



SECOND ORDER KINETICS THERMOLUMINESCENCE BEHAVIOR OF $KY_3F_{10} : HO^{3+}$ PHOSPHOR

A Thesis Submitted to the Department of Physics

Jimma University

In Partial Fulfilment of the Requirement of the Degree of

Masters in Physics(**Condensed Matter Physics**)

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Abstract

The behavior of thermoluminescence glow curve properties of $KY_3F_{10} : H_o^{3+}$ phosphor in view of second order kinetics was studied. Kinetic parameters of the glow curves used to determine the activation energy (E) the initial concentration of filled traps n_o and frequency factor (s) of the different peaks present in the phosphor. Thermoluminescence measurements with different heating rates, with increasing heating rate, the maximum of a Thermoluminescence glow peak shifts to higher temperatures. At a higher temperature, the luminescence is quenched more intensely so that the whole area under thermoluminescence peak decreases. Thermoluminescence measurements were carried out from 350 to 500 K with varying heating rates in the range of 0.5 to 2 K/s. Two thermoluminescence glow peaks centered at Temperature max = 350 and 500 K were observed at heating rate of $\beta= 0.5$ K/s. For low-temperature peak , thermoluminescence intensity decreased whereas that for high-temperature peak increased with elevating the heating rates, which means anomalous heating rate behavior occurred for high-temperature peak.

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Introduction

1.1 Background of the Study

Luminescence is the emission of light by a material as a consequence of absorption of energy [1-3]. A material that emits light is called luminescent material. More precisely, luminescence is produced by the selective excitation of the atomic or molecular energy levels. The atom or the molecule is taken to a higher energy state because of excitation and its fall to ground state results in the emission of light, which is called luminescence. So, in Latin Lumen means light, the term luminescent materials refer to materials that can emit light, especially in the visible range such as crystals, minerals, and chemical substances. Luminescence can be categorized into fluorescence or phosphorescence. Fluorescence is light emission caused by irradiation with light (normally visible or ultraviolet light) and typically occurring within nanoseconds to milliseconds after irradiation [1,3,4]. It involves the excitation of electrons into states with a higher energy, from which radiative decay is possible. Typically, the emitted wave lengths are longer than the excitation wave lengths; otherwise up-conversion fluorescence will occur. Phosphorescence is a light emis-

sion that can occur over much longer times (some times hours) after irradiation. The life time of phosphorescence is usually from $10^{-4} - 10^{-2}$ s, much longer than that of fluorescence [5]. Thermoluminescence is the emission of light from an insulator or semiconductor when it is heated. This is not to be confused with the light spontaneously emitted from a substance when it is heated to incandescence. Thermoluminescence is the thermally stimulated emission of light following the previous absorption of energy from radiation [1]. The term thermoluminescence 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. The word phosphor was invented in the early 17th century and its meaning remains unchanged till today. Early alchemists found a heavy crystalline stone with a gloss at the foot of a volcano, and fired it in a charcoal oven intending to convert it to a noble metal. They found that the sintered stone emitted red light in the dark after exposure to sunlight rather than being converted in to metal. After this discovery, similar findings were reported from many places in Europe, and these light-emitting stones were named phosphors [8]. This word means light bearer in Greek. In other words, a phosphor emits energy from an excited electron as a light. In general, the excitation of electron is caused by absorption of energy from an external source such as another electron, a photon, or an electric field. Thermoluminescence properties of $KY_3F_{10} : Ho^{3+}$ phosphor powder is reported. Potassium triyttrium decafluoride $KY_3F_{10} : Ho^{3+}$ has attracted much attention and has been extensively studied because of its excellent optical properties and potential applications in a wide range of fields: laser applications [12], scintillation and

display devices [13]. It also possesses low-maximum phonon frequency leading to a large number of potential emitting levels as well as high luminescent efficiency. Compared to other low phonon energy materials such as chlorides, bromides, or sulphides, the fluorides present a reasonably high thermal conductivity, a good enough mechanical hardness, and a high chemical stability. The $KY_3F_{10} : Ho^{3+}$ phosphor is a single-site host material for rare-earth ions to occupy which ensure homogeneously broadened absorption and emission spectra. This last point is especially crucial to investigate the multipolar interactions between ions. In addition to all the aforementioned interesting properties, KY_3F_{10} has much higher energy transfer efficiency in it than other fluorides such as BaY_2F_8 and $LiYF_4$, this makes it an interesting material for luminescence applications.

1.2 Statement of the Problem

In this thesis, we want to know the thermoluminescence behavior of $KY_3F_{10} : Ho^{3+}$ phosphor in view of second order kinetic. In consider to Luminescent materials have found wide application in many fields in recent years. Major traditional applications include lighting and emissive display device amplifiers in optical communication and lasers. In addition, phosphors also find applications in X-ray detector systems and scintillators. Developments on the theoretically investigate thermoluminescence properties of $KY_3F_{10} : Ho^{3+}$ phosphor in view of second order kinetics. We have been studied to the theoretical and experimental results of the thermoluminescence properties of $KY_3F_{10} : Ho^{3+}$ phosphor and calculated in the effect of various heating rates on thermoluminescence glow curves of $KY_3F_{10} : Ho^{3+}$ phos-

phor in view of second order kinetics, we develop the following research questions.

1.2.1 Basic Research Questions

1. What is the theoretically thermoluminescence properties of $KY_3F_{10} : Ho^{3+}$ phosphor in view of second order kinetics?
2. What is the effect of various heating rates on thermoluminescence glow curves of $KY_3F_{10} : Ho^{3+}$ phosphor in view of second order kinetics?
3. What is the theoretical and experimental results of the thermoluminescence properties of $KY_3F_{10} : Ho^{3+}$ phosphor in view of second order kinetics?

1.3 Objectives of the study

1.3.1 General objective

The general objective of this research was to investigate "Second Order Kinetics Thermoluminescence Behavior of $KY_3F_{10} : Ho^{3+}$ Phosphor".

1.3.2 Specific objectives

1. To identify the theoretical thermoluminescence properties of $KY_3F_{10} : Ho^{3+}$ phosphor in view of second order kinetics.
2. To describe the effect of various heating rates on thermoluminescence glow curves of $KY_3F_{10} : Ho^{3+}$ phosphor in view of second order kinetics.
3. To describe the theoretical and experimental results of the thermoluminescence properties of $KY_3F_{10} : Ho^{3+}$ phosphor in view of second order kinetics.

1.4 Significance of the Study

The significance of this study was:-

- ★ To determine both analytically on thermoluminescence behavior of $KY_3F_{10} : Ho^{3+}$ phosphor and to the effect of various heating rates on thermoluminescence glow curves of $KY_3F_{10} : Ho^{3+}$ in view of second order kinetics for further understanding.
- ★ To determine the theoretical and experimental results of the thermoluminescence properties of $KY_3F_{10} : Ho^{3+}$ phosphor in view of second order kinetics for further understanding. These phosphors are Ho^{3+} doped KY_3F_{10} , so this study contribution will be important information to any researchers and expects in the same areas.

1.5 Scope of the Study

The scope of this study is delimited to investigating the thermoluminescence behavior of $KY_3F_{10} : Ho^{3+}$ phosphors in view of second order kinetic theoretically and focus only on the theoretical analysis and calculation of the theoretically the thermoluminescence properties of $KY_3F_{10} : Ho^{3+}$ in view of second order kinetics. In addition to determine the effect of various heating rates on thermoluminescence glow curves of $KY_3F_{10} : Ho^{3+}$ phosphor in view of second order kinetics.

1.6 Limitations of the Study

The researcher might face the following limitations:

- ★ Lack of adequate reference and time constraint etc.
- ★ Lack of instability peace

2

Literature Review

2.1 The Concept of Luminescence

Luminescence is the emission of light by a material as a consequence of absorption of energy [1-3]. A material that emits light is called luminescent material or Luminescence is, in some ways, the inverse process to absorption. Absorption of photons of appropriate frequency causes an atomic system shift to the excited states. This atomic system can return to the ground state by spontaneous emission of photons. This de-excitation process is called luminescence. However, the absorption of light is only one of the multiple mechanisms by which a system can be excited. In a general sense, luminescence is the emission of light from a system that is excited by some form of energy [1,3-5]. There are different sources of excitation, namely, UV light, x-rays, γ -rays etc. For instance, some minerals show some kind of luminescence under ultra-violet light exposure and some need x-ray bombardment. The presence of atomic centers whose energy levels are protected from the thermal vibrations of the atoms of the bulk medium, for example, the transitions of inner 4f electrons in lanthanide rare-earth ions, is the specific characteristic which provides

an inorganic solid the luminescent property. Luminescence phenomena can also be observed in organic solids. While the luminescence of inorganic solids is mostly due to impurity atoms or other lattice defects, the luminescence in organic solids is attributed to molecular complexes [15]. In luminescence process, the emission spectrum shifts to a lower energies relative to the absorption spectrum. This shift is called Stokes 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. Depending on the excitation mechanism, luminescence can be categorized in to different types. The most important types of luminescence are :-

- ◆ Thermoluminescence, there-emission of absorbed energy when a substance is heated = Heat.
- ◆ Photoluminescence, a result of absorption of photons = Electromagnetic radiation.
- ★ Fluorescence, photoluminescence as a result of singlet-singlet electronic relaxation (typical lifetime: nanoseconds).
- ★ Phosphorescence, photoluminescence as a result of triplet-singlet electronic relaxation (typical lifetime: milliseconds to hours).
- ★ Raman emission, photoluminescence as a result of inelastic light scattering, (lifetime: nanosecond).
- ★ Cathodoluminescence, a result of a luminescent material being struck by electrons = Electrons.
- ★ Electroluminescence, a result of an electric current passed through a substance=)

Electric field.

- ★ Mecholuminescence, a result of a mechanical action on a solid.
- ★ Sonoluminescence, a result of imploding bubbles in a liquid when excited by sound.
- ★ Radioluminescence, a result of bombardment by ionizing radiation.
- ★ Chemiluminescence, the emission of light as a result of a chemical reaction.
- ★ Bioluminescence, a result of biochemical reactions in a living organism .
- ★ Electro chemiluminescence, a result of an electrochemical reaction.
- ★ Crystalloluminescence, produced during crystallization.

2.2 Theory of Thermoluminescence

Thermoluminescence (TL) is the phenomenon of light emission upon heating a material, which has been previously excited [1]. All types of radiations such as gamma rays, x-rays, alpha particle , beta particle and light rays can excite a material but to widely different extents. Thermoluminescence is the emission of light from an insulator or semiconductor when it is heated or 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 emit light again by simply cooling with re-heating, but it must first be exposure to ionizing radiation [1].

2.3 Simple Model of Thermoluminescence (OTOR)

The simple two level models of thermoluminescence. A simple energy level scheme consisting of two localized levels (one act as trap (TR) and the other act as recombination center (R)) there are just two localized levels, one situated between the demarcation level and the delocalized band (i.e., E_t and E_c or E_h and E_c is shown in Fig. (2.1). It is also called one trap and one recombination center (OTOR) model. The traps are assumed to be electron traps and the recombination centers are hole traps. The traps and the recombination centers get filled up by the respective type of charge carriers following irradiation of the specimen. The electrons are ejected out of the traps (de trapped) and become free to move in the conduction band during the heating stage after absorption of enough energy E corresponding to the trap depth [1]. The absorption of radiation of energy $(h\nu) > E_c - E_v$ (i.e., greater than the band gap energy results in the ionization of valence electrons, producing free electrons in the conduction band and free holes in the valence band (transition 1). The free carriers may either recombine with each other or become trapped at the trap centers. In order for recombination to occur holes first become trapped at cen-

ters (R)(transition 5). Recombination takes place via the annihilation of the trapped holes by free electrons (transition 4). If, in this model, the recombination transition is assumed to be radiative, then luminescence will result [1,4]. The free electrons may also become trapped at level T (transition 2) in which case recombination can only take place if the trapped electrons absorb enough energy E to be released back to conduction band, from where recombination is possible. During the random motion of the electrons in the conduction band following ionization (irradiation) and thermal release, the electrons may recombine with holes trapped at recombination center (R) emitting light. Alternatively, the electrons may also fall back into an empty trap. This is called re trapping. Thus the transport of electrons from the traps to the recombination centers to emit luminescence may be described in terms of rate of excitation, re trapping and recombination These three rates for the OTOR model are given by [2]

$$\text{Excitationrate, } R_{ex} = n_s \exp\left(\frac{-E}{kT}\right) \quad (2.1)$$

$$\text{Retrappingrate, } R_{ret} = n_c A (N - n) \quad (2.2)$$

$$\text{Recombinationrate, } R_{rec} = n_c A_r n_h \quad (2.3)$$

where N and n, respectively are the total and the filled concentration of the thermally active traps, n_c is the concentration of the charge carriers in the conduction band, n_h is the concentration of holes in the recombination center, E is the activa-

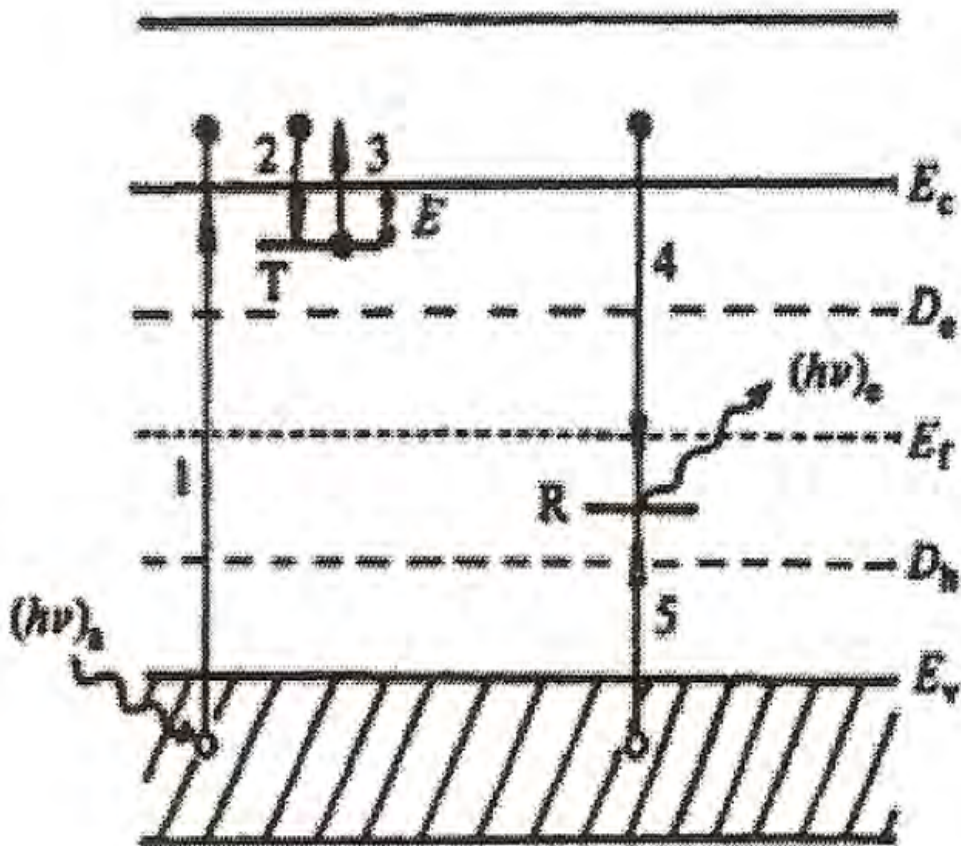


Figure 2.1: Two level model for thermoluminescence. Allowed transitions: (1) ionization; (2),(5), trapping; (3) thermal release (de trapping); (4) radiative recombination and emission of light.

tion energy of the trap, which is also called the trap depth, T is the sample temperature, K is the Boltzmann constant, A and A_r , respectively are the retrapping and the radiative recombination probability coefficients. The values of these coefficients depend on the capture cross sections σ and σ_r of the traps and the recombination centers, respectively: $A = \sigma v$ and $A_r = \sigma_r v$ where v is the velocity electron in the conduction band). The physical scheme used in formulating any particular model of thermoluminescence determines the value of n_h . Since the overall charge neutrality condition should be ensured, the value of n_h is the sum of all the filled traps in the sample, which means the filled active traps n and any deeper level traps which are thermally not affected, at the given temperature T . It is assumed that all the excited charge carriers relax from conduction band instantly either into the recombination center or alternatively into the empty traps, with no significant number of these being left behind in the conduction band. This is called the quasi-equilibrium condition. The fraction η of the excited carriers which produces luminescence during heating stage (luminescence efficiency) is given by the following equation [1].

$$\eta = \frac{R_{ret}}{R_{ret} + R_{rec}} \quad (2.4)$$

The value of η strongly depends on the values of the parameters in equations (2.1) to (2.3). Depending on the existence of other possible routes of relaxation, for example non-radiative recapture in deeper level traps, the denominator in (2.4) may increase. model.

2.4 Garlick and Gibson model

The model proposed by RW [7] for TL intensity was modified by Garlick and Gibson (GG) in 1948 [6] using the same one trap and one recombination (OTOR) model. The assumption made by GG was that an electron which is de trapped in to the conduction band from the trap centers after absorption of thermal energy may either recombine with a hole trapped at recombination center to produce luminescence or may be re trapped by any of the vacant traps. However, in RW model, retrapping is ignored and the de trapped electrons are assumed to recombine directly with the trapped holes emitting light. Using the probability coefficients for re trapping and recombination A and A_r respectively, the recombination and re trapping terms, respectively are proportional to $A_r n$ and $A(N-n)$, where N is the total number of the traps and n is the number of available recombination centers at any time. In the OTOR model n is also equal to the number of filled traps, so that the charge neutrality condition is maintained. The recombining fraction η of this combined probability of transitions for any excited carrier, then is,

$$\eta = \frac{A_r n}{A_r n + A(N - n)} \quad (2.5)$$

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

time, that a trapped electron will escape from the trap, is given by Arrhenius equation, having considered that the electrons in the trap have a Maxwellian distribution of the thermal energies.

$$P = s \cdot \exp\left(\frac{-E}{kT}\right) \quad (2.6)$$

Where P is E is the trap depth (eV), K is the Boltzmann's constant, T the absolute temperature (K), s is the frequency factor sec^{-1} depending on the frequency of the number of hits of an electron in the trap, seen as a potential well. The life time, τ , of the charge carrier in the metastable state at temperature T, is given by

$$\tau = p^{-1} \quad (2.7)$$

$$\tau = s \cdot \exp\left(\frac{-E}{kT}\right) \quad (2.8)$$

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:

$$\frac{dn}{dt} = -p * n \quad (2.9)$$

Integrating this equation:

$$\int_{n_0}^n \frac{dn}{n} = \int_{t_0}^t p \cdot dt \quad (2.10)$$

One obtains

$$n = n_0 \exp\left[-s \exp\left(\frac{-E}{kT}\right) \cdot t\right] \quad (2.11)$$

$$I(T) = -C \left(\frac{dn}{dt} \right) = Cpn \quad (2.12)$$

$$I(T) = -\frac{dn}{dt} = \left(\frac{n}{N} \right) * \left(\frac{n}{\tau} \right) \quad (2.13)$$

$$I(T) = -\frac{dn}{dt} = \left(\frac{n}{N} \right) ns \exp\left(\frac{-E}{kT}\right) \quad (2.14)$$

$$I(T) = \left(\frac{n^2}{N} \right) s \exp\left(\frac{-E}{kT}\right) \quad (2.15)$$

The quantity $s' = \frac{s}{N}$ is called pre-exponential factor and it is the constant having dimension of $cm^3 sec^{-1}$.

$$\frac{dn}{dt} = -n^2 s' \exp\left(\frac{-E}{kT}\right) \quad (2.16)$$

Equation (2.16) is different from that one obtained in the case of first order kinetics, where the recombination probability was equal to 1, since no re trapping is possible. The integration of equation (2.12), considering the temperature as a constant, given the occupancy function $n(n)$ as:

$$n = n_o [1 + s' n_o t \exp\left(\frac{-E}{kT}\right)] \quad (2.17)$$

and then, the TL intensity $I(t)$ is:

$$I(t) = \frac{dn}{dt} = \frac{n_o^2 s' \exp\left(\frac{-E}{kT}\right)}{n_o [1 + s' n_o t \exp\left(\frac{-E}{kT}\right)]} \quad (2.18)$$

Which describes the hyperbolic decay of phosphorescence. The luminescence intensity of an irradiated phosphor under rising temperature, i.e. thermolumines-

cence, is obtained from equation (2.16) integrating yields the value of n at any temperature T and introducing a linear heating rate $\beta = \frac{dT}{dt}$, $dt = \beta dT$:

$$\frac{dn}{n^2} = -\frac{s'}{\beta} \exp\left(\frac{-E}{kT}\right) dT' \quad (2.19)$$

Therefore, by integration, the function $n(T)$ is obtained as:

$$\int_{n_o}^n \frac{dn}{n^2} = -\int_{T_o}^T \frac{s'}{\beta} \exp\left(\frac{-E}{kT'}\right) dT' \quad (2.20)$$

$$n = \frac{1}{n_o \left[1 + \left(\frac{s'n_o}{\beta}\right) \int_{T_o}^T \exp\left(\frac{-E}{kT'}\right) dT'\right]} \quad (2.21)$$

and the intensity $I(T)$ is then given by

$$I(T) = \frac{n_o s' \exp\left(\frac{-E}{kT}\right)}{\left[1 + \frac{1}{N} \left(\frac{s'}{\beta}\right) n_o \int_{T_o}^T \exp\left(\frac{-E}{kT'}\right) dT'\right]^2} \quad (2.22)$$

Plugging this equation in (2.22), one can get the following equation for glow curve [2],

$$I(T) = n^2 \frac{s}{N} \exp\left(\frac{-E}{kT}\right) \left[1 + \frac{n_o s}{\beta N} \int_{T_o}^T \exp\left(\frac{-E}{kT'}\right) dT'\right]^{-2} \quad (2.23)$$

It is worth to mention that, if $n \ll N$ (low dose sample) so that AN becomes much greater than $A_r n$, second order kinetics can be obtained in OTOR model even if $A_r \neq A$. Under this condition, $\eta = \frac{A_r n}{AN}$ and (2.15). $\frac{n}{N}$ gets replaced by $\frac{A_r n}{AN}$ and in (2.5), $\frac{s}{N}$ gets replaced by $\frac{s A_r}{AN}$. Thus,

$$I(T) = n_o^2 \frac{s A_r}{AN} \exp\left(\frac{-E}{k_B T}\right) \left[1 + \frac{n_o s A_r}{\beta AN} \int_{T_o}^T \exp\left(\frac{-E}{k_B T'}\right) dT'\right]^{-2} \quad (2.24)$$

Therefore, it should be noted that in the case of $A_r \neq A$, the second order kinetics is obeyed only in low dose samples ($n \ll N$), whereas it is valid at all doses for the case when $A_r = A$.

2.5 Structural and Electronic Properties of Phosphors

2.5.1 Definition of Phosphor

The word phosphor was invented in the early 17th century and its meaning remains unchanged till today. Early alchemists found a heavy crystalline stone with a gloss at the foot of a volcano, and fired it in a charcoal oven intending to convert it to a noble metal. They found that the sintered stone emitted red light in the dark after exposure to sunlight rather than being converted in to metal. After this discovery, similar findings were reported from many places in Europe, and these light-emitting stones were named phosphors [8]. This word means light bearer in Greek. In other words, a phosphor emits energy from an excited electron as a light. In general, the excitation of electron is caused by absorption of energy from an external source such as another electron, a photon, or an electric field. Phosphors have wide applications in today's science and technology. The applications of phosphors can be classified as light sources represented by fluorescent lamps, display devices represented by cathode-ray tubes, detector systems represented by x-ray screens and scintillators, and other simple applications such as luminous paint with long persistent phosphorescence [21]. Therefore, designing a phosphor for a particular application requires the understanding of the properties of the constituents of the phosphor. In addition to the host material (insulator or semiconductor), inorganic phosphors consist of impurities (dopants or activators) purposely incorporated in small amounts in to the host. The luminescence emission from a given

phosphor depends on many factors. In general, a phosphor with high luminescence efficiency is characterized by properties such as low phonon energy, high optical damage threshold, high quantum efficiency, stability, etc.

2.5.2 Properties of $KY_3F_{10} : Ho^{3+}$ Phosphor

The KY_3F_{10} crystal has a cubic structure (space group Fm3m). The basic building unit consists of the two ionic groups $[KY_3F_8]^{2+}$ and $[KY_3F_{12}]^{2-}$, which alternate along the three crystallographic directions as shown in Figure 2.3. In the first group, the fluorine atoms form an empty cube. In the second unit, they form an empty cub octahedron. This structure could alternatively be described in terms of clusters of octahedral arranged yttrium-center square anti prisms YF_8 which share corners and edges to generate the fluorine cubes and cuboctahedra as shown in Figure 2.2 . The potassium atoms are coordinated to 4 fluorine atoms at the distance 2.765 Å and to 12 fluorine atoms at the distance 3.200 Å .

The 12 fluorine atoms form truncated tetrahedral. The additional four fluorine atoms are located nearby the hexagonal faces forming Friauf polyhedral KF_{16} . KY_3F_{10} crystal was grown for the very first time in 1971 [9]; and since then, it appears to be a very attractive material because it is fairly easy to grow. Two synthesis methods, namely, the Czochralsky pulling technique [10], and Bridgman-Stock Barger method [11] are commonly used as growing mechanisms. Upon doping this crystal with rare earth ions, these ions predominantly occupy yttrium positions. Each rare earth ion is surrounded by eight fluorine ions forming a square anti prism with the C_{4v} point symmetry group(see Fig. 2.3, the distances between Y^{3+} ion and F^- ions

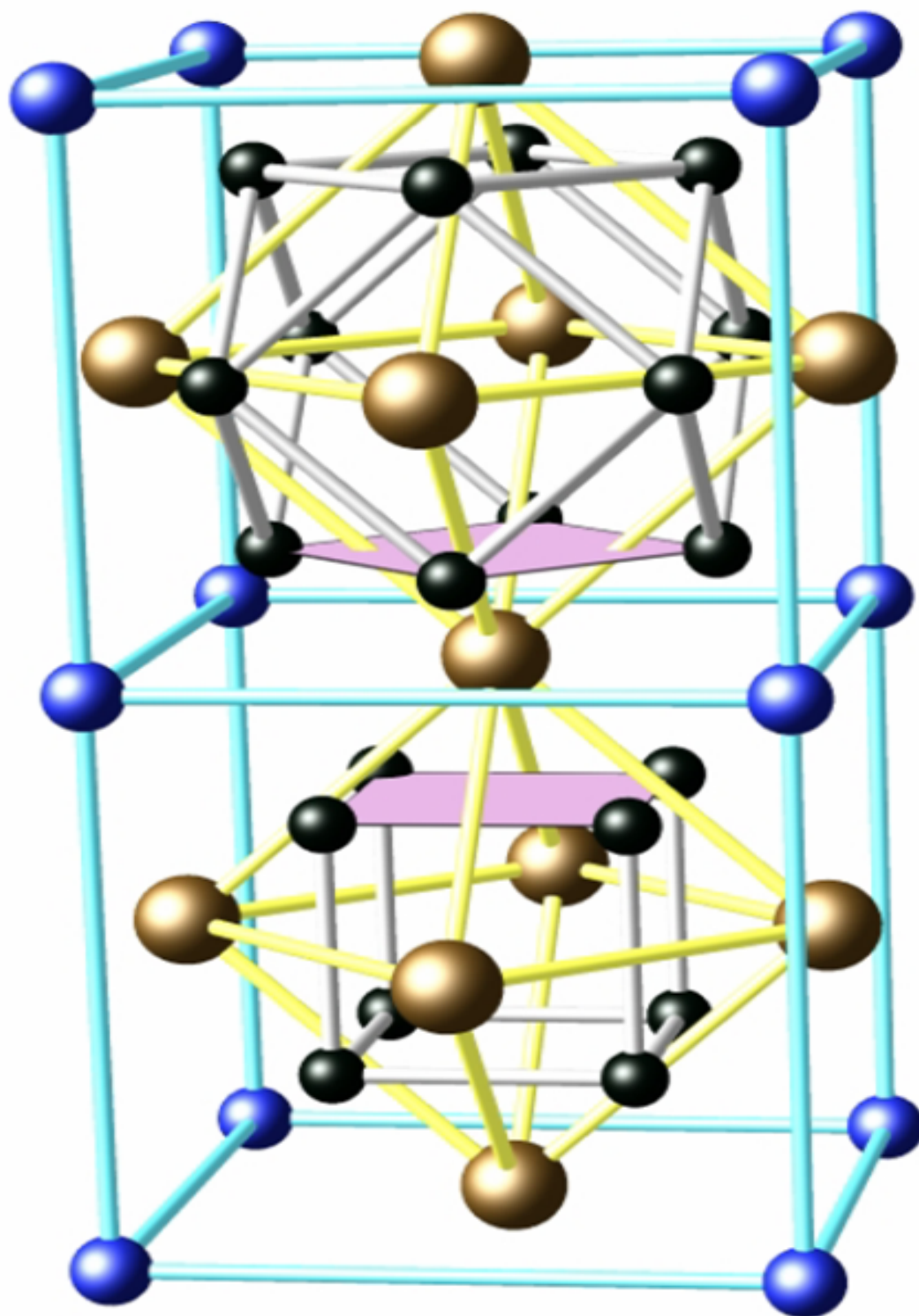


Figure 2.2: The unit cell of the Fm3m structure of KY_3F_{10} . The biggest bronze (grey) spheres substitute for yttrium atoms, the blue (grey) ones for potassium atoms, and the black ones for fluorine atoms. The nearest surrounding of yttrium ions is represented by eight fluorine ions forming a square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

Structure	Tetragonal
Space group	Fm3m
Cell parameters	a=8.161 Å, c=11.53 Å
Number of elements by cell	8
Anisotropy	Isotropic
Melting point	990°C

Table 2.1: Summary of crystallographic properties of KY₃F₁₀

at the corners of the two squares, normal to the C₄ symmetry axis and rotated by the angle of $\frac{\pi}{4}$ relative to one another, is equal to 0.2352 and 0.2202 nm). There are three equivalent rare earth centers oriented along three different C₄ axes of the cubic lattice structure. The compound is chemically and thermally stable, transparent, and isotropic. Once doped with rare earth ions, it has received much attention since it is suitable to build solid state lasers [18-19], white-light emitters [20] and quantum cutting systems to enhance solar cells efficiency.

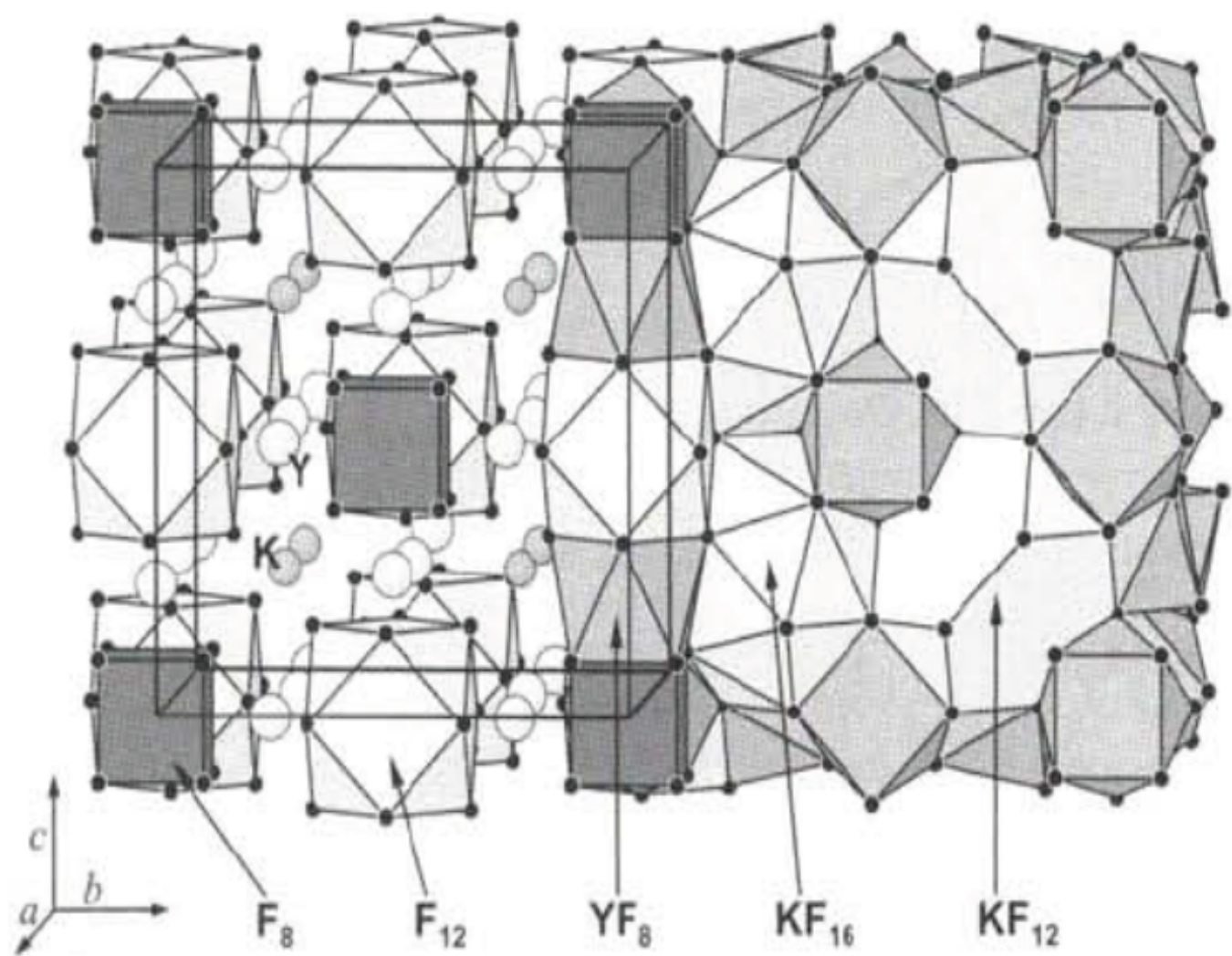


Figure 2.3: Structural composition of KY_3F_{10} .

3

Materials and Methodology

3.1 Methodology

To achieve the stated objectives and problem, analytical methods with computation analysis would be used. To investigate and solve the stated problems we plan to employed analytical method that was derivation of equations based on the theoretical concepts. To calculate the applied equations for numerical computation of the Garlick and Gibson model of intensity in second order kinetics and to determine the theoretical and experimental results of the thermoluminescence properties of $KY3F_{10} :HO^{3+}$ phosphors in view second order kinetics. Inclusions Analyzed numerically with the help of computational tools; uses soft wares.

3.1.1 Analytical

This study was analyzed by the derivation of equations based on the theoretical concepts and applied the equations for the numerical computations of the theoretically investigate the thermoluminescence properties of $KY3F_{10} :HO^{3+}$ phosphors

in view second order kinetics. In addition to investigate the effect of order of kinetics on the shape of TL glow curves of $KY3F_{10} :HO^{3+}$ phosphors in view second order kinetics for this study. In this thesis one of the method or approach used to solve the problem is analytical method.

3.1.2 Computational

Most of the physics problems were not simply to solve analytically. To interpret the result and to observe the thermoluminescence behavior of $KY3F_{10} :HO^{3+}$ phosphors in view of second order kinetic and to study the effect of various heating rates on the glow curves of $KY3F_{10} :HO^{3+}$ phosphors in view second order kinetics computational and graphical methods are employed with the help of MATHEMATICA software. Plotting figures which show the results. Mathematic will be used as alternative software for managing long analytical and numerical expressions. Because it was preferable for simplify and handle bulged equations. Latex to process the edition and compilation of the thesis of with the standard quality.

4

Results and Discussions

4.1 Second Order Kinetics

The rate of chemical reaction is directly proportional to the change in the concentration of both the reactants, it is called bi-molecular kinetics or second order kinetics. The reaction following second order kinetics may be written as [23].

$$-\frac{dn}{dt} = Cn(t)m(t), \quad (4.1)$$

where $n(t)$ and $m(t)$ are the concentration of the reacting substances and C is a constant. A case of non-first order kinetics is obtained if the values of the TL intensity are dependent also on the concentration h of the recombination centers in addition to the concentration of electrons n in traps. According to some early investigators of TL phenomena, second-order kinetics is obtained if the probability of re-trapping is non-zero. For OTOR case in GG model, when $A_r = A$ and the concentration h of recombination center is equal to the concentration n of electrons in traps, it becomes a case of second order kinetics. This means that electrons, which are released thermally from the traps and excited in to the conduction band, have

a higher probability to be re trapped by an electron trap then to recombine with a hole at a luminescence center. In this rate equation,

$$\frac{dn_c}{dt} = s \exp\left(\frac{-E}{kT}\right) n - An_c(N - n) - A_r n_c n_h \quad (4.2)$$

Where A_r is the recombination transition coefficient for electrons in the conduction band with hole centers, n_h is the concentration of trapped holes and s , n , A , n_c , N and E are as defined before. The lifetime of the electrons in the conduction band is assumed to be very short compared to the characteristic time associated with the release and trapping of the electrons in the conduction band n_c will be small compared with the concentrations of the electrons in the traps n . The electron concentration in the conduction band will adjust very quickly to the variations of the concentrations of filled electron and hole traps. Therefore, the rate of change of the carrier concentrations n_c in the conduction band is very small and it can be approximated to zero.

$$\frac{dn_c}{dt} = 0 \quad (4.3)$$

Solving for n_c from equation (4.2) using (4.3) gives:

$$n_c = \frac{s \exp\left(\frac{-E}{kT}\right) n}{A(N - n) + A_r n_h} \quad (4.4)$$

Re-writing equation (4.2)

$$\frac{dn}{dt} = s \exp\left(\frac{-E}{kT}\right) n - An_c(N - n) \quad (4.5)$$

Putting (4.2) in to (4.3) and using $T = T_o + \beta t$ gives:

$$\frac{dn}{dT} = -\frac{s}{\beta} \exp\left(\frac{-E}{kT}\right) n \left[\frac{A_r n_h}{A(N - n) + A_r n_h} \right] \quad (4.6)$$

Here T_o is the initial temperature at time $t=0$ and β is heating rate. Approximations, $A(N-n) \gg A_r n_h$, $N-n \cong N$, $n_h = n + n_c n_h \cong n$ because $n \gg n_c$, Using the above approximations, equation (4.6) becomes

$$\frac{dn}{dT} = -\left(\frac{S}{\beta}\right) \exp\left(\frac{-E}{KT}\right) \frac{A_r n^2}{A N} \quad (4.7)$$

Solving for n from (4.7),

$$n(T) = \frac{n_o}{1 + \frac{A_r}{AN} \left(\frac{s}{\beta}\right) \int_{T_o}^T \exp\left(\frac{-E}{KT'}\right) dT'} \quad (4.8)$$

$$I(T) = -\frac{dn}{dt} = s \exp\left(\frac{-E}{KT}\right) \frac{A_r n^2}{A N} \quad (4.9)$$

Putting (4.8) in to (4.9) we obtain the following second order kinetics thermoluminescence behavior.

$$I(T) = \frac{s n_o^2 \frac{A_r}{AN} \exp\left(\frac{-E}{KT}\right)}{\left[1 + \left(\frac{s}{\beta}\right) \left(\frac{A_r}{AN}\right) n_o \int_{T_o}^T \exp\left(\frac{-E}{KT'}\right) dT'\right]^2} \quad (4.10)$$

$$I(T) = \frac{n_o^2 \frac{s}{N} \exp\left(\frac{-E}{KT}\right)}{\left[1 + \left(\frac{n_o s}{N\beta}\right) \int_{T_o}^T \exp\left(\frac{-E}{KT'}\right) dT'\right]^2} \quad (4.11)$$

where, n_o is the initial concentration of filled traps; s is a pre-exponential frequency factor s^{-1} ; E is the activation energy or trap depth (eV) ; K is Boltzmann's constant $eV k^{-1}$; T is absolute temperature (K), N = the total trap concentration (m^{-3}) and β is the heating rate.

4.2 Thermoluminescence Properties of $KY_3F_{10} : Ho^{3+}$ Phosphor

From absorption, fluorescence and excitation spectra obtained in the temperature range 200K-500K, the crystal-field energy levels for seven of the Ho^{3+} multiples have

been deduced. Corresponding energy level positions from a crystal-field fitting routine are included, with good agreement. The simple model used for the theoretical treatment between delocalized bands, conduction band, CB, and valence band, VB, two localized levels (meta stable states) are considered, one acting as a trap, T, and the other acting as a recombination center, R. The distance between the trap T and the bottom of the CB is called activation energy or trap depth E, this energy is the energy required to liberate a charge, i.e., an electron which is trapped in T, the probability P, per unit of time, that a trapped electron will escape per second. The thermoluminescence glow curve is a measure of the intensity of the emitted light as a function of temperature. This thermoluminescence glow peaks obtained using the computation of the second order kinetics equation, i.e. the Garlick-Gibson equation.

4.2.1 The Effect of The Activation Energy on The Thermoluminescence Glow Curves Properties of $KY_3F_{10} : Ho^{3+}$ Phosphor.

A plot of thermoluminescence intensity versus temperature is known as a glow curve. Analysis of glow curves can provide quantitative information about trap levels. Most notably, one may use glow curve analysis to calculate the depth of the charge carrier traps. The activation energy for releasing charge carriers from the trapping centers, E is called the trap depth or activation energy, the energy needed to release an electron from the trap into the conduction band. The calculated depth

of a trap is referred to as its activation energy. In second order kinetics to calculate activation energy from glow curves based on Thermoluminescence behavior of $KY_3F_{10} : Ho^{3+}$ phosphors. the activation energy increases with temperature, as charge carriers at deeper traps require more thermal energy for release. The most notice able change is the large decrease in activation energy of the highest energy peak after annealing by about 0.836 eV, 0.918 eV, 1 eV. In Garlick-Gibson model (second order kinetic) Thermoluminescence glow curves, calculated using three different values of the activation energies $E_1 = 0.836$ eV, $E_2 = 0.918$ eV and $E_3 = 1$ eV. All other parameters are the same i.e., frequency factor, $s = 2.65 \times 10^{11} sec^{-1}$ and Boltzmann's constant, $K = 8.617 \times 10^5 eV k^{-1}$ and the initial concentration of filled traps and the total trap concentration (m^{-3}), $N = n_o = 10^{10} cm^{-3}$. We get the curves as shown in Figure 4.1.

From Fig 4.1, it can be clearly observed that the intensity maximum shifts to higher temperatures as the activation energy is increased. Moreover, slow decrease of the wide glow peak height was observed with increasing activation energy with $E_1 = 0.836$ eV, $E_2 = 0.918$ eV and $E_3 = 1$ eV. From this result of the Intensity verses of Temperature maximum. The theoretical thermoluminescence behavior of $KY_3F_{10} : Ho^{3+}$ phosphor in view second order kinetics . The shift to higher temperatures can physically be understood by realizing that for higher E values (deeper traps) more energy (higher temperature) is needed to release the charge carriers. In this result efficiency of Crystals of KY_3F_{10} doped with Ho^{3+} phosphor materials are at activation energy increasing and decreasing the intensity shifts to higher temperature, so the energy gap of material decreasing more charge carriers to relies as

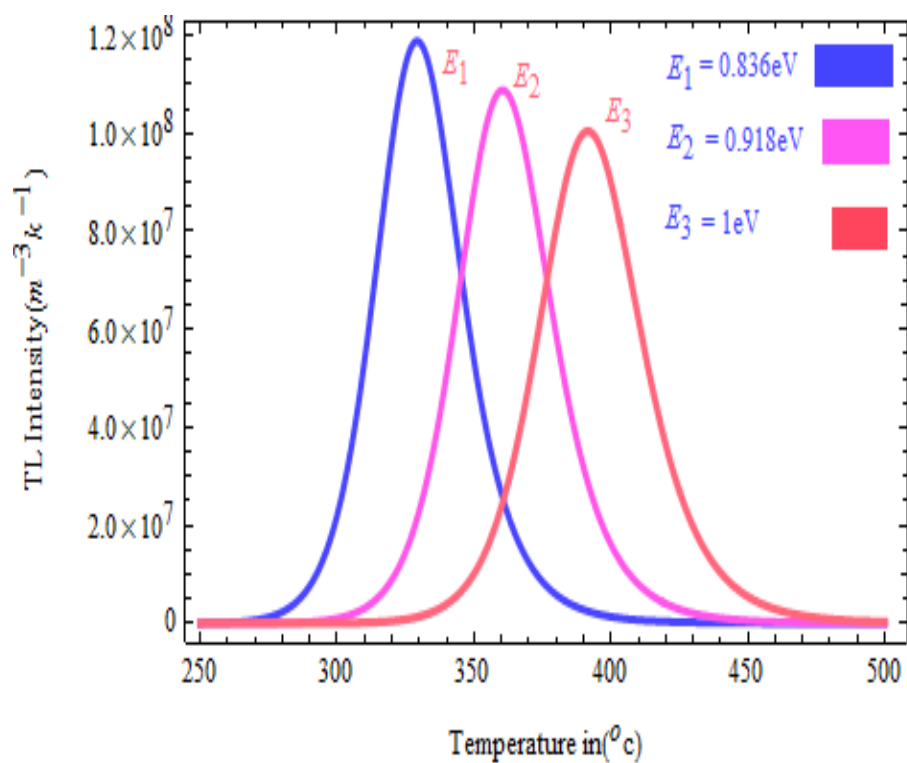


Figure 4.1: second order kinetic of the effect of activation energy on thermoluminescence properties of $KY_3F_{10} : Ho^{3+}$ phosphors $E_1 = 0.836 eV$, $E_2 = 0.918 eV$ and $E_3 = 1 eV$, $N = n_o = 10^{10} m^{-3}$, $s = 2.65 \times 10^{11} s^{-1}$, $\beta = 0.5 ^{\circ} C/s$, in second order of kinetic.

E increases, the glow peak shifts to higher temperature. Higher value of E means stronger binding of the trapped charge and higher thermal energy is needed to release it. The glow peaks for different values of E are shown in Fig.4.1 for constant values of s and b. It can be observed that with increase in the value of E the peak glow curve is reduced.

4.2.2 The Effect of The Frequency Factors on The Thermoluminescence Glow Curve Properties of $KY_3F_{10} : Ho^{3+}$ Phosphor

The term s is called the frequency factor or attempt-to-escape factor. In the simple models s is considered as a constant (not temperature dependent) depending on the frequency of the number of hits of an electron in the trap, with a value in the order of the lattice vibration frequency, namely $10^{12} - 10^{14} s^{-1}$. The frequency factor determines the probability of emission of electrons from electron traps, for high values of the heating temperature. Then the value of the exponential factor $\exp\left(\frac{-E}{kT_M}\right)$ is approximately equal to one. When, there is a high concentration of empty traps in the phosphor material and when the value of the retrapping factor is not negligible then a significant number of electrons are retrapped. This can be seen on the glow curve, as the Thermoluminescence peak shifts to higher values as a result of reducing the velocity of luminescent recombination. Since the filling factor of traps is not known, it is not possible to make a correction of its influence on the rate of Thermoluminescence relaxation. In the initial stage of relaxation, the

relative impact of retrapping is very small, because the total amount of electrons, which are retrapped in phosphor, is small. This means that, in the initial phase, the glow curve does not depend on the retrapping factor and the filling factor. Therefore, the temperature of the maximum will be shifted towards lower temperature values, because significant redistribution of the electrons from the trap will be performed only after the maximum. Garlick-Gibson model (second order) Thermoluminescence curves, calculated using three different values of the frequency factors, $s_1 = 2.65 \times 10^{11} \text{sec}^{-1}$, $s_2 = 2.65 \times 10^{12} \text{sec}^{-1}$, and $s_3 = 2.65 \times 10^{13} \text{sec}^{-1}$. All other parameters are the same i.e., activation energy, $E = 0.918 \text{ eV}$ and Boltzmann's constant, $k = 8.617 \times 10^5 \text{ eV K}^{-1}$ and the initial concentration of filled traps and the total trap concentration (m^{-3}), $N = n_o = 10^{10} m^{-3}$. We get the curves as shown in Figure 4.2 the glow peak shifts to lower temperature as frequency factor (s) is increased. Thus, it is clear that activation energy (E) and frequency factors (s) in second order kinetics have opposite effects on T_m . This is simple to understand since higher frequency factor (s) means faster escape of the trapped charge from the excited state of the trap. Higher frequency factors (s) leads also to increase in peak glow curves. In this results of the effect of frequency factors (s) on thermoluminescence behavior of $KY_3F_{10} : Ho^{3+}$ phosphor in Crystals of materials as the parameter s is varied (see Fig.4.2) but now in the opposite way: as s the frequency factors increases the peak shifts to lower temperatures with an increase of the intensity of glow curve and a decrease in width. A trapping center with a high frequency factor needs less energy (lower temperature) to free a charge carrier.

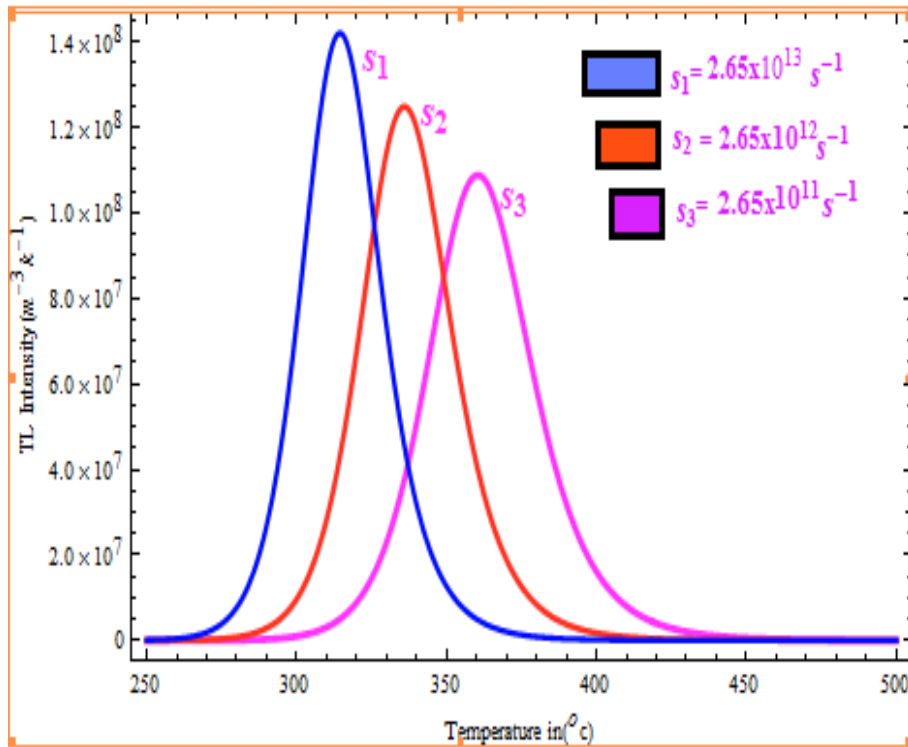


Figure 4.2: second order kinetic of the effect of frequency factors on thermoluminescence properties of $KY_3F_{10} : Ho^{3+}$ phosphors $s_1 = 2.65 \times 10^{11} sec^{-1}$, $s_2 = 2.65 \times 10^{12} sec^{-1}$ and $s_3 = 2.65 \times 10^{13} sec^{-1}$, $N = n_o = 10^{10} m^{-3}$, $E = 0.918 eV$, $\beta = 0.5^\circ C/s$, in second order of kinetic.

4.2.3 The Effect of The Initial Concentration of Filled Traps on The Thermoluminescence Glow Curve Properties of $KY_3F_{10} : Ho^{3+}$ Phosphor

We have simulated the thermoluminescence theoretical for particular second-order. Figure 4.3 ,shows the concentration of filled electron traps and the concentration of free electrons in the conduction band during thermal excitation. the concentration of filled electron traps decreases with increasing temperature, whereas the concentration of free electrons increases to a maximum value at characteristic temperature; above this temperature it decreases. The decrease of the concentration of filled electron traps in slow of decrease of the filled electron traps in second-order kinetics. As a consequence, excitation of trapped electrons to the conduction band leads unavoidably to annihilation by recombination with trapped hole centers, whereas in the second-order process the trapped electrons might need two or more excitations in order to annihilate. Garlick-Gibson model (second order kinetics) Thermoluminescence curves, calculated using three different values of the initial concentration of filled traps, $n_{o1} = 10^{10}m^{-3}$, $n_{o2} = 10^{10.10}m^{-3}$ and $n_{o3} = 10^{10.20}m^{-3}$.the total trap concentration m^{-3} of N (where N = $10^{10}m^{-3}$. All other parameters are the same i.e. activation energy, E = 0.918eV and Boltzmann's constant, $k = 8.617 \times 10^5 eV k^{-1}$,heating rate $\beta = 0.5 k s^{-1}$ and the frequency factor, $s = 2.65 \times 10^{11} sec^{-1}$.We get the curves as shown in Figure 4.3. The initial concentration of filled traps n_o affects both the maximum height of the Thermoluminescence glow

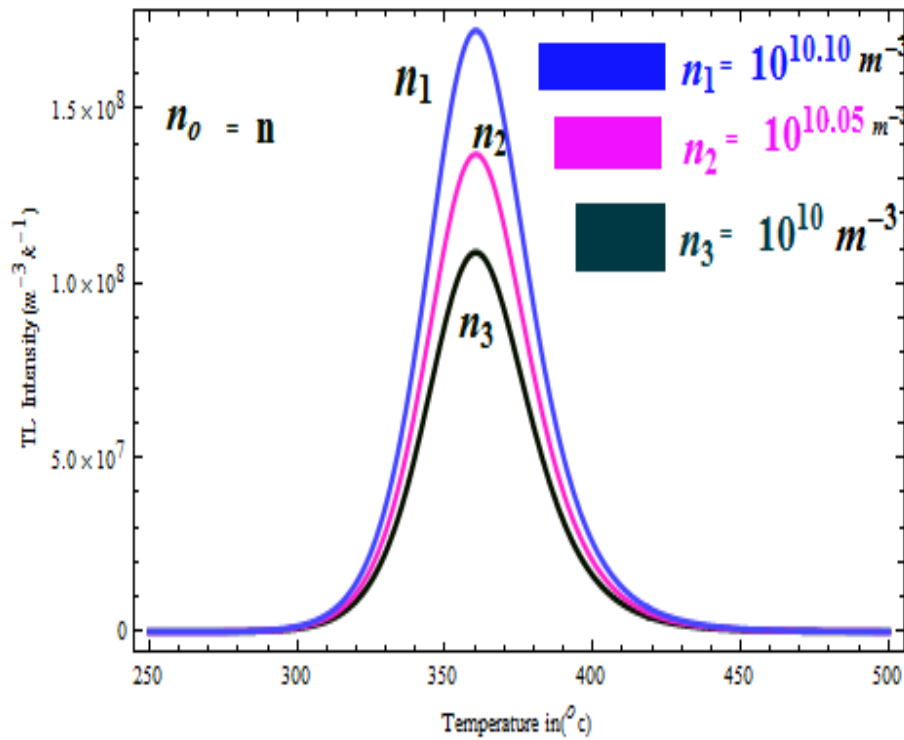


Figure 4.3: second order kinetic of the effect of the initial concentration of filled traps on thermoluminescence properties of $KY_3F_{10} : Ho^{3+}$ phosphors $n_{o1} = 10^{10} m^{-3}$, $n_{o2} = 10^{10.10} m^{-3}$ and $n_{o3} = 10^{10.20} m^{-3}$ $N = 10^{10} m^{-3}$, $E = 0.918 eV$, $\beta = 0.5$ C/s, in second order of kinetic.

curve and the temperature of maximum Thermoluminescence intensity (Tmax), but leaves the overall shape unchanged. This can be understood from the consideration of the fact that in a second-order reaction significant concentrations of released electrons are retrapped before they recombine, in this way giving rise to a delay in the luminescence emission and spreading out of the emission over a wider temperature range. The initial concentration n_0 appears here not merely as a multiplicative constant as in the first-order case, so that its variation at different dose levels change the shape of the whole curve. This is illustrated in Fig.4.3. It is seen that maximum temperature decreases as n_0 increases as the wide of glow curve increase (peak).

4.2.4 The Effect of Various Heating Rates on The

Thermoluminescence Glow Curves of $KY_3F_{10} : Ho^{3+}$

Phosphor

The heating rate is one of the most important parameters in a thermoluminescence measurement. Variable heating rate method is on the shift of the peak thermoluminescence temperature to higher temperature side when the heating rate is increased. It has been found that different heating rates cause different thermoluminescence intensities, which in turn may give rise to a change in the trapping parameters. so, in second order kinetics the variation of glow peak temperature with heating rate for $KY_3F_{10} : Ho^{3+}$ phosphors. To analyze the second order-kinetics the effect of heating rate on thermoluminescence intensity, the Thermolumines-

cence measurements were taken at seven different heating rates of 0.5 C/s, 0.8 C/s, 1 C/s, 1.2 C/s, 1.5 C/s, 1.8 C/s and 2 C/s. Figure 4, depicts the Thermoluminescence intensity versus temperature of $KY_3F_{10} : Ho^{3+}$ phosphor for the different heating rates. It can be clearly observed that the intensity maximum shifts to higher temperatures as the heating rate increased. Moreover, slow decrease of the glow peak height was observed with increasing heating rate and this could be attributed to thermal quenching effect in which the efficiency of the luminescence decreases as the temperature increases due to opening up of competing non-radiative relaxation pathways. In order to be able to study the effect of the heating rate on each glow peak of $KY_3F_{10} : Ho^{3+}$ phosphors at different heating rates. Thermoluminescence glow curves of this phosphor from effect of various heating rate of 0.5 C/s, 0.8 C/s, 1 C/s, 1.2 C/s, 1.5 C/s, 1.8 C/s and 2 C/s at different temperatures and at different heating rates after irradiation. Let us now analyze the evolution of the Thermoluminescence maximum with the heating rate in order to determine the level of the trap beneath the edge of the conduction band. For this thesis, we performed a various heating rate analysis that considers how the traps are emptied at different heating rates while all other parameters are held constant. As the heating rate is increased, the position of the Thermoluminescence maximum T_m shifts toward higher temperatures fig. 4.4, the heating rate β can be related to the T_m of its corresponding peak using an equation of the following. Change in the temperature T_m of the maximum Thermoluminescence intensity of the peak: faster heating rates produce a shift in temperature relatively towards higher values of T. The formation of traps clusters instead of randomly distributed defects causes variation in the kinetics of

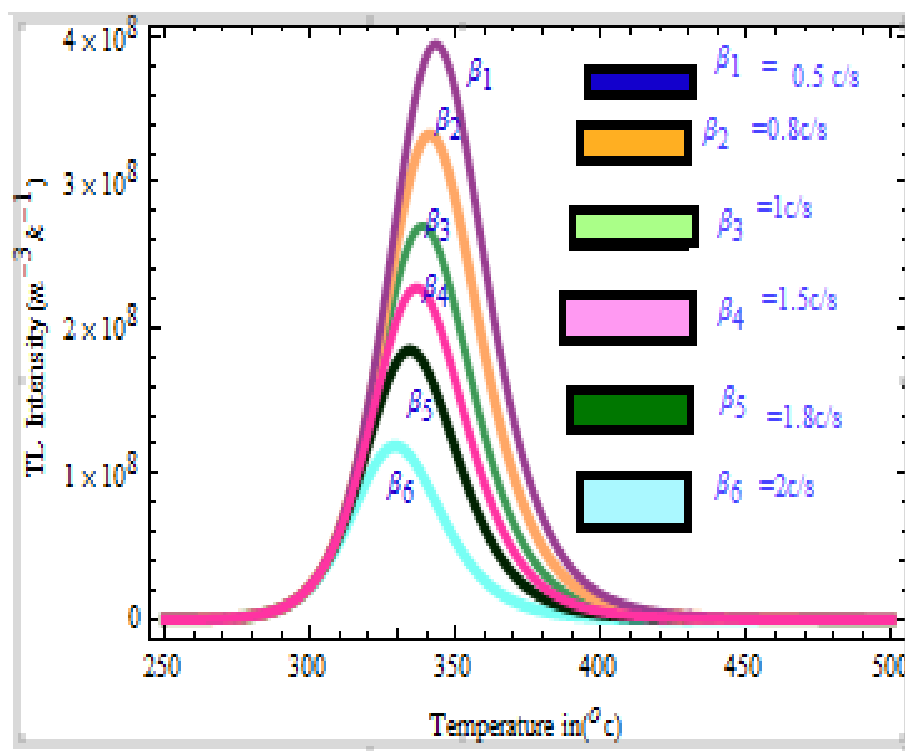


Figure 4.4: second order kinetic of the effect of various heating rate thermoluminescence properties of $KY_3F_{10} : Ho^{3+}$ phosphor $E=0.918\text{eV}$, $N = n_o = 10^{10}m^{-3}$, $s = 2.65 \times 10^{11} s^{-1}$, β of 0.5 C/s, 0.8 C/s, 1 C/s, 1.2 C/s, 1.5 C/s, 1.8 C/s and 2 C/s in second order of kinetic.

trapping and recombination process. Thermoluminescence Intensity versus temperature of $KY_3F_{10} : Ho^{3+}$ for different heating rates. As indicated, the peak of the glow curves decreases and shift to higher temperature region with increasing heating rate. The initial non-zero values of the intensity indicate fluorescence during irradiation. as expected, the intensity maximum shifted to higher temperatures as the heating rate was increased. Moreover, decrease of the glow peak height was observed the glow curves with increasing heating rate. This can be understood as follows. A Thermoluminescence glow peak results from two factors, which change in opposite directions when the time elapses, i.e., the temperature increases, resulting in: (i) an increased escape probability and so a higher rate of recombination, leading to an increased number of photons emitted; and (ii) a decreased number of charge carriers available for recombination. At a lower heating rate, more time elapses during the same temperature increase, allowing more recombination events to occur, so that the charge pairs (electrons and holes) are eliminated faster and the Thermoluminescence maximum is reached at a lower temperature.

5

conclusion

In conclusion, Thermoluminescence properties of $KY_3F_{10} : H_o^{3+}$ phosphor at different kinetic parameters. The thermoluminescence (TL) glow curves of $KY_3F_{10} : H_o^{3+}$ phosphors in second order kinetics. Thermoluminescence intensity increases with increase in the temperature at increases kinetic parameters and then decreases in glow curve. The glow curves slightly shift to higher temperature region for relatively higher heating rate, but with reduced intensity peak and this behavior is not attributed to thermal quenching effect in this particular study. Important Thermoluminescence kinetic parameters; namely the activation energy (E) and the frequency factor (s) are calculated using variable heating rate method. The glow peaks obey second order kinetics. A method for calculating the parameters of Thermoluminescence relaxation for the model of ideal phosphors is based on the concept of kinetics order. We have studied the effect of the activation energy, frequency factor and the initial concentration of filled traps on the glow curves using Garlick-Gibson model. We have observed the following results:

✓ As the activation energy E is increased, the Thermoluminescence glow curve shifts towards higher temperatures, but the curve maintains its overall shape for

these three models.

✓ As the frequency factor s is increased, the Thermoluminescence glow curve shifts towards lower temperatures, but the curve maintains its overall shape for these three models.

✓ The initial concentration of filled traps (n_0) affects both the maximum height of the Thermoluminescence glow curve and the temperature of maximum TL intensity (Temperature max), but leaves the overall shape unchanged in the case of the Garlick-Gibson model. The order of kinetics of all the peaks was found to be, $b = 2$ irrespective of pressure. When the linear heating rate changes, the temperature maximum of the maximum TL intensity of the peak also changes: faster heating rates produce a shift in temperature toward higher values of T_m . The fall in the Thermoluminescence intensity may be attributed to the well-known concentration quenching effect of dopant. Luminescence of a phosphor is affected largely by the impurity concentration in it. If the concentration of impurities increases from a particular amount, they may act as self-quenchers by non-radiative transitions resulting in fall in the intensity of the luminescence.

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