THERMALLY STIMULATED LUMINESCENCE OF $KY_3F_{10} : HO^{+3}$ WITH LINEAR HEATING RATE,

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This is to certify that the thesis prepared by **Gemechu Enshishu** Graduate Studies entitled "**Thermally Stimulated Luminescence of $KY_3F_{10} : Ho^{+3}$ with Linear heating rate,**" 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 work, we have employed for the analysis of TL glow curves of $KY_3F_{10} : Ho^{+3}$ material. The continuous promotion in numerical methods has greatly helped to solve the complex TL kinetic equations (rate equations) which can not be solved analytically. The complexity of the rate equations increase with the number of traps considered. In this thesis, the properties of the thermoluminescence glow curves of $KY_3F_{10} : Ho^{+3}$ has been employed theoretically in view of first order kinetics. 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.

Key Words:-
TL (Thermoluminescence)
KY_3F_{10}(Potassium triyttrium decafluoride)
Ho^{+3} (Holmium ion)

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Chapter 1

Background of the Study

1.1 Introduction

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].

To describe light emitting or luminescent material the Greek word 'phosphor' is usually used and it means 'light bearer'. A phosphor emits energy from an excited electron as light and the excitation of the electron is triggered by absorption of energy from one of the external excitation sources. An excited electron occupies a quantum state whose energy is above the minimum energy ground state. In semiconductors and insulators, the electronic ground state is commonly referred to electrons in the valence band, which is completely filled with these electrons. The excited quantum state often lies in the conduction band, which is empty and separated from the valence band by gap. Therefore unlike metallic materials, small continuous change in electron energy with in the band is not possible. Instead a minimum energy equal to the band gap energy is necessary to excite an electron in semiconductors and insulators, and the energy released by de-excitation is often nearly equal to the band gap. The band gap of semiconductor material is such that at room temperature, very few electrons are promoted from the valance band to the conduction band leaving holes in the valence band. In general, luminescence emission is explained by the transfer of energy from radiation to the electrons of the solid, thus exciting the electrons from a ground state to an excited state. The emission of a luminescent photon takes place when an excited electron returns to a lower energy state [2].

In this study, the investigation of TL properties of $KY_3F_{10} : Ho^{+3}$ phosphor is present and important Thermoluminescence kinetic parameters such as activation energy (E) and the frequency factor (s) was determined by using rate equation approach [3].

1.2 Statement of the problem

Selection of fluoride based materials for improved luminescence performance of a material is highly important. The material Potassium triyttrium decafluoride doped with holmium $KY_3F_{10} : Ho^{+3}$ has attracted much attention and is extensively studied because of its excellent optical properties and potential applications in a wide range of fields. However, the theoretical investigation of the TL properties of $KY_3F_{10} : Ho^{+3}$ 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 this material in view of first order kinetics.

1.3 Research Questions

✓ How we can investigate the Thermoluminescence properties of $KY_3F_{10} : Ho^{+3}$ theoretically in view of first order kinetics?

✓ What is the effect of various heating rate, activation energy(E) and frequency factor(s) on the Thermoluminescence glow curves in view of first order kinetics?

✓ How is the error of theoretical result when compared with experimental results of the Thermoluminescence properties of $KY_3F_{10} : Ho^{+3}$ in view of first 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 properties of the material $KY_3F_{10} : Ho^{+3}$ with linear heating rate in view of first order kinetics.

1.4.2 Specific Objectives

The specific objectives of this study are:

✓ To analyze theoretically the Thermoluminescence properties of $KY_3F_{10} : Ho^{+3}$ in view of first order kinetics.

✓ To determine the effect of various heating rate, activation energy(E) and frequency factor(s) on Thermoluminescence glow curves of $KY_3F_{10} : Ho^{+3}$ in view of first order kinetics.

✓ To analyze how the error of theoretical result when compared with experimental results of the Thermoluminescence properties of $KY_3F_{10} : Ho^{+3}$ in view of first order kinetics?.

1.5 Significance of the Study

This work helps us:

✓ To understand the peculiar properties of Thermoluminescence glow curve of $KY_3F_{10} : Ho^{+3}$ in view of first order kinetics theoretically.

✓ To investigate how the error of theoretical result when compared with experimental results of the Thermoluminescence properties of $KY_3F_{10} : Ho^{+3}$ in view of first order kinetics?.

1.6 Scope of the Study

Due to the time constraint the scope of the study is limited to theoretically investigate the properties, effect of heating rate, on the material $KY_3F_{10} : Ho^{+3}$ phosphor powder by using rate equation in view of first order kinetics.

1.7 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 the material $KY_3F_{10} : Ho^{+3}$ phosphor powder by using rate equation in view of first order kinetics.

1.8 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 and scope of the study.

In Chapter 2, we review the theoretical backgrounds of Luminescence, Thermoluminescence, Thermoluminescence application, types of Luminescence and the properties of $KY_3F_{10} : Ho^{+3}$ and its structure.

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 of $KY_3F_{10} : Ho^{+3}$ with parameter activation energy E, frequency factor s, the dose and the concentration of the trapped electron in the trap and compare the theoretical and experimental result on $KY_3F_{10} : Ho^{+3}$ material.

Finally in Chapter 5, we draw some conclusions.

Chapter 2

Review of Related Literature

2.1 Introduction

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”. Luminescence can be categorized in to fluorescence or phosphorescence. Fluorescence is light emission caused by irradiation with light (normally visible or ultraviolet light) and typically occurring within nanoseconds to milliseconds after irradiation. It involves the excitation of electrons into states with a higher energy, from which radiative decay is possible. Typically, the emitted wavelengths are longer than the excitation wavelengths; otherwise up-conversion fluorescence will occur. Phosphorescence is a light emission that can occur over much longer times (sometimes hours) after irradiation [5]. It involves storage of energy in metastable states and its release through relatively slow (often thermally activated) processes. In other words, phosphorescence is a radiational transition, in which the absorbed energy undergoes intersystem crossing into a state with a different spin multiplicity. The lifetime of phosphorescence is usually from $10^4 - 10^2 s$, much longer than that of fluorescence [6].

After the absorption of radiation, the emission of light takes place in a characteristic time t and this parameter allows us to sub classify the process of luminescence. Conventionally emissions with decay time shorter than 10^{-8} s are assumed as fluorescence and those with decay time greater than that are taken as phosphorescence and this phenomenon is shown in Fig. 2.1.

In luminescence process; the emission spectrum shifts to a lower energies relative to the absorption spectrum. This shift is called Stoke's shift. It is also possible to obtain luminescence at photon energies higher than the absorbed photon energy. This is called anti-Stokes or up-conversion luminescence and it occurs for multilevel systems. Unlike, incandescence, luminescence 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. Its fall to ground state results in the emission of light, which is called luminescence. Excitation takes place usually by UV light, also there are other sources which produce excitation. Not with standing this simple description it is only a few substances which produce luminescence, even though the exciting light is falling on them throughout the day when the sun is shining. This is because that most of the matter is not made of isolated atoms, with the result that the light energy absorbed is dissipated in increasing the rate and the amplitude of the atomic vibrations which we feel as heat. This competitive process of energy dissipation becomes overwhelming as soon as we depart from the low pressure mono-atomic gases and start dealing with

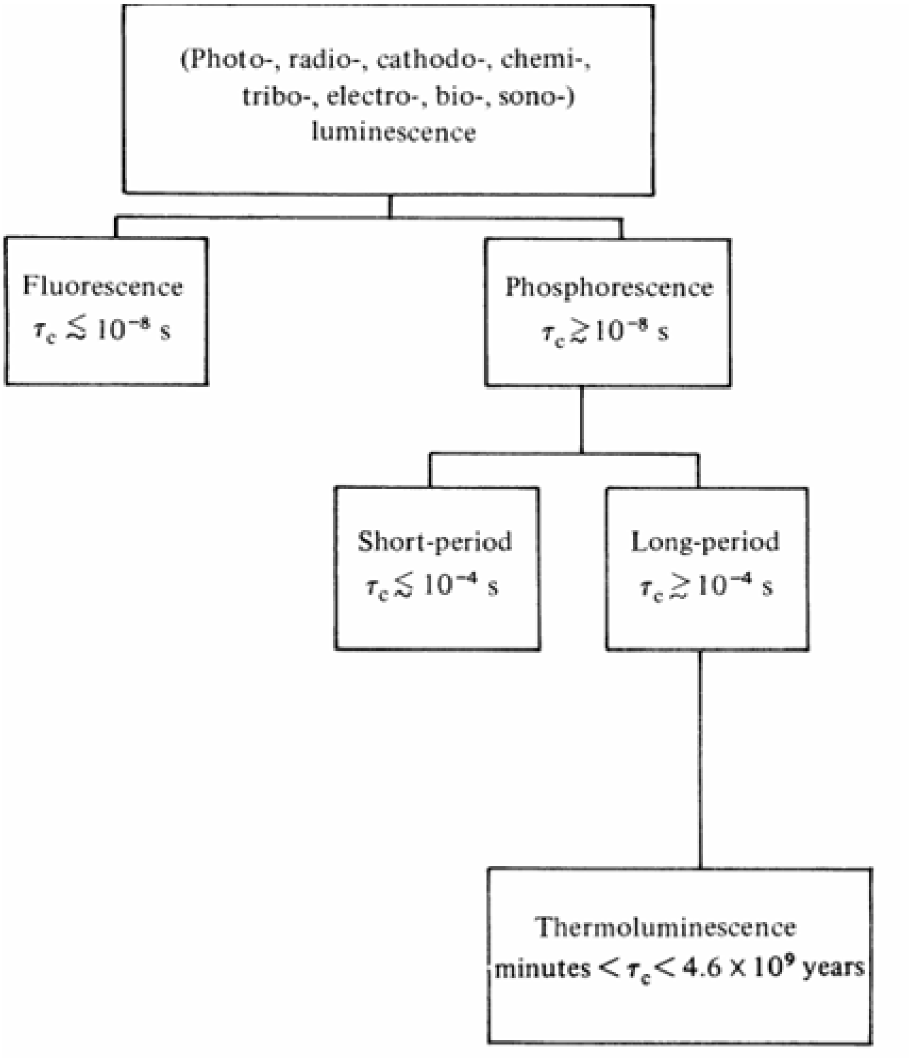

Figure 2.1: The types of luminescence based on the characteristic time t for the emission of light to take place.

condensed matter. Increasing the vibrational energy of the system raises its temperature and reduces the available energy for light emission. A striking example is the element mercury which is luminescent in the gaseous form but is nonluminescent in the liquid state. This however does not mean that luminescence is impossible in the liquids and the solids. The specific characteristic which provides an inorganic solid of the luminescent property is the presence of atomic centers whose energy levels are protected from the thermal vibrations of the atoms of the bulk medium. For example the lanthanide rare-earth ions dispersed in calcium salts and in many other crystals and glasses make very efficient luminescent centers [7].

2.2 Types of Luminescence

According to the type of radiation used to excite the emission, luminescence can be classified in to different types. These are photoluminescence, electroluminescence, thermoluminescence, cathodoluminscence, chemiluminescence, bioluminescence, triboluminescence, radioluminescences(scintillation), Ionoluminescence etc.

Photoluminescence

An electron in a semiconductor or insulator is excited to a higher energy quantum state upon absorption of external energy from electromagnetic radiation. If the electron returns (relaxes) to a lower energy quantum state by radiating a photon, the process is called photoluminescence (PL) [8-9]. In other words, photoluminescence is the process in which a substance absorbs photons and radiates photons back out. Quantum mechanically, this can be described as an excitation to a higher energy state and then a return to a lower energy state accompanied by the emission of photon.

The period between absorption and emission is typically extremely short, in the order of 10 nanoseconds. The PL intensity depends on the measurement temperature and the energy of the exciting light (known as photoluminescence excitation or PLE spectrum).

Electroluminescence

When a material emits electromagnetic radiation as a result of the application of an electric field, the process is called electroluminescence (EL) [10-11]. 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 [12-13].

Cathodoluminescence

Cathodoluminescence (CL) occurs due to the emission of light during electron irradiation [14-15]. In the beginning of the last century it was observed that invisible cathode rays produced by electrical discharges in the evacuated tubes, produced light when they struck the glass walls of the tube. The modern name for cathode rays is electrons and this type of luminescence has retained the name CL. This is a very useful form of luminescence. Beams of electrons are used for many purposes. The electron microscope employs beams of electrons to produce high resolution images of small specimens. In some cases, the beam produces CL from the specimen. This is particularly useful for the study of minerals in rocks where the presence of transition metal trace elements can cause the mineral to give off a distinctive color light.

Chemiluminescence

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

Bioluminescence

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

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 [21] and stated its importance in the process of converting mechanical energy in to light energy. It has been observed that all piezoelectric crystals exhibit triboluminescence and it is sometimes called piezoluminescence. The spectra of triboluminescence light are similar to those of photoluminescence in many substances. The excitation is due to electrification of the cleavages and cracks. Chandra [22] has summarized the mechanism of this emission in different substances.

Radioluminescence or Scintillation

Radioluminescence is produced by ionizing radiation [23, 24]. Some polymers contain organic molecules which emit visible light when exposed to such radiations as x-rays, gamma rays, or cosmic rays. It is also called scintillation because it is used as a technique to detect individual light pulses generated by the incidence of each x or gamma ray photon or a nuclear particle. Such light pulses are called scintillations, since like a spark they are very short-lived. The intensity of the scintillation (light pulse) is directly proportional to the incident gamma ray photon energy when it is totally absorbed. The measurement of the pulse intensity, therefore, provides the means for knowing the gamma ray energy. The mechanism of light emission in radioluminescence and cathodoluminscence is same because in both the cases it is the electrons, incident primarily from cathode rays or the secondary electrons produced after the first interaction of the incident x-ray photon or nuclear particle, which cause the excitation of the luminescent species in the bulk sample.

Ionoluminescence

Another interesting method of producing luminescence is the visible light produced when fast ions collide with organic, in-organics compounds. This is called ionoluminescence and it can also be defined as a phenomenon of non-thermal light emission induced by high energy accelerated particles or ion beams [25, 26]. An early application of ionoluminescence was to luminous clock dials. These relied upon a rather hazardous method of making light that involved radioactivity. A radioactive material, such as radium, was mixed with a material that displays luminescence, such as zinc sulphide. As the radium decays, it emits alpha particles and other radiation.

2.3 Thermoluminescence

Thermoluminescence (TL) is the emission of light phenomenon from some solids commonly called phosphors, which can be observed when it is heated. This should not be confused with the light emitted automatically from the material when it is heated to incandescence. In addition, Thermoluminescence is the thermally stimulated emission of light following the preceding absorption of energy from radiation. The Thermoluminescence is observed under three conditions. Firstly, the phosphors must be either semiconductor or an insulator. Secondly, the material ability to energy store when exposure radiation. Thirdly, the luminescence emission is released by heating the material. However, if the ionizing radiation is incident on a material, may be some of its energy absorbed, the material will store the energy with the release in the form of visible light when the material is heated. Furthermore, the Thermoluminescence material does not emitting light again by simply cooling with re-heating, but it must first be exposure to ionizing radiation [27].

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 [28-29].

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. Such a vacancy can trap an electron and is then called an F center. 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 [30-31].

2.4 Application of Thermoluminescence

The modernization and development in the instrumentation and better understanding of Thermoluminescence have helped the professionals to solve their problems in many fields. The present research on Thermoluminescence has explored its very high application potential in various fields such as archaeology, analysis of defects in solids, radiation dosimetry, geology, forensic sciences, 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 and leaves. Moreover, Thermoluminescence has also interesting applications in space science,thermostimulated luminescence (TSL) photography, radiation physics, petroleum exploration [32-33].

2.4.1 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 [34].

2.4.2 Defects in Solids

TL is very sensitive to traces of impurities or defects within the host material of a given sample and experiments on TL yields useful information on the properties of the various types of defect present within an insulator or semiconductor. This includes the position of the defect with in 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 [35].

2.4.3 Radiation dosimetry

Thermoluminescence has an interesting application in the field of radiation dosimetry [36]. It is clear that the absorption of radiation increases the level of Thermoluminescence observed from a given sample by filling the localized energy levels with trapped electrons while the absorption of heat from the environment tends to reduce the numbers of trapped electrons by de-trapping them.

2.4.4 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 [37].

2.4.5 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) [38].

2.5 Structure of $KY_3F_{10} : Ho^{+3}$ Phosphor

The crystal has a cubic structure space group Fm3m. The basic building unit consists of the two ionic groups$[KY_3F_8]^{2+}$ and $[KY_3F_{12}]^{2-}$ and which alternate along the three crystallographic directions [39] as shown in Figure 2.2. In the first group, the fluorine atoms form an empty cube. In the second unit, they form an empty cuboctahedron. This structure could alternatively be described in terms of clusters of octahedral arranged yttrium-centered square antiprisms which share corners and edges to generate the fluorine cubes and cuboctahedra. The potassium atoms are coordinated to 4 fluorine atoms at the distance $2.765\mathring{A}$ and to 12 fluorine atoms at the distance $3.200\mathring{A}$. The 12 fluorine atoms form truncated tetrahedra. The additional four fluorine atoms are located nearby the hexagonal faces forming Friauf polyhedral KF_{16}.

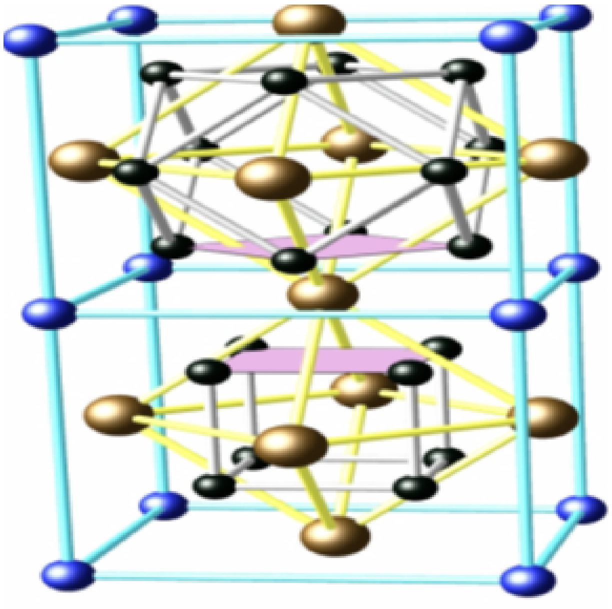

Figure 2.2: The unit cell of the Fm3m structure of KY_3F_{10}. The biggest bronze (grey) spheres substitute for yttrium atoms, the blue (grey) ones for potassium atoms, and the black ones for fluorine atoms. The nearest surrounding of yttrium ions is represented by eight fluorine ions forming a square antiprism with the C_{4v} point symmetry group [40].

2.6 Properties of $KY_3F_{10} : Ho^{3+}$ phosphor

The crystal was grown for the first time in 1971 and since then, it appears to be very attractive materials because it is fairly easy to grow [41]. Fluoride-based materials are very attractive since they possess a reasonably high thermal conductivity, good enough mechanical hardness, and high chemical stability compared with other low phonon energy materials such as chlorides, bromides, or sulfides. In particular, (KY_3F_{10}) host material has much higher energy transfer efficiency in it than other fluorides such as BaY_2F_8 and $LiYF_4$, and this makes it even more interesting for luminescence applications. Because of its excellent material properties such as high chemical and thermal stability, transparency, isotropy, ease of growing, suitability to build solid state lasers, white-light emitters, and quantum cutting systems to enhance solar cell efficiency. KY_3F_{10} doped with holmium and different rare earth elements has attracted much attention and been extensively studied. It is used for various applications in a wide range of fields such as for optical studies, laser applications, scintillation, and displays [42, 43-44].

The KY_3F_{10} and family are usually doped with various trivalent rare earth ions in order produce phosphors with improved luminescence property for different applications though still these studies do not focus on its TL properties. Doping of KY_3F_{10} host with holmium has significant advantage over other rare earth ions because Ho^{3+} ion has a high-gain cross-section and long lifetime of $^5I_7$ upper level emission that results in high efficiency and energy storage capacity [45].

2.7 First order kinetics

First order kinetics mean that: the TL intensity I at any temperature during heating depends only on the concentration of the active traps at that temperature. If the values of I are dependent also on the concentration h of the recombination centers (RC), it becomes a case of non-First order kinetics. In the case of first order kinetics, every charge carrier that manages to escape a trap immediately produces luminescence and is not captured by another trap or no re-trap is allowed and during Thermoluminescence the temperature increases linearly with time. This leads to an exponential after glow decay profile and an asymmetric Thermoluminescence glow peak with a negative skew. The expressions for first order kinetics are only valid in ideal situations, i.e., when the re-trapping probability is negligible. An alternative to the above analytical approach to describe the trap-filling process is to use a set of rate equations, which represent the flow of charges between the valence band, the conduction band, and the electron traps and the hole centers following ionization by irradiation. The rate equations have to be solved numerically to find the number of filled electrons traps at the end of the irradiation which implies the dose. The results of the numerical computations depend on the values of the input parameters used in the equations. An important result, which has implication for theoretical cases is that the population of the filled traps n, produced by irradiation depends on the electron-hole generation rate by ionization, which means that the thermoluminescence output for a given dose would depend on the dose rate as well. The dose rate dependence of Thermoluminescence could have important consequences in dosimetric application [46].

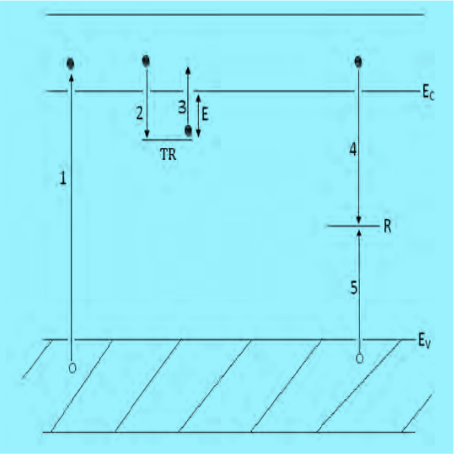

Figure 2.3: During the excitation stage (1) electrons and holes are produced which are trapped (5) in trapping, TR, and Recombination centers, R. During the heating stage (3) electrons are released to the conduction band and move through the Conduction band until they encounter a hole in a recombination center (4). The recombination energy will excite the center and relaxation of the excited center will produce the luminescence [47].

2.7.1 Simple Model of Thermoluminescence

The simplest model to explain TL is the One Trap One Recombination ($OTOR$) model (Figure 3). Absorption of radiant energy with energy greater than the band gap results in the ionization of valence electrons, producing energetic electrons and holes which will, after thermalization, produce free electrons in the conduction band and free holes in the valence band. A certain percentage of the freed charge carriers will be trapped: the electrons at Tr and the holes at R (transitions 5). There is a certain probability that the charge carriers escape from these traps due to thermal stimulation.

2.7.2 Randall and Wilkins Model

The theoretical model for the thermoluminescence emission was first suggested by Randall and Wilkins. They assumed that the retrapping may be negligible ($R_{ret} = 0$)[47].

$$I = cR_{ex} = cns\exp(\frac{-E}{KT}), \tag{2.7.1}$$

where the temperature can be expressed in terms of the linear heating rate as β as $T = T_0 + \beta t$ and c is a constant representing the optical efficiency factor relating the luminescence output to the electron release rate and the measuring instrument's efficiency to collect the light. The constant c influences only the intensity of the glow curve and it doesn't affect the characteristics like the shape of the glow curve and its decay pattern. Therefore its value can be taken to be unity. Now we have [48],

$$\frac{dn}{n} = -s\exp(\frac{-E}{KT}dt^{'}), \tag{2.7.2}$$

Assuming linear heating rate i.e, $\frac{dT}{dt} = \beta ks^{-}1$, this equation may be written as,

$$\frac{dn}{n} = -(\frac{s}{\beta})\exp(\frac{-E}{KT}dT^{'}), \tag{2.7.3}$$

Integrating this equation, the value of n at any temperature T during the heating process is expressed as,

$$n = n_o\exp(-\int_{T_o}^{T}(\frac{s}{\beta})\exp(-\frac{E}{KT^{'}})dT^{'}), \tag{2.7.4}$$

where n_0 is the initial concentration of trapped electrons and T_0 is the temperature at the beginning of the heating process. Substituting this expression for n in (2.7.4) we get the expression for Thermoluminescence intensity I(T), as a function of temperature T as,

$$I(T) = n_o s \exp(-\frac{E}{KT}) \exp[(-\int_{T_o}^{T} (\frac{s}{\beta}) \exp(-\frac{E}{KT'}) dT')]. \qquad (2.7.5)$$

Equation (2.7.5) gives the expression of the glow curve. The integral in this equation can be expressed as,

$$\int \exp(\frac{-E}{KT}) dT = \exp(\frac{-E}{KT}) T + \frac{EXExpIntralEi(\frac{-E}{KT})}{K}, \qquad (2.7.6)$$

where $ExpIntegralEi(\frac{-E}{KT})$ gives the exponential integral function $Ei(\frac{-E}{KT})$.

In this study, theoretical investigation of Thermoluminescence properties, the effect of variable heating rate on $KY_3F_{10} : Ho^{3+}$ phosphor is presented and the experimentally determined value of kinetic parameters such as activation energy (E) and the frequency factor (s) were used (E=0.916 eV, $s = 2.65x10^{11}s^{-1}$) in this work [49].

Chapter 3

Materials and Methodology

This study has been carried out by using the following procedures. These are: materials used and, the methodology.

3.1 Methodology

3.1.1 Analytical

Analytical solution of the rate equations are 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 are employed. Therefore, for numerical calculations, Mathematica Software will be used to determine the effect of heating rate, activation energy(E) and frequency factor(s) on Thermoluminescence glow curves of $KY_3F_{10} : Ho^{+3}$ in view of first order kinetics.

3.1.2 Computational(Graphical)

The properties of Thermoluminescence of the material $KY_3F_{10} : Ho^{+3}$ with linear heating rate will be interpreted graphically with Mathematica.

3.1.3 Ethical Consideration

The University guidelines and regulations are strictly followed and respected. Ethical authorization like proper citations and appropriative verification will be obtained from research review and Ethical committee of College of Natural Science, Jimma University. Any concerned will be informed about the purpose of the study.

Chapter 4

Results and Discussion

4.1 Thermoluminescence glow curve Properties of $KY_3F_{10} : Ho^{+3}$ 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 2.7.4 and 2.7.5 is used and then we can generate by using the parameter E, s, n_o, radiation dose 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 $KY_3F_{10} : Ho^{+3}$ Phosphor.

4.1.1 The variation concentration of electron in traps

It is interesting to note that there was no observed shift of the intensity peak positions to high or low temperature region due to the variation of the initial filled concentration of electron n_o in traps then by using the equation (2.7.4).

This means that the peak characteristics are independent of n_o in the sample , which

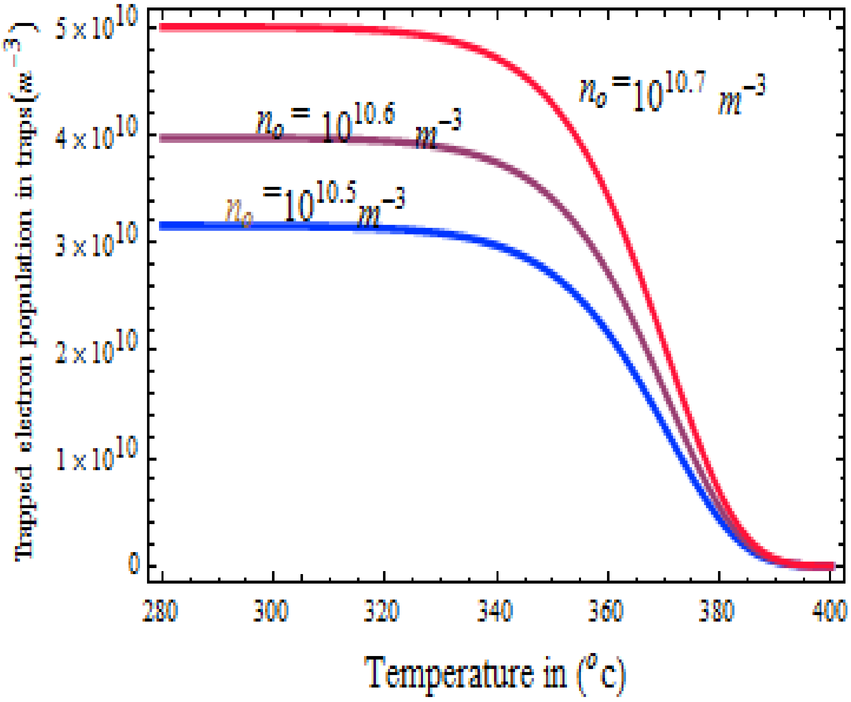

Figure 4.1: Variation of concentration of electron population in traps versus temperature for $KY_3F_{10} : Ho^{+3}$ at different initial concentration n_o of the electron in traps. As indicated, the peak of the glow curve does not change. The glow peak characteristics, namely the peak temperature and the peak shape remain unchanged when the initial filled concentration of the traps is changed

indicate the population of electron in traps. However, the intensity (the area as well as the height of the peak) increases in direct proportion to for given E, s and β. These characteristics are of prime importance in the application of Thermoluminescence in radiation dosimetry as well as in kinetics analysis of the Thermoluminescence glow curves of $KY_3F_{10} : Ho^{+3}$ Phosphor. When the initial concentration of electron in traps n_o is changed the peak characteristics are independent of radiation dose given to the sample. Also the vertical axis represents the trapped electron population in traps at T= T_o. At temperature of 280^oc, 300^oc, 320^oc there is no electron traped to the CB b/se the temperature is not enough to eject it, but at the temperature of 350^oc there is electron traped to the CB and at 400^oc all electrons are excited to CB. However, the intensity (the area as well as the height of the peak) increases in direct proportion to for given E,s and β. These characteristics are of prime importance in the application of Thermoluminescence in radiation dosimetry as well as in kinetics analysis of the Thermoluminescence glow curves of the material.

4.1.2 Effect of Activation Energy E on Thermoluminescence glow curves of $KY_3F_{10} : Ho^{+3}$ 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 (2.7.5) which has been generated by using Mathematica for the graph and the input parameters used are E =0.818 ev, 0.918 ev, 1 ev, $\beta = 1.2^o c/s$, $s = 2.65x10^{11}s^{-1}$,Initial concentration of trapped electron $n_o = 10^{10}cm^{-3}$.

This is useful to determine the properties of Thermoluminescence glow curves of $KY_3F_{10} : Ho^{+3}$ at different values of activation energy E with temperature $T = 0^o c - 450^o c$ and the other parameter is kept constant in these case.

The initial part of the Thermoluminescence glow curves for $KY_3F_{10} : Ho^{+3}$ rises exponentially. In the initial rise part of the Thermoluminescence glow curves for

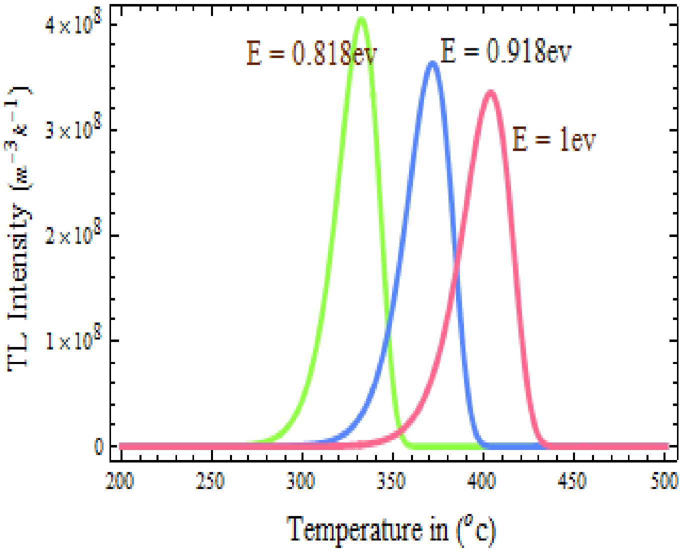

Figure 4.2: The Thermoluminescence Intensity of the glow curve of $KY_3F_{10} : Ho^{+3}$ at three different E values

$KY_3F_{10} : Ho^{+3}$, 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 $KY_3F_{10}:Ho^{+3}$ at different activation energy:-

In Fig.4.2, we varied the activation energy E in equation (2.7.5)from 0.818 ev , 0.918 ev, 1 eV. 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 reduced.

4.1.3 Effect of Radiation dose on Thermoluminescence glow curves of $KY_3F_{10}:Ho^{+3}$ phosphor

Thermoluminescence glow peak, gives the intensity of the emitted light as a function of temperature at a particular exciting radiation dose. Radiation dose plays a crucial role in the filling of the traps constituting a Thermoluminescence material and the Thermoluminescence response of a given sample to a known dose depends on the number of the traps filled by the given dose. A simple way to estimate the number of the filled traps is to assume the filling rate to be directly proportional to the dose and also directly proportional to the vacancies in the traps. The dose at which all of the traps get filled up depends solely on the fraction of vacant traps which get filled up per unit dose. The thermoluminescence intensity of most phosphor materials increases with increasing radiation dose up to a certain level and then decreases. This decrease of the Thermoluminescence glow peak can be attributed to the stronger competition with non-radiative centers at higher doses. At a given temperature of irradiation, many phosphor materials display an intensity of Thermoluminescence which is proportional (or nearly so) to the amount of radiation absorbed, and this leads to the fact that Thermoluminescence may be used as a means of radiation dosimetry. In general the Thermoluminescence glow curve of a good dosimetry is directly proportional to the applied dose. The absorption of radiation increases the level of Thermoluminescence observed from a specimen by filling the localized energy levels with trapped electrons. The absorption of heat from the environment, on the other hand, tends to reduce the numbers of trapped electrons by thermally releasing them. Thus, the intensity of the Thermoluminescence is a competition between trap filling by radiation and trap emptying by thermal excitation.

In Fig.4.3, shown below indicate how I(T) varies if the radiation dose varies from $10^{10.5}m^{-3}$, $10^{10.8}cm^{-3}$ and $10^{11}cm^{-3}$ while E =0.918 eV , $s = 2.65x10^{11}s^{-1}$ and $\beta = 1.2^{o}c/s$ are kept constant. It can be noted that the temperature at the peak stays fixed.

From Fig.4.3, we observed that not only the peak height at the maximum but each point of the curve is proportional to dose. In the application in dosimetry dose is the parameter of supreme importance since this parameter is proportional to the absorbed dose. It is simple to see that the area under the glow peak is equal to the dose.

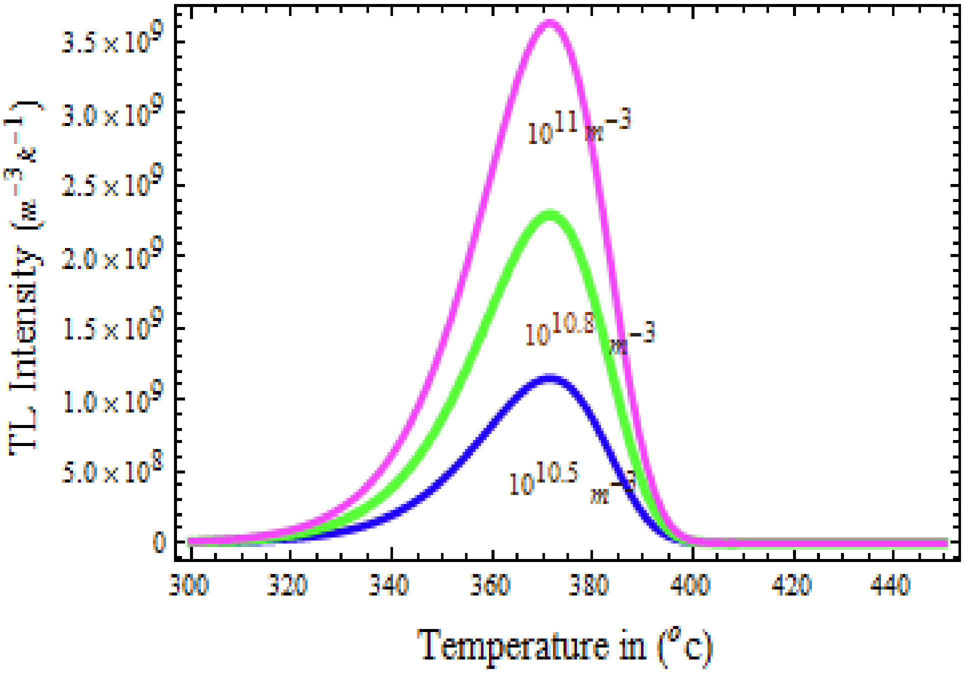

Figure 4.3: The Thermoluminescence intensity versus temperature of the TL glow curves for $KY_3F_{10} : Ho^{+3}$ at three different values of dose by using equation (2.7.5)

These characteristics are very importance in the application of radiation dosimetry as well as in kinetics analysis of the Thermoluminescence glow curves of $KY_3F_{10}:Ho^{+3}$ Phosphor powder. Also as we observed from the above graph when the value of the dose given to the sample was increased up to $10^{11}m^{-3}$ and above this dose then the peak is decreased.

4.1.4 Effect of frequency factor s on Thermoluminescence glow curves of $KY_3F_{10}:Ho^{+3}$ phosphor

Properties of TL glow curve for $KY_3F_{10}:Ho^{+3}$ Phosphor, showing the variation with the frequency factor s from equation 2.7.5 given in literature. Parameter values we used are $n_o = 10^{10}cm^{-3}$, E = 0.918 eV, $\beta = 1.2^oc/s$ with different s (i,e $s_1 = 2.65x10^{11}s^{-1}$, $s_2 = 2.65x10^{12}s^{-1}$, $s_3 = 2.65x10^{13}s^{-1}$) of in which parameter s is varied while the others are kept constant.

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

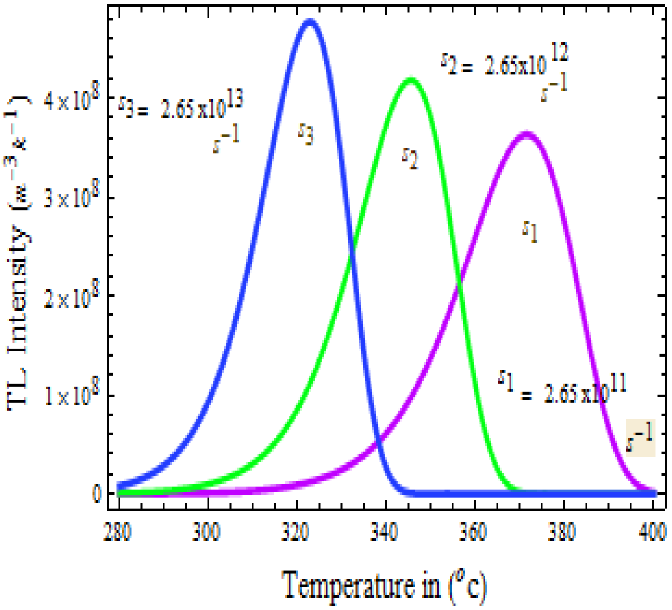

Figure 4.4: The thermoluminescence Intensity of the glow curve of $KY_3F_{10} : Ho^{+3}$ at different frequency factor s values

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.

4.2 Effect of heating rate on Thermoluminescence glow curves of $KY_3F_{10} : Ho^{+3}$ 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 $KY_3F_{10} : Ho^{+3}$ varies at three different value of heating rates. As we expected from the result, 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, Fig. 4.5 shows corresponding Thermoluminescence glow curves of with different heating rate and from the figure we conclude that:-

- Glow peak height increases with the increase of the heating rate
- Peak position shifts toward higher temperature
- Area under the glow curve is not conserved and is a function of heating rate.

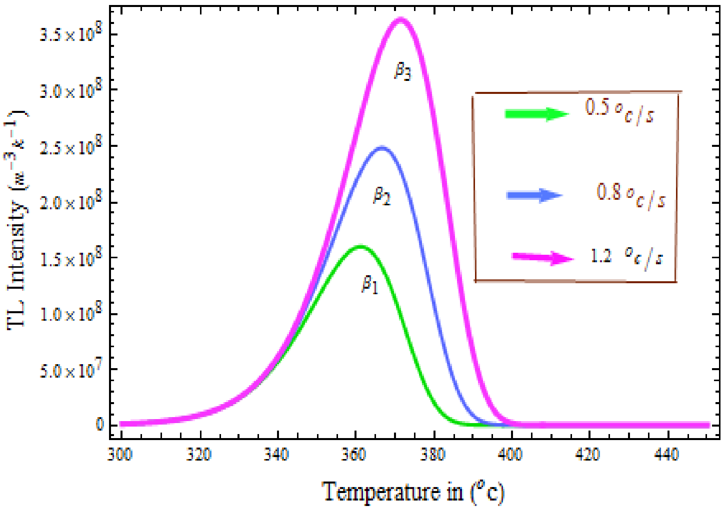

Figure 4.5: Thermoluminescence Intensity versus temperature of TL glow curves for KY_3F_{10} : Ho^{+3} Phosphor at different heating rate (β). As indicated, the peak of the glow curves increase and shift to higher temperature region with increasing the value of β and the other parameter is kept constant E = 0.918 ev, $n_o = 10^{10}cm^{-3}$, $s = 2.65x10^{11}s^{-1}$ while the value of heating rate β is varied from $0.5^oc/s$, $0.8^oc/s$, $1.2^oc/s$

4.3 The comparison of theoretical and experimental result on the Thermoluminescence glow curve of $KY_3F_{10} : Ho^{+3}$ Phosphor

When we compare the theoretical and experimental result on the Thermoluminescence glow curve of $KY_3F_{10} : Ho^{+3}$:-

- ✓ For given values of E and β, the glow peak shifts to lower temperature as s is increased. Thus, it is clear that E and s have opposite effects on temperature.
- ✓ when the value of the dose given to the sample was increased up to $10^{11}m^{-3}$ and above this dose then the peak is decreased. This decrease of the Thermoluminescence glow peak can be attributed to the stronger competition with non-radiative centers at higher doses.
- ✓ But in our work there is some difference between the theoretical and experimental result on the TL glow peak of $KY_3F_{10} : Ho^{+3}$ Phosphor. This means, experimentally as heating rate increase the TL glow peak of $KY_3F_{10} : Ho^{+3}$ Phosphor was decreased and shift to the maximum temperature. But, as we conclude from our work as heating rate increased the TL glow peak of $KY_3F_{10} : Ho^{+3}$ was increased and the glow peak is shift to the maximum temperature as we observe from fig.4.5.

Chapter 5

Conclusion

In this study, the thermoluminescence kinetic parameters such as activation energy E, the effect of dose on TL Intensity, concentration of trapped electron (n_o) and frequency factor s was reported to express the properties of Thermoluminescence glow curve of $KY_3F_{10} : Ho^{+3}$.

The Thermoluminescence intensity increases with an increase in the initial concentration of trapped electrons (n_o) and then decreases by using the equation (2.7.4) 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.

We varied the activation energy E in equation (2.7.5) as 0.818 ev , 0.918 ev , 1 eV.

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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