evaluating The Kinetics

Absorption of radiant energy with energy greater than the band gap results in the ionization of valence electrons, producing energetic electrons and holes.After thermalization, produce free electrons in the conduction band and free holes in the valence band. The probability per unit time of release of electron from the traps is given by

$$p = se^{\frac{-E}{kT}} \tag{2.1.8}$$

E is called the trap depth or the activation energy i.e the energy needed to release an electron from the trap into the conduction band. k is the Boltzmanns constant. When the free electron absorbs enough energy, it to be released back into the conduction band, from where recombination is possible and accompanied by the release of a light emission [16]. where a is the generation of holes and electrons, b is the electron trapping, the c is hole trapping, the d is electron release by heating, the R is recombination center with light emission, E is the activation energy or trap depth, g is hole trap depth, E_f is Fermi level and thus empty in the equilibrium state, and E_g is forbidden energy. If N denotes the total concentration in the crystal concentration of filled traps in the crystal in m^{-3} at time t, and $n_h(t)$is the concentration of trapped holes in the recombination center in m^{-3} and the initial concentration of filled traps at time t = 0 is denoted by n_0 The intensity of TL, I(t) at any time t during heating is proportional to the rate of recombination at R is given by

$$I(t) = -\frac{dm}{dt} \tag{2.1.9}$$

where m is the concentration of the hole at R

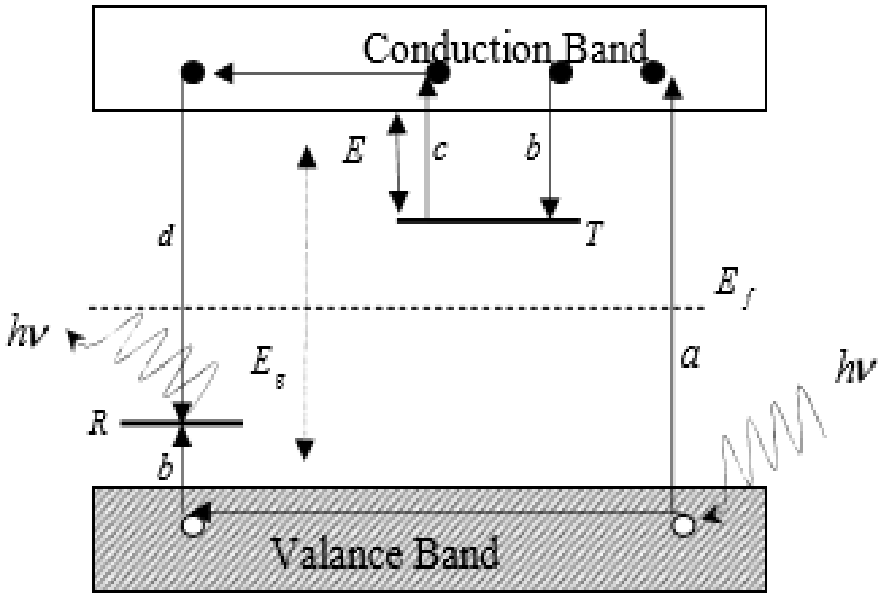

Figure 2.5: The simple level model for thermoluminescence proess(bos,2007)

2.1.8 Order Of Kinetics

Expressions for first,second,General-order TL kinetics in the equations in thermoluminescence processes have been given by Randall-wilkins,Garlick-Gibson and may partridge for first,second,general-order kinetics respectively.

$$I(t) = -\frac{dn}{dt} = nse^{\frac{-E}{kT}} \tag{2.1.10}$$

$$I(t) = -\frac{dn}{dt} = \frac{n^2}{N}se^{\frac{-E}{kT}} \tag{2.1.11}$$

$$I(t) = -\frac{dn}{dt} = n^2s'e^{\frac{-E}{kT}} \tag{2.1.12}$$

Where, s is the pre-exponential factor, n is concentration of the filled electron traps in the crystal, E is activation energy of the electron traps, s is frequency factor

of the electron trap, T is temperature k is Boltzmans constant Linear heating rate $dT = \beta dt$

2.2 Application Of Thermoluminescence

2.2.1 Defect Analysis 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 . 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. 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 recent research on defect analysis in various materials focuses on the determination of the position of the defect (trap) level just beneath the edge of the conduction band. This can be achieved through analysis of TL glow curves by employing various methods[32].

2.2.2 Radiation Dosimetry

TL has an interesting application in the field of radiation dosimetry. Its clear that the absorption of radiation increases the level of TL observed from 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 entrapping 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 TL may be used as a means of radiation dosimetry.

2.2.3 Archeology

The thermoluminescence output from the specimen is mostly attributed to Thermoluminescence sensitive mineral inclusions (mostly quartz) in the host clay matrix of the pottery fired in the kiln (TL clock for dating) sometime in the long past. That event is considered to be the starting of the Thermoluminescence clock for archaeological dating[35].

2.2.4 Geology

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 Thermoluminescence. This bleaching is effective enough to reduce Thermoluminescence level to a negligible value[33].

2.2.5 Forensic sciences

This 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 Thermoluminescence to some selected materials that are commonly encountered in the criminal cases (glass, soil, safe insulation materials etc)[34].

Chapter 3

Materials and Methodology

3.1 Materials

The study was purely theoretical. The main source of information were the published articles, books, the published thesis and manuscripts and dissertation carried out based on the project title. Softwares such as mathematica for plotting graph and computers for search information concerning with this work and for writing on, are additional instruments, which was used to accomplish the study.

3.2 Methodology

Analytical solution of the rate equations are achieved by assuming ret-rapping in case of general order kinetics, whereas, the consideration of re-trapping complicates the rate equations and hence numerical approaches are employed. Therefore, for numerical calculations, Mathematica Software used to determine the effect of heating rate, activation energy(E) and frequency factor(s) on thermoluminescence glow curves of zinc oxide in view of general order kinetics.

3.2.1 Computational(graphical)

The properties of Thermoluminescence of the material zinc oxide with linear heating rate was interpreted graphically with Mathematica.

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Chapter 4

Results and Discussion

4.1 General Order Kintics

May and Partridge (MP) suggested a more general expression for TL emission which would satisfy not only the first order and second order kinetics expressions when b = 1 and b = 2 respectively, but would also include all other possible values of b including its non-integral values between 1 and 2 or even outside this range. the following expression for TL intensity

$$I(T) = -\frac{dn}{dt} = n^b s' e^{\frac{-E}{kT}} \tag{4.1.1}$$

s' frequency factor b kinetics, Therefore, this expression for TL intensity is called general order kinetics. Rearranging

$$\frac{dn}{n^b} = -s' e^{\frac{-E}{kT}} dT \tag{4.1.2}$$

which gives by integration

$$n = n_0[1 + s' n_0^{b-1}(b-1)te^{\frac{-E}{kT}}]^{\frac{1}{1-b}} \tag{4.1.3}$$

can be written

$$n = n_0[1 + s''(b-1)te^{\frac{-E}{kT}}] \tag{4.1.4}$$

where s" =s'n_0^{b-1} The frequency factor s" is constant for a given does and would vary when the does is varied. The intensity is given by

$$I(t) = -\frac{dn}{dt} = s'n^b e^{\frac{-E}{kT}} = s''n_0 e^{\frac{-E}{kT}} x[1 + s''(b-1)te^{\frac{-E}{kT}}] \tag{4.1.5}$$

Assuming a Linear heating rate dT=γdt

$$n = n_0[1 + s''(\frac{b-1}{\beta}) \int e^{\frac{-E}{kT'}} dT']^{\frac{1}{1-b}} \tag{4.1.6}$$

The Temperature dependent expression for the TL glow peak,

$$I(T) = n_0^b s' e^{\frac{-E}{kT}}[1 + \frac{(b-1)n_0^{b-1}}{\beta} \int e^{\frac{-E}{kT}} dT']^{\frac{-b}{b-1}} \tag{4.1.7}$$

$$I(T) = s''n_0 e^{\frac{-E}{kT'}}[1 + s''(\frac{b-1}{\beta}) \int e^{\frac{-E}{kT'}} dT']^{\frac{1}{1-b}} \tag{4.1.8}$$

To get the parameter in general order kinetics the equation above can experienced in the for of

$$\frac{kT_m^2 bs''}{\beta E} e^{\frac{-E}{kT_m}} = 1 + s''\frac{(b-1)}{\beta} \int e^{\frac{-E}{kT'}} dT' \tag{4.1.9}$$

4.2 Thermoluminescence glow curve Properties of zinc oxide Phosphor

The nature of the glow peaks which are generated from the intensity of the emitted light as a function of temperature depends on the properties of the trapping states responsible for the material. To analyze the properties and effect of heating rate equation 4.1.8 and 4.1.6 is used and then we can generate by using the parameter E, s, n_o, and β after this we observed the following graphs(Fig.4.1, 4.2, 4.3, 4.4 and 4.5).Those figures describe briefly the properties of Thermoluminescence glow curves of zinc oxide Phosphor.

4.2.1 Effect of Activation Energy (E) on Thermoluminescence glow curves of zinc oxide phosphor

A crucial role is played by energy levels in the band gap of the material, introduced by defects in the crystal lattice (e.g vacancies or co dopants). These so-called traps are able to capture charge carriers originating from the luminescent centers (electrons in most cases, although hole trapping has been suggested for some material). These charge carriers remain trapped until enough thermal energy is available to help them escape and recombine at a luminescent center. The activation energy required for this is called the trap depth and is supposedly determined by the energy difference between the energy level of the trap and the conduction band (in the case of electron trapping) or the valence band (in the case of hole trapping). A trap which is too shallow (i.e too close to the conduction-or valence-band) will result in a very short afterglow; if the trap is too deep no charge carriers can escape at room temperature and no luminescence will be observed unless the temperature is raised. The Thermoluminescence intensity versus temperature as a function of temperature with different value of E. Calculations are carried out using equation (4.1.8) which has been generated by using Mathematica for the graph and the input parameters used are E =0.64 ev, 0.8 ev , 1 ev, $\beta = 0.2k/s$, $s = 2.35x10^{8}s^{-1}$, Initial concentration of trapped electron $n_o = 10^{10}cm^{-3}$. This is useful to determine the properties of Thermoluminescence glow curves of zinc oxide at different values of activation energy E and the other parameter is kept constant in these case.

The initial part of the Thermoluminescence glow curves for zinc oxide rises exponentially. In the initial rise part of the Thermoluminescence glow curves for zinc

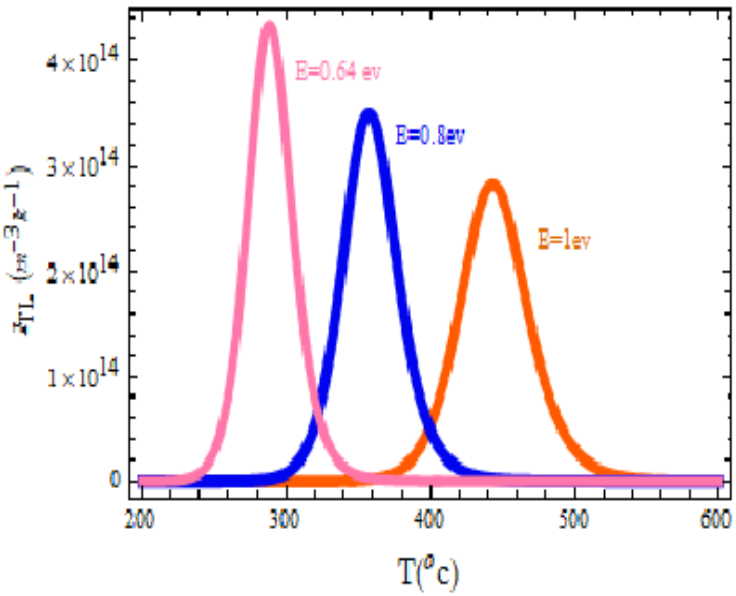

Figure 4.1: The Thermoluminescence Intensity of the glow curve of zinc oxide at three different E values for the b=1.8

oxide, the value of n may be considered constant at n_o which is the initial concentration of electrons in traps. The following are the properties of Thermoluminescence glow curves for zinc oxide at different activation energy:- activation energy E calculated in above given equation 0.64 ev , 0.8 ev, 1 eV and the other parameter are n_o=$10^{10} cm^{-3}$,s=$2.35 * 10^8 s^{-1}$,b=1.8,β=0.2k/s. As E increases the glow curve shifts to higher temperatures with a decrease in the height.From this shift to higher temperatures we understood physically by realizing that for higher E values or deeper traps more energy or higher temperature is needed to release the charge carriers and also, higher value of E means stronger binding of the trapped charge and higher thermal energy is needed to release it. It can be observed that with increase in the value of E the peak height is decrease.

4.2.2 the effect of order of kinetic on the thermoluminescence glow curves of zinc of zinc oxide

As order kinetic increase the height of the glow curves decrease and when kinetic order increase the glow curve shifts to higher temperatures with a decrease in the height.

From this shift to higher temperatures we understood physically by realizing that for higher kinetic order higher temperature is needed to release the charge carriers to re trapped.

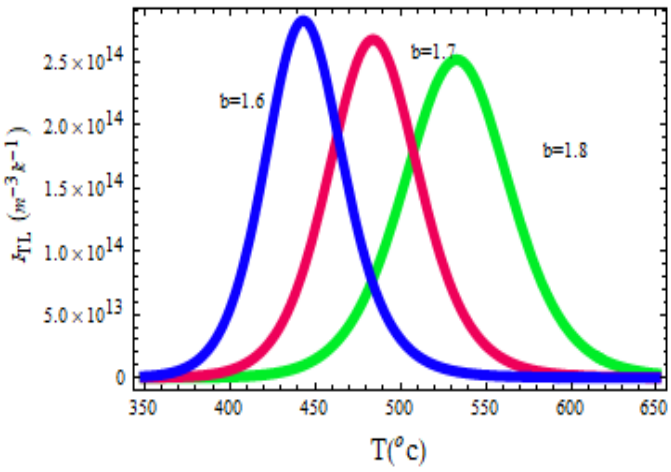

Figure 4.2: The Thermoluminescence Intensity of the glow curve of zinc oxide for b=1.6,1.7,1.8 and E=1evn_o=$10^{10}cm^{-3}$,s=$2.35*10^8s^{-1}$,b=1.8,β=0.2k/s.

4.2.3 Effect of frequency factor on Thermoluminescence glow curves of zinc oxide

Properties of TL glow curve for Zinc oxide Phosphor, showing the variation with the frequency factor . Parameter values we used are n_o=$10^{10}cm^{-3}$, E = 1 eV, β = $0.2^o k/s$,kinetic order of b=1.8 with different frequency factor (i,e $s_1 = 2.35X10^8$,s^{-1}, s_2 = =$1.71x10^8$, s^{-1}, s_3=$1.2x10^8 s^{-1}$) of in which parameter s is varied .

For given values of E and β, the glow peak shifts to lower temperature as s is in-

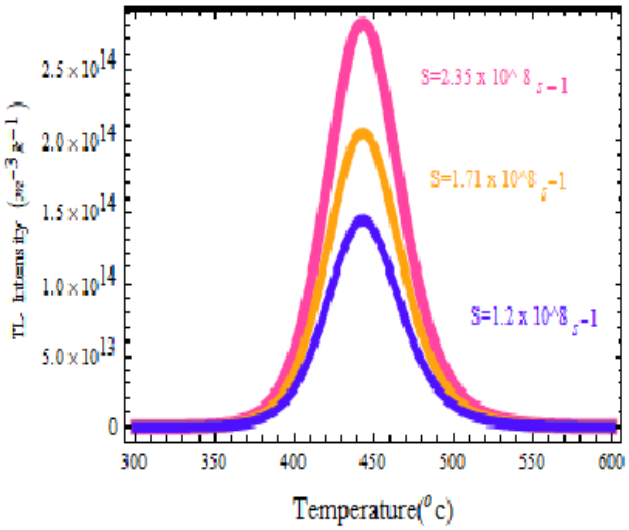

Figure 4.3: effect of frequncy factor on Thermoluminesscenc intensity of the glow curves of zinc oxide at different valve s for b=1.8 the other parameter constant.

creased. Thus, it is clear that E and s have opposite effects on temperature. This is simple to understand since higher s means faster escape of the trapped change from the excited state of the trap. Higher frequency factor s leads also to increase in peak height. Therefore, Similar changes can be noticed as the parameter s is varied but

now in the opposite way: as frequency factor s increases the peak shifts to lower temperatures with an increase of the height and a decrease in width. A trapping center with a high frequency factor needs less energy (lower temperature) to free a charge carrier.

4.3 Effect of heating rate on Thermoluminescence glow curves of zinc oxide phosphor

Heating rate is an important parameter for the determination of the various kinetic parameters of Thermoluminescence glow curves. The glow peak height decreases or increases with increasing heating rate. In this study, the Thermoluminescence glow curves intensity of zinc oxide varies at three different value of heating rates.

as the heating rate increase the intensity of thermoluminescence also increase, the intensity maximum shifted to higher temperatures as the heating rate was increased. Moreover, increase of the glow peak height was observed as increasing heating rate. Change in the linear heating rate β results in the change of the increase of the Thermoluminescence glow curve and faster heating rates produce a shift in temperature relatively towards higher values of temperature as explained above. Generally, glow peak height increases with the increase of heating rate and peak position shifts toward higher temperature.

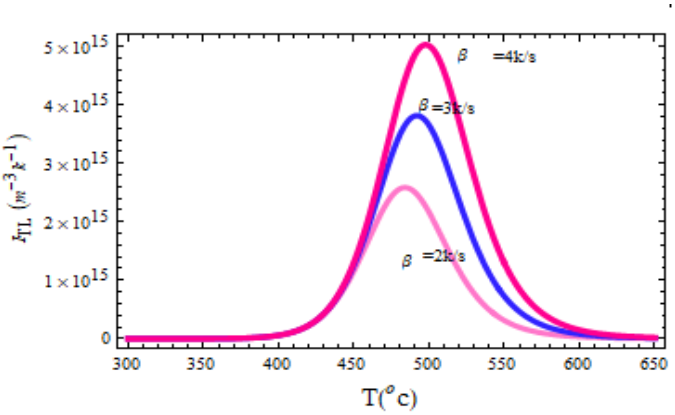

Figure 4.4: Thermoluminescence Intensity versus temperature of TL glow curves for zinc oxide Phosphor at different heating rate (β). As indicated, the peak of the glow curves increase and shift to higher temperature region with increasing the value of β and the other parameter is kept constant E = 1 ev, n_o =10^{10} cm^{-3}, s= $2.35x10^8 s^{-1}$ and b=1.8 while the value of heating rate β is varied from 2k/s, 3k/s, 4 k/s

4.4 The effect of activation energy on the electron concentration in traps of zinc oxide

Thermoluminescence occurs when the trapped electron absorb enough energy in the form of heat to released back to the conduction band from where there recombination of electrons and holes. the energy required from the trapped electron to be released back to the conduction band is called activation energy.

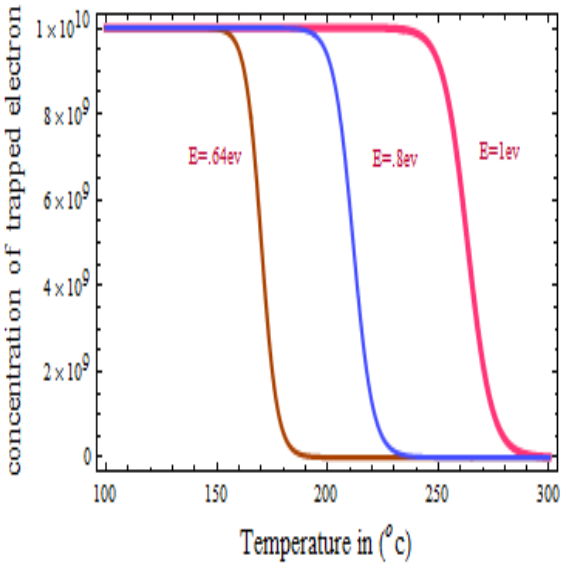

Figure 4.5: The effect of activation energy on the electron in traps of zinc oxide for different values of energy and for b=1.8, E=1ev.

activation energy is the energy(E), expressed in (eV), assigned to a level With in the forbidden band gap between the conduction band (C_B) and the valence band(V_B) of a crystal.This energy is also called trap depth.as in indicated in fig the electrons

in first Trap needed 0.64ev released from trap and re-trapped the hole ,than the concentration of in theE_1 trap decreases as temperature increases and the concentration of electron inE_3 trap increases with Temperature.the higher the activation energy heated at higher temperature to re-trapped.

4.5 The effect of frequency on the electron concentration in traps of zinc oxide

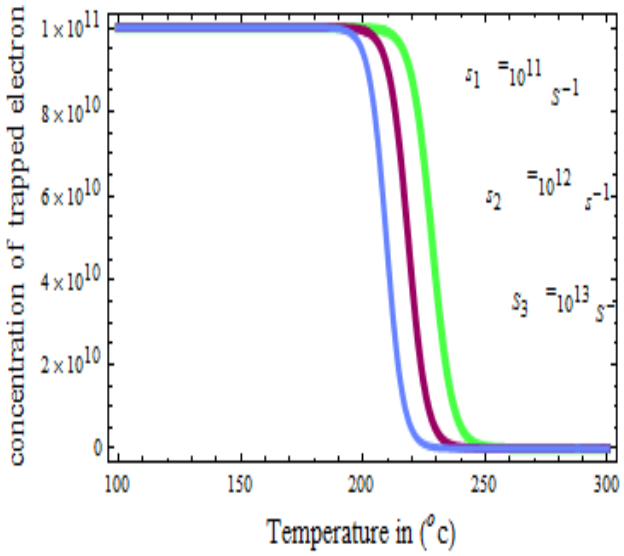

Figure 4.6: The effect of frequency on the electron in traps of zinc oxide for different values of s and for b=1.8 ,E=1ev,

To explain this effects we used the plotted figure here by three General order kinetics TL curves, for three different values of the frequency factor.Allother parameters are the same i.e., activation energy, E = 1 ev and Boltzmanns constant, k = $8.617 * 10^{-5} eVK^{-1}$ and the initial concentration of filled traps, $n_0 = 10^{10} cm^{-3}$ from

this figure, as the frequency factor is increased, the TL glow curve shifts towards lower temperatures, but the curve maintains its overall shape for these three peak.

4.6 The effect of heating rate on the electron concentration in traps of zinc oxide

different values of heating and activation energy, E = 1 ev , Boltzmanns constant, k = $8.617 * 10^{-5} eVK^{-1}$ the initial concentration of filled traps, $n_0 = 10^{10} cm^{-3}$ and frequency factor s=10^{12} from the fig the high heating rate high concentration of electron and high temperature.Than for high concentration of electron high temperature needed to heat the material for electron to Traps.

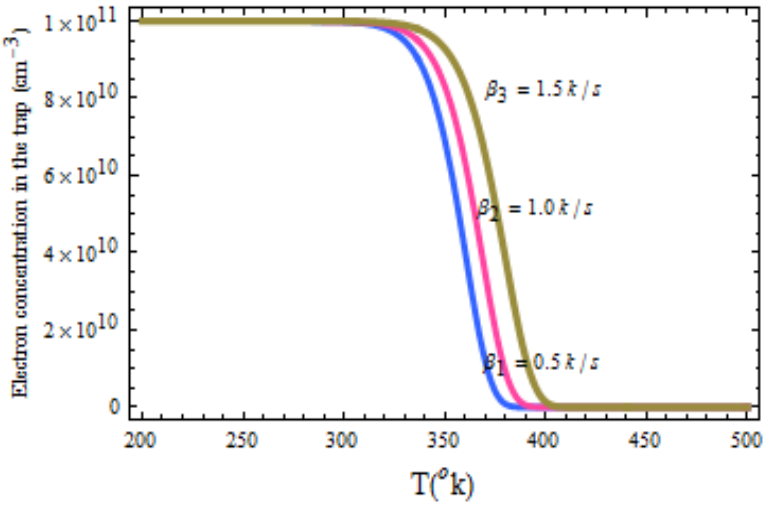

Figure 4.7: The effect of heating rate on the electron concentration in traps of zinc oxide for different vales of frequency and for the b=1.8 the other values parameter constant

Chapter 5

Conclusion

In this thesis, the thermoluminescence kinetic parameters such as activation energy E, and frequency factor s was reported to express the properties of Thermoluminescence glow curve of zinc oxide.shown in Fig.4.1. The Thermoluminescence intensity peak shifts slightly to higher temperature region at relatively high heating rates, but with increasing peak intensity. As E increases the glow curve shifts to higher temperatures with a decrease in the height. For higher E values or deeper traps more energy or higher temperature is needed to release the charge carriers. To study the presence of a trap depth distribution it is interesting to vary the heating rate at which the sample is excited. The reason for this is graphically represented in Fig.4.5, if a phosphor with a continuous trap depth distribution is excited at a higher heating rate, only deeper traps of the distribution are filled. The shallower traps are immediately bleached because of the increased thermal energy available. If we then estimate the trap depth, the resulting value will increase with increasing excitation heating rate. Therefore, similar changes can be noticed as the parameter s is varied but now in the opposite way:As frequency factor s increases the peak shifts to lower temperatures with an increase of the height and a decrease in width. A trapping canter with a

high frequency factor needs less energy or it needs lower temperature to free a charge carrier.

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