CHAPTER I
INTRODUCTION

1.1 HISTORICAL

Thermoluminescence refers to the process of luminescence emission from certain substances on thermal stimulation. The luminescence emission is as a result of the release of energy stored in the material when it is excited by one of usual agents like Ultraviolet rays, X-rays, electrons, electric fields etc. Thermoluminescence forms a part of the study of luminescence which is an important branch of physics and has widened our knowledge regarding the structure of solids and the effects produced by various irradiations. Luminescence, a general term, includes light emission as fluorescence or phosphorescence. Depending upon the excitation method, luminescence is classified as photoluminescence, X-ray luminescence, chemiluminescence, cathodoluminescence, electroluminescence, bioluminescence and so on.

According to Leverenz (1968 a), the first observations on thermoluminescence are stated to have been made by Robert Boyle in 1663. Only in 1903, Wiedeman (1903) recognized it as a new phenomenon and introduced the name "thermoluminescence" while pursuing his work on fluorites. Detailed investigations on
various minerals and glasses followed. The efforts of Daniels et al (1953) and Cameron and others (1961) gave a big momentum to the branch by bringing forward radiation dosimetric applications of TL. In the early stages of development, very significant contributions came from Attix (1962) and Schulman (1963). So far, a large number of investigations have been taken up to explain the phenomenon, to improve upon a variety of thermoluminescent phosphors and innumerable applications, right from radiation dosimetry to thermoluminescence dating of potteries and minerals. The immense value of the phenomenon can be gauged from the fact that three bibliographies have been brought out (Angino 1965, Lin & Cameron 1967 and Spurny 1969, 73). There have been six international conferences concerning the subject and two specialist conferences on TL dating.

1.2 SCENE AND OBJECT OF THE PRESENT WORK

A number of TL phosphors such as Al₂O₃ (Mehta and Sengupta 1976), BaO (Tochilin et al 1969; Busuoli et al 1977); CaF₂ (Nambi 1968 and Schulman 1960); CaSO₄ (Lakshmanan 1978 a and Schmidt 1974); LiF (Cameron 1964 and Suntharalingam et al 1969); Li₂B₄O₇ (Schulman et al 1967) and Mg₂SiO₄ (Hashizume et al 1970) have been successfully employed in radiation dosimetry.
The basic TL phenomenon, TL models have been proposed only for LiF (Click et al 1967 and Zimmermann et al 1967), CaF$_2$ (Herz & Pershan 1967), for certain alkali halides (Mehendra & Radhakrishna 1968) and CaSO$_4$ (Nambi et al 1974). These models are still in the process of evolution and are being polished on the basis of more recent experimental facts.

CaSO$_4$ and BaSO$_4$ phosphors (particularly rare earth doped) are of recent origin in the field of radiation dosimetry. CaSO$_4$ phosphors have high intrinsic sensitivity as compared to other phosphors e.g. LiF, CaF$_2$, Li$_2$B$_4$O$_7$ etc., and have found wide applications in personnel dosimetry (Vohra et al 1980). Barium sulphate phosphor, because of its high effective number ($\bar{Z} = 45.8$) has been usefully employed in dosimetry of low energy electromagnetic radiation. Medlin (1961) studied anhydrite minerals for the TL phenomenon in CaSO$_4$ phosphors. Yamashita (1968) has dealt with selection of a sensitive TL dosimeter. To some extent, the nature of the TL process has been examined by Nambi et al (1974). Still the TL process remains to be completely understood.

Dixon et al (1974 a) and Luthra et al (1974) have investigated the TL phenomena in alkali earth sulphates. However, the effect of UV irradiation on
glow curve structure, application in the field of dosimetry of non-ionizing radiation etc., have not yet been properly explored.

The main object of the present work is to investigate various aspects of the thermoluminescence phenomenon in CaSO₄, BaSO₄ and KF₂ phosphors doped with certain rare earth elements and understand the processes involved. The scope of the study includes preparation of the phosphors with individual dopants, study of effect of the dopant on the TL glow curves produced by UV and Y irradiations, analysis of glow curve parameters, TL emission spectral characteristics, effects of dose rate and temperature during irradiation; and explore further the application of these phosphors for the dosimetry of ionizing and non-ionizing radiations viz: UV rays and microwave radiation.

1.3. REVIEW OF EARLIER WORK

1.3.1. TL mechanism, glow curve and its parameters.

Various models, proposed to explain the mechanism of TL emission, have been reviewed by Braunlich (1966). It is however, generally accepted that TL results from thermal stimulation of electrons (or holes) which are detrapped from their respective sites and their recombination with holes (or electrons) at the recombination centre.
Fig. 1.1 shows a simple model proposed by Schulman (1967) for doped alkali halides. In the process of excitation (Fig. 1.1 A), absorption of electromagnetic radiation ejects an electron from the valence band into higher lying empty band. This leaves a hole in the valence band. Both charge carriers (electrons and holes) freely migrate through the crystal in the conduction and valence band respectively. Just after their production, a fraction of these free charge carriers recombines either through a radiative process with photon emission or through a dissipative process emitting phonons and the remaining fraction gets trapped in metastable energy states in the forbidden band called electron and hole traps.

On thermal stimulation, after absorbing an amount of energy equal to the difference in energy (E) between the trapped and free states, electrons are released from traps and get either retrapped or recombine with hole at impurity centre (or later modified as combination centre), thereby resulting in the light emission. However, according to Braunlich’s (1968) model for wide band gap materials, it is not necessary for electrons to go to the conduction band or thermal release from the traps.

A plot of the luminescence intensity against time or temperature of the phosphor is called a glow
FIG. 1.1. SCHEMATIC DIAGRAM OF THERMOLUMINESCENCE PROCESS IN ALKALI HALIDES (SCHULMAN 1967)
As the phosphor is heated, the TL intensity rises initially and passes through a maximum. Depending upon the variety of trapping levels involved, the glow curve exhibits a number of peaks, each peak representing a particular parameter. The glow curve can be considered as a rough image of the trap distribution. Intensity of the glow peak is, in a way, related to the number of electrons (and holes) released and to the number of specific recombination centers. Therefore, the area under the glow peak can yield good amount of information about the number of trapping sites of a phosphor.

Measurement of TL emission spectra (wavelength distribution of the emitted light) provides information regarding the energy level transitions of the luminescence centres which are responsible for the light emitted.

TL intensity, ab initio, can be calculated by presuming that the trapped electrons have a Maxwellian distribution of thermal energies and the probability 'p' for the thermal release of trapped electron from the trap per unit time is

$$ p = s e^{-E/kT} $$

... (1.1)

and TL intensity will be given by

$$ I_t \propto n_t \cdot p $$

... (1.2)
where

\[ s = \text{Frequency factor, a constant for the trap.} \]
\[ E = \text{activation energy of the trap depth.} \]
\[ T = \text{absolute temperature (°K)} \]
\[ k = \text{Boltzmann's constant.} \]
\[ I_t = \text{TL intensity at time 't'} \]
\[ n_t = \text{Number of filled traps at time 't'} \]

and if \( \beta \) is the heating rate

\[
\frac{\Delta n_t}{\Delta t} = \beta \quad \ldots(1.3)
\]

According to thermodynamic considerations, the factor \( s \) is connected to the capture cross section \( (S_T) \) of the trap by

\[ s = V_c \cdot N_c \cdot S_T \quad \ldots(1.4) \]

where

\[ V_c = \text{thermal velocity of electrons in the conduction band} \]
\[ N_c = \text{density of the available trap levels.} \]

Equation 1.4 expresses the physical concept of a trap as a potential well, in which case \( s \) can be expressed in terms of the product of the frequency with which the electron strikes the sides of the well and the reflection coefficient. Thus 's' is usually termed as the 'attempt-to-escape frequency factor'.

From Eqn. 1.1., the number of traps emptied
per second is

$$\frac{dn}{dt} = -n_t p = -n_t s \exp \left(-\frac{E}{kT}\right) \quad \ldots(1.5)$$

and since

$$I_t \propto n_t \cdot p$$

$$\frac{dn}{dt} = -s n_t \exp \left(-\frac{E}{kT}\right) \quad \ldots(1.6)$$

After integration of Eqn : 1.6 we have

$$\log_e \frac{n_t}{n_0} = -\int_0^T \frac{s}{\beta} \exp \left(-\frac{E}{kT}\right) dT \quad \ldots(1.7)$$

and in turn

$$I_t = -n_0 \exp \left(-\frac{E}{kT}\right) \exp \left[-\int_0^T \frac{s}{\beta} \exp \left(-\frac{E}{kT}\right) dT\right] \quad \ldots(1.8)$$

This is the mathematical formula for the glow curve of a TL phosphor containing single type of traps. It was derived by Randall and Wilkins (1945). According to Eqn: 1.8, the glow curve can be calculated point to point, but for a precise solution, the integral part has to solved numerically.

Keating (1961) extended the work of Randall and Wilkins (1945) to include temperature dependent trapping cross-sections.
Similar rate equations for the thermoluminescence process have been formulated and solved under certain approximations (Shenker and Chen 1972, Arai et al 1975, Maxia et al 1971 and Nakajima 1977). Shape of the glow peak is determined from the solution of these equations by fixing the parameters like retrapping, initial occupancy of the trap, total number of traps present etc. A complete analysis of theoretical derivation of these models, starting from ab-initio has been given by Land (1969).

However, insignificant consideration has been shown to

(i) creation or annihilation of trapping and luminescence centers, either due to radiation damage or by thermally induced changes;

(ii) self-absorption of the emitted light

(iii) thermal quenching;

(iv) tunneling or resonance transfer of energy to the emission centre which is independent of the trapping centres.

According to these models, the TL intensity passes through a maximum after rising initially according to the exponential factor $e^{-E/kT}$. The intensity decreases as the number of filled traps decrease substantially. The glow curve exhibits many peaks, each peak corresponding
to a trap with its characteristic activation energy.

1.3.2. Thermoluminescence characteristics - physical factors.

Electron traps are metastable states or levels in which electrons can be captured and they remain for significant times between absorption of exciting radiation and emission of luminescence. The thermal activation energy ($E$) required to liberate a trapped charge carrier is known as the trap depth.

Optical activation energy in an ionic crystal, as a general rule, is greater than the thermal activation energy. The thermal activation $E$ occurs with the removal of the ionic polarisation due to the trapped electron, but in optical activation the polarisation does not have time to disappear and the energy ($\hbar\nu - E$) is not recovered until later (Curie 1963).

Luminescence centres are the levels which determine the luminescence spectra. Each centre includes some point defect of the crystal. Each trap has its characteristic frequency factor $S$.

(a) Role of impurities

Electron traps are formed by several types of crystal imperfections that have the ability to hold electrons at an excited energy level. Even though
physical processes are not completely known, various
types of electron traps are possible e.g.,

(i) vacancies and imperfections in the crys-
tal lattice produced at the time of the
crystal growth or created at later stage
by means of mechanical pressure, thermal
treatment or by bombardment with energetic
particles.

(ii) distortions produced by impurity ions of
larger or smaller size than those comprising
the crystal lattice.

(iii) various ion radicals produced by irradia-
tion either due to host lattice or impuri-
ties present.

Thus traps could be associated with either the
impurity or the host lattice centers. A comparison of
the TL glow curves of the undoped samples with those of
the doped (with a specific impurity) can help, sometimes,
to identify any glow peak or peaks with a particular im-
purity.

The dosimetric peak (200°C) of TL phosphor
LiF has been correlated with the Li⁺ impurity (Christy

Mers and Pershan (1967) and Sunta (1971) have
shown that, for CsF₂ phosphors, all the glow peaks
occurring in the temperature range 77°K to 700°K are due to host lattice centers. However, the peak at 780°K has been postulated to be associated with Ce³⁺ impurity.

According to Bonfiglioli et al (1959), 495°K and 589°K TL peaks in NaCl are due to host lattice defects only whereas Mahendru et al have correlated 355°K peak with Ce²⁺ and Cd²⁺ (Mahendru and Radhakrishna 1969).

In presence of other impurities, a dopant can act as a 'codopant' also by a useful transfer from one ion to another resulting in higher TL outputs. TLD-100, a well established TL phosphor is LiF codoped with Mg and Ti. Singly doped LiF:Mg and LiF:Ti have very poor emission but LiF:Mg, Ti has been found highly efficient. Another good example is CaSO₄:RE phosphors codoped with Mn or Ce (Bapat 1977). It has been possible to get an improved output with normally inefficient RE dopants by providing efficient emission centers.

(b) Effect of dopant concentration.

As the concentration of an activator is increased beyond a certain extent, it can act as its own poison. It is known as concentration quenching and is related to the resonant transfer of energy from one activator atom to the other, which now has an increased chance of getting dissipated without luminescence at quenching sites such as jogs at dislocations, vacancies.
Even pairs or higher aggregates can act as poisons. Johnson and Williams (1950) have shown theoretically that the luminescence efficiency can be given by

\[ E = \frac{C (s - C)^2}{C + \gamma (1 - C)} \]  \hspace{1cm} (1.31)

where
- \( C \) = mol. conc. of activator
- \( \gamma \) = a constant involving the capture cross sections of luminescent centers and host ions.
- \( z \) = a constant defined in general as the number of lattice positions (quenching) surrounding a given activator ion.

Kedlin (1968) fitted these equations to the concentration quenching of Na\(^{2+}\) and Sb\(^{3+}\) ions in enhydrites.

A different expression for the concentration quenching has been arrived at by Ewles and Lee (1953), making use of the experimental facts that lattice defects can act as luminescent centers and taking into account the competition of these centers in the luminescent process.

Efficiency \( E = \frac{K}{1 + \alpha C^{-1} \exp(\beta C)} \)

where
- \( K \) is a normalizing constant
- \( C \) is the concentration of the activator ions.
n is the number of lattice ions associated with radiative centres; determined experimentally as equal to the reciprocal of the optimum activator conc.;

$\lambda$ constant involving the absorption coefficients of activator and structure centres.

However the concentration quenching of rare earth ions is very specific and has been dealt with by Blaese (1970).

(c) Effect of heating treatment.

At any temperature, a certain concentration of vacancies exists. From thermodynamic considerations it can be shown that the free energy of a lattice with ionic vacancies is less than that of a perfect lattice. As the temperature of the lattice is increased, the number of vacancies also increases. If the material is cooled at a slow rate from high temperature, tendency to achieve a relatively perfect structure exists. However, if the material is suddenly quenched, the vacancies existing corresponding to the higher temperature get frozen in. If the material, besides the vacancies, contains certain impurities, the impurities and the associated defects also get dispersed. At high temperatures, the impurities get more or less uniformly distributed throughout the host lattice affecting the TL response of the material in a
significant manner. These impurities, by providing certain specific defects, can change the trapping parameters or change the TL emission characteristics.

(d) Effect of X, gamma and particulate irradiation.

When X and gamma rays pass through a medium they lose energy in the medium by means of photoelectric effect, Compton interaction and pair-production. The energy of the incident photons and the effective atomic number defined by

\[ \bar{Z} = \left( \frac{\sum Z_i \sigma_i \alpha_i}{\sum \alpha_i} \right)^{1/2} \]

where \( \bar{Z} \) is the fractional content of the elements of atomic number \( Z_i \). \( \bar{Z} \) of the medium determines the type of the interactions that dominate. In general, it can be stated that the passage of electromagnetic radiation through the phosphors produces secondary electrons, which are responsible for the ensuing effects - ionization and displacement. Displacement of atoms is mostly produced when charged particle irradiations (\( \alpha \)-rays, deuterons) etc. take place. These displaced atoms can further cause ionizations along the path. Ionization and displacement effects, in turn, can give rise to vacancies, dislocations etc. These lattice defects serve as useful traps and recombination centers.

(e) Supralinearity and sensitization.

On irradiation with \( \beta \) or \( \gamma \) rays (low LET radiations) TL phosphors typically exhibit a linear response
at low dose levels, and a supralinear response at higher doses. This phenomenon has been studied in TLD-100 (Suntharalingam 1969), CaSO₄: Dy (Lakshmanan 1978 a and Schmidt 1974) Al₂O₃:Si,Ti (Mehta 1976), CaF₂ (Da Cruz 1974) and Mg₄SiO₄:Tb (Yamazaki 1978). The supralinear component appears at exposure levels from 1 to 500 R, depending on the host matrix, its doping, annealing and previous radiation history. A saturation in response is often observed at exposures in the neighbourhood of 10⁵ - 10⁶ R. The only phosphor exhibiting a linear response over the range 20 mR - 10⁴ R is MgF₂:In (Paun et al 1976).

Most TL phosphors, after high level radiation exposures and partial annealing, exhibit enhanced TL sensitivity. This is called radiation induced sensitization. Sensitization can be gamma ray induced (Lakshmanan 1978 a) or it might be UV induced (Shastry and Shinde 1979). If S₀ is the radiation sensitivity of the virgin phosphor and S, that of the sensitized phosphor, S/S₀ is called the sensitization factor. Depending upon the initial radiation exposure level and the nature of the test exposure for determining S and S₀, the sensitization factors vary to a great extent.

It might appear that all the phosphors exhibiting supralinearity will also show radiation induced sensitization but it is not so. Li₂B₄O₇:In exhibits supralinearity
but not sensitization (Burgkhardt et al. 1977). In case of natural fluorite (CaF₂), the 200°C peak is linear but it exhibits radiation induced sensitization. Hence it is obvious that sensitization and supralinearity need not always follow each other.

The earliest attempts to explain these phenomena were based on creation of traps (Cameron et al. 1965) and luminescent centres (Cameron et al. 1966) but as the glow curve shape and TL emission spectra of the sensitized and virgin samples of TLD-100 phosphor were observed to be the same, these models had to be rejected (Pearson and Cameron 1966).

The competing trap model was proposed by Suntharalingam and Cameron (1969). It assumes the presence of a competing trap which has a larger cross section for the capture of charge carriers as compared to the normal dosimetric traps. The total number of deep traps was presumed to be much smaller than the normal dosimetric TL traps. The TL response was formulated as

\[ I(D) \propto N_\circ \left( \frac{1}{1 - \exp(qD)} - N_{cc} \frac{1}{1 - \exp(-\mu D)} \right) \]

where \( N_\circ \) and \( N_{cc} \) are the maxima numbers of total and competing traps, \( q \) is the probability of creating an electron which is bound in any trap, and \( \mu \) is the probability of filling a competing trap. It is presumed here that,
the number of filled dosimetry traps has little effect on the rate of filling the competing traps. However, this assumption is not true when the number of dosimetry traps is not much larger than that of the competing traps. Moreover these competing deeper traps have never been observed directly and the fact that the high temperature TL glow peaks (in TLD-10C) are supralinear (Sunta et al 1972) does not agree with the competing deep trap model for sensitization.

Track interaction model proposed by Claffy et al (1968) has been established mathematically by Attix (1975). The model assumes that for low doses, the secondary electron tracks are separated far enough so that released charge carriers have access to luminescence centres in the same track only, thus TL response is linear with respect to dose. At high doses, the average separation of adjacent electron tracks is comparable to the average separation of luminescence centers along each track. Many luminescence centers are then located within the migrating range of the released charge carriers, thereby increasing the TL efficiency and the resultant TL output in high dose region. Based on the interaction model Dobson and Midkiff (1970) formulated that

\[ I(D) = I_o \left[ 1 - \exp \left( - \frac{\lambda}{D_0} \right) \right] (1 - \gamma \xi) \]  \hspace{1cm} (1.34)
where $I_o$ is the light output at saturation and $D_o$ is the dose value at which a second track is close enough to the trapped charge carrier to compete on equal terms with the original track, the constant $\lambda$ is related to the probability that a new charge carrier is trapped and $\gamma$ is the average probability that a trapped charge carrier does not interact with a luminescent center. The effective number of "nearby" tracks is expressed by $q$

$$q = 1 + \frac{D}{D_0}$$  ...(1.35)

But lower degree of sensitization for post-annealing temperatures lower than 300°C, cannot be explained on this basis (Lakshmanan et al 1979 a). However, based on this model, the numerical agreement in case of TL0-100 and Mg$_2$SiO$_4$ with the experimental results, is good (Yamasaki et al 1978).

There are several other models, TCLC model [Jain et al (1974)], two step mechanism proposed by Mayhugh et al (1970) and Mink and Kos (1976); and detrapping model of Nakajima (1969). However, no single model is able to explain the observations on glow curve shapes, emission spectra, supralinearity threshold, LET dependence, degree of sensitization and the dependence on the activator concentration, simultaneously.

(f) Effects of UV irradiation.
UV photons have energy in the eV region. Band gap of most of the materials studied for thermoluminescence phenomenon lie in the energy region 6 - 12 eV. The UV photon does not have energy sufficient to raise an electron directly from valence band to conduction band. Still low energy UV photons (eV region) are capable of inducing TL in various materials such as Al₂O₃ (Si,Ti) (Mehta 1977), CaF₂:Dy (Bassi et al 1975), SrF₂:Tb (Kirsh and Kristianpoller 1977), MgO (Takeuchi et al 1976), CaF₂:Sm (Becker et al 1973), CaF₂:Th (Batsanov et al 1971), CaSO₄ (Nambi et al 1971), Mg₂SiO₄ (Lakshmanan 1978 b). There are two schools of thought about the processes responsible for the induction of thermoluminescence by UV. One says that it is the multiphoton event giving rise to TL (Bradford et al 1975, Schmid et al 1975). The other school presumes that major role in the process is played by excitons. Excitons transport energy by thermal diffusion. The second theory is supported by the observations on defect formation in alkali halides by low energy irradiations (Townsend 1976). Threshold for the defect formation is observed to be a photon in the exciton absorption band (Konitzer and Hersh 1966, and Townsend and Elliott 1969).

Gamma exposed TL phosphors, on UV irradiation, show a reduction in the TL output. Since UV photons have
sufficient energy to release charge carriers from traps to the conduction band, it seems to empty certain proportion of traps, bringing down the TL output.

If irradiated TL phosphors, heated up to 300°C, are shown to UV or even visible photons, the glow peaks up to 300°C get regenerated. This is referred to as photo-transferred thermoluminescence (PTTL), since charge carriers from high temperature peaks (unerascd during first read out) are transferred to lower temperature peaks. PTTL has been observed in almost all the phosphors.

(g) Electron Spin Resonance studies (ESR).

Paramagnetic defects can be identified by means of ESR. A single crystal or a powder is placed in a magnetic field. The magnetic field causes the unpaired electrons to precess as they spin and the precession rate is dependent on the strength of the field (0-10,000G). An oscillating electric field (∝ 10,000Hz) is applied at right angles to the direct magnetic field. When the precession frequency of the electron matches the microwave field frequency, energy will be absorbed and the electrons will flip their spins. At any temperature, the amount of energy absorbed is directly proportional to the number of unpaired spins or the number of electrons trapped in a specific paramagnetic defect. Electron spin resonance measures static rather than dynamic conditions in the
crystal and the observations are independent of the optical qualities of the crystal.

Delbecq et al (1966) studied TL-ESR correlation in KCl(Tl) for irradiations at 77°K. It was concluded that 208°K and 300°K peaks are due to Cl\textsuperscript{−} and Tl\textsuperscript{0} respectively. On warming up of the material beyond 77°K, Cl\textsuperscript{−}, molecular ion diffuses and recombines with Tl\textsuperscript{0} giving the characteristic Tl\textsuperscript{+} emission.

Iason et al (1968) identified the 150°K Tl peak of CaWO\textsubscript{4} with electrons trapped at tungstate complexes and the 290°K with Nb\textsuperscript{4+} substitutional impurity sitting at tungsten site.

Mera and Pershan (1967) have correlated TL and optical absorption of CaF\textsubscript{2}:RE crystals with ESR data and showed that valence reduction takes place during irradiation and valence reoxidation during TL read out. Hole centers of F\textsuperscript{−} type are stated to take part in thermoluminescence.

Luthra and Gupta (1974) attributed the impurity independent ESR signals in BaSO\textsubscript{4} to various radicals like SO\textsuperscript{4−}, SO\textsuperscript{2−}, SO\textsuperscript{−}, SO\textsuperscript{2} and O\textsuperscript{−}. Thermal annealing behavior of ESR signals and glow peaks showed that the temperatures at which anion radicals are annihilated correspond to the temperatures of the prominent glow peaks.
In case of CaSO₄:RE, from the room temperature decay curves of ESR and TL intensities, Nambi et al (1974) reported that the nature of the traps involved in TL is the same as indicated in the ESR spectra. Different traps are provided by the basic nature of the host material CaSO₄, and glow peaks are attributed to the detrapping of various radicals like SO₄⁻, SO₃⁻ etc. observed in ESR spectra.

Hasimura (1979) arrived at similar conclusions after ESR studies of radical ion centers in irradiated CaSO₄.

1.3.3. Determination of glow curve parameters.

1.3.3(a) Evaluation of E and s

Methods for experimental determination of E and s have been reviewed by a number of workers (Chen and Winer 1970, Walsh and Lightowler 1971, Nicholas and Woods 1964, and Dittfeld and Voigt 1963). Certain methods for determination of E and s are described here in brief.

(i) Urbach's method.

The simplest, although an empirical one, was suggested by Urbach (1930)

$$ E \sim 25 kT_m $$

...(1.9)

Peak temp (°K) is read from the observed glow curve. However, $T_m$ was observed to vary with heating
rate $\beta$, the phosphor thickness etc. and hence the formalism lost its meaningfulness.

(ii) Varying the heating rate (Booth 1954).

By setting the derivative of Eqn: (1.8) equal to zero, an exact solution for the maximum is obtained.

$$T_m^2 = \frac{E\beta}{sK} e^{\frac{E}{KT_m}}$$  \hspace{1cm} \ldots(1.10)

using two heating rates $\beta_1, \beta_2$ ; $E$ can be determined by

$$E = \frac{K T_m T_{2m}}{T_{1m} T_{2m}^2} \left( \log_\beta \frac{\beta_1}{\beta_2} + 2 \log_\beta \frac{T_{2m}}{T_{1m}} \right)$$  \hspace{1cm} \ldots(1.11)

Where $T_{1m}$ and $T_{2m}$ refer to the glow peak maxima temperatures for $\beta_1, \beta_2$, respectively. Based on Eqn. 1.10, a plot of $\log \frac{T_{2m}}{T_{1m}^2}$ against $\frac{1}{T_{2m}}$ will be a straight line with a slope of $-\frac{E}{K}$ (Bube 1950). Here it is presumed that 's' remains constant.

However, as the variation of $T_m$ with $\beta$ is small and the broadening of the peak at low $\beta$ makes estimation of $T_m$ difficult, great reliance is not placed on the method,

(iii) Initial rise method (Garlick & Gibson 1948),
The major assumptions involved in this method are that during initial part of the glow peak, the population of trapped charge carriers is independent of the temperature i.e. indirectly the integral \( \int_0^T \frac{\varepsilon}{\rho} e^{-E/kT} d\tau \) of eqn. 1.8 remains constant and also that the luminescence efficiency remains constant. Under these assumptions

\[ I_t = A e^{-E/kT} \quad \text{...(1.12)} \]

will represent the intensity during the initial rise. The factor \( A \) contains the frequency factor 's' and the concentration of filled traps which are assumed to be constant. Hence, for temperatures well below \( T_m \) such that the reduction in the population of trapped charge carriers is negligible, the intensity \( I_t \) is measured as a function of \( T \). Arrhenius plots (log\( e \) \( I_t \) vs \( \frac{1}{T} \)) are straight lines with slopes \( \frac{E}{k} \) and hence \( E \) can be evaluated.

The method yields value of \( E \) independent of the order of kinetics involved (Halperin and Exner 1960) and it is also not necessary to have a prior knowledge of the concentration of traps and luminescence centers involved and their transition probabilities. In case of disturbance from neighbouring overlapping peaks, it is first cleaned by thermal means as suggested by Hoogenstranten (1958).
(iv) Peak shape methods

These methods are based on the shape of the glow peak whose symmetry is dependent on the number of traps as compared to the luminescence centres available and on the transition probabilities. Luschik (1955), Halperin et al (1960) and Chen (1969a) have given different formulae for calculation of activation energy of a trap for first order and second order kinetics using high-temperature half-width \( \delta = T_2 - T_m \), low temperature half width \( \tau = T_m - T_1 \) and full half width \( \omega = T_2 - T_1 \) at half peak intensity respectively.

By assuming that the area of the half peak towards the fall-off of the glow curve is equal to area of a triangle having the same height and half width, Luschik (1955) has shown that

\[
E = \frac{kT_m^2}{\delta} \quad \text{for first order kinetics} \quad \ldots (1.13)
\]

\[
E = 2 \frac{kT_m^2}{\delta} \quad \text{for second order kinetics} \quad \ldots (1.14)
\]

and

\[
s = \left( \frac{\beta}{\delta} \right) \frac{T_m}{\delta} \quad \text{for both the cases} \quad \ldots (1.15)
\]

Eqs. 1.13 and 1.14 were further corrected by Chen (1969a), as

\[
E = 0.976 \frac{kT_m^2}{\delta} \quad \text{for first order kinetics} \quad \ldots (1.16)
\]

and

\[
E = 1.706 \frac{kT_m^2}{\delta} \quad \text{for second order kinetics} \quad \ldots (1.17)
\]
According to Halperin and Brener (1960)

\[ E = \frac{1.72 \, kT_m^2}{C} \left( 1 - 1.5\Delta \right) \text{for first order kinetics} \quad \ldots (1.18) \]

and \[ E = \frac{2 \, kT_m^2}{C} \left( 1 - 3\Delta \right) \text{for second order kinetics} \quad \ldots (1.19) \]

where \[ \Delta = \frac{2 \, kT_m}{E} \quad < < 1 \]

Chen (1969a), to avoid the iterative solutions of (1.18 and 1.19), approximated them as

\[ E = \frac{1.52 \, kT_m^2}{C} - 3.16 \, kT_m \text{ for first order} \quad \ldots (1.20) \]

and

\[ E = \frac{1.613 \, kT_m^2}{C} - 4 \, kT_m \text{ for second order kinetics} \quad \ldots (1.21) \]

However, Grossweiner showed that for the case of negligible retrapping, \( E \) may be described as

\[ E = 1.51 \, \frac{T_m T_1}{C} \quad \ldots (1.22) \]

The limits of the applicability of this simplification are given by Grossweiner as \( \frac{E}{kT_m} > 20 \) and \( N_C S \sqrt{\rho} \approx 10^{7} / K \).

Making use of the full half-width \( (\omega) \) of a glow peak, Chen (1969a) gave the following formulae

\[ E = 2.29 \, \frac{kT_m^2}{\omega} \text{ for first order kinetics} \quad \ldots (1.23) \]

and \[ E = 3.52 \, \frac{kT_m^2}{\omega} - 2 \, kT_m \text{ for second order} \quad \ldots (1.24) \]

and \( S = \frac{2.67}{\omega} \left( \frac{T_m}{\omega} \right) \quad \ldots (1.25) \)
A general formula for calculating the activation energy has been evolved by Chen (1969b), which is applicable to both first-order and second-order kinetics.

However, in cases where various glow peaks cannot be cleaned by thermal means, Hao (1974) has suggested a novel method of analysis of glow curve pattern starting from the highest temperature end of the glow curve and arriving at the parameters of the lower peaks using Chen's equations 1.23 and 1.24.

Making use of the entire shape of the isolated glow peaks, DeMuer (1970) has developed another universal method for calculating the thermoluminescence parameters.

(b) Determination of the order of kinetics

When charge carriers released on heating have no retrapping, the TL process will follow first-order kinetics (Randall & Wilkins 1945). However, when there is an equal probability of charge carriers getting retrapped or going to the recombination centers, the process is said to be of second order.

The order of kinetics (\( \ell \)) can be determined by using the isothermal decay of the glow peak. In the case of first-order kinetics (\( \ell = 1 \)), decay is exponential. When \( \ell > 1 \), the decay pattern is slower and
plot of \((I_t)^{1/1-1}\) versus decay time \(t\) would be a straight line. The value of \(l\) that produces a straight line will be the actual order of kinetics. (Ray and Fartridge 1964). It is also possible to determine \(l\) by plotting \(\log \frac{dI}{dt}\) vs \(\log I\). The slope of the resulting straight line \((f)\) is related to the kinetics \((l)\) by

\[
l = \frac{1}{2 - f}
\]  

...(1.26)

According to Halperin and Blauer (1960), from the shape of the glow peak, for first order process

\[
\frac{\delta}{\omega} < < \frac{1 + \frac{2kT_m}{E}}{e}
\]  

...(1.27)

and for second order process \(\frac{\delta}{\omega} > \frac{1 + \frac{2kT_m}{E}}{e}\)  

...(1.28)

Since \(\frac{2kT_m}{E} \approx 0.1\), it can be neglected as a first approximation. Without the knowledge of the trap depth, it can therefore, be stated that

\[
\frac{\delta}{\omega} < < \frac{1}{e}
\]  
indicates first order process ..(1.29)

\[
\frac{\delta}{\omega} > \frac{1}{e}
\]  
indicates second order process ..(1.30)

\(l\) may not be independent of the proportion of occupancy of the traps. Recently it has been reported
(Kathuria et al 1979) that the value of 1 depends upon the degree of saturation of the glow peak, when isothermal decay method is used for TLD-100. Near saturation \( 1 \approx 1 \), but it approaches 1.6 as the proportion of empty traps increases from zero to 80%.

1.3.4 Spectral studies - Absorption, fluorescence and TL emission.

A fair amount of understanding can be arrived at regarding the role of impurities and the host matrix after an extensive study of the TL glow curves, absorption, fluorescence and TL emission spectra of doped and undoped specimens.

Absorption studies are generally carried out spectrophotometrically, measuring transmission of crystals. A number of investigations have been carried out on alkali halides, after irradiation and thermal treatments. The most recent studies by Kos and Nink (1979) have identified 250°C TL peak in LiF:Mg, Ti as arising from \( \text{Z}_2 \) centers (\( \text{Mg}^{2+} - \text{F} \) pairs).

Fluorescence spectra help identify the fluorescent ions/species and the energy transfer process. Most revealing conclusions from fluorescent spectra have been in case of CaF\(_2\):Ce, Mn phosphor (Crittenden 1974). CaF\(_2\):Mn is non-fluorescent under the UV light excitation while CaF\(_2\):Ce gives a characteristic Ce\(^{3+}\) fluorescence emission.
Codoping of Ce, Mn in the CaF₂ lattice, however, gives a brilliant Mn²⁺ fluorescence emission in addition to the Ce³⁺ fluorescence emission. The excitation spectrum studies reveal that the fluorescence excitation of Mn²⁺ is through the Ce³⁺ and the process is explained in terms of energy transfer.

TL emission spectral measurements should yield directly information on the nature of the luminescence centers involved in the TL process. However recording absolute TL emission spectra poses a number of problems. Corrections for the spectral efficiency of both the spectrograph and the detection system have to be applied. In addition, there is a loss of spectral intensity in the course of scanning. Hence most of the reported TL spectra are of qualitative nature. TL emission spectra have been measured employing a spectrograph in conjunction with photographic plates/films (Ghosh et al 1958), using interference filters (Schays et al 1963), or making use of prism monochromator with a photomultiplier (Sunta 1970). Using a slow scanning rate, it has been possible to get a resolution of 0.1 nm (Merz et al 1967) for TL emission spectra. Absolute TL emission from a variety of phosphors like Li₂B₄O₇:Mn, CaSO₄:Mn, CaF₂:Mn, LiF and natural CaF₂ have been measured by Gorbics (1966). By the use of advanced instruments
(Mattern et al 1970), it is possible to present TL emission in the form of 3 dimensional curves with intensity as a function of temperature and wavelength.

In rare-earth doped CaF$_2$ samples, Merz et al (1967) identified the emission centres to be the Eu$^{3+}$ ions. Similar conclusions were drawn for Eu doped CaSO$_4$ and BaSO$_4$ phosphors by Nambo et al (1974) and Luthra et al (1974) respectively.

1.3.5 TL processes and models.

Certain models for TL processes have been evolved. Some of these, proposed for certain materials, are discussed here briefly.

According to Medlin (1968), in CaCO$_3$ (calcite) mineral, impurity independent color centers, generated on irradiation, are the trapping sites with Mn$^{2+}$ acting as emission centers. When the material is heated, the color centers act as sensitizers transferring energy to the Mn$^{2+}$ ions.

Rare earth doped CaF$_2$ phosphors have perhaps been the best explained by the model. Merz and Pershan (1967) explained the entire TL process in terms of irradiation induced valency reduction and thermally stimulated valency reoxidation of the Eu ions resulting in the observed TL emission. Most probably, Eu$^{3+}$ displaces Ca$^{2+}$ ion in the lattice and the charge compensation is
provided by an interstitial F ion. On irradiation, electrons released from F- ions are trapped by \( \text{RE}^{3+} \) ions forming \( \text{RE}^{2+} \) ions. Holes are trapped in a V_k centre forming \( \text{F}^- \) centres. On heating \( \text{CaF}_2: \text{RE} \), holes are released and on recombining, with the trapped electron at the \( \text{RE} \) site, leave the newly formed \( \text{RE}^{3+} \) ion in an excited state. TL emitted in this characteristic of \( \text{RE}^{3+} \) emission.

Nambi et al (1974) have attributed the origin of TL in \( \text{CaSO}_4: \text{RE} \) phosphor to the reduction of \( \text{RE}^{3+} \) to \( \text{RE}^{2+} \) by capture of an electron in the radiation process and its reconversion to \( \text{RE}^{3+} \) in the heating process. The reconversion is attributed to a thermally released hole (\( \text{SO}_4^-, \text{SO}_3^-, \text{O}_2^- \) etc.) combining with the electron at the \( \text{RE}^{2+} \) and leaving the residual \( \text{RE}^{3+} \) in excited states. This hypothesis was further confirmed in case of \( \text{CaSO}_4: \text{Eu} \) by Bapat (1977) after a series of fluorescence studies. However, absorption bands characteristic of \( \text{RE}^{2+} \) in gamma irradiated \( \text{CaSO}_4: \text{RE} \) have not been observed so far.

In case of \( \text{BaSO}_4 \) phosphors it has been shown by Luthra and Gupta (1974) that anion radicals formed on \( \gamma \) radiation act as hole trapped centers and the impurity ions function as luminescence centers. The TL mechanism involves the release of holes from the anion radicals. Similar conclusions were arrived at for \( \text{Rare Earth} \)
activated CdSO₄, SrSO₄ and BaSO₄ by Dixon and Ekstrand (1974a). Thermoluminescent emission spectra were obtained for Sm³⁺, Tb³⁺, Dy³⁺ and Tm³⁺ and for divalent Eu in these sulfates.

Various TL glow peaks of Li₂O have been attributed to hole trapped centres (Luthra et al 1977). One of the peaks has been found to be due to holes released from V₁ ions (hole trapped at cation vacancy associated with a neighbouring impurity ion).

In case of various alkali halides, there is a correspondence between colour center bleaching and the TL. Different models of TL in alkali halides have been proposed (Mahendra and Rajahkrishna 1969, Koe and Nink 1979). Bonfiglioli et al (1959) proposed involvement of F centres and V centres. For the most widely studied material LiF, Click et al (1967) proposed that the trapping centre consists of a hole trapped near various groupings of Mg²⁺ ions and vacancies. Holes are transported to the F centre which acts as the emitting centre. This F centre is either in an isolated position or adjacent to a complex structure of Mg²⁺ ions. Zimmerman et al (1967) have stated that the role of Ti impurity is very significant during emission.

In Li₂B₄O₇:Mn glasses, holes trapped on bridging and non-bridging oxygens of the matrix have
been identified as the trapping centres (Shearer 1974). Number of trapped holes after irradiation is reduced and this reduction increases with the impurity content. Un- trapping process occurs over a continuous spectrum of activation energies. Luminescent center is independent of the trap.

1.3.6. TL phosphors for radiation dosimetry.

A variety of TL phosphors has been used for radiation dosimetry in various applications covering a vast range of fields. Since Daniels (1953) introduced the dosimetric aspect, it has grown into a very useful branch. More frequently used phosphors, CaF$_2$ natural, CaF$_2$ (Mn), LiF (TLD-100, TLD-600, TLD-700) Li$_2$F$_2$O$_7$:Mn and CaSO$_4$ (Mn) are now commercially available. CaSO$_4$:Dy, CaSO$_4$:Tm, CaF$_2$:Dy, CaF$_2$:Tm and Mg$_2$SiO$_4$:Tb are of recent origin and have shown promise due to high sensitivity. A review of the literature pertaining to only CaSO$_4$, BaSO$_4$, MgF$_2$ will be given in brief here.

CaSO$_4$ was introduced as CaSO$_4$ (Mn) and used for measurement of UV radiation (Lyman 1935, Nosenko et al 1956). A. G. A. Chalifour et al (1961) used it for dosimetry of ionising radiation and it was Bjarnegard (1962) who established it for low level dosimetry of ionising radiation. However, the fast post irradiation fading of the TL, even at room temperature, was a great drawback.
CaSO₄ (Be) phosphors were introduced by Yamashita et al (1968, 1971). CaSO₄ (Dy) and CaSO₄ (Tm) are now commercially available from Marshaw Chemical Co., USA. These have found favour with various radiation protection and monitoring programmes (Volra et al 1980, Iga et al 1977 and Nambi 1979).

BaSO₄ phosphors, having high effective atomic number (45.8) show greatly enhanced response for low energy electromagnetic radiation and have been proposed for dosimetry of low energy X-ray beams (Dixon and Ekstrand 1974b).

MgF₂(Mn) has been studied by Pass et al 1976 and Braunlich et al 1961). Its wide linear response (20 mR - 10⁵ R) however, has not found its proper utility because of prominent post irradiation fading observed with the material.

1.3.7. Dosimetry of non-ionizing radiation

With the increasing use of non-ionizing radiations such as Ultraviolet (UV) and microwaves, the risk to populations is also increasing. Ultraviolet radiation (100-400 nm) has had a long and distinguished use in clinical medicine. As the binding energies of most of the chemical and biological molecules fall within the range of UV photon energy (eV), the photochemical and biological effects of UV radiation have been abundantly
observed. Germicidal wavelength (254 nm) is being put to maximum use for various applications. With the increasing usage, awareness to the harmful effects of the undesirable exposures to UV radiation is also being realised (McCullough 1977). In fact, World Health Organisation had made strong recommendations against indiscriminate distribution of UV lamps for private users as early as 1972 (WHO 1972).

Rapid advancement in microwave oven technology has also caused some concern since adverse health effects from exposure to high levels of microwave radiation are well recognised.

Obviously to limit exposure of the personnel to these non-ionising radiations, it is imperative to have proper dosimetric systems. UV radiation may be detected and measured by means of its thermal, chemical, electrical and certain solid state effects. Thermal and photochemical techniques can be used for absolute measurement of UV radiation whereas for microwave radiations one has to resort to thermal means.

Of late, UV dosimetry making use of thermoluminescence phenomenon has come in vogue. Intrinsic response to UV as well as the phototransferred thermoluminescence of the phosphors such as MgO (Takeuchi et al 1976),
Cs₂SO₄:Dy (Bassi et al 1975), Be₂SiO₄:Th (Lakshmanan et al 1978), Al₂O₃:Si, Ti (Mehta and Sengupta 1977), CaSO₄:Dy (Chandra et al 1976), CaSO₄:Tm (Nambi et al 1971) and CaF₂:Nd (Sunta et al 1970) have been suggested for UV dosimetry. Earlier CaSO₄:Yb had been used by Lyman (1935) and Tousey (1951) for the same purpose.

For microwave dosimetry, thermoluminescence of Na doped BaTiO₃ phosphor has been investigated. There is a reduction in the TL response of gamma irradiated phosphor when it is exposed to microwave radiation (Lin et al 1976 and Elle et al 1973). Gamma exposure given to the ceramic samples was 10⁵ R and the studies in the range 100 mW/cm² - 400 mW/cm² indicated that microwave induced TL fading in BaTiO₃:Dy and BaTiO₃:Sm could serve as microwave dosimeters.

For thermally stimulated exoelectron phosphors such as CaF₂, BaSO₄, (Ba⁰.₈Sr₀.₂)TiO₃, microwave induced fading was observed only when they were mixed with graphite and exposed to extremely high power densities (Elle et al 1973).