INVESTIGATION OF THERMOLUMINESCENCE PROPERTIES OF ZINC ALUMINATE NANOCRYSTALS

Mengesha Alemayehu Adimas

A Thesis Submitted to

The Department of Physics

PRESENTED IN FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE
JIMMA UNIVERSITY
JIMMA, ETHIOPIA
JANUARY, 2022

JIMMA UNIVERSITY
DEPARTMENT OF
PHYSICS

This is to certify that the thesis prepared by **Mengesha Alemayehu Adimas** Graduate Studies entitled "**Investigation of thermoluminescence properties of zinc aluminate nanocrystals**" 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. .

Dated: January, 2022

Supervisor: ______________________
Dr. Nebiyu Gemechu

Readers: ______________________

____

JIMMA UNIVERSITY

Date: **January, 2022**

Author: **Mengesha Alemayehu Adimas**

Title: **Investigation of thermoluminescence properties of zinc aluminate nanocrystals**

Department: **Physics**

Degree: **M.Sc.** Convocation: **January** Year: **2022**

Signature of Author

Table of Contents

List of Figures

Abstract

Light emission from zinc aluminate nanocrystals have got a great attention in industries for controlling the quality of some glasses, ceramics, semiconductor products, biology and biochemistry for studding the properties(involving different chemical reaction) or contents of proteins,leaves, e.t.c. Thermoluminescence is one of the luminescence, which is the emission of light from an insulator or semiconductor when it is being heated, following the previous absorption of energy from radition. Therefore in this study the mathematical expression for the thermoluminescence intensity of zinc aluminate as a function of temperature has been derived specifically. The thermoluminescence (TL) Properties of Zinc aluminate nanocrystal were investigated in the View of first Order Kinetics. The continuous promotion in numerical methods has greatly helped to solve the complex thermoluminescence kinetic equations (rate equations) which can not be solved analytically. The complexity of the rate equations increase with the number of traps considered. As activation energy increases the glow curve shifts to higher temperatures with a decrease in the height. 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. linear heating rate (β) can be increase the intensity of thermoluminescence also increase and for trapping electron more energy produce on the less linear heating rate and less energy were produced on the high linear heating rate.

Keywords: zinc aluminate nanocrystal, glow curve, thermoluminescence, kinetic parameters.

Acknowledgements

First of all I would like to thank the almighty **God**, my strength, power and leading me to this position.

I would like to express my deep gratitude to my advisor and instructor **Dr. Nebiyu Gemechu** for his constant assistance, invaluable guidance, and encouragement without any reservation during the whole period of my thesis work.

Next, my sincere thank goes to my co-advisor **Dr. Menberu Mengesha** for his insightful comment and continuous encouragement to the accuracy of this thesis.

I would also like to thank my best friend teacher **Tilahun Asmare** for his ideal support and guidance how to use mathematica software.

Finally I would likes to thank **my family** for their moral and economical support for the successes of my work.

Chapter 1

Background of the Study

1.1 Introduction

In order to understand thermoluminescence, it is better to know what luminescent is. In Latin lumin means light, the term luminescent material refer to material that emit light, especially in visible range such as crystal, mineral, and chemical substance. Luminescence is spontaneous emission of radiation from an electronically excited species or from a vibrationally excited species [1-5].

Luminescence occurs when a material absorbs radiation that brings about the transition of electrons from the valence band to the conduction band. This is followed by de-excitation of the electrons back to the valence band via a luminescence center, which converts their energy to electromagnetic waves [1-5].

The emission of light takes place in a characteristic time τ after the absorption of the radiation and this parameter allows us to sub classify the process of luminescence as fluorescence and phosphorescence [5].

Thermoluminescence (temperature stimulated luminescence) is the process in which a mineral emits light while it is being heated: it is a stimulated emission process occurring when the thermally excited emission of light follows the previous absorption of energy from radiation. Energy absorbed from ionising radiation (alpha, beta, gamma, cosmic rays) frees electrons to move through the crystal lattice and some are trapped at imperfections in the lattice. Subsequent heating of the crystal can release some of these trapped electrons with an associated emission of light. There are three essential ingredients necessary for the production of thermoluminescence.

Firstly, the material must be an insulator or semiconductor-metals do not exhibit luminescent properties.

Secondly, the material must have at some time absorbed energy during exposure to radiation.

Thirdly, the luminescence emission is triggered by heating the material.

In addition, there is one important property of thermoluminescence. It is a particular characteristic of thermoluminescence that, once heated to excite the light emission, the material cannot be made to emit thermoluminescence again by simply cooling the specimen and reheating. In order to re-exhibit the luminescence, the material has to be re-exposed to radiation, whereupon raising the temperature will once again produce light emission [5].

There are many other types of luminescence: photoluminescence,mechanoluminescence, chemoluminescence, electroluminescence, bioluminescence, radioluminescence are some example of type of luminescence.[6]

Zinc aluminate is a rare nanocrystal which is well known n-type semiconductor device with large energy band gap (3.8 eV) [7-8]. Zinc aluminate ($ZnAl_2O_4$), naturally occurring as the mineral gahnite, is a member of the spinel family. It has normal spinal structure, high chemical and thermal stability, high mechanical resistance and low surface acidity. Due to this it is suitable for a wide range of applications, such as optical coating or host matrix, high temperature ceramic material. [8-11].

Defect states in $ZnAl_2O_4$ have a significant role in its applicability as a luminescent material.The mechanism of trapping, retrapping and recombination have been depicted through schematic band model diagram. X-ray photoelectron spectroscopy indicated the presence of various types of defects specifically AlZn antisite defect, oxygen and zinc vacancies which are further upheld by photoluminescence and Raman spectroscopy. All results when summed up, predict $ZnAl_2O_4$ to be a quality material for dosimetry.Its conductivity prominently attributed to AlZn antisite defects which is a shallow defect near conduction band edge accompanied by cationic vacancies [12]. Due to complex crystal structure and multiple defect centers such as cationic-anionic vacancies, antisite defects and cationic interstitial, it shows alluring luminescence[13-14].

Informative parameters such as order of kinetics, trap depth and frequency factor from TL emission must be known so that basic mechanism of TL emission and dosimetric properties of material could be critically analyzed[15]. First order kinetics indicates a faster decay while second order kinetics indicates retrapping of charge carriers leading to delayed emission [16]. Trap depth or activation energy (E) is assigned to a metastable state (trap) existing in forbidden band gap region either below the conduction band, above the valence band or rarely in the middle of band gap. These trap states originate from defects in the crystal structure[17]. On irradiating the crystal with a suitable ionizing radiation, free charge carriers are generated which get trapped in these metastable states. On receiving thermal energy, trapped carriers gain much energy to overcome the trap potential barrier and jump to conduction band. Recombination of carriers undergoing transition from conduction band to hole traps lead to TL glow curves. Frequency factor, also known as attempt to escape frequency (s) is number of times per second a charge carrier attempts to escape the potential barrier of trap[17].

1.2 Statement of the Problem

Many researches have been done on the nanocrystals of materials and dosimetery of thermoluminescence materials using different models by heating the material. The possible increase in the intensity of TL from propertise have been studied experimentally. In the experimental techniques used focused on investigating the TL intensity and activation energy as a function of temperature and this results in which only the TL glow peaks were generated but not discussed theoretically. Thermoluminescence properties of zinc aluminate in view of first order kinetics is very important to distingush it from other materials. But in this thesis the effect of activation energy, effect of frequency factor, effect of heating rate on TL glow curve of zinc aluminate nanocrystal and variation of electron concentration in traps in zinc aluminate nanocrystal depended on first order kinetic equation has been studied. Therefore the aim of this thesis to answer the following questions.

1. What is the effect of frequency factor on thermoluminescence glow curves of $ZnAl_2O_4$ nanocrystal in view of first order kinetics?
2. What is the effects of activation energy on thermoluminescence glow curves of $ZnAl_2O_4$ nanocrystal in view of first order kinetics?

3. What is the effect of heating rate on thermoluminescence glow curves of $ZnAl_2O_4$ nanocrystal in view of first order kinetics?
4. What is the effect of variation of concentration of electrons on thermoluminescence glow curves of $ZnAl_2O_4$ nanocrystal in view of first order kinetics?

1.3 Objectives of the Study

1.3.1 General Objectives

The general objective of this study were to investigate thermoluminescence properties of zinc aluminate ($ZnAl_2O_4$) nanocrystals in view of first order kinetics.

1.3.2 Specific Objectives

- To investigate the effects of frequency factor on thermoluminescence glow curves of zinc aluminate($ZnAl_2O_4$) in view of first order kinetics;
- To examine the effects of activation energy on thermoluminescence (TL) glow curves of $ZnAl_2O_4$ in view of first order kinetics;
- To identify the effects of heating rate on thermoluminescence glow curves of $ZnAl_2O_4$ nanocrystal in view of first order kinetics;
- To examine the effects of variation of concentration of electrons on thermoluminescence glow curves of $ZnAl_2O_4$ nanocrystal in view of first order kinetics.

1.4 Significance of the Study

The significance of this study is to investigate the thermoluminescence properties of zinc aluminate nanocrystal. It helps to compare the experimental results with respect to our calculation.This study may be used as a reference for the scientific community to know about the investigation of thermoluminscence properties of $ZnAl_2O_4$ nanocrystals. it also helps as starting for other researchers

1.5 Scope of the Study

Due to the time constraint the scope of the study is limited to the theoretical investigation of TL properties; effect of heating rate, frequency factor, activation energy and concentration of electron on the material zinc aluminate nanocrystal by using rate equation in view of first 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 of the study is limited to investigate; effect of heating rate,effect of frequency factor, activation energy and concentration of electron in trap on the material zinc aluminate nanocrystal by using rate equation in view of first order kinetics.

1.7 Thesis Outline

This study contains five chapters and organized as follows: In Chapter 1, we have discussed some of the background of Luminescence, including the statement of the problem, objectives, significance of study, limitation and scope of the study. In Chapter 2, we review the theoretical backgrounds of Luminescence, In Chapter 3, We discuss some of the methodology we used for our work In Chapter 4, We discuss the properties and the effect of varies heating rate on the Thermoluminescence glow curve properties of zinc aluminate nanocrystal with parameter of activation energy E, frequency factors s and the concentration of the trapped electron in the trap and compare the TL glow curves on zinc aluminate nanocrystal through first order kinetics. Finally in Chapter 5, we draw some conclusions.

.

Chapter 2

Review Literature

2.1 Background of thermoluminescence

The first scientifically recorded observation of thermoluminescence was made in 1963 by Robert Boyle. Boyle also stimulated the luminescence emission by more conventional means by using the heat from a hot iron, from friction and from a candle. In 1676, Elsholtz observed a similar effect from the mineral fluorspar. Early interpretations of the phenomena were that the heat itself was being directly converted to light. Oldenburg (1676), referring to the thermoluminescence of a phosphor called 'phosphorus smaragdinus', wrote that the material received its light 'from the fire itself'. Most of the other observations at the time supported this or similar views. Du Fay (1726) thought that the luminescence was due to 'a sulphur' which actually burned on heating, but later he was to provide what was possibly the first clear evidence that the observed phenomenon (i.e., thermoluminescence) was nothing more than delayed phosphorescence. His experiments on natural quartz showed that the thermoluminescence could be reactivated by exposure of the sample to light. Heat only stimulated the emission, but was not its cause[5,18]. Deribere (1936) reported that, in 1821, Calloud, a chemist from Annecy in France, discovered that heating sulphate of Quinine produced an intense blue luminescence between 100 and 1800C. This observation was confirmed shortly afterwards by Pelletier. In 1867, Becquerel also reported luminescence from fluorspar as it was heated. It is difficult to pinpoint exactly when the word thermoluminescence was first used in the published literature, but it is certainly used in 1895 by Wiedemann and Schmidt (1895) in what Becker (1974) describes as ' probably the first careful investigation of experimentally radiation-induced thermoluminescence under its modern name' A major difference between the work of Wiedemann and Schmidt and that of earlier investigators is that these authors induced the thermoluminescence themselves by irradiating the specimens with an electron beam in the laboratory'. This type of thermoluminescence is sometimes referred to as 'artificial' whereas the earlier observations were on natural thermoluminescence, i.e., that induced by natural radioactivity in the environment. Wiedemann and Schmidt studied a wide variety of synthetically produced phosphors. However, the fact that the thermoluminescence from natural specimens could be regenerated in the laboratory was first published by Trowbridge and Burbank (1898). These authors drained the natural thermoluminescence from fluorite by heating it and then re-excited the thermoluminescence by exposing the specimen to X-rays. The connection between phosphorescence and radiation was the subject of extensive examination in the late nineteenth century and the study of radiation-induced thermoluminescence received a boost from Marie Curie in 1904 when she wrote in her doctoral thesis; ' certain bodies, such as fluorite, became luminous when heated; they are thermoluminescent'.Their luminosity disappears after some time, but the capacity of becoming luminous afresh through heat is restored to them by the action of a spark and also by the action of radiation[5][18].

2.2 types 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. The phenomenon of luminescence can be classified as follows[6][19]

2.2.1 Photoluminescence(PL)

In photoluminescence (photon luminescence) as its name indicate, Emission of the light is the result of the ex-citation by electromagnetic radiation/photons. It is a process in which a molecule absorbs a photon in the visible region, exciting one of its electrons to a higher electronic excited state, and then radiates a photon as the electron returns to a lower energy state. It includes both fluorescence and phosphorescence that we have seen above. Photoluminescence has a very broad application area from whitening substances in washing powder to plasma screens for large scale displays. The period between absorption and emission is typically extremely short, in the order of 10 nanoseconds. There is special type of luminescence which has a very slow decay with the emission continuing for minutes or hours. This type of luminescence is called long lasting or persistent luminescence and it is commonly used in road safety and exit marking[6].

2.2.2 Thermoluminescence(TL)

The term thermoluminescence (TL) consists of two words: thermo, meaning heat and luminescence, meaning emission of light. These words may appear to mean that the emission of luminescence is caused by heat. This however is not totally true, since heat has only a secondary role in this case. When heat is the primary cause, the emission is called incandescence, for example, the light coming from a hot filament lamp or a burning charcoal. The primary agents for the induction of Thermoluminescence in a material are the ionizing radiations, namely the X-rays, or radiations from radioactive elements to which the sample is pre-exposed. In some materials, ultraviolet light also may excite Thermoluminescence.When the sample is subsequently warmed up, luminescent light is emitted. The act of warming up stimulates the release of the stored energy in the sample due to pre-exposure to the ionizing radiations. The release of this stored energy produces the luminescence. Therefore, some authors have appropriately used an expanded expression for this emission calling it radiation induced thermally stimulated luminescence. Some others have abbreviated it to radiothermoluminescence to signify that the Thermoluminescence is induced by the radiations. Some authors call it thermally stimulated luminescence (TSL). Presently however, most workers of this field have become accustomed to the abbreviated term Thermoluminescence. Thermoluminescence(TL)is defined as the emission of light from a semiconductor or an insulator when it is heated, due to the previous absorption of energy from irradiation. The graph of the amount of light emitted during the Thermoluminescence process as a function of the sample temperature is known as a Thermoluminescence glow curve. On subsequent heating the energy may be released and some of it may be in the form of light, which we call thermoluminescence (TL).

The underlying mechanism involves the role of:-

- crystal defects which allows the storing of energy derived from exposure to radiation through the trapping of carriers at these defect centers.
- subsequent release of stored energy as visible light when these trapped carriers, after having been freed by thermal stimulation, recombine at the luminescent centers provided by impurity atoms in the solids[20-21].

The fundamental principles which govern the production of Thermoluminescence are essentially the same as those which govern all luminescence processes and hence Thermoluminescence is one member of a large family of luminescence. 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. The basic effect leading to the production of Thermoluminescence is the trapping of charge carriers, i.e. electrons and holes, produced during exposure to an external source at defect sites in the material. Defect sites can be divided into two categories:- i, Those inherently present in the material ii, Those produced by external means, such as deliberately doping the sample with impurities. A well-known example of the first category is a negative ion vacancy. Such a vacancy can trap an electron and is then called an F center. 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 [22-23]. In addition to the above mentioned disciplines, the method of Thermoluminescence 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[24]. Moreover, Thermoluminescence has also interesting applications in space science, thermostimulated luminescence (TSL) photography, radiation physics, and petroleum exploration [25].

The other types of luminescence are:-

1. Electroluminescence:When a material emits electromagnetic radiation as a result of the application of an electric field, the process is called electroluminescence (EL) [26-27]. 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 [28-29].

2. 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 [30-31]. The chemical reactions are the enzymic oxidations. For example, the oxidation of luciferin in the presence of enzyme luciferase is responsible for occurrence of bioluminescence. 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.

3. 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 mechanoluminescence. B. V. Bukvetskii et al, described the phenomenon of triboluminescence as the glow resulting from crystal destruction or friction [32] 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.

4. Chemiluminescence:Chemiluminescence is produced as a result of a chemical reaction usually involving an oxidation reduction process [33-34]. 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.

5. Cathodoluminescence(CL):it occurs due to the emission of light during electron irradiation [35-36]. 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.

6. radioluminescence:It is a phenomenon by which light is produced in a material by bombardment with ionizing radiation such as beta particles, x rays or gamma rays[5].

2.3 Luminescence and Stokes Law

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 (Stokes law). 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 blackbody radiation, involves two steps:

(1) The excitation of electronic system of a solid material to higher energy state, and

(2) subsequent emission of photons or simply light. The emission of light takes place at characteristics time $'\tau'$ after absorption of the radiation, this parameter allows us to sub-classify the process of luminescence into fluorescence and phosphorescence.

Luminescence can be classified on the basis of duration of emission $'\tau_c'$ in to two parts:

1. Fluorescence where $\tau_c < 10^{-8}s$ (Temperature independent process), and
2. Phosphorescence where $\tau_c > 10^{-8}s$ (Temperature dependent process). The Phosphorescence phenamenon can be further divided into two parts:

(a) short period $\tau_c < 10^{-4}s$, and

(b) long period where $\tau_c > 10^{-4}s$ is called Thermoluminescence (TL), the emision depends from minutes $< \tau_c < 4.6x10^9$ years falls under long period category. Each process mentioned above has its own significance and advantage in the field of science and technology Solids exhibiting property of luminescence are usually referred to as Phosphors. The Fluorescence emission is seen to be spontaneous as $'\tau_c' < 10^{-8}s$, thus fluorescence emission is seen to be taking place simultaneously with absorption of radiation and stopping immediately as radiation ceases. Phosphorescence on the other hand is characterized by delay between radiation absorption and time $'t'_{max}$ to reach full intensity. Also phosphorescence is seen to continue for some time after the excitation has been removed. If the delay time is much shorter it is more difficult to distinguish between fluorescence and phosphorescence[37].The family tree of luminescence phenomena is shown in fig. 2.1.

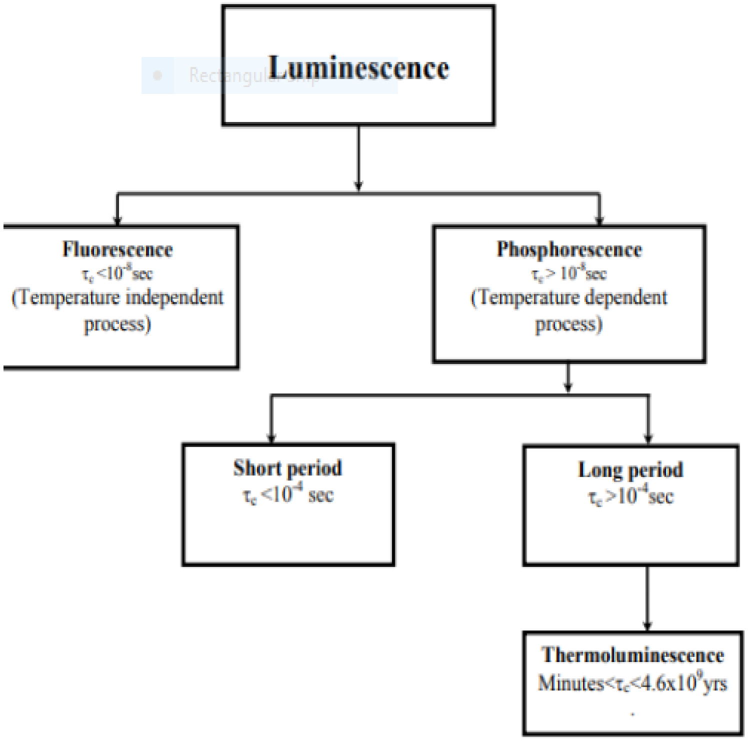


Figure 2.1: Classification of luminescence on the basis of duration of emission(Mckeever,1985)

2.4 Defects in solids

Defects in solids may be defned as all kinds of imperfections such as impurities, interstitials and vacancies within the atomic structure of the solid [38]. Impurities refer to the random placement of foreign atoms into the crystal lattice structure. Vacancies are unoccupied sites or missing atoms in the lattice structure. Interstitials are irregularly occupied sites. The most common type of defect are point defects which can be classified in two major categories depending on their origin: Intrinsic defects consist of vacancies and self interstitials. Extrinsic defects arise from substitutional or added impurity atoms in the lattice. Defects may also arise from interstitial impurities which are impurity atoms at irregular lattice sites. Radiation itself and transitional atoms in the lattice can also produce impurities. If defects are not present (in a perfect crystal), electrons are allowed to exist in certain discrete energy levels. These allowed energy levels are called delocalized energy bands, either valence band or conduction band. The separation of two consecutive delocalized energy bands is called the energy band gap or forbidden energy band. No electron is allowed to exist in the forbidden bands. The presence of point defects and their distributions in a material structure introduces local energy levels in the forbidden energy band [39]. These local energy levels host an anion vacancy or an excess anion. An anion vacancy may capture a free electron from the conduction band and thereby act as an electron trap. An excess anion may capture a free hole from the valence band and in that way act as a hole trap. If the defective level can return an electron or hole back to the band it came from, then the defect is called a ”trap .. center”. The defective level where a charge carrier of opposite sign can be captured to produce electron-hole recombination is called a ”recombination center”[38].

2.5 Traps and Recombination Centers

The locations where electron and holes are caught up are called trap.A hole may be captured at a location where positive charge is lacking or a negative charge is in excess, for example at a positive ion vacancy or at an interstitial negative ion. 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 [40]. 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 [41]. 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 [41,42]. An essential feature of all luminescence process in the change in occupancy of the various localized energy sates to another,several kinds of transition are possible and some are disused below. The interaction between an incident radiation and atoms in a luminescence material may be described schematically using the energy band diagram as shown in fig 2.2. In the figure,the letter denote that the following processes,(a) ionization;(b) electron(solid circle) trapping;(c) electron release(de-trapping);(d) band-to-center recombination;(e) hole(open circle)Trapping;(f) hole release;(g) band-to-center recombination;(h) band to-band recombination;and(i) center-to-center recombination; respectively.

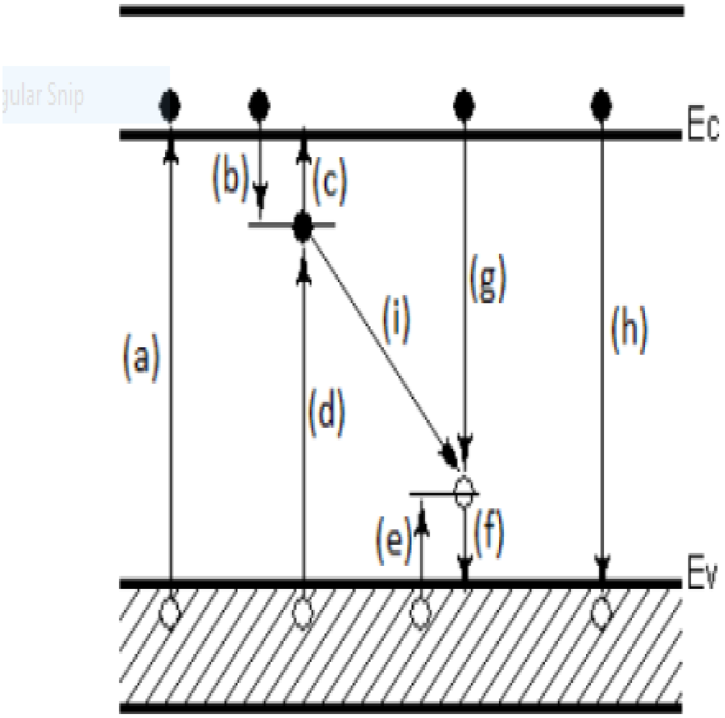


Figure 2.2: Schematic illustration of common types of electronic transition involving the conduction band Ec and valence band Ev(Mckeever,1985)

The primary interaction between ionizing radiation and the atoms electronic structure 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 [43]. There 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 (i)

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 [44]

2.6 The one trapping one recombination center (OTOR) model [simple TL 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. 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 Figure 2.3). The highest level indicated by T is situated above the equilibrium Fermi level (Ef) 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 $hv > Eg$ results in ionisation 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 with each other or become trapped. In the case of direct 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 ($< 10^{-8}s$) recombination of free electrons and holes under emission of light is called radioluminescence. However, in semiconductors and insulators a certain percentage of the charge carriers are 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

$$p = s\exp(\frac{-E}{KT}) \tag{2.6.1}$$

where p is the probability per unit time. The term s is called the frequency factor or attempt to-escape factor. In the simple model s is considered as a constant (not temperature dependent) with a value in the order of the lattice vibration frequency, namely $10^{12} - 10^{14}s^{-1}$. E is called the trap depth or activation energy, the energy needed to release an electron from the trap into the conduction band (see Figure 2.3). Thus, the non-equilibrium state is metastable and will exist for an indefinite period, governed by the rate parameters E and s. The return to equilibrium can be speeded up by raising the temperature of the TL material above T_o. This will increase the probability of detrapping and the electrons will now be released from the trap into the conduction band. The charge carrier migrates through the conduction band of the crystal until it undergoes recombination at recombination centre R. In the simple model this recombination centre is a luminescent centre where the recombination of the electron and hole leaves the centre in one of the higher excited states. Return

to the ground state is coupled with the emission of light quanta, i.e. thermoluminescence. The intensity of TL I (t) in photons per second at any time t during heating is proportional to the rate of recombination of holes and electrons at R. [45-47].

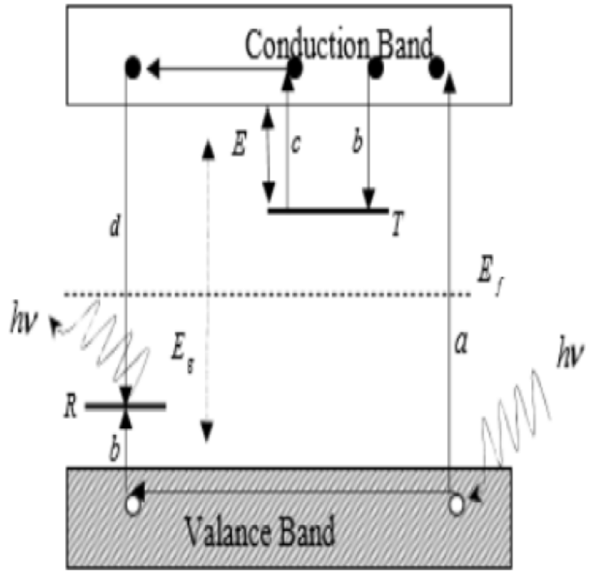


Figure 2.3: Energy band model showing the electronic transitions in a TL material according to a simple two-level model: (a) generation of electrons and holes; (b) electron and hole trapping; (c) electron release due to thermal stimulation; (d) recombination. Solid circles are electrons, open circles are holes. Level T is an electron trap, level R is a recombination centre, Ef is Fermi level, Eg is the energy band gap(bos,2007)

2.7 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.

$$I(t) = \frac{-dn}{dt} = ns\exp(\frac{-E}{KT}) \tag{2.7.1}$$

$$I(t) = \frac{-dn}{dt} = \frac{n^2}{N}s\exp(\frac{-E}{KT}) \tag{2.7.2}$$

$$I(t) = \frac{-dn}{dt} = n^b s^{'}\exp(\frac{-E}{KT}) \tag{2.7.3}$$

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,N is total electron concentration, s is frequency factor of the electron trap, T is temperature k is Boltzman's constant.

Chapter 3

MATERIALS AND METHODOLOGY

3.1 Materials

The investigation of thermoluminescence properties of zinc aluminate ($ZnAl_2O_4$) nanocrystal has been studied theoretically. So, the books, articles, journals, published thesis and dissertations carried out based on the thesis title were sources of information. Computer and software were essential instruments, which have been used to accomplish the study..

3.2 Methodology

3.2.1 Analytical

Analytical solution of the rate equations were achieved by assuming negligible re-trapping in case of first order kinetics, whereas,the consideration of re-trapping complicates the rate equations and hence numerical approaches were employed. Therefore,for numerical calculations, Mathematica Software has been used to determine the effect of electron concentation(n_o), heating rate(β), Activation energy(E) and

Frequency factor(s) on thermoluminescence glow curves of zinc aluminate($ZnAl_2O_4$) nanocrystal in view of first order kinetics.

3.2.2 Computational(Graphical)

The properties of Thermoluminescence of the material zinc aluminate nanocrystal with linear heating rate were interpreted graphically with Mathematica.

Chapter 4

RESULT AND DISCUSSION

In this chapter, we seek to investigate the effect of activation energy,frequency factor, heating rate and concentration of electrons in the traps , the TL intensity as a function of temperature (the glow curve) of Zinc Aluminate ($ZnAl_2O_4$) nanocrystal in the view of first order kinetics by employing the method which is based on mathematica software.

4.1 First order kinetics

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. In TL phenomena, first order kinetics means electron retrapping is assumed to be zero and the TL intensity I at any temperature T during heating depends only on the concentration n of electrons in the active traps at that temperature [45,46,48]. In 1945, Randall and Wilkins extensively used a mathematical representation for each peak in a glow curve, starting from studies on phosphorescence. Their mathematical treatment was based on the energy band model and yieds the well-known first order expression. The life time, τ, of the charge carrier in the metastable state at temperature T, is given by.

$$\tau = p^{-1} \tag{4.1.1}$$

If n is the number of trapped electrons in T, and if the temperature is kept constant, then n decreases with time t according to the following expression:

$$\frac{dn}{dt} = -pn \tag{4.1.2}$$

integrating this equation

$$\int_{n_0}^{n} \frac{dn}{n} = -\int_{t_0}^{t} p.dt \tag{4.1.3}$$

one obtains

$$n = n_0 \exp[-s \exp\frac{-E}{KT}.t] \tag{4.1.4}$$

Where n_0 is the number of trapped electrons at the initial time $t_0 = 0$. Assuming now the following assumptions:

- irradiation of the thermoluminescent material at a low enough temperature so that no electrons are released from the trap,
- the life time of the electrons in the conduction band is short,
- all the released charges from trap recombine in luminescent center,
- the luminescence efficiency of the recombination centers is temperature independent,
- the concentrations of traps and recombination centers are temperature independent,

- no electrons released from the trap is retrapped

According to the previous assumptions, the TL intensity, I, at a constant temperature, is directly proportional to the detrapping rate, $\frac{dn}{dt}$:

$$I = -c\frac{dn}{dt} = cpn \tag{4.1.5}$$

where c is a constant which can be set to unity. Equation (4.1.5) represents an exponential decay of phosphorescence. Using Equation (4.1.4) in Equation (4.1.5) one obtains:

$$I(t) = n_0 s \exp(\frac{-E}{KT}) \exp[-st \exp(\frac{-E}{KT})] \tag{4.1.6}$$

Usually TL is observed as the temperature is raised as a linear function of time according to:

$$T(t) = T_0 + \beta t \tag{4.1.7}$$

Introducing a constant heating rate $\beta = \frac{dT}{dt}$, from equation (4.1.3) we have:

$\int_{n_o}^{n} \frac{dn}{n} = (\frac{-s}{\beta}) \int_{T_0}^{T} \exp[\frac{-E}{KT} dT]$

$ln(n) - ln(n_0) = (\frac{-s}{\beta}) \int_{T_0}^{T} \exp(\frac{-E}{KT}) dT$

and again

$$n = n_0 \exp[(\frac{-s}{\beta}) \int_{T_0}^{T} \exp(\frac{-E}{KT}) dT] \tag{4.1.8}$$

then using equation (4.1.5)

$$I(T) = n_0 s \exp(\frac{-E}{KT}) \exp[(\frac{-s}{\beta}) \int_{T_0}^{T} \exp(\frac{-E}{KT}) dT] \qquad (4.1.9)$$

Where n_0 is the total number of trapped electrons at time $t = 0$. As the temperature increases, the intensity initially increases (detrapping of the trapped charge carriers and recombination takes place which initiates luminescence), than reach a maximum and finally decreases (as the number of charges carriers becomes depleted. $Equation$(4.1.9) is the well-known Randall-Wilkins first-order expression of a single glow peak. The peak has a characteristic asymmetric shape being wider on the low temperature side than on the high temperature side. $[46 - 48]$.

4.2 Thermoluminescence glow curve Properties of zinc aluminate nanocrystal

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 4.1.9 is used and then we can generate by using the parameter E, s, no, and β after this we observed the following graphs ($Fig.$4.1, 4.2, 4.3 and 4.4).Those figures describe briefly the properties of Thermoluminescence glow curves of zinc aluminate nanocrystal.

4.3 Effect of Activation Energy (E) on Thermoluminescence glow curves of zinc aluminate nanocrystal

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 $E = 1.031ev, 1.035ev, 1.043ev, \beta = 2k/s, s = 9.23x10^{11}s^{-1}$, Initial concentration of trapped electron $n_o = 10^{10}cm^{-3}$. This is useful to determine the properties of Thermoluminescence glow curves of zinc aluminate 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 aluminate rises

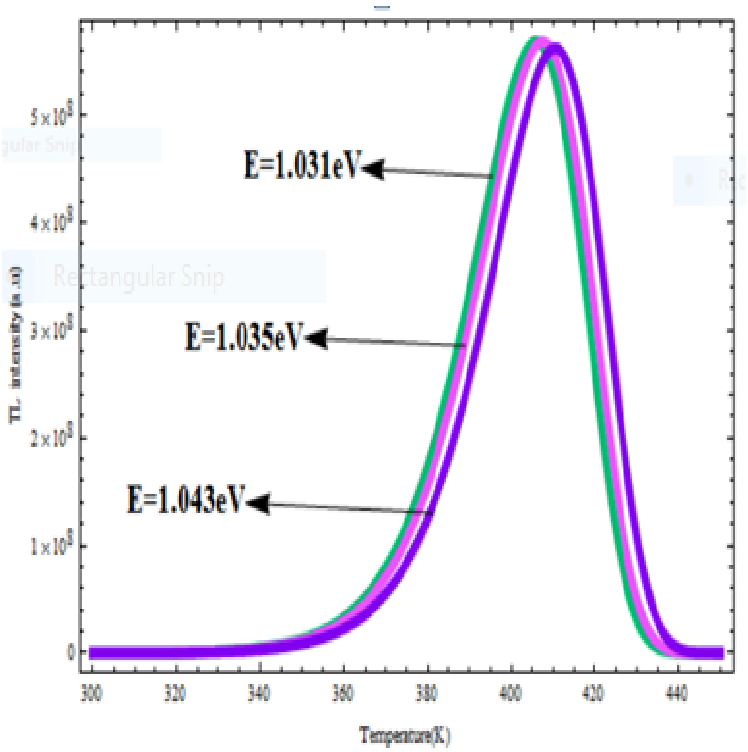
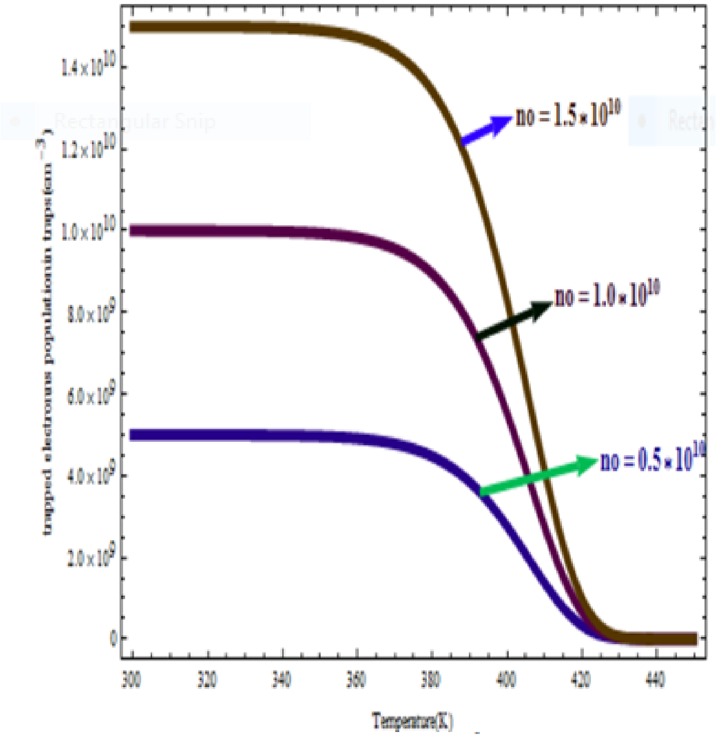


Figure 4.1: . The Thermoluminescence Intensity of the glow curve of zinc aluminate at three different E values.

exponentially. 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.

4.4 Effect of variation of electron concentration (n_o) on Thermoluminescence glow curves of zinc aluminate nanocrystal

Figure 4.2 shows the effect of electron concentration in the trap as a function of temperature for a constant radiation dose of $n_o = 0.5 \times 10^{10} cm^{-3}, n_o = 1 \times 10^{10} cm^{-3}, n_o = 1.5 \times 10^{10} cm^{-3}, E = 1.031 eV, \beta = 2K/s$ and $s = 9.23 \times 10^{11} s^{-1}$. The effect of variation of electron n_0 concentration on the thermoluminecence properties of zinc aluminate nanocrystal is observed that the concentration of trapped electrons population decrease as the temperature increase just above $380K$, reaching its minimum values



vs T.png

Figure 4.2: The effect of variation of electron concentration in trap on the Thermoluminescence Properties of Zinc aluminate nanocrystal

approximately between 425K and $430K$ and at temperature of $300K \rightarrow 380K$ the trapped electron is not released from the center of trap because the temperature is not enough to eject it, but above the temperature of 425K the trappd electron start to excite from the trap center. When the initial concentration of electron in traps nois changed the peak characteristics are independent of radiation dose given to the sample. Also the vertical axis represents the trapped electron popuulation in the traps versus temperature.

4.5 Effect of frequency factor on Thermoluminescence glow curves of zinc aluminate

Properties of TL glow curve for Zinc aluminate nanocrystal, showing the variation with the frequency factor . Parameter values we used are $no = 10^{10}cm^{-3}, E = 1.031eV, \beta = 2k/s$ with different frequency factor $(i, es1 = 6.83 * 10^{11}s^{-1}, s2 = 9.23 * 10^{11}s^{-1}, s3 = 1.23 * 10^{12}s^{-1}$ of in which parameter s is varied. For given values of E and β, the glow peak shifts to lower temperature as frequency factor s is increased. Thus, it is clear that E and s have opposite effects on temperature. This is simple to understand since higher frequency factor 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 canter with a high frequency factor needs less energy (lower temperature) to free a charge carrier.

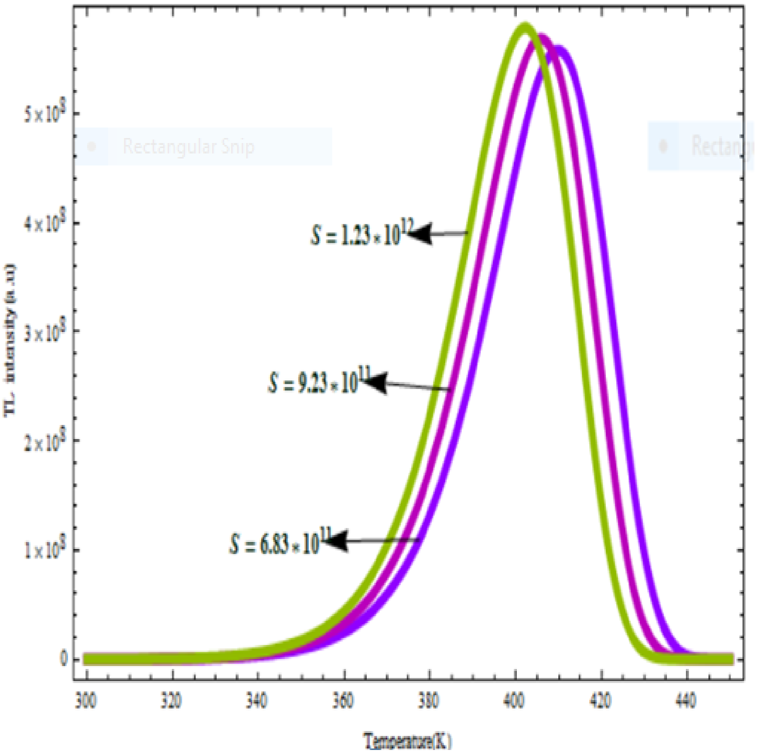


Figure 4.3: effect of frequncy factor on Thermoluminesscenc intensity of the glow curves of zinc aluminate at different value frequency factor s and other parameters are constant.

4.6 Effect of Linear Heating rate (β) of the thermoluminescence glow curves of zinc aluminate

Heating rate is an important parameter for the determination of the various kinetic parameters of Thermoluminescence glow curves. In this study,Parameter values we used are $E = 1.031eV, n_o = 10^{10}cm^{-3}, s = 9.23 * 10^{11}s^{-1}$ with different heating rate $\beta = 1K/s, \beta = 2K/s$ and $\beta = 3K/s$. The Thermoluminescence glow curves intensity of zinc aluminate 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.

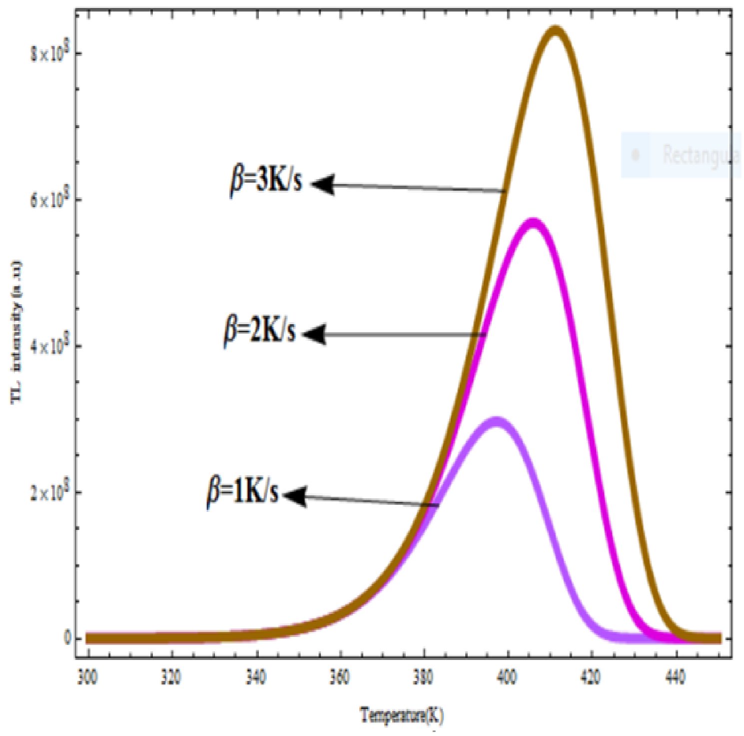


Figure 4.4: The Thermoluminescence intensity versus temperature of the TL glow curves for zinc aluminate at three different values of heating rate

Chapter 5

Conclusion

In this thesis, the Thermoluminescence kinetic parameters such as activation energy (E), concentration of trapped electron population (no), heating rate (β) and frequency factor (s) was used to express the thermoluminescence glow curve of Zinc aluminate ($ZnAl_2O_4$) nanocrystal through first order kinetics.

The thermoluminescence intensity increases with an increase in frequency factor (s) and then decreases with increase in activation energy . 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.

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.

The concentration of trapped electron population(no) decrease as the temperature increase just above 380K, reaching its minimum values approximately between 425K and 430K and at temperature of $300K \rightarrow 380K$ the trapped electron is not released from the center of trap because the temperature is not enough to eject it, but above the temperature of 425K the trapped electron start to excite from trap center.

The Thermoluminescence intensity peak shifts slightly to higher temperature region at relatively high heating rates, and with increasing peak intensity.

generally, we can understand that different frequency factors s and different activation energies E show similar changes but in the opposite way can be noticed. As the energy E is increased or as the value of frequency factors (s) is decreased, the TL glow curve shifts toward higher temperatures sid. Thus, it is clear that E and s have opposite effects on maximum temperature (TM). This is simple to understand since higher s means faster escape of the trapped change from the excited state of the trap.

Bibliography

[1] D.D. Busch, Nikon D200 Digital Field Guide, 2006, Wiley Publishers, Indianapolis, IN.

[2] L.L. Noto, M.Sc. Thesis, 2011, University of the Free State, South Africa.

[3] Gaft , M. , Reisfeld , R. , and Panczer , G.(2005) Luminescence Spectroscopy of Minerals and Materials , Springer ,Berlin

[4] Adirovitch, E. I., (1956). La formule de Becquerel et al Loielementaire du decline de la luminescence des phosphorescrys-talline. J.Phys. Radiation, 17, 705-708.

[5] Nebiyu Gemechus's M.sc. thesis in 2009, university of Addis Abeba, Ethiopia

[6] N. Thejo Kalyani, ... S.J. Dhoble, in Principles and Applications of Organic Light Emitting Diodes (OLEDs), 2017

[7] Ravikumar, B.S. et al. Plant latex mediated green synthesis of ZnAl2O4:Dy3+ (1-9 mol%) nanophosphor for white light generation. J. Alloy. Compd. 585, 561-571 (2014).

[8] https://www.britannica.com/science/crystal-defect

[9] V. Ciupina, I. Carazeanu, G. Prodan; J. Optoelectronics and Advanced Materials; 6, 1317 (2004).

[10] Tzing WS and Tuan WH. The strength of duplex Al2O3- ZnAl2O4 composite. Journal of Materials Science Letters. 1996; 15:1395-1396. http://dx.doi.org/10.1007/BF00275286

[11] Zawadzki M, Wrzyszcz J, Strek W and Hreniak D. Preparation and optical properties of nanocrystalline and nanoporous Tb doped alumina and zinc aluminate. Journal of Alloys Compounds. 2001; 12:279-282. http://dx.doi.org/10.1016/S0925-8388(01)01031-3

[12] Dixit, H. et al. First-principles study of possible shallow donors in ZnAl2O4 spinel. Phys. Rev. B 87, 174101 (2013).

[13] Jain, M. et al. Enhanced near-infrared luminescence in zinc aluminate bestowed by fuel-blended combustion approach. J. Alloy. Compd. 797, 148-158 (2019)

[14] Pathak, N. et al. Exploring Defect-Induced Emission in ZnAl2O4: An Exceptional Color-Tunable Phosphor Material with Diverse Lifetimes. Inorg. Chem. 57, 3963-3982 (2018

[15] Kirsh, Y. Kinetic analysis of thermoluminescence. Phys. Status Solidi 129, 15-48 (1992).

[16] Furetta, C. Handbook of Thermoluminescence (World Scientific, Singapore, 2010), second edn.

[17] Sunta, C. Unraveling Termoluminescence, vol. 202 of Springer Series in Materials Science (Springer, 2015)

[18] Delft University of Technology, Faculty of Applied Sciences, 2629 JB Delft, The Netherlands.

[19] Claudo Furetta, Hand book of thermoluminescence Cambridge university press,480.

[20] T. Calder on, REVISTA MEXICANA DE FISICA S, 54, 21 (2008).

[21] A. Akin, E. Ekdal, Y. Arslanlar, M. Ayvacikli, T. Karali, N. Can, Luminescence,30, 830(2014).

[22] Bos, A.J.J. Theory of thermoluminescence. Radiat. Meas. , 41, 45-56, [CrossRef],2006.

[23] Carlota Sajnani, New Phytologist, 175, 120 (2007).

[24] Vinay Kumar, et al, Adv. Mater. Lett. 6, 402 (2015).

[25] Daniel Richter, Geoarchaeology: An International Journal, 22, 671 (2007).

[26] S. Bhushan, Nucl. Tracks 10, 215 (1985).

[27] Ullrich Mitschke and Peter Bauerle, J. Mater. Chem. 10, 147 (2000).

[28] Anatoly P. Pushkarev J. Mater. Chem. C, 2, 1532 (2014).

[29] M.T. Jose, S.R. Anishia, O. Annalakshmi, V. Ramasamy, Radiation Measurements 46(2011).

[30] H.D. Haddock, Mark A. Moline, and James F. Case, Annu. Rev. Mar. Sci. 443(2010).

[31] B. V. Bukvetskii, N. V. Petrochenkova, and A. G. Mirochnik, Russian Chemical Bulletin, International Edition, 64, 2427 (2015).

[32] Weijie Zhou et al, J. Mater. Chem. C, 3, 9161 (2015).

[33] Fernando Heering Bartoloni, et al, J. Org. Chem. 60, 374 (2015).

[34] R. S. Chandok, etal, Indian Journal of Pure and Applied Physics, 44, 519 (2006).

[35] K. T. Hillie and H. C. Swart, Appl. Surf. Sci, 183, 304 (2001).

[36] L. Oosthuizen, H. C. Swart, P. E. Viljoen, P. H. Holloway and G. L. P. Berning, Appl. Surf. Sci, 120, 9 (1997).

[37] Wunderlich, Christian-Heinrich. "Light and economy: an essay about the economy of prehistoric and ancient lamps. " Lychnological news (2003): 251-64.

[38] Adirovitch, E. I., (1956). La formule de Becquerel et al Loi elementaire du decline de la luminescence des phosphorescrys- talline. J.Phys. Radiation, 17, 705-708.

[39] D. Curie, Luminescence in crystals, John Wiley Sons Inc. New York, (1963).

[40] X. Qin, Y. Ju, S. Bernhard, N. Yao, Mater. Res. Bull, 42, 1440 (2007).

[41] S.W.S. McKeever, Thermoluminescence of solids, Cambridge Solid State Science Series, Oklahoma State University, 1988.

[42] McKeever S.W.S.(1985). Thermoluminescence of Solids, Cambridge University Press.

[43] B.M. Ilich, Sov. Phys. Solid State., 21, 1880 (1979).

[44] Agersnap, Larsen N., Whitley, V. and McKeever, S.W.S.(1998). Thermal quench ing of F centre luminescence inAl2O3:C. J. Appl.Phys., 84, 3364-3373.

[45] A.J.J. Bos / Radiation Measurements 41 (2007) S45- S56.

[46] J.T. Randall and M.H.F. Wilkins, Proc. Roy. Soc. A184 (1945)366.

[47] N.G. Debelo F.B. Dejene V.N. Mal'nev T. Senbetab, B. Mesfin and K. Roro-Private Bag X13, Department of Physics, University of the Free State, QWA-QWA Campus, South AfricaDepa rtment of Physics,Addis Ababa University, $P.O.Box$1176, Addis Ababa, Ethiopia R and D Core (Energy Initiatives),Council for Scientific and Industrial Research, P.O. Box 395, Pretoria, South Africa (Received October 24, 2015; in final form February 22, 2016).

[48] Aristotle University of Thessaloniki, Nuclear Physics Laboratory, 54006 Thessaloniki, Greece

JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCES
PERFORMANCE CERTIFICATE FOR MASTER'S DEGREE

Name of Student: **Mengesha Alemayehu Adimas** ID No. **S30800/09**

Graduate Program: **Summer, M.Sc.**

1. Course Work Performance

Course Code	Course Title	Cr. hr	Number Grade	Rank **	Remark
Phys699	**M.Sc. thesis**	**6**			

** Excellent, Very Good, Good, Satisfactory, Fail.

Thesis Title

Investigation of Thermoluminescence properties of zinc aluminate nanocrystal

2. Board of Examiners decision Mark × in one of the boxes. Pass ☒ Failed ☐
If failed, give reasons and indicate plans for re-examination.
____
____

3. Approved by: Name and Signature of members of the examining Board, and Department Head

Committee member	Name	Signature	Date
Chairman	________	________	________
External Examiner	________	________	________
Internal Examiner	________	________	________
Major Advisor	________	________	________

________________ ________________ ________________
Department head Signature Date

School of Graduate Studies
Jimma University
College of Natural Sciences
MSc. Thesis Approval Sheet

We the undersigned, number of the Board of Examiners of the final open defense by **Mengesha Alemayehu Adimas** have read and evaluated his/her thesis entitled “**Investigation of Thermoluminescence properties of zinc aluminate nanocrystal**” and examined the candidate. This is therefore to certify that the thesis has been accepted in partial fulfilment of the requirements for the degree Master of Science in **Physics (Condensed Matter Physics)**.

Name of the Chairperson	Signature	Date
Name of Major Advisor	Signature	Date
Name of Internal Examiner	Signature	Date
Name of External Examiner	Signature	Date

SCHOOL OF GRADUATE STUDIES

DECLARATION

I hereby declare that this M.Sc thesis is my original work and has not been presented for a degree in any other University and that all source of materials used for the dissertation have been duly acknowledged.

Name: Mengesha Alemayehu Adimas

Signature: _________________
email:mengeshaa800@gmail.com

This M.Sc dissertation has been submitted for examination with my approval as University advisor.

Name:Dr. Nebiyu Gemechu

Signature: ____________________

Place and date of submission:

Department of Physics

Jimma University

Jun, 2022