Chapter-1

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Luminescence is the emission of light from a substance after absorbing energy. The wavelength of the emitted is not of the incident radiation but is the characteristics of the luminescent substance. There are varieties of luminescence phenomena observed in nature or in manmade articles and the nomenclature given to these are invariably related to the exciting agent which produces the luminescence. The various luminescence phenomena can be sub classified according to the type of radiation used to excite the phosphors. Photoluminescence (excitation by optical or ultra-violet light), Radioluminescence (nuclear radiations.) [1] and Cathodoluminescence (electron beam) [2] are the types of luminescence which uses radiation as the excitation energy. In addition to this, there are also some other types of luminescence phenomena such as Chemiluminescence (generated by chemical energy) [3], Triboluminescence (mechanical energy) [4], Electroluminescence (electrical energy) [5], Bioluminescence (biological energy) [6] and Sonoluminescence (sound waves) [7]. There are also many fascinating phenomena in nature which are related to luminescence emission. The glow worms, fire flies, some bacteria, fungi and varieties of sea creatures are some examples of self-luminescent creatures which can found in nature. The polar lights called auroras are another spectacular phenomena related to luminescence which are produced by the excitation of the atmospheric oxygen and nitrogen by high energy cosmic ray particles particularly during the solar flares. In the luminescence phenomena the emission of light takes place a characteristic time $\tau_c$ after the absorption of the radiation. According to this parameter the process of luminescence can also be broadly classified into two sub groups; fluorescence ($\tau_c < 10^{-8}$ s) and phosphorescence ($\tau_c > 10^{-8}$ s) as shown in the figure 1.1 [8,9]. Furthermore phosphorescence can be subdivided into two main types namely, short period ($\tau_c < 10^{-4}$ s) and long period ($\tau_c > 10^{-4}$ s) phosphorescence. Thermoluminescence and optically stimulated luminescence phenomena comes under the long period phosphorescence.
Photoluminescence is light emission produced by excitation with the light photons itself [10]. The fluorescent lamp used in household and general lighting is a principal example of this phenomenon. The host is doped with desired activators for PL, by adjusting the relative concentrations of these activator impurities one can produce desired modification in the colour of the light emitted during the process. There are a large variety of organic and inorganic phosphors which are available and used in consumer items like in road and traffic signals, displays, laundry whiteners, etc., in addition to the host of those used in industrial and scientific applications [11–26]. One of the high technology subjects called light amplification by stimulated
emission of radiation (LASER) is also a kind of photoluminescence in which emission is coherent [27].

1.1.1. Excitation and Emission Spectra

Figure 1.2 shows a typical spectrum of the excitation and emission of a fluorochrome. These spectra are generated by an instrument called a spectrofluorimeter, the sample is strongly illuminated by a colour of light that is found to cause some fluorescence. A spectrum of the fluorescent emission is obtained by scanning with the analysing spectrometer using this fixed illumination colour. The colours of the visible spectrum can be broken up into the approximate wavelength values:

(a) Violet and indigo 400–450 nm
(b) Blue and aqua 450–500 nm
(c) Green 500–570 nm
(d) Yellow and orange 570–610 nm
(e) Red 610 to approximately 750 nm

On the short-wavelength end of the visible spectrum is the near-ultraviolet (near-UV) band from 320 to 400 nm, and on the long-wavelength end is the near-infrared (near-IR) band from 750 to approximately 2,500 nm. Energy transfer mechanism from one dopant (sensitizer) to another (luminescent center) is sometimes used to enhance the sensitivity of a phosphor. Earlier, several researchers have tried to sensitize this phosphor by co-doping with different rare earth metals. Energy transfer between pairs of rare earth ions at dilution level below the self quenching limits has been known to take place generally through multipolar interaction like dipole–dipole interactions or dipole–quadrupole interactions. The optical absorption leading to emission can also take place by the host lattice itself (band absorption). Generally, luminescence of phosphors involves two processes: excitation and emission. Many types of energy can excite the phosphors but PL occurs when excited by photon (often ultra-violet). The process of emission is a release of energy in the form of photon. The basic luminescence mechanisms in luminescent centers are illustrated as follows. In the host lattice with activator, the activator is directly excited by incoming energy; the electron on it absorbs energy
and is raised to an excited state. The excited state returns to the ground state by emission of radiation.

Figure 1.2: The schematic diagram with illustrations of excitation and emission process of photoluminescence phenomena in a phosphor material.

1.2 Thermoluminescence (TL)

Thermally Stimulated Luminescence (TSL) or Thermoluminescence (TL) is the emission of light when heated an insulator or a wide band gap semiconductor which has previously absorbed ionizing or non-ionizing radiation [9]. The basic requirements for producing TL are first, the material should be an insulator or a wide band gap semiconductor, second, the material should have for some time absorbed energy during exposure to radiation and third, the luminescence emission is to be triggered by heating the material. So, thermoluminescence (TL) in a sample may be described as a two-step process: (1) induction (excitation) of TL by exposure to ionizing radiations, (2) stimulation of TL emission by heating subsequent to
exposure. The necessary condition for the induction of TL in a material is that the concerned material should contain certain types of defects in its regular structure which means that very pure and defect free materials would not show TL. Moreover, these defects should be capable of capturing electrons or holes during exposure to ionizing radiations and the captured charges should be retained in that state until the sample is heated to an appropriate temperature to read the TL. These defect structures may be called the TL centers as these structures are present as isolated entities and are not a part of the regular lattice, which is a continuous repetition of the unit cell of a crystalline material. The main function of irradiating the material with ionizing radiations is to produce free electrons and holes in abundance by the interaction of the incident radiation with atoms of the bulk sample. But majority of the electrons and holes undergo recombination almost instantaneously during irradiation and in the process one may see the radioluminescence. Some of these free electrons and holes diffuse in the lattice and are ultimately captured (trapped) in the defect centers and in order to produce luminescence emission during thermal stimulation by the trapped charge carriers (electrons and holes), it is necessary that the sample material contains also such defect species which capture the charge carriers liberated from the traps during heating and in the process undergo electronic transitions leading to the emission of light which are known as recombination centers or luminescent centers.

1.2.1. Interactions with Radiations

The radiations may divide into the following four categories for the purpose of discussing the interactions of the incident radiations, which lead to the induction of TL in insulating solids like phosphors and minerals as: (a) Heavy charged particles, such as alpha particles and protons. (b) Light charged particles, which essentially consist of electrons which are also named as cathode rays or beta rays depending on their origin. Positrons are also included in the same category which have same mass as electrons, but are positively charged. (c) Electromagnetic radiations, i.e., gamma and X-rays and this category also include the vacuum ultraviolet rays. (d) Neutral particle radiations such as neutrons which will not be discussed in this chapter. There are also other particle radiations like mesons which are present in cosmic rays but are not important for the present discussions.
1.2.1.a. Heavy Charged Particles

Alpha particles and protons will be considered and discussed under this category. Alpha particles consist of two protons and two neutrons which are like a helium nuclei. So alpha particles thus have double the charge of protons and are four times as heavy whereas the protons are 1,840 times more massive than electrons and carry one unit of positive charge. The interaction of these heavy charged particle radiations may be divided into two types: (i) inelastic collisions with atomic electrons. (ii) elastic collisions with the nuclei of the atoms of the target material. The inelastic collisions are the predominant mechanism by which these charged particles lose their kinetic energy in a target sample. As the alpha particles are positively charged, alpha particles and protons exert a coulomb force of attraction on the electrons and pull some of these away from their binding with the parent atoms. Being relatively massive as mention above, alpha particles have short range and consequently high specific ionization. Some of the collisions of the alpha particles with atomic electrons are so hard that the ejected out electron produces its own track of interactions with electrons of other atoms which are called delta rays. Alpha particles from usually available radioactive sources (4–7 MeV) produce a few tens of thousands ion pairs each when incident into a solid insulating medium in which the excitation of TL is caused by these ions (electrons). Alpha particles and protons produce densely ionized isolated tracks in the sample volume due to which the ionization is non-uniform with a large part of the sample volume remaining un-irradiated. The efficiency of TL induction by the heavy charged particles is therefore low which is only 4 % of that by b, X and gamma rays for a given dose [28].

1.2.1.b. Light Charged Particles

The beta particles, energetic electrons, and positrons will be considered and discussed under this category. The effect of both the electrons and positrons on the matter is similar. But in the case of the positron, it ultimately annihilates itself by combining with an electron giving rise to a pair of 0.51 MeV gamma photons. Let us consider the direct interaction between an incident electron and the target matter in which an electron with velocity v is moving in the matter. The electron has a radial electric field so, as it moves through the interstitial spaces of the atoms, it exerts Coulomb force of repulsion on the orbital electrons of the target medium. The energy
transferred to the orbital electrons depends on the length of the time the incident particle spends in the vicinity of the orbital electron and the approach distance. If enough energy is imparted, the orbital electron gets ejected out. Some of the interactions may occur at close distances, with the result that the bound orbital electron may be ejected with sufficiently high energy which is called delta rays like that of the alpha particles. These electrons dissipate their energy in the same manner as the original incident beta particle. The energetic beta particles lose energy in yet another manner in which a beta particle passes through the Coulomb field of a nucleus, it experiences a strong force and loses its energy by the so called process of bremsstrahlung emission. As we all know the Bremsstrahlung radiations are X-rays produced by the “braking action” of coulomb field of the nucleus on the passing electron. This process of energy loss becomes important for beta particles with energies above several MeV and is greater for target elements of high atomic number, since higher the atomic number, greater is the nuclear charge and hence greater is the braking action. The bremsstrahlung radiations interact in the sample as that of the X and gamma rays which will be discussed in the later part. The beta particles do not have a straight line path unlike that of the alpha of particles. At lower energies the path of an electron is likely to be tortuous due to multiple scattering in the Coulomb field of electrons or nuclei in its path. Thus the ionization produced in the sample is uniform for a beta ray beam.

1.2.1.c. Electromagnetic Radiations (X and Gamma Rays)

The X-rays are produced by the stoppage of fast moving cathode ray electrons in a target, which is discussed above as the bremsstrahlung radiation while the Gamma rays are emitted from the nuclei of the radioactive elements during their disintegration. But there is no basic difference between the properties of X-rays and gamma rays except for the difference in their origin. When incident on a material the X-rays and gamma rays interact in the following three ways: (i) Photoelectric effect (ii) Compton effect and (iii) Pair production. In photoelectric effect, an electron is knocked out usually from the inner orbit of the target atom and the knocked out electron which is called photoelectron carries with it almost all the energy of the incident photon. The kinetic energy $T$ of the photoelectron is given by

$$T = E - W$$

(1.1)
where $E$ is the incident photon energy and $W$ is the binding energy of the atomic orbit from which the electron is removed which is also called the work function. The cross-section $\sigma$ of photoelectric interaction is approximately given by $\sigma = AZ^4/E^{3.5}$ where $A$ is a constant and $Z$ is the atomic number of the target material. This equation suggests the strong dependence of photoelectric effect on $Z$ and $E$. For example, in LiF phosphor, most of the interactions would take place in Fluoride ion as $Z$ of F being much higher than that of Li. Compton Effect is a scattering phenomenon in which the incident X or gamma photon knocks out an electron from an orbit of the target atom by imparting part of its energy to the orbital electron. The incident photon is scattered and the remaining energy is carried with it. And the scattered photon may undergo another Compton collision or it may interact photoelectrically, in either case imparting energy to yet another electron. The Compton scattering cross-section is a complicated function of the energy of the incident photon and the angle of scattering which is independent of the atomic number $Z$ of the target material. However, the Compton mass absorption coefficient (given in units of cm$^2$ g$^{-1}$) depends on the density of the electrons thus; it is greater for lighter elements since the number of electrons per atomic number is higher for lighter elements. In the third type of interaction, namely the pair production, the X or gamma photon gets converted into a pair of positive and negative electrons as the photon passes near the nucleus of an atom. The effect takes place only when the incident photon energy is more than 1.02 MeV, which is the sum of the mass equivalent of one electron plus one positron. In this case, the excess energy of the incident photon over 1.02 MeV is carried by the electron and the positron in the form of their kinetic energy. The positron after losing its kinetic energy recombines with an electron producing two gamma photons of energy 0.51 MeV each which is called annihilation. The gamma photons produced after annihilation, interact in the medium either by photo-electric or Compton process. The process of pair production is in a way the reverse of bremsstrahlung process, in which both the process takes place in the field of the atomic nucleus. In the photon energy range of our interest the Compton effect predominates in most of the materials out of the three processes of X and gamma ray interaction mention above. The photoelectric effect becomes comparable with Compton effect, only at low energies, approximately below 30 keV.
in the case of low Z elements such as Li, Be, and B. For medium Z elements of importance in TL such as Al, Ca, Mg, Si, etc., its contribution is significant below 100–200 keV. However, Pair production makes significant contribution only above about 2–3 MeV. Above discussion shows that the interactions of X or gamma ray photons produce energetic electrons, which carry the energy of the incident photon in the form of their kinetic energy liberating a large number of bound electrons from atoms of the target medium by exerting electrostatic force on them as discussed above. The most loosely bound electrons have the maximum chance of getting knocked out. In other words, the electrons are knocked out from the valence band of a solid phosphor, since it is this energy state which has a minimum binding energy. The energy deposition by X and gamma ray photons in matter is thus a two step process with the production an energetic electron as the first step and this produced electron is indistinguishable from any other incident electron like a beta ray or cathode ray. This electron interacts in the matter exactly as described earlier in the case of beta particle, in the second step. Thus, the TL induction rate per unit dose therefore is similar for beta and X/gamma rays of similar linear energy transfer (LET) [10].

1.2.2. Thermoluminescence equations

The main equations governing the Thermoluminescence (TL) processes were developed by Randall-Wilkins [29], Garlick-Gibson [30] and May-Partridge [31] for first, second, and general orders, respectively:

\[
I(t) = -\frac{dn}{dt} = ns \exp\left(-\frac{E}{kT}\right)
\]  

(1.2)

\[
I(t) = -\frac{dn}{dt} = \frac{n^2 s}{N} \exp\left(-\frac{E}{kT}\right)
\]  

(1.3)

\[
I(t) = -\frac{dn}{dt} = n^b s' \exp\left(-\frac{E}{kT}\right)
\]  

(1.4)

Where

\(I(t)\) = intensity at time \(t\)

\(n\) = concentration of trapped electrons at time \(t\) (m\(^{-3}\))
\( t = \text{time (s)} \)

\( s = \) a constant characteristic of electron trap, called the “frequency factor”.

\( E = \) the activation energy or trap depth (eV)

\( k = \) Boltzmann’s constant (eV K\(^{-1}\))

\( T = \) the absolute temperature (K)

\( N = \) the total trap concentration (m\(^{-3}\))

\( b = \) the kinetic order, a parameter with values typically between 1 and 2

\( s' = \text{effective pre-exponential factor for general order kinetics (m}^{3(b-1)}s^{-1})\)

In a typical experimental situation a linear heating rate \( \beta \) is used to heat the sample, resulting in the temperature varying as \( T = T_0 + \beta t \), where \( \beta = \) linear heating rate (K s\(^{-1}\)), and

\( T_0 = \) temperature at time \( t = 0 \) (K)

Equation (1)-(2) can be integrated by assuming a linear heating rate \( \beta \), and the following equations are obtained:

\[
I(T) = n_0 s e x p \left( -\frac{E}{kT} \right) \exp \left[ -\frac{s}{\beta} \int_{T_0}^{T} \exp \left( -\frac{E}{kT'} \right) dT' \right]
\]  

(1.5)

\[
I(T) = n_0^2 s e x p \left( -\frac{E}{kT} \right) \left[ 1 + \frac{n_0 s}{\beta N} \int_{T_0}^{T} \exp \left( -\frac{E}{kT''} \right) dT'' \right]^{-2}
\]  

(1.6)

\[
I(T) = n_0 s'' \exp \left( -\frac{E}{kT} \right) \left[ 1 + \frac{s''(b - 1)}{\beta} \int_{T_0}^{T} \exp \left( -\frac{E}{kT''} \right) dT'' \right]^{-\frac{b}{b-1}}
\]  

(1.7)

Where

\( I(T) = \) intensity at temperature \( T \)

\( n_0 = \) number of trapped electrons at time \( t = 0 \) (m\(^{-3}\))

\( s'' = s' n_0^{(b-1)} = \) an empirical parameter acting as an “effective” frequency factor for general-order kinetics (in s\(^{-1}\)).

The general-order kinetics equation is completely empirical and in general will have no relationship to actual physical models.
1.2.3. Applications of Thermoluminescence

The present day progress on research in this field owes to the wide application of this phenomenon. Some of the main applications of the thermoluminescence will be discussed below.

1.2.3.a. Radiation dosimetry

The absorption of radiation increases the level of thermoluminescence observed from a specimen by filling the localized energy levels with trapped electrons and the absorption of heat from the environment, on the other hand, tends to reduce the numbers of trapped electrons by thermally releasing them. So, the intensity of thermoluminescence from a specimen is the result of a competition between trap tilting by radiation and trap emptying by thermal excitation. At a given temperature of irradiation, many materials display an intensity of thermoluminescence which is proportional (or nearly so) to the amount of radiation absorbed leading Daniels and colleagues to propose that thermoluminescence may be used as a means of radiation dosimetry [32]. The first proper application of thermoluminescence to dosimetry was in 1953 when LiF was used to measure radiation following an atomic weapon test conducted [33]. LiF was found by Daniels to be a particularly good material for use in radiation dosimetry because of its high sensitivity. Studies to measure internal radiation doses received by cancer patients treated with radioactive isotopes [32] in which the patients swallow small LiF pellets and the pellets were recovered after passage through the digestive system. The accumulated dose received by the patients was obtained by measuring the thermoluminescence from the pellets and comparing it with that produced in similar crystals which had been irradiated with a known dose of radiation. Following the pioneering work of Daniels and colleagues the application of thermoluminescence to radiation dosimetry has seen an immense increased of effort and a vast literature now exists on this topic. Most of the research has been devoted to the discovery and development of materials suitable for thermoluminescence dosemeters. Much research was (and still is) carried out on the development of ideal dosemeters and for a detailed history of the development of thermoluminescence dosimetry in general the reader is referred to several books and articles on the topic [34–58]. A TL material for the purpose of dosimeter should have the following properties:
1. The materials are desired to give simple isolated glow curve preferably a single glow peak at low temperatures (180-250\(^\circ\)C). However, in case of complex glow curves at least the main peak should be well dominant compared to the hump peaks [47].

2. It is expected to have high gamma ray sensitivity. Fading loss must be as low as possible [49].

3. The phosphor should be stable at high temperatures.

4. The phosphor must be resistive to extreme climatic conditions and chemically inert.

5. It should not be toxic in case of in-vivo and in-vitro experiments. For the use in personnel and medical dosimetry, it is important that the dosimeters have effective atomic numbers close to that of the human tissue [59].

1.2.3.b. Age determination (Dating)

After establishing the relationship between thermoluminescence intensity and absorbed radiation dose, it is only a short step to the use of thermoluminescence as a means of age determination. The natural thermoluminescence from rocks is directly related to the radioactivity from uranium, thorium and potassium present within the material which results in the accumulation of a so-called 'geological' dose. If the rate of irradiation from the radioactive minerals is established, and if the rate of thermal release of the thermoluminescence during the rock's irradiation is assumed to be negligible, then the length of time over which the rock has been irradiated (i.e., its 'geological age') can be determined from:

\[
\text{age} = \frac{\text{absorbed dose}}{\text{dose rate}}
\]  \hspace{1cm} (1.8)

The proper development of thermoluminescence as a means of age determination did not begin in earnest until the discovery of natural thermoluminescence from samples of ancient pottery. This observation led to the development of thermoluminescence as a means of archaeological dating. The basic assumption is that the ingredients of the pottery (i.e., the clay) lose their accumulated geological dose when the pot is fired during its manufacture. So, the high
temperature experienced during firing the thermoluminescence level is re-set to zero. The newly formed pot is now subjected to natural radiation from the radioactive elements naturally present in the clay and surroundings which accumulates an absorbed dose which is proportional to its 'archaeological age, i.e., the time since firing. This age is also calculated from the same equation (1.8). The method of thermoluminescence dating progressed through the 1960s and 70s via the development of proper methods of extracting the thermoluminescent grains from pottery in order to facilitate the calculation of the natural dose rate. So as a result, the quartz-inclusion [60] and fine-grain [61] methods were introduced. A rather different method of dating, relying not on the thermoluminescence due to the archaeological dose, D\textsubscript{a}, but upon changes in the thermoluminescence sensitivity of the specimen induced by D\textsubscript{a}, was also introduced in 1971 (the so-called 'pre-dose' technique; [62]). In addition to these major innovations, there are also many valuable improvements in technique which have helped to overcome a plague of complexities which is the result that thermoluminescence dating is now establishing itself among archaeologists as a respectable method of age determination. Several research articles and books on thermoluminescence dating are available in the literatures [63–89].

1.2.3.c. Geology

Geology is one of the popular disciplines to accept the TL technique in its fold in a variety of applications, such as dating of mineralization, igneous activities, sedimentation and evaluation of growth rate of beaches and sand dunes. The TL technique has been found useful in dating specimens of geologically recent origin where all other conventional methods available fail. In a geological specimen, the TL would start building up from the time of its crystallization and would normally continue throughout its existence due to the radioactivity present within the minerals and in the surrounding materials, till it saturates. If one selects a material with a negligible radioactivity in it such as quartz, the accumulated TL mostly represents the environmental dose rate at a place from where the geological specimen was collected. Accumulation of TL can be affected by natural light especially the ultraviolet component. So, in geology the sunlight bleaching is considered to be the basis for dating the geological event. The exposure of sand grains to sunlight during their weathering and transport through wind and water results in bleaching of their
geological TL which is effective enough to reduce thermoluminescence level to a negligible value. These bleached sand particles, once embedded in a sand dune or bleach, get shielded from further exposure to sunlight which helps particles to acquire more TL due to radiations exposure from their new environment within the sand dune or on the seashore [90]. At present using this single grain technique age of geological samples can be estimated up to 50 million years with an accuracy of +5% or −5%.

1.2.3.d. Forensic science

The major study in forensic sciences is to evolve and standardized methods to compare evidentiary materials with similar materials of known origin, which are invariably available only in minute quantities. So the samples are required to be analyzed non-destructively for evidence purposes. Thermoluminescence can offer an attractive technique in selected materials that are commonly encountered in the criminal cases such as glass, soil, safe insulation terials, etc... This can be used as exclusionary evidence i.e. when the TL characteristics do not match, then it can be said with certainty that a particular sample has not come from a known source. To reduce the probability of any coincidental matching and improve the confidence of the TL measurements whose signal to noise ratio may be bad, in which examination may be made of the TL glow curves from the virgin samples as well as after a heavy artificial gamma or X-ray irradiation and also of the emission spectra [91].

1.2.3.e. Biology and Biochemistry

Application of TL technique in the study of biological and biochemical systems is increased in recent times and necessarily all the measurements are done in the LNT-RT range. The attempts of applying TL techniques have been successful in the study of hydroxyl and amino benzoic acids, proteins, nucleic acids, plant leaves, algae and bacteria. The TL results could indicate the proper stability of the benzoic acid or the ortho form of the benzoic acid, the inter and intra molecular transfer of radiation damage in nucleic acids, proteins and their constituents could be correlated with their TL behaviour; the photosynthetic electron transport routes in the Z diagram could be correlated with TL and additional routes delineated and the interaction between salts and proteins could be understood from the TL patterns [92–97].
1.2.3.f. Quality control in Industry

The application of TL in the control of feldspars in ceramic products has been described as early as 1938. The TL given out by a ceramic after artificial irradiation is directly indicative of its feldspar contains at trace levels where any other type of quantitative analysis is time consuming. Thus in ceramic industry where a particular process is repeated many number of times to produce batches of the same materials, any controllable variations in the feldspar contents can be checked quickly and efficiently using this method. The efficiency of certain surface catalyst like Al₂O₃ can be quickly and efficiently evaluated by their TL sensitivities of the product. The lattice defects which permit the adsorption reactions might also play a role in the TL emitted by these substances and the nature and intensity of TL may be gainfully correlated with the catalytic activity of the surface catalyst. The TL glow curve in such a case could be used as criterion in controlling the preparative parameters of a desired catalyst in a product. In principle, TL method could be employed in the quality control of many of the glass, ceramics and semiconductor products. Moreover, recently it has been shown in the case of textile fibres that the low temperature TL glow curve changes can be correlated with the structure differences and/or chemical traces impurities. But these have not yet received the attention of the industries [98–100].

1.3 Optically Stimulated Luminescence (OSL)

Optically stimulated luminescence (OSL) is the luminescence emitted from an irradiated insulator or semiconductor during exposure to light which is similar phenomena like that of the TL phenomena [101]. So, the OSL intensity is also a function of the dose of radiation absorbed by the sample and thus can be used as the basis of a radiation dosimetry method. OSL is not to be confused with the related phenomenon of photoluminescence (PL) that can be stimulated from similar materials, but which is generally not dependent upon irradiation of the material. In comparision with thermoluminescence (TL) technique, optically stimulated luminescence (OSL) is becoming more popular in radiation dosiemetry because of (i) faster and multiple readout, (ii) very high sensitivity, (iii) no infra-red/black body radiation, (iv) absence(no role) of thermal quenching and (v) possible use of
phosphor in plastic (withstanding even low temperature) binders [102,103]. The OSL dosimeter assembly must be light tight and should be carefully processed in complete dark. Additional details about advantages and disadvantages of the dosimetry carried out using OSL and TL processes can be found from the debate of McKeever and Moscovitch [39]. One of the disadvantages which are associated with the OSL technique is that the optical stimulation itself introduces background counts. This is because at a given stimulating wavelength ($\lambda$), the optical filter available never attenuates the stimulating photon intensity perfectly i.e. 100%. It is also worth mentioning that the stimulating light is $10^{18}$ orders of magnitude stronger than the emitted luminescence [104]. So, the background signal due to stimulating light is over and above the photomultiplier tube’s dark current and noises associated with electronic circuits. Further, there are also evidences indicating the presence of shift in the wavelength of stimulating light ($\lambda \pm \Delta \lambda$, especially for blue LEDs) due to scattering (Raman) which can cause variation in the background counts and widening of OSL curves [105,106].

The more commonly used stimulation profiles in OSL are continuous wave (CW; stimulating intensity is constant) and linearly modulated (LM; intensity increases linearly with time) and each has its advantage and disadvantage. In CW-OSL, the luminescence is recorded very fast and the CW-OSL signal looks like a decay curve. Also in CW-OSL, the background count rate or net background is nearly constant but in the case of LM-OSL, the recording of luminescence is slow but peak shaped and the background count rate increases (non-linearly) with stimulation time. If optically sensitive traps having different values of photo ionisation cross-sections are participating in the OSL process, well separated multiple peaks can also be obtained. The peak height of the LM-OSL glow curve is decided by the number density of the traps participating in OSL process and the recombination efficiency whereas the peak position is decided by the optical stimulation rate, retrapping and recombination cross-sections and the radiation dose. It is worth mentioning that due to long recording time the LM-OSL is not useful in dosimetric applications but it is very useful in characterisation of traps participating in OSL process. OSL is mainly applied in three areas of dosimetry: i) personal dosimetry [107,108], ii) environmental dosimetry [109–113] and iii) retrospective
dosimetry [113–121]. Moreover OSL has also found applications in dating as well detection of artificial irradiation of foodstuff [122] and radiation medicine where an optical fibre OSL dosimeter measures the dose received by patients during radiotherapy or diagnostic radiology [123].

1.3.1. Theoretical background

The equation for optically stimulated luminescence (OSL) in general order kinetics model can be written as [124–126]

\[
I = \frac{dn}{dt} = f \frac{n^b}{N^{b-1}}
\]  

(1.9)

Where \(n\) is the density of filled traps \((m^3)\), \(N\) is total density of available traps \((m^3)\) and \(b\) is the order of kinetics. This also means that out of \(N\), \(n\) are filled and \((N-n)\) are empty. The optical excitation rate, \(f\) is closely associated with; (i) The excitation/photo ionisation cross-section \((\sigma_p)\) of trapped electrons for stimulating radiation, (ii) Energy = frequency/wavelength of the stimulating light and (iii) The intensity, \(I\) of stimulating light. The factor \(f = \sigma_p I/h\nu\) can further be written as \(f=\sigma_p(\lambda)\varphi(\lambda)\), where \(\varphi(\lambda) = I/h\nu\). Since for a given wavelength \(\lambda\), \(\sigma_p\) is constant and the variation of \(f\) is dependent on stimulating light flux; \(\varphi(\lambda)\). It is important to note that \(f= \sigma_p\varphi\) is constant with respect to time for CW-OSL whereas for LM-OSL, \(f= \sigma_p\varphi = gt\) increases linearly with time, where \(g\) is a constant \((s^2)\). It is worth mentioning that CW-OSL represents same physical information as LM-OSL and both describe the same phenomenon under different excitation/stimulation profiles. For \(b= 1\), the Eq.(1.9) represents first order kinetics and is given by

\[
I = \frac{dn}{dt} = nf
\]  

(1.10)

And for \(b = 2\), the Eq.(1.9) becomes

\[
I = \frac{dn}{dt} = f \frac{n^2}{N}
\]  

(1.11)

which represents second order kinetics.
1.3.2. Order of kinetics

1.3.2.a. First order kinetics

A CW-OSL curve follows first order kinetics if it is fitted by single decaying exponential and the decay constant/pattern is always independent of radiation dose and is unaffected by optical bleaching. For all these experimental conditions, the plot of ln(I_{CW}) versus time is a straight line where I_{CW} is CW-OSL intensity. Further for LM-OSL curves, the peak position t_m is always independent of radiation dose as well as optical bleaching. The shape factor μ_g (The shape/geometrical factor μ_g is defined by the ratio of [δ/ω = (t_2-t_m)/(t_2-t_1)] where t_m is the time corresponding to maximum intensity of the LM-OSL peak (I_m) and t_1 and t_2 are the value of the time for the rising and falling portions of the LM-OSL curve at I_m/2) lies in the range 0.55–0.58 for LM-OSL curves following first order kinetics. Further the numerical values of ω/t_m, δ/t_m and τ/t_m are around 1.602, 0.92 and 0.68, respectively for LM-OSL curves obeying first order kinetics [127]. It is important to note that the CW or LM-OSL curves obeying first order kinetics exhibit linear dose response.

1.3.2.b. Non-first order kinetics

In this case, the decay pattern for CW-OSL curve is not a perfect decaying exponential and the decay constant/pattern is dose as well as order of kinetics dependent. The decay constant for CW-OSL curves is influenced by optical bleaching. Further for LM-OSL curves, the peak position t_m is dose dependent and shifts toward higher side in time with the decrease of radiation dose. Also under optical bleaching, the peak position t_m for LM-OSL curves shift towards higher side in time. The value of the shape factor μ_g for second order kinetics lies in the range 0.65–0.68 for LM-OSL curves whereas the shape/geometrical factor μ_g values in the range 0.59–0.65 correspond to order of kinetics between one and two. Further the numerical values of ω/t_m, δ/t_m and τ/t_m in the range from 1.60–2.10, 0.92–1.40 and 0.68–0.70, respectively represent order of kinetics between one and two. It is worth mentioning that non-first order CW-OSL curves may be fitted as sum of two, three or more first order exponential fits, however that may not be the actual situation always. Higher values of μ_g (>0.68), ω/t_m, δ/t_m and τ/t_m may represent LM-OSL curve resulting from superposition of more than one LM-OSL curves obeying first or non-first order kinetics or their mixture. Further the prevalence of mixed order kinetics is
not ruled out. Comprehensive details regarding the analysis of LM-OSL curves using peak shape methods based upon general and mixed order kinetics can be had from the papers of Kitis et al. [127,128].

1.4 Introduction to Li$_2$B$_4$O$_7$ dosimeter

Since the last three decades lithium tetraborate (Li$_2$B$_4$O$_7$/LTB) have been using as one of the promising thermoluminescence (TL) dosimeter as its atomic number is near tissue equivalent effective atomic number ($Z_{\text{eff}} \approx 7.4$). It is one of the widely studied phosphor for applications in the field of personal and clinical dosimetry. Schulman in 1967 reported LTB doped with Mn for the first time, but the luminescence intensity was poor [129]. Further, Takenaga 1980 improved the TL sensitivity by Cu doping [130]. The sensitivity of the LTB TLD was further improved by co-doping Cu with other dopants Ag, In and P [131–133]. Though the sensitivity of the LTB was much increased with the Ag doping, the problem of fading becomes the main drawback again [134]. Huy et al., (2008) studied the effects of Cu, Ag and P dopants in the LTB glass system [133]. EPR studies of the LTB systems were also carried out by different researchers in order to understand the incorporation sites of the dopants in the crystal system. For Cu dopant in the LTB single crystal, each charge state of the Cu forms a well-defined low symmetry species in the LTB lattice. While Cu$^{2+}$ has a frozen-in substitutional position near to Li site with strong distortion of its surroundings, Cu$^+$ has a dynamic excited state with an overall C$_2$ symmetry suggesting interstitial incorporation of the monovalent ion [135–138]. In case of LTB glass doped with Mn and Cu, the Mn$^{2+}$ ions are incorporated into the octahedral and tetrahedral sites of the tetraborate glass network as isolated centres and small exchange-coupled clusters for low and high Mn concentration, whereas the Cu$^{2+}$ ions are incorporated into the octahedral sites of the glass structures as isolated centres, exclusively for low and high Cu concentration [139]. For the LTB single crystals doped with Ag, it was observed that during an exposure at room temperature to ionizing radiation, holes are trapped at substitutional Ag$^+$ ions and form paramagnetic Ag$^{2+}$ ions. At the same time, electrons are trapped at interstitial Ag$^+$ ions and form defects that have the unpaired spin shared by the interstitial ion and a neighboring substitutional ion [140,141]. Recently
LTB nanophosphors doped with Cu were started to develop for the applications in radiation dosimetry of high dose measurements. Singh et al., (2011) synthesize nanoparticle of LTB:Cu using combustion for the first time [142]. The TL dose response of this nanophosphor was observed to have a very wide range of linear dose response in the range of 100 Gy to 1000 Gy. Soheilian et al., 2016 also synthesized nanocrystalline LTB:Cu using different synthesis methods (High temperature solid state reaction, wet reaction and combustion method) and studied their TL characteristics [143]. The LTB:Cu pellets synthesized using the wet reaction was observed to have higher TL response. With doping of Ag, the LTB phosphors become sensitive to optical stimulation of traps [144]. The OSL properties of the LTB doped Ag and co-doped Cu and Ag microcrystalline and single crystals were also had been reported earlier. The authors suggested the LTB doped with Ag and co-doped Cu, Ag crystals as a potential phosphor for the used in real time OSL dosimetry and imaging applications in neutron based radiography [145,146].

1.5 Introduction to CaB$_4$O$_7$ dosimeter

CaB$_4$O$_7$ have an effective atomic number of~12.5 which is very close to the effective atomic number of bones [147]. Calcium Tetraborate (CaB$_4$O$_7$) is a well-studied phosphor as a high sensitive TLD phosphor which shows excellent dosimetry properties required for a TLD [148]. TL properties of Cu doped CaB$_4$O$_7$ was first reported by Fukuda et el., [149]. Fukuda et al., [150] also studied the TL properties of doped and undoped CaB$_4$O$_7$ phosphor. Later on Fukuda et al., also studied the TL properties of Dy, Eu and Pb doped CaB$_4$O$_7$ phosphor [151,152]. TL studies of CaB$_4$O$_7$ doped with Dy was also reported by Tekin et al., [153]. There are also several reports on TL properties of RE (rare earth) doped CaB$_4$O$_7$ [154–158]. TL and OSL properties of the CaB$_4$O$_7$:Ce phosphor was also reported by Palan et al., [159] which shows high sensitivity and excellent TL and OSL properties. Haghiri et al., [160,161] synthesized the CaB$_4$O$_7$ nanoparticles doped Mn and Cu using co-precipitation method and reported its TL properties showing wide range of dose linearity. Though the TL properties of this phosphor is well-studied and established,
there are still rooms for study regarding the OSL properties of RE and transition metal doped CaB$_4$O$_7$ phosphors.

1.6 Motivation of present work

Borate based phosphors are becoming more important because of the ease of synthesis in bulk quantities, simple glow curve structure, increased neutron and gamma sensitivity, near tissue equivalence in some cases and simple thermal treatment procedure. The aim of the present work was to be able to propose a borate based TL phosphor for each of the dosimetric application such as clinical or personnel or environmental monitoring and study these materials in terms of their structural, morphological properties, dosimetric characteristics, analysis of kinetic parameters and mechanism of TL emission as well as unravelling the kinetic parameters of the OSL process. In the present work, two borate based phosphors, namely, lithium tetraborate and calcium tetraborate are investigated as candidates for clinical as well as personnel dosimetry applications because of their near tissue equivalence (LTB: 7.4 and CTB:12.5 which is near bone tissue equivalent). Lithium tetraborate and calcium teraborate are well studied in the literature. However, some of the TL characteristic properties such as temperature of the dosimetric peak of Ag doped lithium tetraborate, fading and hygroscopic nature of both lithium and lanthanide ions doped calcium tetraborate have been studied in the present work. This is achieved by preparing the lithium tetraborate using solid state sintering method and using different initial materials for synthesis and different sintering temperatures. In this present work, the TL and OSL studies and dose response properties by beta radiation of LTB nanoparticle doped with Cu, Ag and co-doped Cu, Ag are discussed in details. The aims of the present work are to synthesize nanoparticles of LTB doped with Cu, Ag, and co-doped Cu, Ag and study their TL and OSL characteristics. Various samples of LTB doped with different concentrations of Cu and Ag are prepared and studied their effects with doping concentration. The kinetic parameters of both TL and OSL glow curves were evaluated and the dose responses of these prepared samples were also studied. Calcium tetraborate are synthesized using solution combustion method doped with lanthanide ions and investigated their TL and OSL properties as well as dose
response for the applications in medical dosimetry applications. In this study the synthesized CaB$_4$O$_7$ nanoparticles doped with different concentrations of Dy, Tm and Tb using combustion method and study the luminescence properties (PL, TL and OSL). The stabilities of the prepared nanoparticles are also studied by observing fading characteristics of the TL and OSL. The $\gamma$- dose response of these phosphors is also studied. Further, the studies on mechanism of TL as well the OSL in these phosphors have been very few. The TL mechanism may depend on the preparation method since the defect centers can be different in different methods. A systematic and detailed PL studies have been carried out to understand the defect centres created by the dopants in the materials. The correlation between TL and OSL process of the synthesized nanoparticles are also studied in details using optical bleaching techniques and observing TL readings after OSL readout of the samples.

1.7 Scope of the thesis

The dose absorbed by the phosphor to be used in personnel dosimetry should ideally correspond approximately to that absorbed by the human tissue in the same radiation field over a wide range of photon energies. This implies that effective atomic number of the phosphor must be close to that of the human tissue (7.4). Conventional high sensitive phosphors such as calcium fluoride and calcium sulphate though have a high sensitivity the effective atomic numbers are higher. At photon energies below 100 KeV, the response of these phosphors for a given absorbed dose of radiation becomes significantly greater than that of the biological tissue. The lack of tissue equivalence may be compensated by proper filtering of the low energy photons which reduces sensitivity of the phosphor and the precision of the absorbed dose assessment. TL materials with reasonable tissue equivalence such as lithium fluoride do not have high enough sensitivity for assessment of absorbed dose for low dose measurement and in addition to this lithium fluoride based phosphors have complex glow curve structure and require complicated thermal treatment for re-use.

This thesis presents luminescence (PL, TL, OSL) studies of borate based phosphors. Two borate based phosphors, viz., lithium tetraborate and calcium tetraborate nanoparticles have been synthesized and characterized. The synthesis
method used to prepare borate phosphors are solid state sintering method and solution combustion method, which is easy, fast and can be employed to prepare materials in bulk quantities. The thesis is organized as follows. Instrumentation and methods employed during the analysis of the TL and OSL glow curves are discussed in chapter 2. Synthesis procedure, structural and morphological characterization of phosphors studied using XRD, FTIR and TEM are discussed in chapter 3. Detailed luminescence studies of the LTB nanoparticles such as PL, TL and OSL are discussed including the estimation of kinetic parameters using different methods are presented in chapter 4. Similarly, detailed luminescence studies of the CTB nanoparticles such as PL, TL and OSL are discussed including the estimation of kinetic parameters using different methods are presented in chapter 5. Principal conclusions including important findings of the work and scope for the future work are discussed in chapter 6.
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