Chapter 1

Introduction

The use of Thermally Stimulated Luminescence (TSL) also called thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) is growing in a variety of applications like geological and archaeological dating, testing of ancient artifice to detect forgery, personnel dosimetry, medical dosimetry, environmental dosimetry, retrospective dosimetry, study of extra-terrestrial materials like meteorites and lunar materials, material characterization and many other emerging applications. The many nuances of the working of the TL and OSL phenomena are an area of active research and it calls for the development of more versatile instruments by which such research can be undertaken. Most of the research in this field has been carried out using a Photomultiplier Tube (PMT) which does not give any information about the spatial distribution of luminescence.

The study of spatial distribution of luminescence is important because it provides lots of advantages over the conventional system where the integrated luminescence form the sample is studied. The spatial distribution of luminescence from the sample allows the measurement of the luminescence behaviour of many individual grains of the sample. This enables the separation of mineral specific signal without the need to physically separate the various minerals form the sample [1]. If the sample is perfectly homogeneous or if the dose distribution is perfectly evenly spread, the emitted luminescence from each and every part of the sample will be exactly the same. Since this is usually not the case with the naturally occurring samples used in geological or archeological dating, a study of the spatial distribution of the emitted luminescence would inform us about the extent of homogeneity of the sample and the spread of the dose distribution in the sample.

For TL or OSL dating, grains of quarts or feldspar of specific size are extracted from the sample. It is not always feasible to extract quarts or feldspar from the given sample. Such situations arise when the dating of rock surfaces, dating of the fusion crust of meteorites, archaeological tools made of stone, antique statues and sculptures is needed. For such situations a technique and instrument for luminescence dating of the surface is required. Even though attempts have been made for it [2] a routinely applicable protocol and a proper instrument capable of achieving this is yet to be developed.

Even in a sample comprising of only the same kind of mineral like only quartz or only feldspar, all the grains do not contribute equally to the emitted luminescence [3]. This is due to the fact that the dose distribution in the sample is not perfectly homogeneous.

Some attempts have been made to study spatial luminescence using a Charge Coupled Device (CCD) camera. The drawback of a CCD camera is that they are not sensitive enough to detect very low level light which puts a limit to their utility for research. After undertaking a feasibility study for the proper light detector, a high-end Electron Multiplying CCD (EMCCD) which is capable of detecting light at the photon counting level has been employed in the present study.

Some applications of TL/OSL like personnel dosimetry, medical dosimetry and environmental dosimetry require development of proper phosphors with suitable characteristics like linear dose response, ability to detect low level dose, high dose saturation at a high level, etc. A nano scaled Calcium Fluoride is synthesized and characterized. Along with the TL and OSL characteristics of the phosphor its structural and optical characterization is also undertaken.

TL and OSL are basically a sub-set of the luminescence phenomena. The primary causes of TL and OSL are the same as the primary causes of the luminescence phenomena in general. Thus in order to get a more complete picture and to place TL and OSL in its proper context, the luminescence phenomena in general needs to be considered.

1.1 Luminescence

Luminescence is the emission of light from a substance on excitation by some form of energy. The electronic state of the substance is excited by such kind of external energy or trigger. When this excited electron comes back to its ground state it emits a luminescent photon. The irradiation can be due to alpha, beta, gamma, X-ray or some other appropriate source. The external energy or trigger could be chemical energy, mechanical energy, electrical energy, biochemical energy, sound energy, pressure, light energy, heat energy, etc. Depending upon the type of trigger the luminescence is named. For the above mentioned triggers the corresponding luminescence is named as chemiluminescence, triboluminescence, electroluminescence, bioluminescence, sonoluminescence, piezoluminescence, optically stimulated luminescence and thermoluminescence respectively.

The above classification of luminescence is based on its trigger source. A more fundamental classification of luminescence can be done based on the delay time between the absorption of the energy which causes the electron to move from the ground state to an excited state and the emission of the photon when the excited electron returns to its ground state. If this time delay is more than 100 nano-seconds then the luminescence is known as phosphorescence, and if the time delay is less than 100 nano-seconds then it is known as fluorescence. Both fluorescence and phosphorescence are important phenomena which are utilized in a wide variety of applications.

The spontaneous emission of light with the excitation source is characteristic of fluorescence. Here the electron directly comes down to its ground state from its excited state without going into a metastable state. It is temperature independent. In the case of phosphorescence, the electron goes into a metastable state from its excited state. It then requires some external trigger like heat or light in order to come from its metastable state to the ground state emitting light in the process. Phosphorescence is temperature dependent. The brightness and decay time of the phosphorescence would depend on the temperature. Phosphorescence will be brighter and the decay time will be shorter if the temperature is higher. In the case of lower temperature the decay time will be longer and the phosphorescence will be less bright. This dependence of phosphorescence on temperature can be used to distinguish it from fluorescence which is independent of temperature.

TL and OSL fall under the phosphorescence phenomena. Here the delay time between excitation and emission could range from a fraction of second to millions of years [4]. This time delay is dependent, along with other parameters, on the activation energy of the traps and the ambient temperature. The traps are formed due to the defects in the crystals.

1.2 Thermoluminescence

1.2.1 Theoretical Basics

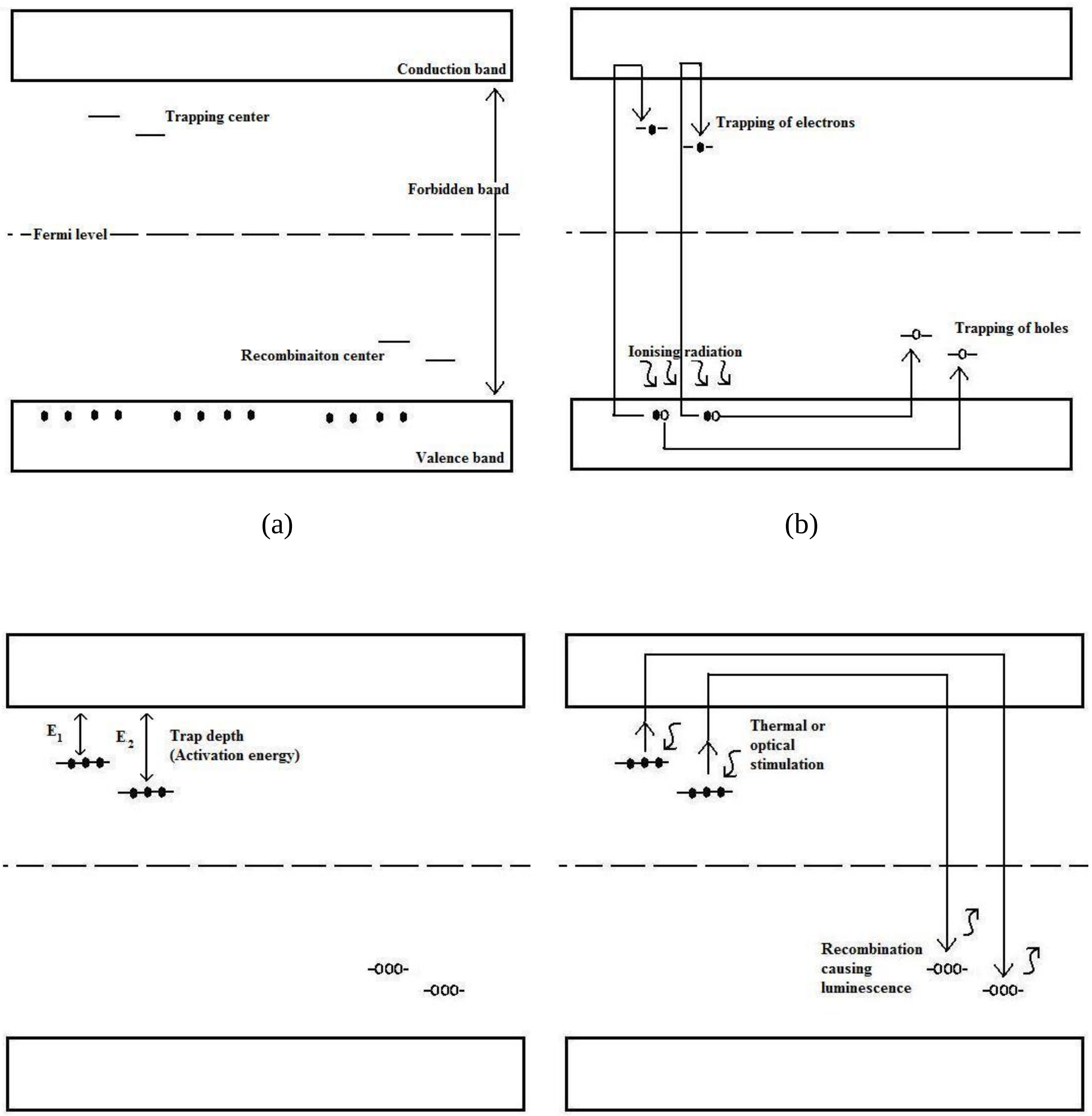
In order to perform TL, the material should first undergo irradiation. Then this material should be subjected to thermal irradiation. Due to this the substance will emit luminescence.

This process is explained using the energy band model shown in figure 1. This model can be used to understand the basic phenomena of luminescence. This model is applicable because of the connection between conductivity and luminescence. It is established that photoconductivity (increased electrical conductivity caused by the presence of light) is due to the release of charge carriers during luminescence. This validates the energy band model which is described by authors like Randall and Wilkins [5] and, Garlick and Gibson [6], as suitable for understanding the luminescence process which involves the transport of an electrical charge through the lattice [4].

Crystals are formed by the periodical arrangement of atoms or molecules. This arrangement is not completely perfect as there are always some atoms or molecules that are not in their proper place causing defects in the crystal. Many of the important properties of the crystal are due to the presence of such defects. The defects are also influenced by the method of preparation of the crystal.

The defects could be caused due to a number of reasons. Vibration due to thermal energy is one of the causes for the displacement of the atoms from their lattice positions. At any temperature above the absolute zero temperature, there are some intrinsic imperfections in the crystals in the form of vacant lattice site or interstitial atoms. Schottky defects and Frenkel defects are examples of intrinsic defects. Schottky defect is a vacant lattice site from which the regular atom has been removed. Frenkel defect is an irregularity in the crystal structure which is localised in the lattice.

Extrinsic imperfections are created by the addition of impurities, also called activator, to the crystal. If the added impurity or activator occupies a position between the host atoms then it is called interstitial impurity and if occupies a lattice site from which a host atom has been expelled then it is called substitutional impurity. For synthetic crystals, the added impurity would be at part per million level, purity of host would be very high and it will be well crystallized. The imperfections or defects created in the crystal are the places where the electron-hole produced due to irradiation gets trapped. On the application of proper stimulating energy, the trapped charge is released and it recombines, emitting photons in the process.



(a) (b)

(c) (d)

Figure 1: a) Scenario before ionisation; b) Ionisation; c) Trapping centres with occupied trap charges—holes and electrons; d) de-trapping and recombination

The phosphor material has a valance band, a forbidden band and the conduction band. The electrons that are in the valence shell occupy energy levels represented by the valence band and the electrons which have escaped from the valence band and are free to move about in the crystal occupy energy levels represented by the conduction band. In a pure crystal there are no energy states in forbidden band which the electrons can occupy. Since most of the crystals are not pure and contain imperfections or defects they provide localized metastable energy states within the forbidden band. These metastable energy states are the traps where the electrons or holes created due to ionizing radiation are trapped. If they are not trapped then the free electrons move in the conduction band and the holes move in the valence band.

The electrons are trapped nearer to the conduction band and these trapping sites are called electron-trapping centre. Likewise the holes are trapped nearer to the valence band and these sites are called hole-trapping centre. The amount of time spent in the traps by the electrons depends on the nature of trap and its environment. The lifetime of the electron in the trap is given by Arrhenius equation as

$$\tau = s^{-1} \exp\left(\frac{E}{kT}\right) \text{...............................}(1)$$

where

τ is the lifetime,

s is the frequency factor. It represents the interaction between a bound electron with the lattice phonons and a transition probability.

E is the energy trap depth which is the energy difference between the trap and the bottom of the conduction band,

k is the Boltzmann constant,

T is the absolute ambient temperature of the phosphor.

The lifetime τ can range from fraction of a second to 10^8 years. It is strongly dependent on the temperature and the trap depth. The trap depth typically ranges between 0.5-2.0 eV, giving lifetime ranging from 1 s for very shallow traps to 10^{15} s for very deep traps [4]. Since the frequency factor s represents the interaction between a bound electron with the lattice phonons and a transition probability the maximum value expected for s is the lattice vibration frequency which is 10^{12} - 10^{14} s^{-1}. It also includes an entropy term and is weakly temperature dependent [4]. Randall and Wilkins [5] have reported the value of s to be around 10^{-8} s^{-1} in the phosphors studied.

Some of the trapped charges which are de-trapped from their metastable state by a thermal and/or optical stimulation, radiatively recombine with holes producing luminescence at the recombination site which is called recombination centre. The spectrum of the emitted luminescence depends on the recombination site as the recombination occurs in the excited state of the atom, from where a de-excitation causes luminescence. The rate at which the trapped electrons are de-trapped determines the intensity of luminescence and is represented by [4,7]

$$I = C\left(\frac{dn}{dt}\right) \text{......................................}(2)$$

Where,

I is the luminescence intensity,

C is the proportionality constant,

n is the number of electron present at an instant t.

It follows that the phosphor has to be either a semi-conductor or an insulator. Since materials that are conductors do not have the forbidden band, no trapping sites are available where the luminescence causing electrons can be trapped.

Though thermoluminescence and incandescence are both caused due to heat, the luminescence mechanism is very different in both the cases. In thermoluminescence, luminescence is caused due to the transition of the electron from the metastable state to the ground state due to heat which acts as a stimulant or a trigger. In incandescence, luminescence is due to the high state of agitation of the atoms because of the temperature of the material. The vibrations of the atoms at the room temperature produce radiation in the far infrared region of the spectrum. With the increase in temperature these vibrations shift towards the visible region.

In order to observe TL the material is usually linearly heated to a certain temperature at a constant rate. At the same time the light emitted from the material is recorded with reference to the temperature at which it was emitted. This is represented with a light emitted versus temperature graph which is called ‘glow curve’. Figure 2 shows a typical glow curve. The glow curve could have one or more distant peaks. The temperature at which the peak occurs is related to the traps in the materials. Specifically, it depends on the activation energy of the traps. Traps corresponding to higher activation energy will cause peaks at a higher temperature region. An extensive description of the TL process using the different models and TL parameters is given in chapter 5 which deals with the TL/OSL characteristics of the nano CaF_2 along with its annealing parameter optimization.

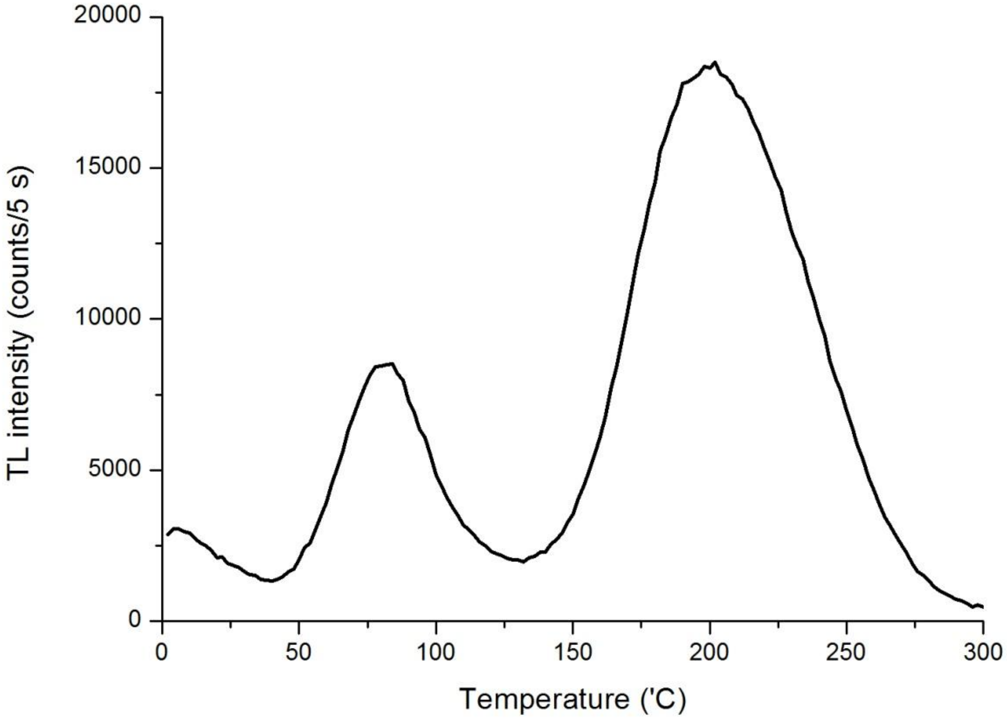


Figure 2. Glow curve from a TL phosphor

1.2.2 Historical Account

TL might have been observed as early as the Middle Ages by the medieval alchemists who are speculated to have known that certain material glow faintly when heated in dark [8]. Initially it was claimed that the emitted luminescence was from the heat itself which was converted to light till Du Fay [9] proved that the observed luminescence was actually delayed phosphorescence and heat only stimulated the emission and was not its cause. The first reported TL was by Robert Boyle on 28th October 1663 in a paper that he read before the Royal society. In it he reports about a diamond that gave glimmering light when he held it in dark in the warm part of his naked body for quite some time.

Thermoluminescence from extraterrestrial minerals was first reported by Herschel [10]. One of the earliest uses of the term thermoluminescence was in 1895 by Wiedemann and Schmidt [11]. The work of Wiedemann and Schmedt pioneered the use of induced TL where they irradiated a specimen with electron beam in a laboratory. Prior to this the TL observations were due to exposure to natural radioactivity in the environment. They used many synthetic samples for this study. The regeneration of thermoluminescence form natural samples in the laboratory was first reported by Trowbridge and Burbank [12]. They bleached the natural thermoluminescence form fluorite by stimulating it with heat and then regenerated the thermoluminescence by X-ray irradiation of the sample. The study of radiation induced thermoluminescence received a boost from the works of Marie Curie [13]. This work was part of her doctoral thesis. The study of the spectra of the emitted luminescence was done for the first time by Morse in 1905 [14].

Urbach [15] used thermoluminescence to study the trap distribution in the sample. This is possible because the electron trap depth determines the temperature at which the peak of the glow curve occurs. The peak will occur at higher temperatures for electrons having higher trap depth. The number of peaks indicates the presence of electron traps at different levels. A peak may be made up of many closely placed peaks. This is due to the distribution of the electron trap depth in near proximity. Deconvolution of the broad peak would give the many individual peaks which constituted the broad peak.

Though research work on TL had been going on no real breakthrough was achieved till Randall and Wilkins [5] proposed the first order kinetic model theory of thermoluminescence and a method to find out the kinetic parameters of the TL process.

The work on the first order kinetics by Randall and Wilkins was followed by Garlick and Gibson's work on the second order kinetics [6]. In the first order kinetics, Randall and Wilkins assumed that once the electron is released from the trap, it will not be re-trapped but will only recombine emitting photon. Garlick and Gibson did not agree with this and they assumed comparable re-trapping and recombination probabilities [4]. Further researchers found cases where neither the first nor the second order was followed. Such cases were reported by Partridge and May [16], Muntoni *et al.* [17], Capelletti and de Benedetti [18], Chen [19] and Taylor [20]. There might be a case where two electrons are trapped in the same trap. In such a case the order of kinetics will be 1.5 [21].

Prior to 1940s TL was used only for mineral identification due to the poor sensitivity of the then available photomultiplier tubes. It was only from the early 1950s that TL's use for measuring exposure to nuclear radiation was developed [22]. It was applied to archaeological dating after sufficiently sensitive and reliable photomultiplier tubes became commercially available in the early 1960s [23 – 25] and to geological dating in the early 1980s [26]. TL dating was able to go up to the Palaeolithic ages by dating materials like burnt flint [28].

1.2.3 Applications

The applications of TL are numerous. The principle of TL is used in many fields of research. Two areas where TL is extensively used are radiation dosimetry and dating (geological as well as archaeological). The study of the emitted light during TL provides rich information which is useful in diverse scientific disciplines such as archaeology, geology, medicine, solid-state physics, biology and organic chemistry. It is also used for material characterization in collaboration with other methods.

The aim of using TL in radiation dosimetry is to infer the amount of incident radiation. The amount of light emitted during TL is a function of the amount of radiation incident on the phosphor. Better phosphors are being developed for radiation dosimetry. The characteristics of an ideal phosphor are linear dose response, reproducibility, high accuracy, no fading problems, no thermal quenching, high sensitivity, etc. High sensitivity means that the amount of light emitted per unit dose and unit mass should be more. This will enable the measurement of very low level dose. The peak used for dosimetry should not be at a low temperature one otherwise it will lead to fading at room temperature itself. At the same time if the peak is at a high temperature black body radiation will cause luminescence which is independent of the incident radiation. Ideally the peak should be around 200 ˚C [28].

In personnel dosimetry the amount of radiation that a person is subjected to is measured. This is specially used for the workers of nuclear plants. The workers wear a badge which contains a TL phosphor. Using this badge the amount of radiation that could have been incident on the worker is inferred. Not only the workers’ exposure to radiation needs to be monitored but also the radiation incident on the surrounding environment of a nuclear plant needs to be monitored periodically to safe guard against any unintentional radiation leakage. This is called environmental dosimetry. Here the amount of radiation present in the atmosphere is measured. Medical dosimetry is used to measure and control the amount of radiation given to patients, especially cancer patients.

TL is also used to determine the dose of absorbed radiation to environmental or locally available materials in situations where conventional, synthetic dosimeters were not in place at the time of radiation exposure. This is called retrospective dosimetry. It is used in cases like radiation exposure due to nuclear accident. For retrospective dosimetry, commonly occurring materials are used. The use of even common salt has been found suitable for retrospective dosimetry [29].

TL dating can measure age in the range 40,000 to 10,00,000 years whereas carbon dating can date up to 50,000 years. It is used in both geological and archaeological dating. Natural dosimeteric materials like quartz and feldspar are used for this. Quartz or feldspar is extracted from the sample to be dated. This quartz or feldspar would have been constantly irradiated by ionizing radiation emitted by natural radioactive isotopes of U, Th, and K. This results in trapping of the electrons or holes at the defect sites. The continuous irradiation over the time results in accumulation of charges in traps having lifetime of $\sim 10^6$ y. The concentration of charges in such traps is proportional to the radiation dose received by them or alternately the time of irradiation. When trapped charges are evicted from the trapping site by means of heat or light, they recombine at recombination sites to give luminescence. Proper measurement of the emitted light can be used to estimate the age of the sample. There are several well defined procedures which are used on daily basis for estimation of age of a sample. The basic equation for dose estimation is:

$$\text{Age} = \text{absorbed dose} / \text{dose rate}$$

Dating of geological samples help in inferring the past climatic conditions. In archaeology it is used to detect forgeries.

TL is also used, in a limited way, for the characterization of materials. It can give information about the various types of defects present in the solid as the spectral characteristic of the emitted light also depends upon the defects in the substance. The peaks in the glow curve and their de-convolution can give a distribution of the ‘defect energies’ present in the material [4].

TL is used for extra-terrestrial materials also. It has been used in the study of meteorites and lunar materials [30]. The amount of radiation in space needs to be known before a manned mission could be sent to space to ensure the safety of the astronauts.

1.3 Optically Stimulated Luminescence

1.3.1 Theoretical Basics

The basic functioning of the OSL phenomena is very similar to that of the TL phenomena. OSL is the phenomena in which light is emitted from the substance when the trapped charges are released due to optical stimulation. Here too, the energy band model can be used to explain the working of the OSL phenomena as shown in figure 1.

This is a very simple model. In reality other parameters like re-trapping come into play. For this model the concentration of charge, i.e. electrons will change under optical stimulation as follows:

$$np = -\frac{dn}{dt} \text{.........................(3)}$$

Where,

n = concentration of trapped electrons

p = Transition probability per unit time for the trapped electron to escape to the conduction band under optical stimulation.

The solution of equation 3 gives the following equation:

$$n(t) = n_o \exp(-pt) \text{...................(4)}$$

Here n_0 is the initial concentration of trapped charges.

Equation 4 implies that the decay of the charge concentration will be exponential with respect to stimulation time. The intensity of light emitted is proportional to the rate of electrons escaping from their traps. From equation 3 and 4 we get

$$I(t) \propto -n_0 p \exp(-pt) \text{...........(5)}$$

Equation 5 gives the intensity of the OSL emission. Since light is used here as the stimulant instead of heat, it is also called photostimulated luminescence (PSL). The traps from which the charges are released during OSL may not necessarily correspond to the traps from which the charges are realised during TL. Irrespective of this difference the amount of emitted light is directly related to the amount of electrons trapped due to the irradiation. Thus OSL is also directly related to the amount of irradiation just like TL.

Like the ‘glow curve’ associated with TL, the ‘decay curve’ or the ‘shine down curve’ is associated with OSL. The emission from the material decays with time as the material is optically stimulated. Figure 3 is an example of an OSL decay curve. The OSL characteristics of the phosphor are described in chapter 5.

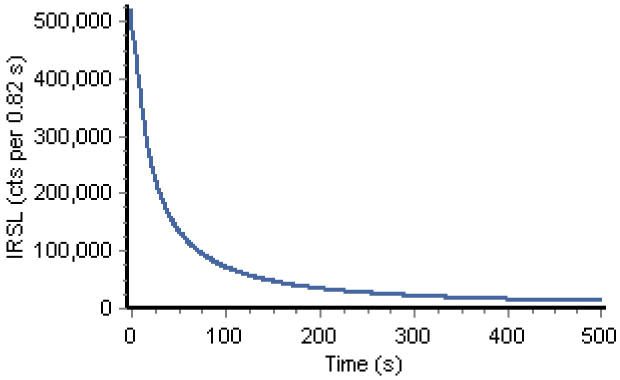


Figure 3. OSL decay curve

Just as TL is not to be confused with incandescence, OSL is not to be confused with Photoluminescence (PL). In PL, due to the absorption of light, there is an excitation of an electron in the crystal defect. When this electron returns to its ground state there is an emission of luminescence. The intensity in PL is related to the concentration of the excited defects and not to the irradiation of the material as is the case for OSL. Thus the mechanism of OSL and PL is fundamentally different, though in both the case the emission of light is due to optical stimulation.

1.3.2 Historical Account and applications

The earliest unambiguous reference to OSL is found in Edmond Becquerel [31] and Henri Becquerel [32] where they reported the quenching of phosphorescence from Zinc and Calcium Sulphides when these materials were exposed to infrared illumination after being exposed to ionizing radiation [33]. Other researchers of the time like Harvey [34] noted that the intensity of the phosphorescence could either increase or decrease due to the infrared light. Later this phenomenon was called *photophosphorescence*. Mandeville and Albrecht [35] used the term *photostimulation phosphorescence,* and *co-stimulation phosphorescence,* to describe the luminescence emitted from alkali halides during optical stimulation following gamma irradiation. Schulman *et al.* [36] called this phenomenon as *radiophotostimulation*. While describing the emission in ultraviolate region under stimulation by a light of 410 nm from X-ray irradiated BeO Albrecht and Mandeville [37] used the term *photostimulated emission.* Pradhan *et al.* [38] gives the credit for discovering the use of OSL for radiation dosimetry to Albrecht and Mandeville [37] while for Yukihara and Mckeever [33] this credit would belong to Fowler [39].

More work in the line of use of OSL for radiation dosimetry was mainly carried on by Antonov-Romanovsky *et al.* [40], Bräunlich *et al.* [41], Sanborn and Beard [42] and Wallack [43]. Their work could not establish OSL as an effective tool for dosimetry. The reason for this failure was that they were working with Sulphide materials. Sulphides do not have deep traps. The electrons trapped in its shallow traps are not stable at room temperature since the electrons in shallow traps will have low activation energy. Thus this phosphor was not reliable for dosimetry.

Then from 1970 onwards other materials were investigated but not much development was done till the work of Huntley *et al.* [44]. They used OSL from natural quartz to estimate the dose absorbed by this mineral in nature. The dose rate was found by the examining the naturally occurring radioactive substances around the mineral like Uranium, Thorium and Potassium. Using the value of dose and dose rate the age of the substance since the last resetting can be inferred. They used green light of 514.5 nm wavelength from an Argon laser for stimulation. This work opened the door of OSL to the field of archaeological and geological dating.

In the field of radiation dosimetry the next major boost came from the area of material development. It was the development of anion-deficient Al_2O_3, doped with carbon (Al_2O_3:C) which was a sensitive dosimetry phosphor for thermoluminescence [45]. Even though this material was a very sensitive thremoluminescent phosphor, it was found to be highly sensitive to light. This apparent shortcoming was explored by Markey, Colyott and McKeever [46] to use it as an OSL phosphor. Al_2O_3:C has been accepted for personal and environmental dosimetry. It has also been accepted by the National Council on Radiation

Protection and Measurements (NCRP) for the dosimetry of astronauts and the habitable volumes of spacecrafts [47].

OSL is also used as a real-time *in vivo* dosimetry technique for radiotherapy beams and for applications in mammography and CT dosimetry. Al_2O_3:C based OSL systems have many necessary qualities of a medical dosimeter such as high sensitivity, high special resolution, availability in different shapes and sizes, no or few dependencies on beam parameters, capability of measurements of absorbed dose in real time for both photon and electron beams, and temperature independence for the ease of calibration and use [27]. OSL dosimetry has many advantages and disadvantages over TL as discussed by McKeever and Moscovitch [48] and others. In many places OSL dosimetry has replaced TL dosimetry [49, 50].

Applications of TL/OSL have been extended to retrospective dosimetry where radiation dose incident on an area of nuclear accident is inferred. Materials from the site are used as dosimeters. Even electronics items have been investigated for their use as retrospective dosimeter. Normally it is the feldspar or quartz extracted from the bricks or pottery or other suitable item that is used as dosimeter [51-55].

The use of OSL for on-board dosimetry of long duration manned space mission is also explored. It is not possible to wait till the spacecraft returns to earth to determine the radiation exposure of the astronauts for long duration manned spaced mission. An on-board OSL based dosimeter reader is suitable because it can be made lightweight and can have low energy consumption. This would not be easily possible for a TL based dosimeter reader as the heating would consume much energy.

In medical dosimetry, the high sensitivity and the optical nature of OSL dosimetry is very beneficial. Due to high sensitivity the dosimeters could be made small which in turn can give greater spatial resolution. The optical nature of this process makes it possible to use optical fibres to access difficult to reach locations, including inside the patient body. With OSL real-time dosimetry is also possible in interventional radiography.

Many different modes of stimulation have been explored for OSL. Huntley *et al* [44] had used the Continuous-wave OSL (CW-OSL) stimulation mode. In the CW-OSL the sample is stimulated with a light of constant intensity. Linear modulation OSL (LM-OSL) was used by Bulur [56] and many others [57-59]. In LM-OSL the sample is stimulated with a light whose intensity is linearly increased to a pre-determined level. Pulsed OSL (POSL) was employed by Akselrod and McKeever [60]. In POSL the stimulating light is switch ON and OFF at a fixed rate. The luminescence emitted from the sample is measured during the OFF state of the stimulating light. Due to this the interference between the stimulating light and the emitted light is avoided. McKeever *et al*. [61] and Bos and Wallinga [62] proposed other stimulation modes like exponential and sinusoidal.

1.4 TL/OSL Instrumentation

A system for TL/OSL mainly consists of a thermally stimulating unit, optically stimulating unit, control unit and a photodetector unit. Figure 4 depicts a basic TL/OSL system. Normally resistive heating is used for the thermal stimulation unit. Non-contact methods of heating like gas heating, laser heating have also been employed since they provide better thermal conduction. For optical stimulation appropriate LEDs, lasers or lamps can be used. If LEDs are used then they are grouped together so that their individual optical power is added up at the sample position providing the sample with sufficient optical power. This is required since the LEDs are not as optically strong as the laser. The disadvantage of using many LEDs is offset by its cheap cost and simpler power driver circuit.

For the control unit, a microcontroller has been generally used. In the present study the use of Field Programmable Gate Array (FPGA) has been successfully employed benefiting from its superior performance. For photo-detection normally a PMT is used. The output of the PMT is proportional to the total luminescence from the material. However, the spatial difference of luminescence from the sample cannot be known. The information on spatial distribution of luminescence has many advantages over the conventional ones [1,63-65]. Therefore, an image detector which can give spatial distribution of luminescence is employed in the system developed here after undertaking an extensive feasibility study, given in chapter 2, to find the most suited detector.

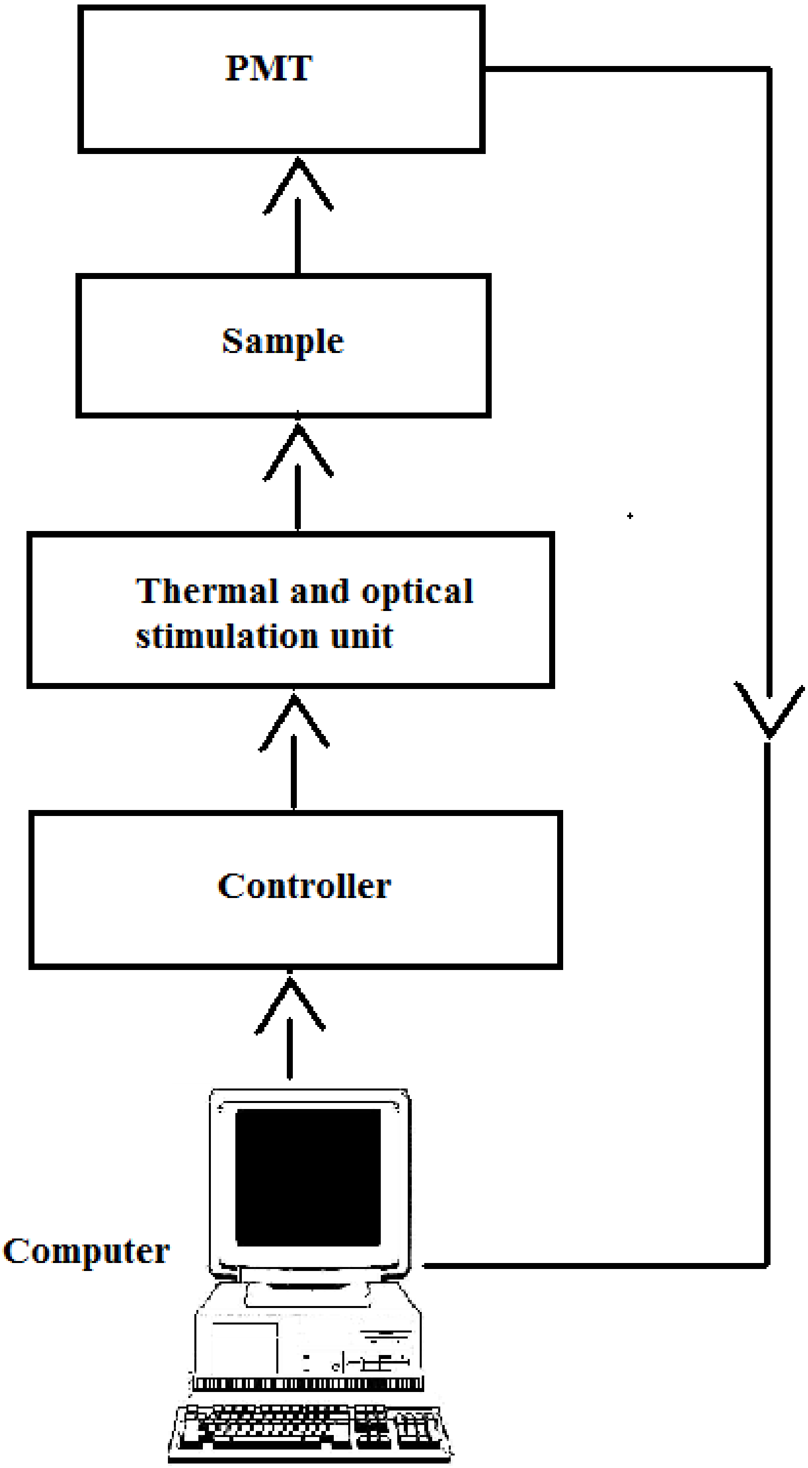
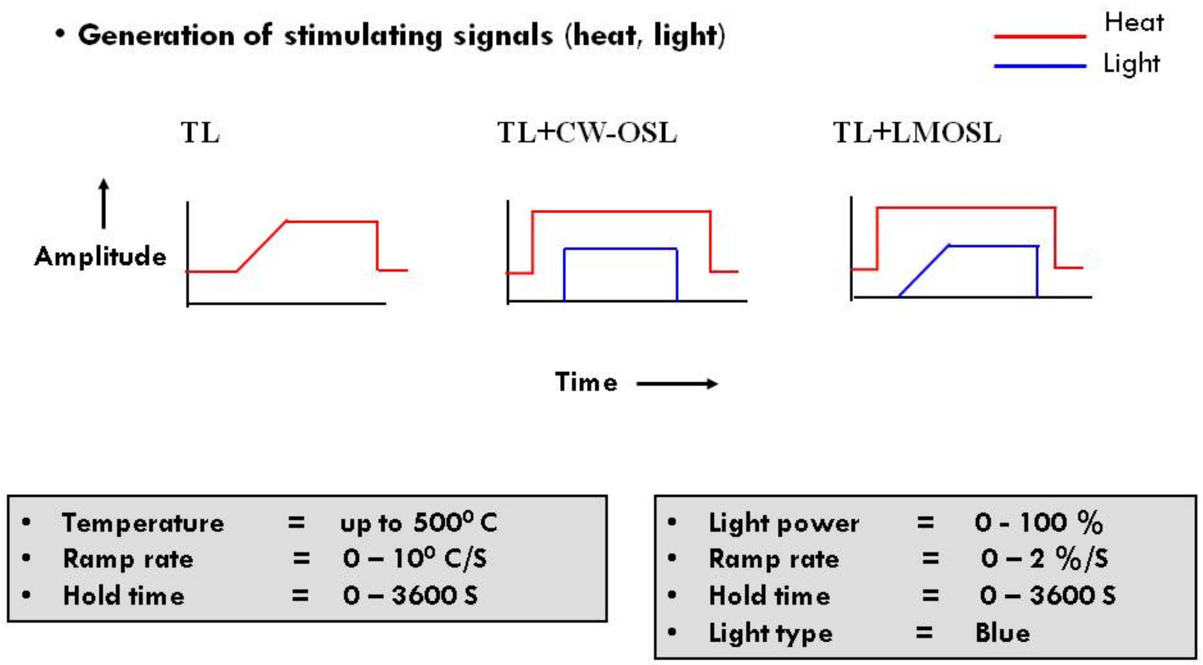


Figure 4. A basic block diagram of a typical TL/OSL system

The manner in which the material is stimulated is important. Certain materials need stimulation in a definite manner like heating with a definite rate up to a particular temperature. Similarly optical stimulation has to be done in a definite manner like increasing the intensity of light linearly up to certain intensity(Lm-OSL) or stimulating with light kept at a fixed intensity (CW-OSL).

In the present study, one of the target parameters for TL was to provide thermal stimulation at a linearly variable heating rate ranging from 0.5 ˚C/s to 10 ˚C/s up to a maximum of 500 ˚C and to be able to maintain this temperature up to an hour. The target parameter for OSL was to provide optical stimulation at a linearly increasing rate ranging from 0.1 %/s to 2 %/s up to the maximum intensity which corresponds to 20 mA current passing through the blue diodes. OSL could be done in either LM-OSL or CW-OSL mode at any elevated temperature ranging from room temperature to 500 ˚C.

The basic technical requirements of the system are given in figure 5.



- Temperature = up to 500° C
- Ramp rate = 0 – 10° C/S
- Hold time = 0 – 3600 S

- Light power = 0 - 100 %
- Ramp rate = 0 – 2 %/S
- Hold time = 0 – 3600 S
- Light type = Blue

Figure 5. Technical requirements of the TL/OSL system

Since research in TL developed much before OSL came into the picture, the instrumentation for TL preceded the instrumentation for OSL. However the first TL that was reported was obtained without the help of any instrumentation. As mentioned above it was reported by Robert Boyle where he used the natural heat from his body for stimulation. Later he also used artificial methods to stimulate emission from diamond. He used heat form a hot iron, from friction and from a burning candle.

A basic TL/OSL system is shown in figure 4. It mainly consists of a computer, a controller, stimulation unit and the light detector. The light detector is usually a PMT which is till now one of the most sensitive low light detector. To detect emission form quartz and feldspar a bialkali PMT like EMI 9235 which has the peak detection at 400 nm is used. For detection in the red region PMTs with S-20 cathode like RCA 31034 and EMI 9658 are used. These red PMTs have higher dark counts. Peltier element coolers are used to cool them to bring down the dark counts. PMTs can be operated in analogue mode or digital mode. Analogue mode is suitable for higher intensity light and digital mode is suitable for low intensity light as shown in chapter 2 while discussing about the various light detectors.

The initially developed systems did not have a computer and the control was done using analogue electronics. Randall and Wilkins [5] had developed their own system for TL. It was quite a rudimentary system where the luminescence could be measured every 10 seconds. It required two observers—one to follow the glow curve and other to note the corresponding thermocouple readings.

A manual TL reader was also developed by Oxford [66, 67]. This was a simple servo loop based system where the temperature signal was compared to a voltage ramp and the difference was used to power the heater supply.

For the heating of the sample, theoretically many different approaches like induction heating, gas-jet heating, infrared hating, ultrasonic heating, laser heating, and resistive heating could be used. The most easy and widely used method of heating is the resistive heating. Both Risø National Laboratory, Denmark and the Daybreak Nuclear and Medical systems, USA uses this form of heating with success. Normally the heating strip is made up of Kanthal, though in the past Daybreak had used Nikrothal as the heating strip. It is important that the thermal resistance between the phosphor and the heater plate be same for all the experiments. Samei *et al.* [68] have reported the effect of variation in thermal resistance on the glow curve.

Since a linear heating rate is needed, it was achieved mechanically or electronically. Now with the progress in electronic technologies, linear heating rate is achieved electronically only. Mechanically it could be achieved by attaching a synchronous motor to the variac. Almost all the TL systems are also able to perform isothermal TL. In isothermal TL, instead of a linear heating rate, the TL is measured at a constant temperature.

The manual one at a time systems were then automated for large throughputs [69]. The first automatic TL reader capable of measuring twelve samples in sequence using planchette sample changer was developed at Risø [70]. Establishment of the Nordic Laboratory in 1977 at Risø gave a major boost to the research along with the development of more effective instruments for TL. These instruments were controlled by PC based software. Microprocessors were used as the main control element in such systems. By the 1980s fully automated systems with the facilities for *in situ* beta radiations were commercially available [71].

For OSL, initially lasers were used as is seen in the case of Huntley *et al.* [44]. OSL properties of quartz were characterised using argon lasers as the optically stimulating source [72-75]. An automated 50 sample OSL reader was developed [73] which used different types of krypton, argon and red dye lasers as the optical stimulating source. Due to the expensive nature of laser based stimulating unit not much research was undertaken in this area till cheaper stimulating units based on filtered lamps and light emitting diodes were made available. It led to the massive use of this technique for dosimetry [49].

The use of IR stimulation for OSL was first shown by Hütt *et al.* [76]. After this many optically stimulating units based on IR stimulation were developed [77-79]. IR LEDs were used as the stimulating light source in these units. Schott BG-39 filter had to be used in front of the PMT to prevent the IR stimulating light being detected along with the emitted luminescence.

Stimulation from blue LEDs is more effective than from that of IR LEDs. This is because as the wavelength decreases the energy of the light increases. Due to this blue light stimulation gives more benefits than stimulation form a higher wavelength light. When blue stimulating light is used a U340 filter is used in front of the PMT to prevent the stimulating light entering the PMT along with the emitted luminescence.

A feedback mechanism is also arranged in the optical stimulation unit to control the intensity of the stimulating light. For this a photodiode is used on which one of the LEDs connected with the stimulating bunch of LEDs is focused. The output of this photodiode is suitably amplified and is used to control the intensity of the stimulation.

Daybreak Nuclear and Medical Systems, USA has also played a major part in the development of the instruments for TL/OSL since the last thirty years or so. They have expertise in the application of TL for archaeological dating. This is used to detect fake artifices. Their services are offered commercially to verify ancient artifices.

A considerable amount of interest has been developed for spatial study of luminescence of TL and OSL. Spatial luminescence offers many benefits over the non-spatial luminescence (integrated luminescence) obtained by a PMT. Due to spatial luminescence from the sample the mineral specific signal can be separated without physically separating the various minerals form the sample [1].

Attempts have been made to study the spatial distribution of luminescence since the last three or four decades using scanning and imaging systems [80, 81]. Along with the laser based single grain system from Risø, another laser scanning systems have also been developed for spatial mapping. They have been used for spatial measurements of OSL from porcelain, Al2O3:C, quartz crystals, brick and concrete [82, 83]. Confocal microscopy has also been used for spatial luminescence as it allows depth discrimination [84]. Prior to the development of sensitive image sensors spatial luminescence studies were attempted by film based cameras [85-92]. Bialkali photocathode and microchannel plate were also used to detect spatial intensity patterns [93, 94]. These detectors were cumbersome and not user friendly.

Progress in this field of spatial luminescence studies were made only after the CCDs came in. CCDs were then employed by many to study the spatial luminescence [1, 95, 96]. They mainly focused on examining the luminescence in the visible range only. Some measurements were also made in the UV region by coating a UV phosphor on the camera. This phosphor would emit in the visible region when a light of wavelength in the UV strikes it [1]. The capabilities of the CCD are further improved by the use of Electron Multiplying Charge Coupled Device (EMCCD). Recent work has focused on the potential of EMCCDs with imaging of infra-red radiofluorescence measurements on feldspar [97] and TL from siliceous rock slices [98]. Clark-Balzan and Jean-Luc Schwenninger have shown the potential of EMCCD for OSL dating [65].

At present two types of automated systems are marketed by Risø National Laboratory (48 sample reader) and the Daybreak Nuclear and Medical systems (24/57 sample reader) [99]. These systems provide for a variety of possible operations that includes ramping of temperature or maintaining a constant temperature with or without optical stimulation, ramping of optical stimulation, pulsed optical stimulation and measurement of light after pulsed stimulation. Almost all possible configuration of thermal and optical stimulation can be created using its software interface.

Risø systems have the facility of automatic background correction. In this process, after TL has been done on the sample, one more cycle of TL is repeated on the same sample. The result of this latter TL is subtracted from the former TL. The latter TL is considered to be background. Previously a double beam detection technique was proposed [61] for measurements of low level TL wherein two similar samples, one "irradiated" and another "clean" are heated simultaneously with identical heating rates and the difference in the outputs of the two identical photomultipliers facing the samples, are automatically plotted in a recorder. This method has been claimed to be of immense help in detecting low level-high temperature TL usually exhibited by geological samples.

The heater plate used in the Risø system has a depression where the sample plate is placed. Due to this arrangement there is more contact between the heater plate and the sample plate. A gold rivet is used to fix the thermocouple below the heater plate. This arrangement is meant to provide better conduction between the heater plate and the thermocouple. The diameter of the thermocouple is 0.5 mm [71]. Due to this it will be able to sense temperatures up to 700 ˚C. In the case of the Daybreak system, the thermocouple is spot welded below the heater plate for optimal contact.

Both the systems have the provision for using Nitrogen gas during the heating to provide better heat conduction and to avoid any possible oxidation of the sample. Nitrogen gas is also used for the rapid cooling of the heater plate so that it is ready for the next measurement. Risø systems also have the provision for evacuation of the atmosphere of the sample chamber. The irradiation source is turned facing the sample or in the opposite direction using the Nitrogen gas to rotate the stainless steel wheel on which it is mounted. Unlike the pneumatically control of irradiation source in the Risø system the Daybreak systems perform this function electromechanically.

The Risø system consists of three parts: the host computer, mini-sys control computer and the TL/OSL reader hardware. The mini-sys computer has all the direct hardware control of the automated reader incorporated in it like maintaining proper timing, sample positioning, data acquisition and error checking. It is connected with the host computer with a serial cable. It uses RS232 communication protocol and functions as a slave computer. The Daybreak system basically consists of only two units: the host computer and the TL/OSL reader hardware which incorporates in it all the electronic control circuitry.

Generally beta source is used for irradiation but alpha source and x rays have been also used for irradiation for the TL/OSL research [100, 101]. Eventhough x ray radiation offers the advantage of no legal hassles regarding the legality of using radioactive substances, it is not a direct replacement for beta source. During irradiation the sample could be heated in order to avoid the filling of the shallow traps as happens in the case of natural samples.

There are some other companies that have also developed TL instruments. Thermo Scientific have their Harshaw model of TLD readers. Most of its models are based on LiF based TLD badges only and those suitable for research work are very expensive. Rexon (USA) and Panasonic are some of the producers of TLD readers. Panasonic uses optical heating which is a non-contact way of heating. A tungsten lamp is used for the heating purpose. A number of TL systems have been developed in BARC, Mumbai for routine personnel monitoring of radiation workers and for medical and research applications [102-105]. ELSEC-Littlemore Scientific Engineering Company, UK, is also one of the prominent companies manufacturing research instruments.

Most these systems employ a high sensitivity photomultiplier tubes, using a bialkali photocathode and an extended range in the UV, provided by a quartz window. These systems are however bulky and expensive and need at present is for more compact, transportable and inexpensive systems [106].

1.5 TL/OSL Phosphors

Phosphors are materials that emit light due to some exposure and/or stimulation. TL/OSL phosphors have the ability to store energy due to ionizing radiation in the form of electrons trapped in the defects of crystals. Under thermal or optical stimulation, the trapped electrons are de-trapped and combine with holes emitting light in the process. Quartz, feldspar, calcium fluoride etc are among the naturally occurring TL/OSL phosphor. Synthetic phosphors like BeO, CaF_2, $CaSO_4$ and Al_2O_3 have also been developed [107]. The development of anion-deficient Al_2O_3 doped with Carbon (Al_2O_3:C) was a milestone in the field of synthetic phosphor development [108]. It gave a boost to the use of OSL for dosimetric applications. It is also commercially produced by Landauer Inc., USA. This phosphor is used for space dosimetry [109], personnel dosimetry and medical dosimetry, where it has a potential for single pulse dosimetry in real time for radiotherapy applications [107,110-112]. There are now a large number of such synthetic phosphor but only Al_2O_3:C has been much of a commercial success.

1.6 Chapter-wise details

The thesis is presented in six chapters. The organization of the thesis in different chapters is given below.

Chapter 2 *Feasibility study of various light detectors for TL/OSL applications*

Since the requirements of light detectors for TL/OSL research are very critical, especially when used for geological or archeological dating purpose, where the emitted luminescence can be very faint, a feasibility study of various light detectors is done. Light detectors for both spatial luminescence studies and non-spatial luminescence studies are presented. A very high sensitive light detector with sufficiently large detector area, low dark noise, high signal-to-noise ratio, good dynamic range, etc is required here. Photomultiplier tubes have been conventionally used for such applications. They have many limitations like high voltage requirement, sensitivity to magnetic field and they are bulky. This called for a feasibility study of various light detectors like P-N photo diode, P-I-N photo diode, Photo Transistor, Avalanche Photo Diode (APD), Photo Multiplier Tube (PMT), Hybrid Photo Detector (HPD), Single Photon Avalanche Diode (SPAD), Silicon Photo Multiplier (SiPM), Digital Silicon Photomultiplier (dSiPM), Charge Coupled Device (CCD), Complementary Metal Oxide Semiconductor (CMOS) Sensors, Intensified CCD (ICCD), Electron bombardment CCD (EBCCD), and Electron Multiplying Charge Coupled Device (EMCCD) to find a better replacement.

Chapter 3: *Development and evaluation of the TL/OSL system*

In this chapter the indigenously developed FPGA-EMCCD based system for imaging both TL and OSL is described. The flexibility and versatility of FPGA has been explored in the development of this high-end system. The control logic used in the FPGA which gave a precise control over the thermal and optical stimulation is enumerated. The choice of components and the design of the system are explained. The use of EMCCD as a detector for spatial analysis as well as the coupling optics between the EMCCD camera and the sample is presented. The use of Labview for developing a user-friendly Graphical User Interface (GUI) and for FPGA interface with the system is described. Designing of a compact high frequency transformer has also been shown.

The results of the tests performed on the system for different parameters of TL and OSL is given. The dose recovery tests were done on the developed system and on commercially available standard systems of Risoe and Daybreak for the sake of comparison. The results are given in the chapter.

Chapter 4: *Synthesis and thermal, optical and structural characterization of the phosphor*

This chapter reports the synthesis of nano-CaF_2. The structural properties of the phosphor are investigated using XRD. To investigate its optical property, Ultra Violet/Visible Absorption Spectroscopy and PL are employed. This chapter describes all these investigations, their results and conclusions.

Chapter 5: *Annealing parameter optimization and TL/OSL characteristics*

The various experimentations performed to find the optimal annealing parameters which would give the best thermoluminescence response are reported here. This chapter describes the influence of the annealing parameter on the phosphor in terms of its effect on the TL sensitivity, peak position (T_m) and full width at half maximum (FWHM). The annealing parameters that are optimised are the annealing atmosphere—air vs vacuum, annealing temperature and duration.

The TL/OSL characteristics of CaF_2 are also examined in this chapter. The chapter describes how the various parameters are derived using different methods. The dose response and linearity of dose response is also reported along with the effect of heating rate on the glow curve. The behavior of the phosphor under UV and blue light stimulation is investigated. The emission is studied using different filter combinations to get insight into the spectral characteristics of the emission. The correlation between the TL causing traps and the OSL causing traps is investigated. The RL response of phosphor is also presented.

Chapter 6: *Summary and future outlook*

This chapter summarizes the work carried out in this thesis and concludes it. It also presents the scope for further work regarding instrumentation, material and for further advancement of the understanding of matters related to luminescence.

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