CHAPTER II

THERMOLUMINESCENCE AND ITS APPLICATIONS

A. The Concept of Luminescence :

The emission of light from materials has been a subject of interest for many centuries. The clubs and arms made of limestone used to glow in the 'stone age'. This may be oldest observation of the phenomenon. The glow from micro-organisms, fungi and insects were also observed. Classical literature contains many references to luminescence and many of them, were associated with super-natural stories, myths and legends. It was only in the 17th century that science came to the rescue of man to solve the puzzle. Emission of light from liquids and solids thus became a topic of interest, speculation and debate.

Luminescence is a general term which includes the phenomenon involving the absorption of energy by a substance and its re-emission as visible or near-visible radiation. The term was thus defined by Wiedemann in 1889[14]. Luminescence is however, to be distinguished from thermal radiation, since the phenomenon does not follow Kirchoff's Law for absorption and emission. The energy absorbed by the material giving rise to the luminescence may be the ultraviolet light, X-rays, Cathode-rays or any other corpuscular radiation. If luminescence is produced by the absorption of electromagnetic radiation; then it is known as photoluminescence. Other prefixes are usually self explanatory; like the Cathodoluminescence produced by electron bombardment, chemiluminescence; effect due to chemical reaction, Bioluminescence, a biological process, Sonoluminescence, triggered by Ultrasonic waves in liquids and Triboluminescence where visible light is released during grinding and pulverizing of the solid.

When luminescent material is excited by radiation or cathode rays, emission occurs during the excitation and in the case of some solids for considerable periods, after the excitation has ceased. The emission during excitation is referred as fluorescence, while that which persists after excitation has ceased is known as phosphorescence or after - glow. Phosphorescence of duration greater than a microsecond has never been observed in the normal liquid state but longer persistence can occur in very viscous media. Phosphorescence of long duration is usually confined to crystalline solids of inorganic constitution whose luminescence is due to activation by traces of a specific impurity. Such solids require special preparation, the inclusion of the impurity being effected by heat treatment. This term is often loosely applied to all materials which are synthesized by heat treatment and become luminescent. In general, solids which show phosphorescence of long duration also show emission when warmed with uniform heating rate after excitation. This phenomenon is known as thermoluminescence (TL).

Thermoluminescence (TL) may be exhibited by other phosphors with after glow of shorter duration, if they are excited at a sufficiently low temperature and then allowed to warm up in the dark.

B. Thermoluminescence (TL) :

The phenomenon of thermoluminescence must have been observed as far back as the stone age, the limestones giving off the glow when heated. The glowworms had been mentioned in the 1500 B.C. Chinese literature. However, it was not until 1603 that the first investigations began with a synthetic material. An Italian alchemist V. Cascariolo heated a mixture of $BaSO_4$ and Coal, which after cooling exhibited a bluish glow at night. This could be restored by exposing it to sunlight. In october 1663, the British scientist. Sir. Robert Boyle reported to the Royal Society that when a diamond is heated, light is emitted. However, the 'glimmering light' he observed then was named thermoluminescence only in 1903 by the German scientist E. Wiedemann during his explanation of the property of fluorite minerals. In 1904, Madam Curie referred the thermoluminescence in her doctoral thesis too. "Certain bodies such as fluorite become luminous when heated, they are thermoluminescent". Much work had been done by 1940 and a clear understanding of the phenomenon reached.

Thermoluminescence (TL) is the phenomenon of light emission upon heating a material which has been previously excited. When a material is exposed to ionizing radiations like, alpha, beta, gamma and X-rays or UV-rays or when it undergoes certain chemical reactions or mechanical stress ; a certain percentage of the liberated charge carriers (electrons and holes) may be trapped at certain imperfections in the lattice which are called traps. If these traps are deep enough, the charge carriers remain trapped for thousands of years before they are released by sufficient stimulation. This stimulation can be achieved by transfer of optical or thermal energy to these excited solids.

The return of these trapped charge carriers to a stable state due to the stimulation by external energy (e.g. heat) is always associated with the release of absorbed energy (by the charge carriers) mostly in the form of heat. A small fraction of the absorbed energy is also released in the form of light during this process. This form of emission of light is called thermoluminescence (TL).

The basic physical processes involved in the thermoluminescence are reasonably well understood.[15,16] A thermoluminescent solid must contain two different types of atomic or molecular defects or impurities. One of them acts or functions as an electron trap or hole trap. The second essential defect or impurity is the centre responsible for the emission of light. Consider first the role of the charge trapping centres. When the crystal is exposed to ionizing radiation, electron-hole ionization pairs are formed. Usually a very large fraction of the ionization-induced charges recombine in milliseconds or less at a variety of defects and impurities, termed as recombination centres. Often the recombination process is accompanied by light emission, which is classified as fluorescence, phosphorescence or collectively radioluminescence. Important for the thermoluminescence process are the remaining electrons and holes not undergoing immediate recombination, which are captured (trapped) by defects or impurities usually referred to as electron, hole or charge traps. Consider next the centres which emit light when the crystal is subsequently heated. The most easily visualized luminescent centre and one of the most commonly occurring is a hole trap. When previously irradiated crystals are heated, thermally released electrons wander about until they interact with a trapped hole on an emission centre. As part of the ensuing electron-hole recombination, or charge neutralization process, the electron makes one or more electronic transitions which are accompained by photon emission. Such centres can be called recombination luminescent centres. A second type of luminescent centre is an electron trap which contains a ground state and at least one or more higher energy states. When a thermally released electron encounters such a centre, it is initially trapped in one of the upper levels. Usually the life-time of the excited state is very short and the trapped electron quickly makes a transition to the ground state with the emission of light. When the crystal reaches a higher temperature, the trapped electrons may be thermally released. However, at higher temperature, it is more likely that the trapped electron will recombine with a thermally released hole with or without the emission of light. When functioning as an emission centre this type of defect may be called a transition luminescent centre. Thus a single type of defect or impurity may be an electron trap, a luminescent centre, a recombination centre or some combination of these.

To an appreciable extent, there is a duality or reciprocal character associated with the sign of the charge which interact with the various centres. In the preceding paragraph the words electron and hole can usually be interchanged without violating the physical principles, however, the processes occasioned by this charge interchange procedure would be encountered only rarely.

The defects and impurities responsible for luminescence and thermoluminescence must be able to introduce localized electronic states into the crystal lattice.

Qualitatively such centres are easily understood. If a normal lattice atom is replaced substitutionally by an atom whose valence is either more or less than the replaced atom, local charge imbalance is created. Substitutional impurities lacking an electron would tend to trap ionization electrons and impurities containing an excess electron (lack of a hole) would tend to lose an electron (capture a hole). Equally important are lattice defects which create local charge imbalance. For example, the defect formed by a missing negative ion in alkali halide, such as NaCl, tends to trap an electron. The well known F centre is formed when an ionization electron is trapped on a Cl^- vacancy in a alkali halide or on similar negative ion vacancies in other types of crystals. F centres may be, in the proper circumstances, electron traps (to form dielectron or F' centres), recombination centres and both transition and recombination - type luminescent centres.

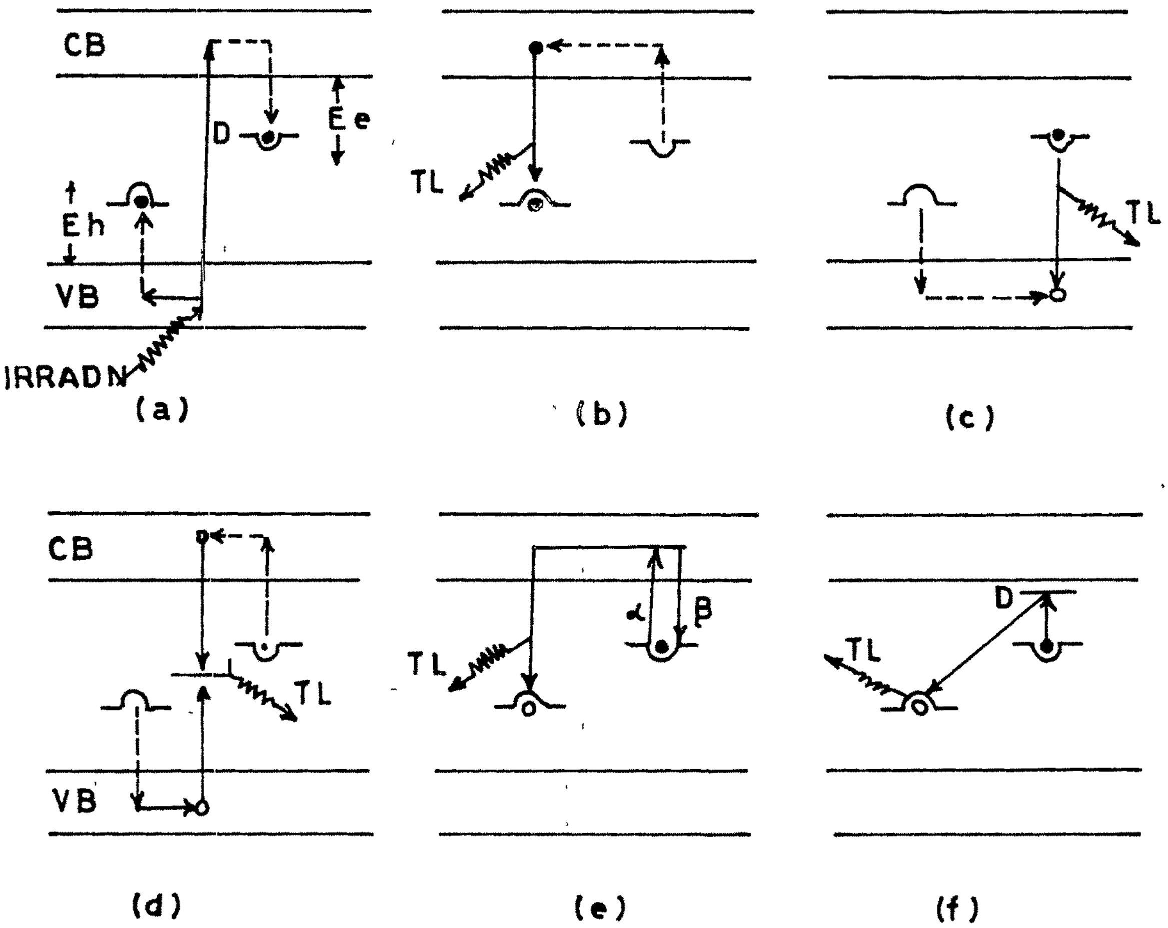
Another type of centre important for thermoluminescence processes is the substitutional impurity having the same valence as the atom, or molecular ion, it replaces. In these cases, the atom functions as an electron trap, as a hole trap, or in both ways. The properties of such centres depend on the detailed electronic interactions between the impurity atoms and the neighbouring atoms.

C. Understanding of the TL-phenomenon :

(1) The Band Theory of Solids.

The phenomenon of thermoluminescence can be best understood in terms of 'band model'[16,17] shown schematically in Fig. II-1. The normal energy state (ground state) of the electrons in a material (before excitation or irradiation) is represented by the valence band. The next higher allowable energy states of all the electrons overlap and constitutes the conduction band. The energy gap between these two states is called the forbidden band. The forbidden band can be imagined to contain some acceptor / donor metastable levels which are basically responsible for the observed thermoluminescence.

Theory demands that no electron can exist in the material with energy states falling in the forbidden gap. When the material is excited by any ionizing radiations (Fig. II-1:a) some electrons (originally in the valence band) are excited and they attain energy states corresponding to the conduction band. Normally these electrons cannot remain excited indefinitely, that is



BAND MODEL DIAGRAM FOR THE TL IN AN INSULATING CRYSTAL (a) - UPON IRRADIATION; (b) - (f) ALTERNATIVE PROCESSES UPON HEATING.

FIGURE : II-1

the life-time of an electron in the conduction band is very short and the electron attains its ground state immediately giving away the energy to warm up the crystal lattice or in the form of light.

However, an impurity atom (with an appropriate ionic size and charge) present in the material can have energy states in the forbidden band. These are the metastable energy states having appreciable life-time . An excited electron can find itself in this state, rather than getting back to its normal valence band state. Now, one says an electron is 'trapped'. In analogy, it is also visualised that a 'hole' (absence of an electron) is trapped at an energy state very close to the valence band. Depending upon the energy level of the electron trap with respect to the conduction band (or the hole trap with respect to the valence band) - called the trap depth, the electron will remain trapped for a definite period; the greater the trap depth, the greater will be the life-time of the electrons in the trapped state for a given temperature.

This stage corresponds to energy storage after the initial excitation of a material. If now the material is warmed, the heat energy supplied is able to stimulate the electrons out of the traps (detrapping) and the electrons return to the ground state; if the conditions are favourable (for example, if the particular atom has a light emitting property) for the emission of light in this 'return process' then thermoluminescence occurs (Fig. II-1:b). Alternatively, a hole may be excited into the valency band where it wanders until it combines with an electron at the trapped counter-part emitting the thermoluminescence (Fig. II-1:c).

If the traps are not very deep, detrapping and recombination may already occur at a substantial rate around room temperature resulting in a short half-life of the stored energy. This is called phosphorescence but strictly speaking it is thermoluminescence at the room temperature. Only if the traps are deep enough to result in sufficient storage stability at room temperature (half - lives of trapped electrons at least several months normally corresponding to glow peak temperature greater than about 150°C), the effect becomes of dosimetric interest. The glow curve generally exhibits many peaks, each corresponding to a trap with a different energy depth.

In many phosphors it is possible that the electrons and holes are detrapped more or less simultaneously and they recombine at an entirely new site

(fig. II-1 ; d) called luminescence centre or recombination centre. The TL glow curve will in this case represent an effective thermal activation energy needed by the trapped electron/hole to surmount a potential barrier between the trap and recombination centre.

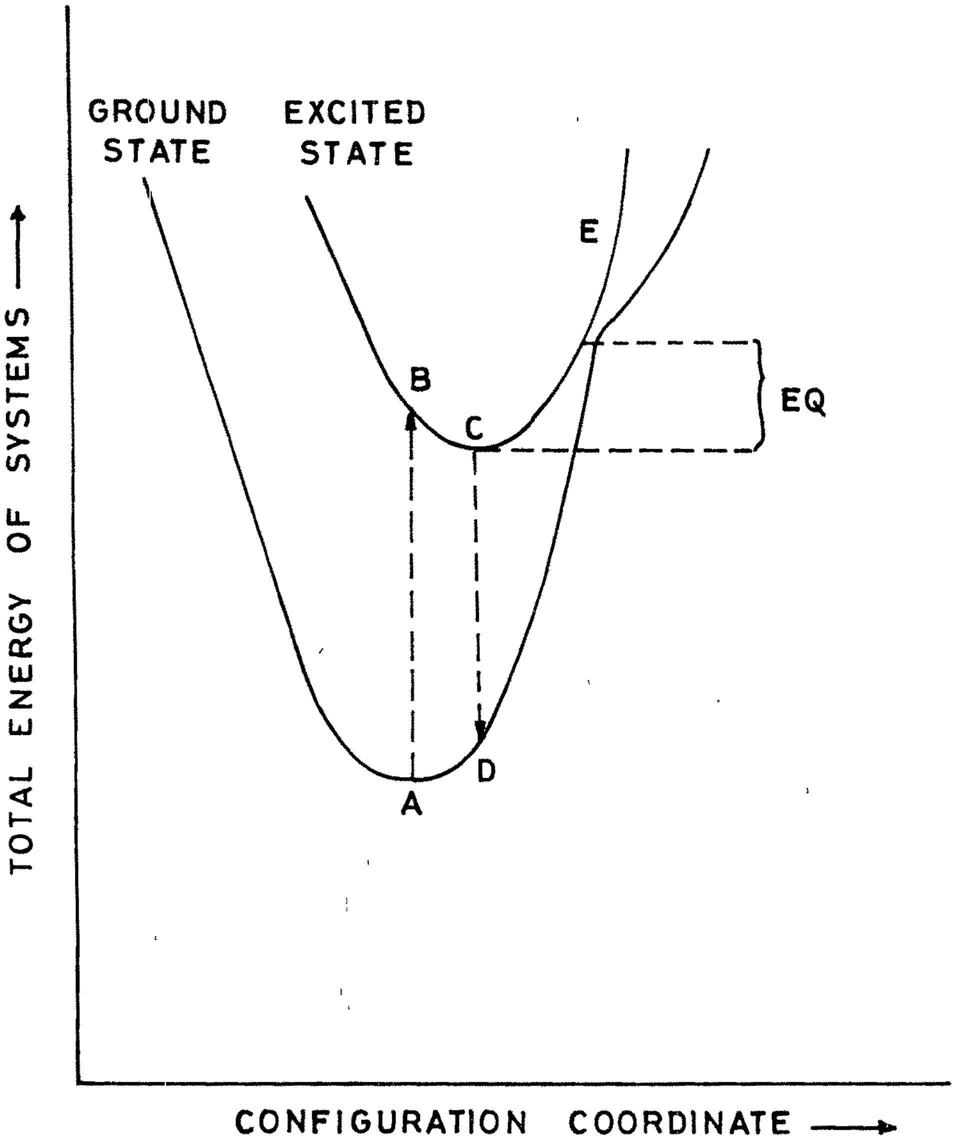
In reality, a trapped charge when detrapped has a finite probability of getting retrapped (β in fig. II-1;E). When this retrapping probability is significant, the shape of the glow curve is different from the case when it is absent. Also the recombination probability for the detrapped charge carrier may in most cases change with time (i.e., as the heating proceeds) depending on the number of available unused recombination centres. Such a process is called a second order or bimolecular process usually while the simplest case where the recombination has a constant probability with time, is called a first order or mono-molecular process. There are also practical situations where the detrapped charge carriers recombine directly without having to be excited into the conduction/valence bands. This is a, case of TL involving isolated luminescence centre and process follows first order kinetics (fig. II-1 ; f).

All the foregoing discussions take into account only the ionisation effects of the excitation irradiation, one should not however forget about the displacement effects resulting from elastic/inelastic collisions of the atom of the phosphor with the impinging radiation. This effect is more significant for the case of particulate radiations (like, alpha, beta, gamma, neutron, cosmic rays). The important thing about this displacement effect is that atoms are physically moved which results in the creation of interstitials, and vacancies. In relation to thermoluminescence, these constitute defects which have potential to influence the trapping and emission processes.

2. Configuration Co-ordinate Curve Model :

Luminescence in atomic gases is adequately described by the concepts of atomic spectroscopy, but luminescence in molecular gases, in liquids and in solids introduce two major new effects which need special explanation. One is that the emission band appears on the long wavelength (low energy) side of the absorption band, the other is that emission and absorption often show as bands hundreds of angstroms wide instead of as the line found in atomic gases.

Both of these effects may be explained by using the concept of configuration co-ordinate curves[18] shown in fig. II-2 . As in the case of atomic gases the ground and excited states represent different electronic states of the luminescence centres, that is the region containing the atoms or electrons or both involved in the luminescent



CONFIGURATION COORDINATE CURVES FOR A SIMPLE LUMINESCENCE CENTER.

FIGURE : II - 2

transition. On these curves the energy of the ground and excited state is shown to vary parabolically as some configuration co-ordinate, usually the distance from the luminescent centre to its nearst neighbours. There is a value of the co-ordinate for which the energy is a minimum, but this value is different for the ground and excited states because of the different interactions of the luminescent centre with its neighbours. Absorption of light gives rise to the transition from A to B. This transition occurs so rapidly that the ions around the luminescent centre do not have time to rearrange. Once the system is at B it gives up heat energy to its surroundings by means of lattice vibrations and reaches the new equilibrium position at C. Emission occurs when the system makes the transition from C to D and once again heat energy is given up when the system goes from D back down to A. This loss of energy in the form of heat causes the energy associated with the emission C to D to be less than that associated with the absorption A to B.

When the system is at an equilibrium position, such as C of the excited state curve, it is not at rest but migrates over a small region around C because of the thermal energy of the system. At higher temperatures these fluctuations cover a wider range of the configuration co-ordinate. As a result the emission transition is not just to point D on the ground state curve but covers a region around D. In the vicinity of D the ground state curve shows a rapid change of energy, so that even a small range of values for the configuration co-ordinate leads to a large range of energies in the optical transition.

This explains the broad emission and absorption bands that are observed. An analysis of this sort predicts that the widths of the band (usually measured in energy units between the points at which the emission or absorption is half its maximum value) should vary as the square root of the temperature. For many systems this relationship is valid for temperatures near and above room temperature.

Two other phenomena which can be explained on the basis of the model described in fig. II-2 are temperature quenching of luminescence and the variation of the decay time of luminescence with temperature. On the scheme of fig. II-2 this is interpreted as meaning that the thermal vibrations become sufficiently intense to raise the system to point E. From point E the system can fall to the ground state by emitting a small amount of heat or infrared radiation. If point E is at an energy E_Q above the minimum of the excited state curve, it may be shown that the efficiency 'η' of luminescence is given by eqn. d,

$$\eta = 1 + C \exp (- E_Q/kT)^{-1} \qquad \text{------} \quad (d)$$

where C is a constant, k is Boltzmann constant and T is the temperature on the Kelvin scale.

The temperature quenching tends to occur most strongly for centres that would have stayed in the excited state for a relatively long period of time. As a result, the decay time of the emission that occurs in this temperature region is largely characteristic of centres in which transitions to the ground state have been rapid; therefore, the decay time of the luminescence is observed to decrease.

D. Theory of Thermoluminescence :

Thermoluminescence may be treated as a kinetic process. It has been found that it is neither a first order nor a second order process. Instead an empirical general order equation has been proposed. For simplicity, consider the thermoluminescence originating in a solid containing a single type of charge trapping centre and a single type of luminescent centre[15]. During irradiation a fraction of traps will acquire charges. When the sample is heated, the thermally released charges will interact with the luminescent centres and light will be emitted either by charge capture or by recombination. Let N_o be the trapping centre concentration and n_o the concentration of trapped charges when the irradiation is terminated. Next assume that all or a constant fraction of the charges released when the crystal is heated, find their way to luminescent centres. Also, assume that each charge interacting with an emission centre causes a photon to be emitted. This is equivalent to assuming that nonradiative transitions involving the luminescent centre are negligible. Under these conditions, which appear to apply in numerous cases, the light intensity is proportional to the number of charges untrapped per unit time. In turn, the number of charges released per unit time is equal to the trapped charge population multiplied by the probability that each charge will escape. The escape probability is given by the usual expression,

$$P = S \exp (- E/kT)$$

where 'S' is pre-exponential factor or attempt to escape frequency,

'E' is the activation energy for thermal untrapping,

'k' is the Boltzmann constant and

'T' is the temperature in degree Kelvin (°K).

the intensity 'I' at any time 't' is given by

$$I = -\frac{dn}{dt} = (\text{const})\, nse^{-E/kT} \quad \ldots\ldots\ldots \quad (1)$$

Here, 'n' is the trapped charge concentration at time 't'.

In the usual TL measurement the sample is irradiated at a temperature low enough to ensure that the term exp ($-E/kT$) is negligible and light emission is undetectable. Subsequently, the sample temperature is increased in a controlled manner as the light emission is recorded. Usually the temperature is increased linearly. There are two reasons for this. First, a precise and reproducible linear temperature increase is the easiest to achieve experimentally. Secondly, a linear temperature programme leads to a simple solution of equation 1. In this case temperature and time are related by the simple expression,

$$T = T_o + \beta t \quad \text{or} \quad dT = \beta\, dt.$$

where β is the heating rate in degree per unit time. Using this relation one can obtain the following expression for the luminescent emission as a function of time or temperature, for a single type of trapping centre,

$$I = n_o S e^{-E/kT} \exp\left(-\int_o^T \frac{S}{\beta} e^{-E/kT}\, dT\right) \quad \ldots\ldots (2)$$

The physical situation leading to equation 1 and 2 occurs when retrapping is negligible, that is, when all but a negligible number of thermally released charges find their way to luminescent centres without undergoing retrapping in the trapping centres. Most commonly this occurs when the concentration of luminescent centres greatly exceeds the concentration of trapping centres, or, if the concentrations are approximately equal, the charge capture cross-section of the luminescent centre is much larger than the corrosponding cross-section of the trapping centre.

When retrapping is non-negligible ; equation 1 must be replaced by one that includes retrapping. This may be done to varying degree of approximation, some of them leading to equations which have not been solved analytically. The only approximation that has been widely used is based on the following situation. For each charge trapped in a trapping centre there is an opposite sign charge trapped in a recombination or luminescent centre. Light is emitted when thermally released electrons find, their way after being retrapped one or more times, to the trapped holes or thermally released holes interact with trapped electrons.

In such cases, the emission is controlled entirely by the competition between thermal untrapping and retrapping and the recombination. This approximation leads to the equation,

$$I = -\frac{dn}{dt} = (\text{const.})\, n^2\, Se^{(-E/kT)} \quad \text{- - - -(3)}$$

This equation differs from equation 1 only in that n term is replaced by n^2. In this case dependence of thermoluminescence intensity on temperature obtained with the usual linear temperature rise is given by

$$I = n_o^2 \;\; S \exp^{(-E/kT)} \times N_o \left\{ 1 + \frac{n_o}{N_o} \int_o^T \frac{S}{\beta} \exp^{(-E/kT)} dT \right\}^{-2}$$

$$\text{- - - - - - (4)}$$

All the parameters in equation 4 have been defined above including N_o which is the charge trap concentration. The curve describing the emission from a single type of trap is usually referred to as a glow peak. A curve may contain one or more glow peaks and is usually termed a glow curve. However, in both first and second order kinetics the peak temperature depends on the heating rate and on ratio ($\frac{n_o}{N_o}$) for second order kinetics. Thus the specification of glow peaks by glow peak temperatures, while widely used and often useful, must be regarded with continuous attention to the fact that this parameter is a function of heating rate.

E. Factors Affecting Thermoluminescence[17] :

1. Effect of impurities :

An impurity which causes thermoluminescence in an otherwise dead phosphor is often called an 'activator'. In the case of thermoluminescence, the role played by an activator may be more than just being the emission centre ; its presence may create more traps responsible for the thermoluminescence. Thus three distinct categories of activators may be distinguished as far as thermoluminescence is concerned :

i) causes increased trapping,
ii) causes increased emission,
iii) causes both increased trapping and emission.

An important aspect about the role of activator is the phenomenon of concentration quenching ; an activator atom, to be an effective emission centre, has to be guaranteed with a minimum ' free lattice space ' around it without another activator atom of the same type being present. Hence, as the activator concentration increases in the crystal, the luminescence increases at first, reaches a maximum at an optimum concentration corresponding to the above mentioned minimum lattice parameter and then starts diminishing for further increases in the concentration.

2. Effect of Thermal Treatments :

Thermoluminescence properties exhibited by a phosphor very much depend upon the kind of thermal annealing experienced by it prior to the irradiation or excitation. Annealing is the process which reduces internal strain and surface energy. It is also generally true that more defects are produced at higher temperatures of annealing. The number of defects retained by the crystal lattice depends on the cooling rate employed to cool the crystal to the ambient temperature from the annealing temperature. From this it is obvious that a 'standard annealing' procedure be adopted for reproducible results in thermoluminescence studies. In some cases the TL sensitivity changes by the annealing treatment which can be identified with certain crystalline phase-changes in the phosphor. These changes are more pronounced when the sample is quickly quenched to the ambient from the annealing temperature. This is perhaps due to "freezing in" some kind of mixed phase defects.

Many phosphors, particularly the non-oxide ones, if heated in air-specially in humid air - at high temperatures become less sensitive to TL due to OH poisoning. Hence vacuum or inert atmospheric heating should be preferred for high temperature annealing treatments.

3. Effect of Irradiation Dose :

In many phosphors the thermoluminescence properties change considerably depending upon the total irradiation dose. The changes are significant when this integral dose is quite high and given in an acute exposure. The effect can be easily studied by first heavily irradiating the phosphor, removing the TL by heating and then studying the TL properties at lower levels of irradiation doses. The more significant effect of such heavy irradiation are

i) TL - sensitisation i.e. increase in thermoluminscence (TL) sensitivity

ii) Damage of TL : at increased doses of irradiation crystal damage like, production of voids, aggregates, strain location etc., can occur which can reduce the TL-output with or without a change in the TL-emission spectrum.

iii) TL-spectral change : spectral changes in the TL-emission have also been observed with increasing doses.

4. Effect of LET of irradiation :

The ionisation capacity of a radiation in a medium is usually signified by the linear energy transferred (LET) to the medium by the incident energy. The usual LET response which is observed in most of the TL-phosphors is decrease of sensitivity with increase of LET of the incident radiation. In a phosphor higher temperature peaks are observed only at high doses of low LET radiation, the same may be observed even at low doses for high LET radiation.

5. Effect of Stress, Crystallisation and Particle size :

These effects have been pursued in detail in the case of thermoluminescence exhibited by geological samples : factors, such as stress, crystallisation, decomposition and particle size are almost inseparable in these cases and hence are considered together. The application of stress can arise out of operations such as crushing, grinding, packing, pellettising etc. Some of the physico-chemical processes like crystallisation and decomposition may result in storage of energy in the material which may in turn appear as thermoluminescence when heated. Also the crystallisation temperature as well as other physico-chemical conditions decide essentially the type and quantity of lattice defects present in the crystal and this in turn decides the TL sensitivity of the material. The effect of particle size assumes importance when thermoluminescence of powder samples are studied. The size of particle influences tremendously the excitation of a phosphor as well as the emission output by scattering and self absorption characteristics.

6. Storage Effect :

This is essentially a 'fading' effect on the thermoluminescence (of a previously irradiated phosphor) at a constant temperature. There are special cases however where there is a slight increase rather than decrease in the TL-output and hence the effect in general will be referred as storage effect. The fading characteristics of a phosphor can be best described by the life-time, T of the particular trapping state wherein greater life-time (T) value will mean less fading. Another type of abnormal fading which could be seen mostly during short interval after irradiation - hence called short term fading - is perhaps due to a combination of the usual thermal decay and a tunnelling transfer among traps. Typically such an abnormal fading exhibits a small 'build-up' during the initial part of the otherwise normal decay curve.

7. Thermal Quenching Effects :

The luminescence efficiency is generally a temperature sensitive factor, efficiency decreasing with increase of temperature. This is so because of a competition between radiative transitions and non-radiative transitions - de-excitation of material by thermal agitation - which increases with temperature. In the case of TL -phosphor having one kind of luminescence centre and several thermal activation energies, this will mean that the higher temperature peaks are observed under decreased luminescence efficiency conditions dictated by the thermal quenching.

8. Electro - Static Effects :

It has been observed that application of high electric fields on a TL phosphor during the heating enhances the TL-output and sometimes affects the nature of the emission too. This effect is thought to be due to either i)Field ionization of electron traps or ii) acceleration of electrons after thermal release from traps and subsequent impact ionization. If the first factor prevails, one could observe thermoluminescence even without heating. In most of the materials however, the second factor is operative. Occasionally, there can be a quenching effect too of this applied electric field.

9. Effect of Infra-red Stimulation :

The possibility of achieving the release of stored energy by infra-red stimulation rather than thermal stimulation has been realised very efficiently only in the case of alkaline earth sulphide phosphors with double activators. Unfortunately however such effects are seen efficiently only in phosphors with shallow traps where fading is quite high.

10. Effect of UV Rays.

The effect of ultra-violet irradiation on TL phosphors has been mostly pursued from the point of view of its applications in measuring UV exposures and not many investigations have been reported enlightning the basic physical processes involved. A somewhat successful explanation has been provided only in the case of alkali halides especially NaCl, KCl and KBr.

An excitonic process of defect creation by UV irradiation has been found to lead to mathematical expressions which explain satisfactorily the wavelength dependence of the UV excited thermoluminescence in these phosphors ; very short wavelength light has been found to excite the phosphor by ionisation. From the point of view of effects produced which are useful in various applications, it is convenient to consider three categories.

10 i) Intrinsic UV Response/UV Induced TL :

Upon UV excitation by an appropriate frequency, a valence electron of the lattice or a ground state electron of an impurity atom is excited to a metastable state upon subsequent thermal stimulation, luminescence is emitted as it would after a X - or gamma irradiation and heating. The TL glow curve obtained after the two kinds of excitation are not usually the same and in general the TL sensitivity to UV excitation is very small. The TL glowcurve shape and the sensitivity are also wavelength dependant.

Among the more sensitive TL phosphors, Mg_2SiO_4: Tb is the only case whose intrinsic UV response is quite high. Other equally gamma sensitive phosphors like $CaSO_4$ exhibit a UV sensitivity almost 10^4 times smaller ;

$CaSO_4$(Dy) has been reported however to have sufficient intrinsic response as to be able to measure 253.7 nm UV exposures in the range of 400 to 4×10^4 erg. mm^{-2}.

10 - ii) UV Induced TL Bleaching and Desensitisation :

If an already irradiated TL phosphor is exposed to UV rays one may observe some bleaching (or erasure) effect in the gamma induced TL. The bleaching efficiency is usually not the same for all the glow peaks as each peak may have a different λ dependence for the bleaching effect. The mechanism involved is that electrons in metastable levels (trapped by the prior gamma irradiation) are freed by the UV excitation.

A more important effect is the desensitisation effect by UV irradiation. This is in fact a damage effect in the sense that TL sensitivity increased artificially by irradiation or thermal treatment of a phosphor can be reversed at least partially by exposure to UV rays. If the luminescence centres are the activated hole centres as has been argued in the case of TL of natural quartz, the sensitisation process can be expected to leave a large number of activated luminescence centres ; the UV irradiation may be expected to neutralise these activated centres by the excitation of valence electrons and hence the desensitisation occurs.

10 - iii) UV Induced Transfer TL.

This is in fact a special case of UV bleaching ; however it is considered here that when an electron is freed from a metastable level it has a good chance to get retrapped at some other level (a different trap). Thus a redistribution of a trapped carrier population takes place among the various types of traps present in the phosphor and a TL glow curve is generated with different relative intensities among the various peaks. The effect is best seen in a phosphor which has been heavily gamma irradiated and partially drained by insufficient heating (i.e. TL corresponding to deeper traps are remaining residual in the sample). When such a sample is exposed to UV light, electrons are freed from these deeper traps and a good fraction of them are retrapped at shallower traps. Hence when the TL is read after the UV exposure, one find a reduction in the high temperature peak and a regeneration of the lower temperature peaks. This has been best demonstrated in the case of fluorite TL phosphor.

The phenomenon of UV transfer is quite efficient in most of the TL phosphors and can be successfully employed to measure even low levels of UV exposure. It is to be remembered that this effect is also extremely λ - dependant.

F. Applications of Thermoluminescence :

Thermoluminescence is perhaps one of those rare physical phenomenon which is more successfully applied than understood. Its application potential was first proposed in 1953 and since then with the development of better instrumentation and basic understanding, its applications have engulfed a whole spectrum of disciplines such as Geology, Archaeology, Biology and Biochemistry, Forensic Science, Radiation Dosimetry, Radiation Physics, Solid State Physics, Space Science, Spectroscopic analysis, TL - photography and so on. The important aspects of these applications[16,17,19] are briefly summarized, in the following sections.

1. Geology :

Geology is one of the earliest disciplines to accept the TL technique in its fold in a variety of applications such as dating of mineralisation, 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 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 mineral and in the surrounding materials, till it saturates. If one selects a material with a negligible radioactivity in it (e.g. quartz), the accumulated TL mostly represents the environmental dose. Therefore, if one can evaluate the environmental dose rate at a place from where the geological specimen was collected, it is easy to calculate the age of the sample as :

TL Age = Dose to produce a TL, equivalent
to the natural TL in a sample.

Accumulation of TL can be affected by natural light, especially its ultraviolet component. 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. This bleaching is effective enough to reduce thermoluminescence level to a negligible value. These bleached sand particles, once embedded in a sand dune or a beach, get shielded from further exposure to sunlight. This helps particles to acquire more TL due to radiations exposure from their new environment within the sand dune or on the seashore.

2. Archaeology :

Thermoluminescence technique has been found to be highly successful in dating ancient pottery samples. This method is suitable because of the following reasons : i) it gives the exact date of kiln firings of the sample (the other methods mostly depend on the shape and style of pottery and hence correlate with the civilization to which it belonged), ii) TL dating is possible even beyond 30000 years, iii) authentication and detection of forgery can be quickly and easily done by using this method.

The dating is done by reading the TL-output from a pottery sherd. The TL from the specimen is mostly due to TL sensitive mineral inclusions (mostly quartz) in the host clay matrix of the pottery. The method of dating pottery is very much similar to that done in geological samples. In archaeology, a more precise and definite event is the basis - the kiln firing. The potter must have fired the pottery in the kiln sometime in the long past. That event is considered to be the starting of the 'TL Clock' for archaeological dating. Whatever TL has been stored earlier in the mineral - inclusion due to internal and external irradiations over the geological times (since crystallisation) is considered to be erased during the kiln firing.

After the onset of the 'TL Clock' (kiln firing) the pottery starts building up TL due to internal irradiation from radioactive emanation of uranium (U), thorium (Th) and Potassium (K) contents in the clay and external radiations from the radioactive contents of surrounding materials and the cosmic background at the excavation site. Typically the total irradiation rate is of the order of 1 rad per year of which the major part is from internal radiations and the remaining due to soil irradiation and cosmic rays. Once an accumulated TL in the specimen has been measured and expressed in terms of absorbed dose by proper calibration techniques and if the total irradiation rate for the specimen could be established, the archaeological age can be obtained by simply dividing the former by the latter,

$$\text{i.e.}\quad \text{Age} = \frac{\text{Accumulated dose}}{\text{Annual dose rate}}$$

But in practice many complicating factors come in the way of evaluating the age.

3. Biology and Biochemistry :

Application of TL techniques in the study of biological and biochemical systems is increasingly favoured in recent times and necessarily all the measurements are done in the LNT-RT range. The attempts have been successful in the study of hydroxy and amino-benzoic acids, nucleic acids, proteins, plant leaves, algae and bacteria. The TL results could indicate the poorer stability of the orthoform of the bezoic acids; 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.

4. Forensic Sciences :

The major study in forensic sciences is to evolve and standardise methods to compare evidentiary materials with similar materials of known origin which are invariably available only in minute quantities and are required to be analysed nondestructively for evidence purposes. Thermoluminescence can offer an attractive technique in selected materials that are commonly encountered in criminal cases viz : glass, soil, safe insulation materials, etc. This can be used as an exclusionary evidence i.e. when the TL characteristics do not match, it can be said with certainity that a particular sample has not come from a known source. To reduce the probability of any coincidental matching and improve the confidence on the TL measurements whose signal to noise ratio may be bad, 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 TL emission spectra.

5. Quality Control in Industry :

Even as early as 1938, the application of TL in the control of feldspars in ceramic products has been described. The amount of TL given out by a ceramic after artificial irradiation is directly indicative of its feldspar content 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 material, any uncontrollable variations in the feldspar contents can be checked quickly and efficiently.

The efficiency of certain surface catalyst like Al_2O_3, can be quickly and efficiently evaluated by their TL sensitivities. 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 emitted may be gainfully correlated with the catalytic activity. The TL glow curve in such cases could be used as a criterion in controlling the preparative parameter of a desired catalyst.

In principle, TL method could be employed in the quality control of many of the glass, ceramic and semiconductor products; recently it has even been shown in the case of textile fibres that the low temperature TL glow curve changes can be correlated with structure differences and / or chemical tracer impurities. However these have not yet received the attention of the industries.

6. Radiation Dosimetry :

Most of the developments in the understanding and applications of the TL owe their origin singularly to the efforts made in the use of this phemomenon in the field of Radiation Dosimetry and in the research for more sensitive dosimetric phosphors. The main basis in the Thermoluminescence Dosimetry (TLD) is that TL output is directly proportional to the radiation dose received by the phosphor and hence provides a means of estimating unknown irradiations. Also, TL can provide a perfect passive measurement i.e. integrated irradiation levels over extended periods of the order of even years. Thus it finds immense use in the monitoring of doses received by radiation workers on a routine basis : weekly/monthly/yearly depending upon whatever a situation may warrant. It should however be borne in mind that most of the TL phosphors are not tissue equivalent (in terms of energy absorption by irradiation) and hence the relevant dose which is medically significant to a radiation worker from protection point of view is not readily obtained. Some of the phosphors like LiF, $Li_2B_4O_7$, BeO etc which are nearly tissue equivalent score 4 definite points over others like $CaSO_4$, CaF_2, Mg_2SiO_4 etc which are however more sensitive.