CHAPTER - II

THERMOLUMINESCENCE AND ITS APPLICATION

A Luminescence Concept

Luminescence is a process which involves at least two steps:the excitation of the electronic system of the solid and the subsequent emission of photons. These steps may or may not be separated by intermediate process. Luminescence is phenomenon of emission of light from a substance caused by the release of stored energy through some type of prior incident radiation. Depending on the time interval between the excitation and emission, luminescence can be classified into two categories. If the delay is shorter than 10^{-8} seconds, the process is termed as fluorescence, otherwise it is known as phosphorescence. The radiation is usually in visible region of the electromagnetic spectrum; however since the same basic process may yield infrared and ultraviolet radiation. Such emission in excess of thermal radiation is also described as luminescence.

Luminescence is however, to be distinguished from thermal radiation. Since the phenomenon does not follow Kirchoff's Law for absorption and emission. The energy obsorbed by the material giving rise to the luminescence may be the ultraviolet light, X-rays, cathod-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.

Many kinds of luminescence emission were observed from lightning, aurora, fireflies, and certain sea bacteria long before there were written records. Awareness of their kinship, however, did not develope until about three thousand years after the reference to fireflies and glowworms in the Chinese Shih Ching (Book of Odes) in the period 1500 - 1000 B.C. Luminescence of solids was reportedly first observed in 1603 by the Bolognian Vincenzo Cascariolo. Since then emission of light from liquids and solids thus became a topic of interest, speculation and debate.

B Thermoluminescence

Thermoluminescence is the phenomenon of light emission upon heating a material which has been previously excited or in other words it is the thermally stimulated release of stored energy in the form of light from a pre-excited material. The phenomenon of thermoluminescence was observed for the first time by Robert Boyle in 1663. He found that the diamond worn by him emitted light due to body heat. 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) appears when a solid sample (usually an insulator or a semiconductor) is heated after being irradiated at low temperature, by some kind of radiation (X or gamma rays, particle beams,uv light etc.). Part of the energy absorbed by the sample in course of the radiation, may be released during the heating, in the form of light. The emission exhibited by substance without exposing it to ionizing radiation prior to heating is known as Natural Thermoluminescence (NTL).

The phenomenon of TL can be explained by the following simple Model:The irradiation excites electrons from the valence to the conduction band. Most of the excited electrons return to the valence band after a very short time (10^{-8}sec.) giving rise to luminescence which can be detected during the irradiation. Some of them, however, are trapped in local trapping levels within the forbidden band (these traps are usually associated with lattice defects such as vacancies, interstitials or impurities). Each trapped electron leaves a hole in the valence band which is soon trapped in a hole-trap (or recombines with a trapped electron). Since the valence band is full, a direct transition of a trapped electron to this band is improbable. However, a trapped electron (or hole) can be thermally raised to the conduction (valence) band, move in the crystal, and finally recombine with a trapped charge carrier of the opposite sign.

The site of a possible recombination is referred to as a recombination centre. If those recombinations are radiative, and take place during the heating of the sample (which is, of course, done after the irradiation is ceased), TL is observed.

When the phosphor is heated rapidly, the emission is seen as a flash of light. In the case of certain materials like fluorites, calcites etc. it is visible to naked eyes, but is usually detected by the photomultiplier tube in other materials and crystalline solids. The plot of TL-intensity versus temperature is known as glow curve. The TL-glow curve contains many glow peaks and each glow peak is associated with one type of defect in the crystals.

The trap is emptied as the phosphor is warmed above the temperature of excitation. The energy required to release charge carriers from the trap is called the activation energy (E). The "shallow" traps with low activation energy empty first and at each temperature 'T' those with life-time of a fraction of second or so are principally responsible for the observed thermoluminescence. If there is only one type of trap with only one value of activation energy, the TL is very weak at T = Ti (initial temperature) but then increases with T, reaches a maximum for the glow peak temperature T_m and then decreases to zero as the traps are all emptied. If the trap distribution consists of different groups of trap, then these groups are observed as TL - maxima in the TL - glow curve. The TL characteristics of any material is customarily labeled by a few parameters such as the order of kinetics obeyed by the TL process, the activation energy of trap depth and the frequency factor. There are many approaches practiced to determine these experimentally. Knowing the glow peak temerature T_m, it is possible to find out the activation energy. Urbach has given the approximate numerical relation

$$E\ (ev) = \frac{[T_m(^\circ k)]}{[500]}$$

deduced from the experiments on KCl:Tl and it gave the right order of magnitude of 'E' for a number of phosphors.

Initial Rise method is the simplest procedure to obtain an estimate of trap depth and is independent of the order of Kinetics involved. The method basically assumes the following:

i in the early rising range of temperature, i.e $T << T_m$, the rate of change of trapped carrier population is negligible and hence intensity strictly proportional to exp $(-E/KT)$,

ii the frequency factor essentially remains the same at all temperatures, and

iii there is no overlap of glow peaks belonging to different trapping levels. The material to be investigated can be heated repeatedly many number of times in such a way that each heating is terminated at a temperature where the TL intensity reached is hardly 1 % of the peak intensity. The ln I versus 1/T plots are made for each heating cycle. The slope of these lines is equated to E/K and E is evaluated. There are however theoretical and experimental considerations that limit the applicability of this method.

Another method used for the estimation of activation energy is Different Heating rate method. Using two different linear heating rates q_1 and q_2 and finding corresponding peak temperature T_{m1} and T_{m2}, one can calculate the trap depth as

$$E = \left[\frac{K . T_{m1} . T_{m2}}{T_{m1} - T_{m2}} \right] \ln \left[(q_1/q_2)(T_{m2}/T_{m1})^2 \right]$$

Another way is to use several different heating rates and plotting ln (T_m^2/q) versus $1/T_m$ which should yield a straight line with slope E/K. This method would yield E rather than E -W as was obtained by Initial Rise method. Thus, use of both these methods can lead to a good estimate of W, the non-radiative energy released in recombination of charge carriers. An alternative method for calculating the activation energy is the peak shape method. T_m, T_1 and T_2, which are respectively the peak temperature and temperatures on either side of T_m corresponding to half the peak intensities, are dependent upon the shape of the glow peak. Activation energy of a TL glow peak can be determined using high temperature half-width δ $(T_2 - T_m)$, low temperature half width $T(T_m-T_1)$ and full half width $\omega(T_2-T_1)$ of a glow peak. Chen, summed up the three methods by the following equation

$$E(ev)=Ca(KT_m^2/a)-ba(2KT_m)$$

'a' represents the various half-widths, Ca and ba are the constants and their values depend upon the geometrical factor μg (δ/ω). There are many other methods by which activation energy and frequency factor of a TL glow peak can be determined.

C **Models for Thermoluminescence**

Many phosphors exhibit an increase in electronic conductivity during the absorption of energy from radiation. When excited by optical or ultraviolet light the induced decrease in the electrical resistivity is termed photoconductivity, but a more general term, which includes similar effects induced by nuclear radiations in wide band gap insulators, is radiation-induced conductivity.

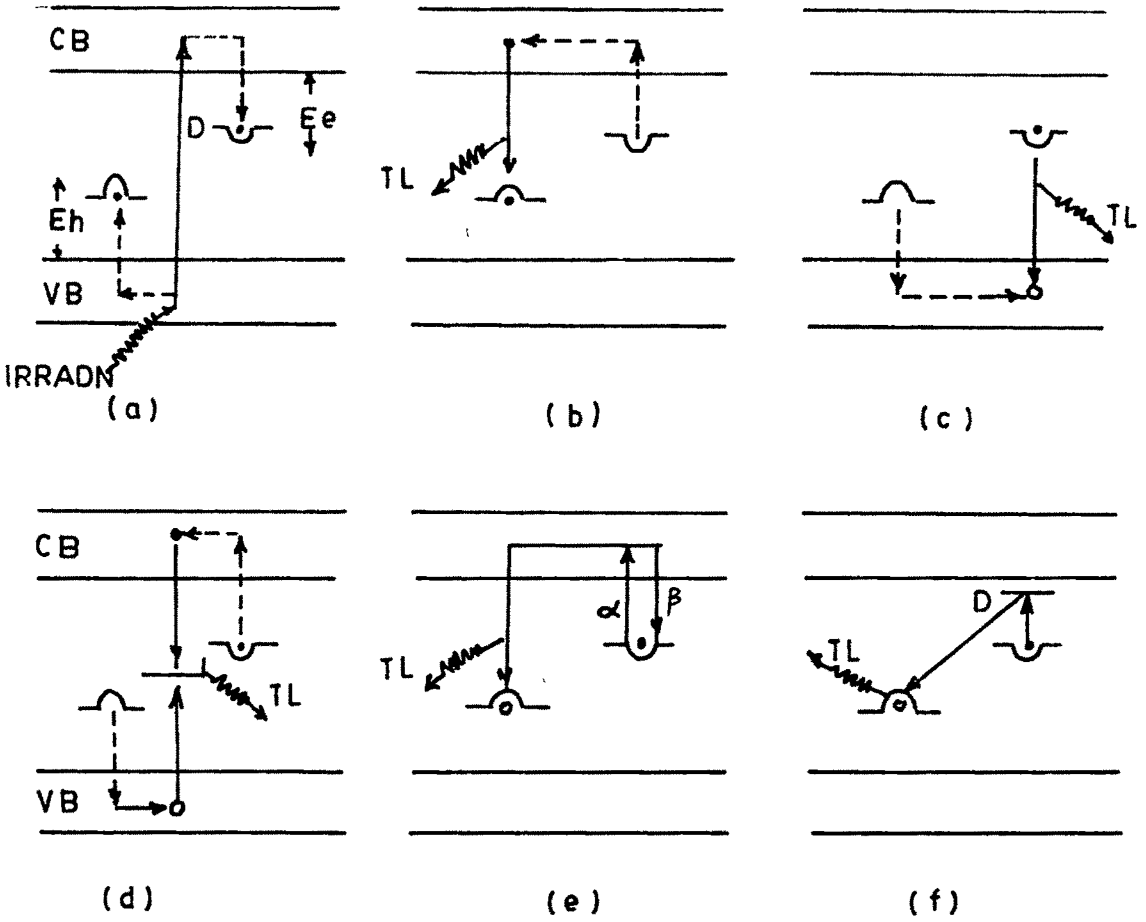
In sulphide phosphors (e.g., CdS, ZnS) it was discerned at the beginning of the present century that conductivity phenomena and luminescence were closely associated and it became evident that photoconductivity arose from the liberation of charge carriers during luminescence. These ideas were fundamental in establishing the energy band model as a means of interpreting luminescence phenomena in many phosphors because this model is especially useful in providing an understanding of processes which involve transport of an electronic charge through the lattice.

Practically all interpretations of luminescence phenomena are based on a band theory model or on a configurational coordinate model. The two models are mutually exclusive, but in no way incompatible, and in fact, complement each other in explaining luminescence phenomena. Both of them have inherent defect however. The configurational coordinate model ignores the charge transport through the lattice while the energy band model neglects the atomic rearrangement that occurs dúring luminescence.

1. The Band Theory Model :

The phenomenon of thermoluminescence can be best understood in terms of 'band model' 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



(a) (b) (c)

(d) (e) (f)

FIG II-1 BAND MODEL DIAGRAM FOR THE TL IN AN INSULATING CRYSTAL (a) - UPON IRRADIATION (b) - (f) ALTERNATIVE PROCESSES UPON HEATING 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 condction band. Normally, these electrons cannot remain excited indefinitely, that is, 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 visualized 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 ionization 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 radation. 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. Configurational Coordinate 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 configurational coordinate curves 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 transition. On these curves the energy of the ground and excited state is shown to vary parabolically as some configurational coordinate, usually the distance from the luminescent centre to its nearest neighbours. There is a value of the coordinate 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

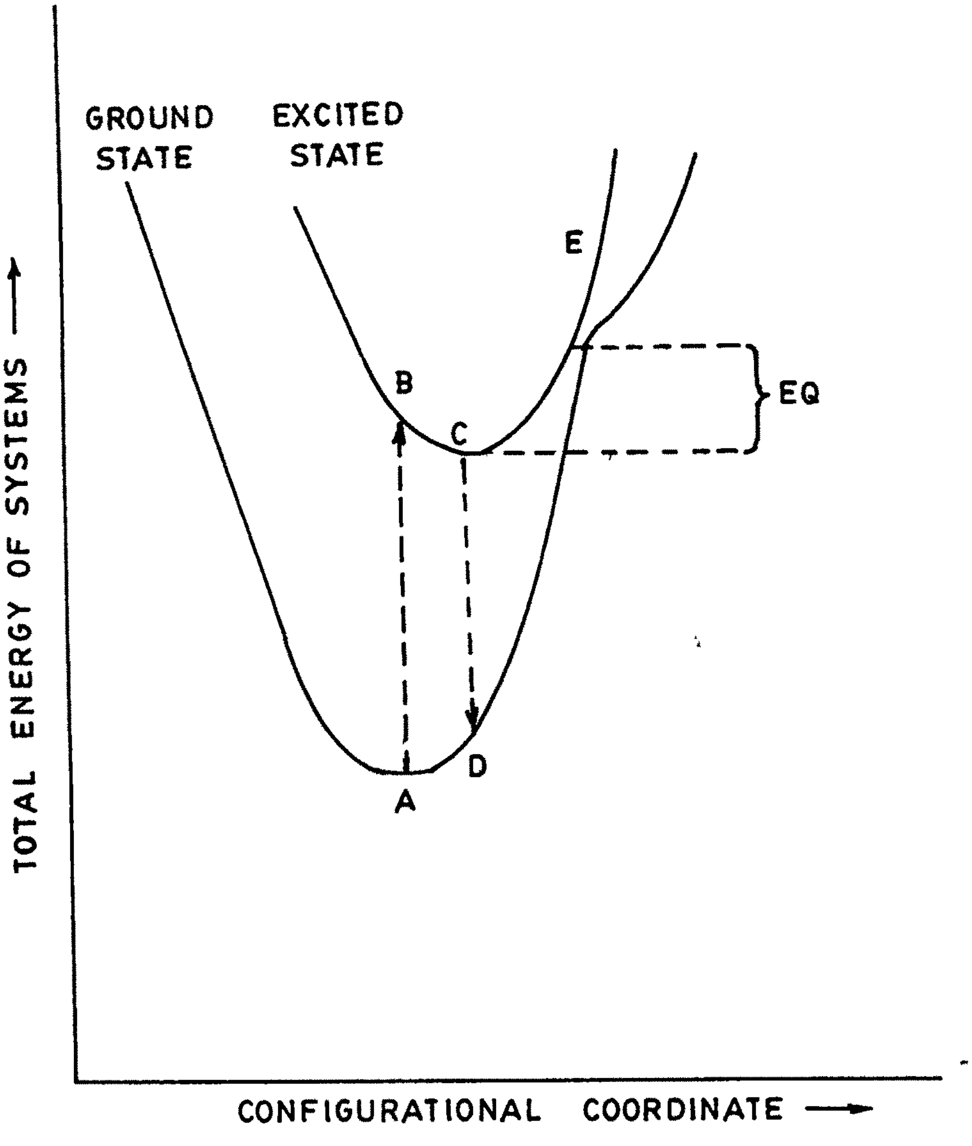


FIG. II-2 CONFIGURATIONAL COORDINATE CURVES FOR A SIMPLE LUMINESCENCE CENTER from A to B. This transition occurs so rapidly that the ions around the luminescent centre do not have time to rearrange. Once the system is at B it gives up heat energy to its surroundings by means of lattice vibrations and 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 configurational coordinate. 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 configurational coordinate 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 temperature 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 equation (a),

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

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. 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_0 be the trapping centre concentration and n_0 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

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

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,

$$T = T_0 + \beta t \text{ or } dT = \beta dt.$$

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,

$$I = n_0 S e^{-E/kT} \exp\left(- \int_0^T S/\beta \; e^{-E/kT} dT\right) \ldots\ldots\ldots\ldots\ldots (2)$$

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 corresponding 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,

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

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

$$I = n_0^2\ S\ \exp^{(-E/kT)} \times N_0 \left\{ 1 + n_0/N_0 \int_0^T S/\beta \quad \exp^{(-E/kT)} dT \right\}^{-2} \quad \ldots(4)$$

All the parameters in equation 4 have been defined above including N_0 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 (n_0/N_0) 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

1 Effect of Impurities

Impurities are responsible for many luminescent phenomena, an impurity which causes TL in a dead phosphor is called an activator. In the case of TL, the role of an activator may be more than just being an emission centre; its presence may create more traps responsible for TL. As far as TL is concerned the role played by an activator may cause increased trapping and/or 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

Changes in sensitivity (via defect creation and/or destruction) can be induced by thermal treatments. The thermoluminescence properties exhibited by a phosphor very much depend upon the kind of thermal annealing experienced by it prior to the irradiation or excitation. The annealing treatments are inducing defect clustering reactions which are in term increasing or decreasing the sensitivities of the individual peaks. Annealing is the process which reducess 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 is to 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 becomes 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 sensitization i.e. increase in thermoluminescence sensitivity.

II Damage of TL at increased doses of irradation 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 change in the TL - emission have also been observed with increasing dose.

4 Effect of LET of Irradiation

Linear energy transfer (LET) is defined as dE/dl where "dE" is the energy loss by charged particle travelling a distance "dl" due to collisions. The ionization capacity of a radiation in a medium is usually signified by the linear energy transferred 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, Crystallization and Particle Size

These effects have been pursued in detail in the case of TL exhibited by geological samples: factors, such as stress, crystallization, decomposition and particle size are almost inseparable in these cases and hence are considered together.

(i) Effect of Stress:

The application of stress can arise out of operations such as crushing, grinding, packing, pellettizing etc. The different deformation processes which may arise out of such operations can be micro-cracking, formation and annihilation of crystal dislocations, integranular gliding, rupturing, pressure twining and so on. These can ultimately affect the TL exhibited by the specimen in many ways.

During pressure application there are dislocation loops and vacancies which can excite valence electrons or de-excite any trapped electron during their translation in plastic flow. The excited valence elctrons if get trapped, give rise to TL which can be observed as a direct consequence of applied stress. If de-excitation of trapped electrons occurs, then obviously there will be a decrease in the observed TL as compared to the same irradiated sample prior to stress application. Such effects are not readily seen in the artificial phosphors usually employed in TL studies; but are clearly observed to affect the natural TL arising out of internal and external irradiation from different sources over geological times, exhibited by mineral samples.

(ii) Crystallization and Decomposition Effects:

Some of the physico-chemical processes like crystallization and decomposition may result in storage of energy in the material which may in turn appear as TL when heated. Also the crystallization temperature as well as other physico-chemical conditions decide essentially the type and quantity of lattice defects present in the crystal and thus in turn decide the sensitivity of the material. Thus, it can be easily understood why a laboratory made TL phosphor exhibits TL even before any irradiation and also why the same phosphor prepared under even slightly differing conditions exhibit widely different sensitivities.

(iii) Effect of Particle Size:

This assumes importance when TL of powder samples are studied. The size of the particle influences tremendously the excitation of a phosphor as well as emission output by scattering and self-absorption characteristics. This effect has perhaps been well investigated only for LiF phosphor. Theoretically at least, the particle size effect should be the same in all materials and extremely energy dependent in the 20-30 KeV range for smaller size particle. This is born out of energy balance considerations between total electron energy leaving a grain and that entering it, including that generated within, during irradiation.

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 in temperature. This is so becuase of a competition between radiative transitions which are almost temperature independent and non-radiative transitions - de-excitation of material by thermal agitation-which increases with temperature. In the case of a 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 thermal quenching.

A direct measurement of thermal quenching of TL is somewhat possible by employing two extremely different heating rates for the same irradiation of the phosphor and measuring the total light emitted in each case. At high heating rates luminescence peak appears at higher temperatures and hence should be affected by thermal quenching if present.

8 Electro-Static Effect:

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 TL 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 realized 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:

Generally, the thermoluminescence response of dosimeter materials to UV rays is of two distinct types, namely, the glow which can be stimulated by illuminating 'virgin' dosimeters with ultraviolet light, and that which can only be stimulated after firstly irradiating the specimen with ionizing radiation (alpha, beta, etc.). Since the ultraviolet wavelengths usually employed are not energetic enough to cause band-to-band ionization, the mechanism responsible for the TL production following illumination of a virgin sample may be due to the creation of excitons and their subsequent decay to electrons and holes. On the other hand, the TL which can only be induced by ultraviolet light if the sample has been previously irradiated is probably due to the phototransfer of charge from deep traps.

F Application of Thermoluminescence:

The increased use of TL became evident in the late 1940's and early 1950's, since then with the development of better instrumentation and basic understanding of the phenomenon, applications of TL got extended to a whole spectrum of disciplines such as archaeology, biology, biochemistry, forensic sciences, geology, radiation dosimetry, radiation physics, solid state physics, space science, spectroscopic analysis, etc. Some of the important applications of TL are described below:

(i) Radiation Dosimetry:

Following the pioneering work of Daniels and Colleagues in 1950's, the application of TL to radiation dosimetry has seen an immense escalation of effort and a vast literature now exists on this topic. Most research has been devoted to the discovery and development of materials suitable for thermoluminescence dosimeters.

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. Recently, TLDs have been proved to have manifold advantages over other dosimeters. TLDs measure the integrated radiation dose for a period at a particular site. Therefore, they can be used as 'watchdogs' around nuclear installations.

Even very low levels of radiations, like the natural radiation background, can be measured by exposing the TLD for long periods, a week or a month or even a year and evaluating the total dose received over the particular period.

TLDs are also widely used for radiation dose estimation in medical fields like in diagnostic radiology, radiation therapy and nuclear medicine, some of the striking applications are in interstitial intracavitary radiation therapy and in the therapy of thyrotoxicosis.

(ii) Geological Applications:

Survey of literature shows that the occurrence of natural thermoluminescence from rocks has been known since long and several early observations have already been reported. The relationship between the natural raidoactivity and the natural thermoluminescence (NTL) led directly to the use of TL as a means of arriving at the geological age of the specimen, the principle is that the TL is a measure of the abserved radiation dose since the specimen was last heated, which, in the case of a rock, is its time of formation.

However, age determination is not the only way that TL is utilized in geology. In some instances TL is more sensitive for detecting traces of radioactivity than conventional means e.g. a Geiger counter or scintillation counter. Thus the technique has found widespread application in radioactive mineral prospecting. Some minerals are found to exhibit a particular glow-curve shape when extracted from one area, but the same mineral gives an entirely different glow curve if extracted from another. Thus TL has also found use in source identification. TL is also found to be useful in the study of meteorites and lunar material.

(iii) Archaeology:

Like geological dating, TL technique also provides an objective scientific method for determining the age of potteries. TL dating of articles of antiquity can successfully be used in crime work to differentiate authentic samples, from spurious ones. The mineral constituents like quartz, feldspar etc. of potteries have the capacity for accumulating TL energy. Potteries are prepared by firing the clay in temperature range over 700°C. Therefore, all previous effects of irradiation are driven off when the pottery is manufactured. These potteries receive irraidation from the radioactive impurities in the clay fabric itself (U.Th.K) and in the surrounding burial media. Cosmic radiation also makes a very small contribution. However, the total dose experienced over long periods of archaeological burial will be quite appreciable.

The accumulated dose, the NTL energy carried by the sample and the annual dose rate of the TL energy received by the potteries from radioactive impurities determine the age of the pottery.

The formula is as follows:

$$\text{Age} = \frac{[\text{Accumulated dose}]}{[\text{Annual dose rate}]}$$

(iv) Forensic Science:

In the present context, Forensic Science means the science used in courts of law or the science applied for the detection and prosecution of crime. A major task in forensic science laboratories is to identify an evidentiary material with a similar material of known origin. Some of the commonly encountered contact traces in criminal cases are glass pieces, soils, fibre, etc. But, quite often, the material available as evidence is very small in quantity. Evidently, thermoluminescence can offer an effective tool in such comparisons and "source-identifications". TL can be used as an exclusory evidence, when TL patterns do not match, it can be said with reasonable confidence that a particular source is not connected with the evidentiary material.

(v) Defects in Solids:

In principle, experiments on TL can be expected to yield useful information on the properties of the various types of defect present within an insulator or semiconductor. It has been known that TL is particularly sensitive to traces of impurities within the specimen. In most instances the exact role of the impurities is unknown but in most materials their presence is considered essential for TL to occur. There have been countless studies of the effect of impurities on the TL properties of various materials. In general terms, it is believed that the impurities give rise to the localized energy levels within the forbidden energy gap and these are crucial to the TL process. As a means of detecting the presence of these defect levels, the sensitivity of TL is unrivalled.

(vi) Other Applications:

Applications of TL would also include the use of suitable phosphors for image storage device, a test for fire damage in building materials, a quality control tool for ceramics and in biology the technique is finding increasing usage.