INTRODUCTION
1.1 INTRODUCTION

"Of all gifts to earth, the first and the greatest was darkness. Darkness preceded light that we remember in Genesis. Darkness seems natural and universal to man and requires no explanation and no cause, but we postulate it, whereas light being to our minds merely the cleansing vibration that dispels black, requires some origin, some lamp whence to shine. From the appalling torch of the sun down to the pale belly of the glow worm, we deens light a derivative miracle, proceeding from some conceivable source. We can conceive darkness without though of light; but we can conceive light without darkness."

Modern scientific invention has proved to be a boon by providing light sources to human beings. There are two types of light sources, namely, the hot light sources (incandescence) and the cold light sources (luminescence). The general term "luminescence" implies luminous emission which is not purely thermal in origin. Long before written records, many kinds of luminescence emission were observed from lightening, aurorae, fireflies and certain see bacteria. Answerness of their origin did not develop until. Luminescence continues to be a rewarding field for scientific study and practical applications and it provides a fascinating variety.

When certain matters absorb energy, then a part of the absorbed energy may be re-emitted as electromagnetic radiations in the visible or near-visible region of the spectrum, in excess of thermal radiation. Such cold emission
of light is known as luminescence, with the understanding that this term does not include the emission of black-body radiation, which obeys the laws of Kirchoff and Wein.

Thus, the process of luminescence involve two steps: (i) the excitation of electronic system of a solid to higher excited states, and (ii) the subsequent emission of photons or simply light.

The excitation is pre-requisite for luminescence, i.e., the emission of light takes place a characteristic time $\tau_c$ after the absorption of the radiation and this parameter allows one to classify the process of luminescence. Thus, we can distinguish between fluorescence in which $\tau_c < 10^{-8}$ second and phosphorescence or after glow in which $\tau_c > 10^{-8}$ second (Garlick 1949, Curie 1960). A large number of substances, both organic and inorganic, show the property of luminescence, but principal materials used in various applications of luminescence, involve inorganic solid insulating materials such as alkali and alkaline earth halides, phosphates, borates and sulphates. Luminescent solids are usually referred to as phosphors. A vast majority of inorganic phosphors owe their luminescence ability to small concentrations of selected chemical impurities, structural defects, or a combination of the two; these entities are called activators. Among the most widely used impurity activators in inorganic phosphors are manganese, the rare earths, thallium, lead, tin, antimony, copper and silver. They are generally incorporated in the
host-crystal lattice in mole fractions ranging from $10^{-5}$ to $10^{-2}$.

1.1-1 TYPES OF LUMINESCENCE

It may be said that all types of light emissions except incandescent emission, are luminescence. A system emitting luminescence is losing energy, and if the light emission is to continue indefinitely, some form of energy must be supplied from elsewhere. Most of the types of luminescence are classified according to the source from which this energy is derived. Among the different types of luminescence, some of them are given below:

(i) Photoluminescence

It is produced by absorption of photons of energies from a few to several electron volts, for example, from ultraviolet radiations.

(ii) Cathodoluminescence

It is produced by energetic electrons or cathode rays.

(iii) Electroluminescence

It is produced by the voltage applied to the luminescent substances.

(iv) Mechanoluminescence or Triboluminescence

It is produced due to the mechanical deformation of solids.
(v) Chemiluminescence
   It is produced due to the energy released by chemical reaction.

(vi) Thermoluminescence
   It is produced when a substance is warmed to a moderate temperature which releases the previously absorbed radiation.

(vii) Radioluminescence
   It is excited by one or all radioactive disintegration products.

(viii) Roentgenoluminescence
   It is a specific case of radioluminescence produced by X-rays.

(ix) Sonoluminescence
   It is produced by ultrasonic waves.

(x) Bioluminescence
   It is produced by energy from biochemical reactions.

(xi) Galvanoluminescence or Voltaluminescence
   It is a luminescence phenomenon accompanying the passage of electric current through aqueous solutions.

(xii) Lyoluminescence or Aquoluminescence
   It is produced during dissolution of certain coloured crystals (by high energy radiations) in aqueous solutions.
(xiii) Crystalloluminescence

It is produced during the growth of the crystals from solutions.

(xiv) Magnetoluminescence

It is the change in photoluminescence intensity due to the application of magnetic field.

There are further sub-classifications of luminescence, such as: photo-electroluminescence, electro-photoluminescence, mechano-thermoluminescence, thermo-mechanoluminescence etc. The first prefix in such luminescence denotes the controlling and the second denotes the source of power that stimulates it.

1.2 PHENOMENON OF THERMOLUMINESCENCE

In Solid State Physics, the primary methods of probing the defect structures, their deformation, distribution and interaction among themselves are optical measurements. Related measurements are utilised either to support or contradict the traditional views built upon the understanding of the underlying electronic processes. The concept of trapping is of central importance in the understanding of defect structures and processes. An important and convenient method of investigating the nature of traps and trapping levels in crystals is the thermal glow method which includes thermoluminescence (TL) thermally stimulated current (TSC), thermally stimulated electron emission (TSEE) or exo-electron
emission (EEE), and thermally stimulated capacitor discharge (TSDC) (Chen 1969). Of all the methods, the experimental simplicity of thermally stimulated large amount of work.

When an insulator subjected to ionizing radiation is heated, the energy stored in the crystal as a result of the irradiation process, liberates in the form of visible light in addition to the normal thermal radiation. Heating the crystal immediately after it, gives rise to only the thermal emission. The additional visible light emitted during first heating is called Thermoluminescence (TL). The designation of this phenomenon as thermoluminescence is not a very logical one, since in the conventional sense of other luminescence process, the prefix 'thermo' suggested that the heat is the primary excitant which is not. For this reason, some workers prefer to call it thermo-stimulated luminescence (TSL).

The first mention of the discovery of thermoluminescence dates back to October 28, 1663, when Robert Boyle reported to the Royal Society in London, the observations of a strange "glimmering light" on warming a diamond in the dark. Most of the early work of this subject was restricted to natural minerals and glasses and it was only about three decades later when crystal growing techniques became common that the interest shifted to the TL of phosphors grown in the laboratory. Although considerable works had been done before on TL in the context of solid state physics, it was in 1953 that the use of this phenomenon in measuring doses of ionizing
radiations was first proposed by Farrington Daniels of the United States of America. Subsequently, John R. Cameron and his students in the Medical Physics Department of the University of Wisconsin made an intensive study on the development of lithium fluoride TLD phosphor (Cameron et al 1968). In 1961, Harshaw Chemical Company (USA) began collaborating with Cameron's group and in a couple of years a new phosphor LiF:Mg,Ti known as TLD-200 was developed by them. Later, Harshaw also made available lithium fluoride phosphors TLD-600 and TLD-700, which were composed of isotopically enriched lithium-6 and lithium-7, respectively. These three types of LiF materials are being used today.

Thermoluminescence is a type of delayed phosphorescence, where the photon energy is released when a crystalline substance is heated from low temperature to a higher value. The substance is irradiated with ionizing radiations such as $\alpha$, $\beta$, $\gamma$, as well as X-rays, cosmic rays, electron beams and other fast particles. The total light emission is proportional to the overall radiation dose irrespective of the dose rate. A thermoluminescence "glow curve" represents all the measured light quanta emitted by a substance when its temperature is increased. Finally, the temperature reaches a point when all the glow is discharged and the substance loses its all radiation history. Upon cooling and reheating, no further TL is observed until the sample is exposed to an additional dose of ionizing radiation.
The phenomenon of thermoluminescence can be best understood in terms of a "band model" as shown schematically in Fig.1.1. In the first stage, ionizing radiation produces electrons and holes in the solid. These carriers wander until the electrons in the conduction band fall into an electron trap and the holes in the valence band fall into a hole trap. On heating, a trapped electron may get excited into the conduction band where it wanders until it recombines with the holes as shown in the second stage. Alternatively, a trapped hole may get excited into the valence band where it wanders until it recombines with an electron as shown in the third stage. The energy of emitted light is related to the trap depth while the intensity of light provides a measure of the number of trapped electrons. Therefore, overall radiations dose may be measured. These traps may be of different depths and span a range 0 to 4 eV. As the thermal ejection of relatively stable trapped electrons leads to the production of TL, the deeper traps require higher temperature.

Theory of TL 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 where the rate of escape of trapped electrons is proportional to the intensity of emitted light per unit time. TL is perhaps one of those rare physical phenomena which are more successfully applied than understood.
Fig. 1.1 The process involved in thermoluminescence: (1) Thermal Excitation, (2) Electronic Migration and (3) Luminescence
In general, the mechanism of the TL is believed to be as follows. When an crystalline phosphor subjected to ionizing radiation, the radiation produces free electrons and holes in the phosphor. Most of these electrons and holes combine promptly resulting either in emission of light or lattice vibrations. The remaining electrons and holes are trapped at the defect sites which may be present in the host lattice inherently or due to some foreign impurities. On heating the irradiated crystals, electrons (or holes) are released from the traps (defect sites) and wander in the medium till they undergo recombination. A part of the recombination energy is emitted in the form of light called Thermoluminescence (TL). The energy required to release the electrons (or holes) from the trap is called the Activation energy (E). Normally, a number of trapping sites exist having different activation energies. On heating the material, charge carriers (electrons or holes) are released from these traps at different temperatures. These results in the appearance of a number of glow peaks, each glow peak representing one type of defect in the crystal. The plot of light intensity versus temperature of the sample is called the glow curve. The emitted thermoluminescence is a measure of radiation dose observed by the phosphor. The dose can bee estimated if the thermoluminescence response to unit radiation dose (TL sensitivity) is known.

The generally accepted picture of thermoluminescence has
its origin in the energy band theory of solids, from which a simple explanation of the observed luminescence properties of various types of material can be obtained. When the Schrödinger wave equation is solved for an electron subjected to a periodically varying potential, such as that due to lattice of ion cores in a solid, it is found that the electrons may occupy broad energy bands separated by the forbidden gaps. At the absolute zero of temperature insulators and semi-conductors have fully occupied bands and an uppermost empty band. At temperature, $T > 0$, some electrons are excited across the forbidden gap from the filled band (valence band) to the empty band (conduction band) leaving behind, effectively positive holes in the valence band (Fig. 1.2).

The simple band scheme given above applies only to perfect crystals. In real crystals, there are always various defects present. These include vacant lattice sites, interstitial atom and impurity atoms. These defects upset periodically of the lattice and disturb normal band structure relating in the presence of localized energy levels within the forbidden gap. Electrons moving through the conduction band (or holes in the valence band) can be trapped at these defect sites [Fig. 1.3(a)].

Upon irradiating the sample with ionizing radiation, some electrons gain sufficient energy to be raised from the valence to the conduction band. Most of the excited electrons return to the valence band after a very short time ($\approx 10^{-8}$
Electron energy band structure in a solid. At temperatures above absolute zero, a few electrons will be excited across the forbidden gap into the conduction band, leaving holes in the valence band.
(a) Trapping of charges
(b) Thermal release of charges leading to TL

FIGURE - 1.3
Schematic representation of TL process.
sec) giving rise to luminescence, which can be detected during irradiation. Some of them, however, are trapped at local defect centres [Fig.1.3(a)]. When the sample is heated, these trapped electrons can gain enough thermal energy to escape from the traps back to the conduction band. From there, they may make direct transitions back to the valence band or alternatively, they may become retrapped or combine with trapped holes [Fig.1.3(b)]. If the electron levels are close to the conduction band, then this thermal detrapping will occur at ambient temperatures and if recombination with holes leads to light emission, then the resulting process is phosphorescence. Deeper traps will require some heating if the electrons are to be released, and thus we have thermoluminescence. Recombination with holes can lead to energy release in the form of phonon or photon emission. The trapped holes are often referred to as "recombination centres", and if the energy release through photon emission predominates then they are known as "Luminescent Centres". All of the above description can equally well apply to the thermal release of holes, which would then move through the valence band the luminescent centres. It is purely a matter of convention that the phenomenological description of TL usually refer to the electron motion.

1.3 KINETICS OF THERMOLUMINESCENCE

The thermoluminescence of alkali halides has been the
subject of investigation for a long time. In this study the important point is to establish a correlation between thermoluminescence and thermal stability of the radiation induced colour centres, mainly F-centres. There are different views about the role of F-centres in thermoluminescence process. According to a group of workers, the F-centres play the role of electron traps in TL process (Jain and Mahendru 1965, 1970). However, some workers believe that F-centres act as recombiantion centres for holes which are thermally released from traps (Timsok and Martieussen 1962, Klick et al 1967).

In brief, we shall discuss the kinetics of TL as it is very important aspect of the phenomenon.

1.3-1 FIRST ORDER KINETICS

Randall and Wilkins (1945) were the first to provide a theoretical analysis of the TL phenomenon. They made the following assumptios :

(i) No direct transition takes place from the defect to the recombination centre.

(ii) The number of defect sites is small as compared to the luminescent centres.

(iii) The recombination life-time in the conduction band is small.
(iv) No retrapping or trapping into any other trap or recombination into other recombination centre (except for the one populated to be directly relevant to this particular peak) is allowed.

The rate of depopulation of the defect is given by (Townsend and Kelly 1973)

\[
\frac{dn}{dt} = -n \left( N_c S v \right) \exp \left( -\frac{E}{kT} \right) + A n_c (N-n) \quad \ldots \quad (1.1)
\]

In the first term on the right hand side of equation (1.1), \( n \) is the electron concentration in the defect, \( N_c \) is the density of states in the conduction band, \( S \) is the electron capture cross-section in the conduction band and \( v \) is the velocity of electrons. The second term allows for the probability of a back reaction with \( A \) as the defect's electron capture cross section, \( N \) is the total concentration of the shallow levels and \( n_c \) is the electron concentration in the conduction band.

As it is assumed that retrapping is negligible and if the recombination lifetime \( \tau \) is very short, the electron concentration in the conduction band \( n_c \) will remain necessarily constant. So, in general, we have

\[
\frac{dn_c}{dt} = -\frac{n_c}{\tau} + \frac{dn}{dt} \quad \ldots \quad (1.2)
\]

when \( \tau \) is short, \( dn_c/dt \) is negligible as compared to the
other terms. If we raise the temperature at a constant rate $\beta$
from the initial temperature $T_o$, the relation between the time
and temperature is given by

$$T = T_o + \beta t$$

So, equation (1.2) becomes

$$\frac{n_c}{\tau} = \beta \frac{dn}{dt} \quad \cdots (1.3)$$

This equation gives the movement of electrons from the
conduction band to the deeper levels which provides the
luminescence, so $n_c/\tau$ is proportional to the light
intensity $I$.

In the case of no retrapping i.e. $A = 0$, and equation
(1.1) may be written as

$$\beta \frac{dn}{dt} = -n \left( N_C S \upsilon \right) \exp \left( -\frac{E}{kT} \right) \quad \cdots (1.4)$$

or

$$\beta \frac{dn}{dt} = -n \, s \, \exp \left( -\frac{E}{kT} \right) \quad \cdots (1.5)$$

where $s = N_C S \upsilon$ is called the "frequency factor" and has the
units of second$^{-1}$.

Integration of equation (1.5) gives

$$\frac{dn}{n} = - \int_{T_o}^{T} \frac{s}{\beta} \exp(-E/kT) \, dT + C$$
or \[ \log n = - \int_{T_0}^{T} \frac{s}{\beta} \exp(-E/kT) \, dT + C \]

where \( C \) is the constant of integration.

At \( T = T_0 \), \( n = n_0 \), therefore we have

\[ C = \log n_0 \]

Now, the above equation may be expressed as

\[ n = n_0 \exp\left[ - \int_{T_0}^{T} \frac{s}{\beta} \exp\left( - \frac{E}{kT} \right) \, dT \right] \quad \ldots (1.6) \]

Using equation (1.5), the intensity of luminescence may be given by

\[ I = \eta \frac{dn}{dt} = \eta s n \exp\left( - \frac{E}{kT} \right) \quad \ldots (1.7) \]

where \( \eta \) is the probability of radiative electron-hole recombination.

Substituting the value of \( n \) from equation (1.6), we have

\[ I = \eta n_0 s \exp\left( - \frac{E}{kT} \right) \exp\left[ - \int_{T_0}^{T} \frac{s}{\beta} \exp\left( - \frac{E}{kT} \right) \, dT \right] \quad \ldots (1.8) \]

where \( E \) is the trap-depth, \( k \) is the Boltzmann constant, \( n_0 \) is the initial concentration of filled traps and \( T \) is the temperature of the crystal (\(^{\circ}\)K).
It can be easily observed from equation (1.8) that the intensity of luminescence increases as T increases, reaches to an optimum value for a particular temperature $T_m$ and then falls off for any further increase in temperature.

At $T = T_m$, $\frac{d}{dt} (\log I) = 0$

Thus, we obtain

$$\left[ \frac{d}{dt} (\log I) \right]_{T=T_m} = 0$$

or

$$\frac{d}{dT} \left[ \log (\eta n_o s) - \frac{E}{kT} - \int \frac{s}{\beta} \exp \left( - \frac{E}{kT} \right) dT \right]_{T=T_m} = 0$$

or

$$\frac{E}{kT_m^2} - \frac{s}{\beta} \exp \left( - \frac{E}{kT_m} \right) = 0$$

or

$$\frac{\beta E}{kT_m^2} = s \exp \left( - \frac{E}{kT_m} \right) \quad \cdots (1.9)$$

The fact that $n_o$ does not appear in equation (1.9) immediately proves the first order characteristic that $T_m$ does not depend on $n_o$.

Equation (1.9) can also be expressed as

$$\frac{\beta E}{kT_m^2} = \frac{sk}{E} T_m^2 \exp \left( - \frac{E}{kT_m} \right) \quad \cdots (1.10)$$

On changing the heating rate, $\beta$ must change $T_m$ in such a way
that equality still holds. The term $T_m^2 \exp\left( \frac{-E}{kT_m} \right)$ is monotonically increasing with $T_m$, therefore, increasing $\beta$ will immediately cause $T_m$ to increase.

Using equations (1.8) and (1.9), the expression for maximum intensity may be written as

$$I_m = \eta \ n_o \ s \ \exp\left( \frac{-E}{kT_m} \right) \ \exp\left[ \int_{T_0}^{T_m} \frac{E}{kT^2} \ dT \right]$$

or

$$I_m = \eta \ n_o \ s \ \exp\left( \frac{-E}{kT_m} \right) \ \ldots \ (1.11)$$

Using equation (1.11), Randall and Wilkins obtained the following expression for the trap depth "E",

$$E \approx 25 \ k \ T_m \ \ldots \ (1.12)$$

where $T_m$ is the glow peak temperature.

If the sample is maintained isothermal at temperature $T$, then solution of equation (1.7) is given by

$$I(T) = I_o \ \exp\left[ -s \ \exp\left( \frac{-E}{kT} \right) \ t \right] \ \ldots \ (1.13)$$

The above equation shows that at constant temperature, TL intensity falls exponentially with time. Plot of TL intensity versus time for fixed temperature is known as isothermal decay. Contributions from several types of traps may exist and it may not be exponential as predicted by equation (1.13), but these contributions are due to several exponentially decaying components.
1.3-2 SECOND ORDER KINETICS

Garlick and Gibson (1948) modified the equation (1.7) by taking into account the retrapping. Randall and Wilkins assumed that all the charge carriers released thermally from the traps recombine. Garlick and Gibson made different assumptions that a free electron has equal probability for going to a recombination centre or getting retrapped.

If "N" be the total number of traps of which "n" are occupied at time "t", then the probability that a released electron will go to the recombination centre is given by

$$\frac{n}{(N-n) + n} = \frac{n}{N}$$

where (N-n) is the number of empty traps.

Hence, $\frac{dn}{dt} = -s \frac{n^2}{N} \exp(-E/kT)$, and the equation for luminescence intensity becomes,

$$I = -\eta \frac{dn}{dt} = \eta s' n^2 \exp(-E/kT)$$

... (1.14)

here $s' = S/N$ is known as the "pre-exponential factor".

The solution of equation (1.14) is given by

$$I = \eta s' \left[ \frac{n_0}{n_0 + \int_{T_0}^{T} \frac{s}{\beta} \exp(-E/kT') \, dT'} \right] \times \exp(-E/kT)$$

... (1.15)
For constant temperature T, the solution is

\[ I = \frac{I_0}{(1 + I_0 p t)^2} \] \hspace{1cm} \cdots (1.16)

where \( p = s \exp(-E/kT) \)

Equation (1.16) represents the second order kinetics. A number of methods have been suggested for obtaining trapping parameters starting with either of the equation (1.7) or (1.14). These methods have been reviewed by several workers (Braunlich 1968, Kivits and Hagebuck 1977).

A typical example of glow curves obtained with first and second order kinetics is shown in Fig.1.4.

1.3-3 GENERAL ORDER KINETICS

Antanov-Ramanovskii (1951) has suggested a TL kinetics differing from that of Randall and Wilkins. In this kinetics, the probability of recombination is not taken as complementary to the trapping but considered independently. They proposed the following equation for TL intensity

\[ I = \eta \frac{\text{dn}}{\text{dt}} = \eta s \frac{B}{A (N-n) + B} \frac{n m}{\exp(-E/kT)} \]

where A and B are probabilities, respectively of retrapping and recombination, and the instantaneous concentrations of trapped charges and recombination centres are n and m respectively.
Computed TL peaks of first-order (curve a) and second-order (curve b) kinetics. In the first order peak, $E=0.4 \text{ eV}$ and $s=10^{10} \text{ m sec}^{-1}$. In the second-order peak, $E=0.4 \text{ eV}$ and $s=10^{11} \text{ m sec}^{-1}$. $n_0$ is chosen in curve b so that the two maxima coincide. Both curves are normalized.
The general order equation (1.17) is valid under more exacting conditions than those stated here (Maxia 1978). For A=B, we obtain Garlic and Gibson equation and for A << B, we get back Randall and Wilkins equation. However, solution of equation (1.17) cannot be obtained in the way it has obtained for equations (1.7) and (1.14). A numerical solution or any analytical solution after substituting some of the quantities from experimental observations is usually attempted to obtain the trapping parameters E, S, A and B.

May and Portridge (1964) have suggested that the order of kinetics need not be 1 or 2, but may assume an intermediate value. The semiempirical equation for general order kinetics given by them is

\[ I = -\eta \frac{dn}{dt} = \eta s^b n^b \exp(-E/kT) \quad \ldots \quad (1.18) \]

where b, the order of kinetics lies between 1 and 2 and 1/b gives the fraction of electrons going to recombination centres.

Solving equation (1.18) and applying the condition of maximum, we obtain a reasonable approximation for most of the cases.

\[ \frac{\beta E}{k T_m^2} = s'' \exp(-E/kT_m) \left[ 1 + (b-1) \frac{2 k T_m}{E} \right] \quad \ldots \quad (1.19) \]

where \( s'' = s^b n^{b-1} \) and \( \beta \) is the heating rate (°K/min). Using
equation (1.19), frequency factor $s''$ can be calculated for $b=1$ and it is given by

$$s'' = \frac{\beta E}{k T_m^2} \exp\left(\frac{-E}{k T_m}\right) \quad \ldots (1.20)$$

Chen (1969) has related equation (1.18) with experimentally obtainable quantity $\mu g$ known as "form factor". He also suggested a reasonable method (which does not require prior knowledge of "b") based on the accurate measurement of the temperature of TL peak maximum ($T_m$), low temperature half width ($\tau$) and high temperature half width ($\delta$).

Methods using $\delta$ and $\tau$ along with $T_m$ were developed by Luschik (1955), Halperin and Braner (1960) and Chen (1969), later summed up in the form of following equations:

$$E_i = Ca \left( \frac{k T_m}{a} \right) - Ba \left( 2 \frac{k T_m}{a} \right) \quad \ldots (1.21)$$

where $a$, $Ca$, $Ba$ are constants and $E$ is the activation energy. This equation may be expressed in the following forms depending upon $\tau$, $\delta$ or $\omega$.

$$E_\tau = \left[ 1.51 + 3(\mu g - 0.42) \right] \frac{k T_m^2}{\tau} \quad \ldots (1.22)$$

$$E_\delta = \left[ 0.976 + 7.3(\mu g - 0.42) \right] \frac{k T_m^2}{\delta} \quad \ldots (1.23)$$
\[
E_m = \left(2.52 + 10.2(\mu g - 0.42)\right) - 2kT_m^2 \tag{1.24}
\]

where \(T_m\) is the temperature at which maximum intensity is observed, \(T_1\) and \(T_2\) are temperatures on low and high temperature side, respectively at which the intensity falls to half of the maximum value.

\[
\delta = T_2 - T_m, \quad \omega = T_2 - T_1
\]

\[
\tau = T_m - T_1 \quad \text{and} \quad \mu_g = \delta/\omega
\]

Except for extreme values of \(\mu g\) (<0.423 and >0.52), the trap depths obtained by using equations (1.22), (1.23) and (1.24) are consistent.

For obtaining trapping parameters from glow curves, the simultaneous equation involving \(E\) (trap-depth) and \(A/B\) (retrapping ratio) were obtained by Moharil and Kathuria (1982, 1983a,b). A method for obtaining \(A/B\) from isothermal decay of TL has also been suggested.

The energy levels involved and the transition are shown in Fig. 1.5.

1.4 THERMOLUMINESCENT MATERIALS

Several materials exhibit TL. Among natural materials selected rocks, minerals, soils, ice and certain plants shows TL after proper excitation; among man-made materials are potteries, ceramics, glasses, a good number of semiconductors
Fig 1.5 Energy levels in the forbidden gap of a solid. $n$, $m$ and $n_c$ are the concentration of trapped electrons, hole centres and free electrons, respectively. $A_m$ and $A_n$ are the recombination and trapping probabilities.
and insulators including polyethylene and PVC. The presence of trace amount of chemical impurities, for example, dysporium (Dy), terbium (Tb) or Samarium (Sm) in fluorites greatly affects TL, sometimes increasing it, sometimes decreasing it. The most important TL material are Lithium fluoride (LiF), Lithium borate (Li$_2$B$_4$O$_7$), Calcium sulphate (CaSO$_4$) and Calcium fluoride (CaF$_2$) etc.

Lithium fluoride was first investigated by Danials et al in 1953. It is an alkali halide with a density of 2.64 gm/cm$^3$ and photon effective atomic number $Z_{\text{eff}} = 8.2$. It is resistant to chemical attack and is only slightly soluble in water. LiF:Mg:Ti is currently the most commonly used family of TL phosphors. Cameron et al (1961) and Harshaw chemicals produced a commercial LiF phosphor as TLD 100 and its isotropic variants TLD 600 and TLD 700.

Lithium-Borate (Li$_2$B$_4$O$_7$) phosphor doped with 0.1% wt/wt manganese was introduced by Schulman et al (1965). It had the advantages of a low effective atomic number, $Z_{\text{eff}} = 7.4$ (slightly lower than that of air), low production costs, simple preparation and good photon energy tissue equivalence; a simple glow peak structure with a composite low temperature, peak between 55$^\circ$C and 90$^\circ$C and a dosimetry peak at 200$^\circ$C, and major disadvantage was its sensitivity. One tenth of LiF due to its yellow/orange spectral emission at 600 nm (Gorbics 1965) and high intrinsic TL efficiency (0.073 compared with 0.04 per LiF).
The calcium sulphate with calcium-fluoride (CaF$_2$) was of the earliest TL material has been used to measure the intensity of ultraviolet radiation. Wantanabe (1951) was the first to prepare synthetic CaSO$_4$ doped with Mg for ionising radiation dosimetry.

The application of fluorites to ionizing radiation dosimetry was reported by Schayes et al (1965). Calcium fluoride (CaF$_2$) is not tissue equivalent and has a photon effective atomic number $Z_{\text{eff}} = 16.3$. It is an extremely sensitive material and generally good displays. They have many advantages: they are cheap, abundant in nature and different fluorites exhibit a complex array of glow peaks, most have thermally stable dosimetry peaks at approximately 260°C and 275°C. Their TL emission is in the ultraviolet blue and green regions of the spectrum.

Beryllium oxide is used extensively as an electrical insulating and refractory materials, and also used as a neutron moderator in nuclear reactors. Few type of BeO used as TL phosphor (Moore 1957, Gammage 1957, Busuoli et al 1977). BeO is tissue-equivalent and consist photon effective number $Z_{\text{eff}} = 7.13$.

Other TL material like Al$_2$O$_3$ is refractory material and is used for many industrial applications. Its various forms contain many different impurities including Ca, Cr, Ti, Ni, Mg, Na and Fe etc. The TL properties of Al$_2$O$_3$ in its various
forms have been investigated (Ricke and Daniels 1957, McDougall and Rudin 1970, Mehta and Sengupta 1976).

Hashizume et al (1971) were the first to manufacture a Magnesium orthosilicate (Mg$_2$SiO$_4$). TL phosphor containing the rare earth terbium as a dopant.

MgB$_4$O$_7$:Dy:Tm was recently produced TL material (Prokic 1980). Its main advantage appear to be a (i) TL sensitivity between 5 and 10 times that of LiF, (ii) Fading similar to that of Li$_2$B$_4$O$_7$:Mn, (iii) Simple annealing indicate that the reproducibility of absorbed dose measurements is very good.

Prokic also developed TL material of CaSO$_4$:Dy:Tm in 1980, is available in the same forms as MgB$_4$O$_7$. Its dosimetry glow peak is at 230°C and the useful measurement range of absorbed dose is 10$^{-6}$-10$^3$ Gy.

Thermoluminescence of alkali-halides, alkaline earth fluorides, calcium sulphate, barium sulphate, aluminium oxide, quartz, diamond, zinc sulphice and calcite has been investigated among many other substances. Atleast 5 (five) bibliographies have been published on TL of various materials and its different aspects (Angilo et al 1965, Lin and Cameron 1968, Spurny 1969, Spurny and Sulcova 1973, Nambi 1975).

1.5 THERMOLUMINESCENCE APPLICATIONS

Solid state luminescence is an area of great scientific
and modern technology and the TL studies is an additional charming feature to its cap. The research on TL may be very useful to obtain some information on the elementary excitation mechanism. Some of the most important TL application is as follows:

1.5-1 RADIATION DOSIMETRY

The first proper application of TL to dosimetry was in 1953, when LiF was used to measure radiation following an atomic weapon test (quoted in Cameron, Suntharalingam and Kenny 1968). LiF was found by Daniels to be a particular good material for use in radiation dosimetry, because of its high sensitivity. This material can be used as small pellets. We used at Hospital of the Oak Ridge Institute of Nuclear Studies to measure internal radiation doses received by cancer patients treated with radioactive isotopes (Daniels, Boyd and Saunders 1953). By having the patients swallow small LiF pellets, which were after passage through the digestive system, the accumulated dose received the patients was obtained by measuring the TL from the pellets and comparing it with that produced in similar crystal which has been irradiated with a known dose of radiations. Many TLD phospor like LiF, CaSO₄, CaF₂ and CaSO₄:Dy have been investigated for the γ-dose estimation. In the absence of any TLD, materials like roof-tiles and wall-bricks could be used to evaluate the radiation dose. Though these materials yield very low TL, it is enough to detect very high radiation dose involved in
nuclear accidents. TLD's are also widely used for radiation dose estimation in medical fields like in diagnostic radiology, radiation therapy and nuclear medicine.

1.5-2 FORENSIC SCIENCE

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 etc. But, quite often, the material available as evidence is very small in quantity. Evidently, TL can offer an effective tool in such comparisons and "source identification". Though very few attempts have been made so far in analysing evidentiary materials, this way, available results indicate that TL can be used as a 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.

1.5-3 AGE DETERMINATION

The application of TL on age determination was first suggested by Daniels and colleagues (Daniels et al 1953), who offered the premise that the natural TL from rocks is directly related to the radioactivity from uranium, thorium and potassium present within the material. This radioactivity results in the accumulation of a so-called "geological-dose", if the rate of irradiation from the radioactive minerals is established, and if the rate of thermal release of the TL
during the rocks irradiation can be shown to be negligible, then the length of time over which the rock has been irradiated can be determined from

\[
\text{age} = \frac{\text{absorbed dose}}{\text{dose rate}}
\]

In this process, we observed civilization more than 10,000 years old, Prof. M.J. Ailken and his group at "Oxford University", England have done pioneering work in the application of TL techniques in archaeology. In India, the BARC and the Physical Research Laboratory, Ahmedabad, have been working in this field.

1:5-4 DEFECT IN SOLIDS

(Experiments on TL can be expected to yield useful information on the properties of various types of defects present in the crystal).

Thermoluminescence's experiments define various types of defect present within an insulator or semiconductor. Wiedeman and Schmidt (1895), show that the TL is particularly sensitive to traces of impurities, the specimen. There have been countless studies on the effect of impurities on TL properties of various materials and not able work of Wicke and colleagues and of Daniels, Cameron and colleagues (for example, Ricke and Daniels 1957). Thus, it is believed that the impurities give rise to the localized energy levels with the forbidden energy, which are very sensitive to TL process. TL technique
is capable of detecting as few as $10^9$ defect levels in a specimen.

### 1.5-5 GEOLOGY

TL study are very useful for Geology, where the potentialities await to be fully exploited are one prospecting and earthquake prediction. However, age determination is not the only ways that TL is utilized in geology. TL is also used for detecting traces of radioactivity in active mineral. 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. Thus, TL has also found use in source identification.

### 1.6 REVIEW AND SCOPE OF THE WORKS ON THE STUDIES OF THE EFFECT OF DEFORMATION ON THERMOLUMINESCENCE

The plastic deformation has considerable influence on the electrical and optical properties of solids. It has been found that the plastic deformation of crystals also affect considerably the TL of crystals. The studies on the influence of plastic deformation on the TL properties of crystals are not only of general scientific interest, but they are also beginning to be of significant practical importance in connection with the creation of efficient new method for the mechanical activation of the various traps present in the solids.
The phenomenon of mechanoluminescence (ML), namely the emission of light during post-irradiation deformation of irradiated alkali halides is well known. This effect has been investigated by various workers (Walton 1977, Chandra 1985, 1996, Molotskii 1981). Mechanoluminescence is believed to arise due to the fact that moving dislocations produced during deformation can capture electrons from F-centres. Thus, the moving dislocations may transport electrons to the recombination centres giving rise to ML or it may be retrapped in some other traps giving rise to new thermoluminescence (TL) peaks. Thus, the post-irradiation deformation may affect considerably the TL of crystals.

The enhanced F-centre coloration in deformed alkali halide crystals has been a topic of considerable interest. Since approximately the same amount of enhancement could be introduced by merely heating and slowly cooling the undeformed crystals initially the enhancement in early stage of coloration was attributed to the break up and dispersion of small precipitates of impurity already known to have a strong influence on the early stage coloration rather than to the vacancies created by dislocation interaction. Later on an exclusive study was made on the growing of the F-band in undeformed, deformed and heat-treated crystals between liquid hydrogen temperature and room temperature. The similarity in forms and temperature dependence of the initial coloration in a freshly cleaved crystal and the coloration after plastic
deformation suggested that both the early and late stages of coloration obtain vacancies from the same source, and it has been concluded that the source of vacancies is dislocation debris resulting from dislocation interaction and not from the dislocation lines themselves. The effect of pre-irradiation deformation on TL should be related to the enhanced darkenability of deformed crystals.

The two cases namely the deformation prior to irradiation and deformation subsequent to irradiation are related to one another but differ slightly. Deformation prior to irradiation modifies the existing traps and/or create new traps which then can be filled during irradiation, however, the deformation subsequent to irradiation modifies the existing traps create new but unfilled traps, and/or cause a redistribution of trapped electrons or holes among these traps due to the passage of dislocations in the vicinity of the traps.

Panizza in 1964 was the first to report that the plastic deformation may change considerably the TL of crystals. Jain and Mahendru (1965) have studied the influence of plastic deformation on the thermoluminescence of pure KCl crystals. Two TL peaks are observed one at 135°C and the other at 190°C. Plastic deformation introduced a new peak at 270°C. The growth of 135 and 190°C peaks are suppressed by the plastic deformation of crystals. The results obtained with the crystals deformed after irradiation show that the both peaks
gets reduced and the $270^\circ C$ peak increases with the deformation of the crystal. It is shown that because of the heat generated or other unknown factor the second stage F-centre bleach and the electrons liberated from the F-centres are trapped in the new vacancies generated during the deformation process to form the centres giving rise to the $270^\circ C$ peak.

Ausin and Alvarez-Rivas (1973) have studied the effect of plastic deformation on the thermoluminescence of $\gamma$-irradiated KCl crystals. The effect of plastic deformation on the thermoluminescence of normally pure Harashaw KCl samples $\gamma$-irradiated at room temperature has been studied up to $450^\circ C$. In samples plastically strained prior to irradiation, a new glow peak appears. It has been found that this glow peak does not follow either first or second order kinetics. It is shown that the phosphorescence decay curves of the glow peak are the superposition of five exponential processes. The activation energies and the pre-exponential factors of these decays are given. Besides these glow peaks, in samples strained after irradiation a glow peak at higher temperature has been observed, which follows second order kinetics. The study of thermal annealing of the F-centres while the temperature of the sample is linearly increased shows that there is an annealing step corresponding to each strain-induced glow peak. These results are discussed to explain the thermoluminescence of as cleaved $\gamma$-irradiated samples. It is reported that the F-centre behaves as a
recombination centre for the interstitial atoms thermally released from traps. At some stage in this process an electron-hole recombination takes place and light is emitted. The relation of these results to the well-known enhancement of the F-colorability by ionizing radiation and also to the enhanced thermal stability of the F-centres in plastically deformed samples is discussed.

Srinivasan and Dewerd (1973) have investigated the effect of plastic deformation on the thermoluminescence of LiF (TLD-100) single crystals. It is shown that without exposure to ionizing radiation, plastic deformation up to fracture does not induce a thermoluminescence response. After subsequent exposure to ionizing radiation the intensity of the thermoluminescence glow peak decreases with the amount of plastic deformation. This is explained in terms of a relative decrease in the concentration of free dipoles and low-order dipole complexes which act as trapping centres for peaks II and V. This decrease is shown to be associated with an interaction of these defect structures with the dislocations introduced during deformation.

Bradbury and Lilley (1976) have studied the effect of deformation on the thermoluminescence of LiF and TLD-100 dosimeter crystals. The response to ionizing radiation of LiF and TLD-100 dosimeter grade LiF, following various amounts of plastic deformation has been investigated. The decrease in thermoluminescence with increasing plastic strain has been
interpreted in terms of following two models: (i) the thermoluminescence traps are destroyed by intersection or interaction with dislocation lines and, (ii) New thermoluminescence traps are created by dislocation intersection which then compete with the previously existing traps. The latter model has been found to be more applicable.

Dewerd et al (1976) have studied the relation between deformation and thermoluminescence defect centres in LiF (TLD-100). The plastic deformation after exposure to ionizing radiation is shown to increase the F-band absorption in LiF (TLD-100) while decreasing the absorptions at 310 and 380 nm which are related to thermoluminescent traps. The rate of change with deformation of the three bands indicates that F-centres are created when 310 and 380 nm absorption centres are destroyed. The results are interpreted in terms of removal of F-centres from the defect complexes causing the 310 and 380 nm absorption bands. This implies that the F-centres may be an integral part of the thermoluminescence traps in this material.

Hook III and Drickamer (1978) have studied the TL of ZnS, ZnS:Cu:Cl and ZnS:Ag:Cl as a function of pressure to 40 Kbars. The major features of the TL spectra were a low temperature peak which shifted to lower temperature with increasing pressure and a high temperature peak which shifted rapidly to higher temperature. They found that entire spectrum decreased in intensity which is consistent with Houses measurements of steady state intensity.
Kos and Mieke (1978) have reported the effect of deformation on the thermoluminescence of titanium doped LiF. It is shown that the glow curve of an undeformed LiF:Ti sample consists of two peaks, one at 120°C and the other at 170°C. It has been found that the plastic deformation suppresses both the peaks to a degree dependent on the applied stress deformation. The higher temperature 170°C peak is affected more than the low temperature peak (at 120°C). Plastic deformation results in the production of additional vacancies due to dislocation interactions. It is assumed that only the additional anion vacancies are important for the decrease of the TL because the occupation of these additional anion vacancies by electrons leads to an enhancement of F-centres, thus increasing the non-radiative transitions. In the case of deformation prior to irradiation not only the original anion vacancies form F-centres during irradiation but also the additional anion vacancies are responsible. This results in the increase of the ratio of non-radiative to radiative transitions and accordingly the TL decreases. In case of deformation subsequent to irradiation only the original anion vacancies are converted to F-centres. On heating the crystal a number of electrons liberated from Ti$^{3+}$ centres are captured by the additional anion vacancies and so lost for radiative transitions. Gartia et al (1982) have shown that the post-irradiation deformation affects considerably the TL of Ca doped NaCl.
Kirk (1979) stated that controlled deformation places various dislocation densities within the solids. The dislocations so formed in ionic solids can act as paths of enhanced mobility for point defects.

Jain (1982) studied the effect of plastic deformation on the TL of pure and doped LiF crystals before and after irradiation. His results indicated that there is a linear relationship between normalized peak height and plastic strain.

Gartia et al (1982) studied the effect of deformation on TL in NaCl:Ca\(^{2+}\) crystals and have shown that a new TL peak can be stimulated by the deformation, which may be termed as deformation stimulated TL.

Elyas et al (1983) have studied thermoluminescence of coloured alkali halide crystals after plastic deformation. Change in the thermoluminescence intensity and the glow profile are found due to the plastic deformation caused by the application of periodic uniaxial pressure in X-irradiated KBr, KCl, KI, LiF, TLD-100 and NaCl crystals. Trap-destruction model and trap competition model have been discussed for the decrease in the TL intensity of the crystals. The increase in TL intensity of some of the glow peaks is possible by the creation of new defects which act as traps, which are intrinsic in the crystal. If during the plastic deformation some of the interstitial atoms are released from one trap and
are retrapped again in some other trap, then the TL intensity corresponding to the first trap may decrease and the TL intensity corresponding to the other trap may increase. If the deformation of a crystal creates some traps which are different in energy than the intrinsic traps, then a new glow peak may appear.

Manam et al (1983) studied the effect of post-irradiation deformation on TL spectra of KCl:Ca. Deformation does not cause any appreciable change in the recombination mechanisms and sites as revealed by the occurrence of the peaks in TL emission in the same spectral region. They concluded that the deformation causes only a preferential redistribution of the traps.

Chandra et al (1983) have studied the effect of plastic deformation on the thermoluminescence of γ-irradiated NaCl and KCl crystals. The overall thermoluminescence (TL) intensity of γ-irradiated NaCl crystals initially increases and then decreases with the number of newly created dislocations. However, the overall TL intensity of γ-irradiated KCl crystals increases with the increasing number of newly created dislocations. The TL spectra are recorded for different plastic deformation at different temperatures. It is found that the plastic deformation has no considerable effect on the TL spectra of γ-irradiated NaCl and KCl crystals. Trap-destruction model and trap-competition model are discussed for the decreases in the TL intensity with
deformation of the crystals. The physical ideas behind the
increase in the relative intensity of glow peaks and the
appearance of new glow peaks are explored.

Joshi and his coworkers (1984) have found that the
defformation induced TL of NaCl:Ca (T) exhibits marked changes
in its pattern when subjected to thermal cycling. This is
suggested to be due to the break-up of the impurity-vacancy
dipole aggregates and subsequent rearrangement of the free
dipoles.

Narasimha Reddy and Subba Rao (1984) made an interesting
investigation on influence of plastic deformation on post
$\gamma$-irradiation TL of NaCl:Ba crystals. They observed that in
the glow of deformed crystal low temperature peak decreases
and a new peak appears at high temperature. They concluded
that the peak appears due to creation of new traps by
deformation which are filled up by F-centre electrons
liberated from traps responsible for low temperature peak
because of passage of moving dislocation (created during
deformation), in the vicinity of traps.

Acharya et al (1985) have studied the effect of plastic
deformation on the thermally stimulated luminescence of KCl:Sn
single crystals. A plastically deformed single crystal of KCl
doped with SnCl$_2$ and briefly exposed to X-rays yielded three
glow peaks at 63, 110 and 210°C. The glow peaks at 110 and
210°C show emission bands at 520, 415 and 390 nm. The 415 nm
emission dominates at 210°C and the 390 nm dominates at 110°C. The plastic deformation and subsequent annealing do not change the emission spectra. Further irradiation of F-bleached sample enhances the 63°C glow peak. Based on these observations the role of plastic deformation in the mechanism of coloration of KCl:Sn system has been discussed.

Manam and Ratnam (1985) have investigated the effect of post-irradiation deformation on the thermally stimulated luminescence of KCl:Na crystals. It is reported that the deformation does not appreciably alter the mechanism and the site of recombination as is indicated by the occurrence of TL emissions in the same spectral regions in undeformed and deformed crystals. It, however, causes a preferential redistribution of traps as is shown by the changes in the relative intensities of these emissions. Results of deformation induced TL glow curves together with TL spectra lead them to conclude that early (first) stage and late (second) stage F-centres are responsible for the 435 and 540 nm emissions, respectively in these crystals.

Getkin and Shiran (1986) investigated the effect of post irradiation deformation on the TL of nominally of dislocations (due to deformation) in irradiated crystals was accompanied by the charge transfer from colour centres to vacancy clusters formed during the deformation. The process of charge transfer was found to be non-radiative.
In most of the cases the materials investigated were in the form of powders (Moharil and Deshmukh 1967, 1977, Moharil et al 1979, Kamavisadar 1982) and for this reason, a surface effect is probably more likely to be the cause than the processes involving dislocations.

Sayanna and Reddy (1987) have studied the effects of mechanical and thermal deformation on the thermoluminescence of KCl:Mn crystals. The effect of pre- and post-irradiation deformation on KCl:Mn crystals has been investigated. Two glow peaks around 85°C and 190°C were observed. In crystals deformed prior or after the irradiation, a new glow peak is observed around 215°C. When the as-received crystal was quenched from 500°C, again the TL peaks at 85°C and 190°C were observed, however, a new peak around 215°C was emerged. This investigation has shown that TL peak around 215°C, which was not present in as irradiated samples can be created by pre- or post-irradiation deformation or by thermal deformation (quenching). These results are explained on the basis of the distribution of dislocations and dipoles under the stress and thermal conditions.

Patey et al (1989) observed interesting changes in the TL intensities of single crystals microcrystalline powders of alkali-halides. The TL intensities of alkali halide powders were found to be much smaller than those for single crystals. The decrease in the intensity was found to be more for finer
particles. The percentage of decrease of TL output for different peaks of the same materials was found to be different. Inspite of their interesting observations, Patel et al (1989) failed to give any specific reasons for the dependence of the intensity of glow peaks on the particle size; but felt that their studies could give fillip to further experiments on similar lines in getting the information about the difference between single crystals and powders in the context of defect-creation, creation, stabilisation, ionisation, recombination etc.

Gopal Reddy and Narasimha Reddy (1991) have studied the TL in plastically deformed NaCl crystals doped with 1 mole% of yttrium. In plastically deformed crystals, they observed four glow peaks at 55, 70, 130, and 190°C, they reported that plastic deformation not only enhanced the TL output of 70 and 130°C peaks but also after their peak positions. They attributed this shift in peak positions to the perturbation at th emitting sites caused during the redistribution of defect centres on staining the crystal.

Baer and Drickamer (1991) have reported the effect of pressure on the TL of various alkali halide crystals. The temperature dependence of the TL was shown to be greatly affected by pressure and there is a large decrease in the peak temperatures and trap depth of potassium halides at their transition pressure which is approximately 1.9 GPa. They have also shown that there are significant increase in the
calculated trap depths of alkali halides in the NaCl structure. They tried to explain the results on the basis of model proposed by Ausin and Rivas according to that if the halogen atoms are mobile, then increasing the pressure would make it more difficult for those atoms to move from one interstitial site to the other and phase transition would change the relative location of all the interstitial sites. It was shown that KCl has an increase in the cation to anion distance at the transition and this may account for the decrease in peak temperature. Further, they have shown that the glow peak due to plastic deformation in common, but not well understood.

Baer and Drickamer (1992) have also observed the shift in the temperature of glow peaks of γ- and X-irradiated quartz as a function of pressure. It is observed that an increase in pressure increases the glow peak temperature, but decreases the trap depth. This suggest that the TL is not due to any one step process. They concluded that creation of oxygen vacancies cannot be responsible for the TL causes. Further, they realized that the ambiguities in the literature make it difficult to assess their results on the 180°C glow peak of quartz.

Recently, Zakrevskii et al (1995) have studied the effect of deformation on the thermoluminescence of irradiated LiF crystals. It ahas been shown that the plastic deformation of irradiated alkali halide crystals destroys colour centres
which one effective barriers for moving dislocations, namely, impurity electron and hole colour centres. It is concluded that the elastic interaction of a colour centre with a dislocation in the process of its deformational destruction is important.

The pressure affects considerably the natural TL (arising out of internal and external irradiation from different sources over geological times) exhibited by mineral samples. D'Albissen and Fornaca-Rinaldi (1968) have reported that the natural TL of CaCO$_3$ is optimum for a particular value of the applied stress. Nambi et al (1977) have shown that in some minerals the applied pressure may create permanent lattice defects which can directly aid or kill the TL process in the mineral. This leads to what is known as sensitisation/desensitisation of TL material by stress application.

The investigation of the effect of plastic deformation on the TL of crystals may be important for the following points of views:

(i) In modern technology we encounter with increasing frequency the situation when materials experience ionizing radiations and are also subjected to mechanical stresses, that cause their plastic deformation. This makes it necessary to investigate these
effects simultaneously and estimate the participation in the radiation defect formation of plastic deformation and also the influence of radiation defects on the properties of crystals.

(ii) Any systematic work on the effect of mechanical treatment on the thermoluminescence (TL) should include the extent of mechanical treatment done on the samples, such as how much shaking, rubbing etc. had been done and whether or not such mechanical treatment has given uniformly to all parts of the sample. Such work should attempt to determine the TL as a function of degree of mechanical treatment or pressure given to the samples.

(iii) Although in normal use, dosimeter crystals are not deformed, however, rapid cooling following annealing can cause the generation of dislocation densities equivalent to several percent plastic strain. This needs that the dependence of TL intensity of the dosimeter materials on the plastic deformation should be well known.

(iv) The mechanical bleaching effect in r-irradiated alkali halide was found to be as
high as 40%, which has direct bearing on certain applications. In the TL dating of lunar and terrestrial rocks, this effect would introduce significant errors due to the lack of knowledge of the strain history of the material and accordingly the amount of bleaching of the natural radiations dose received by the materials on which dating calculations are based. Similarly, it is necessary to know the mechanical history of the materials used in environmental dosimetry, personal dosimetry and accidental dosimetry.

(v) The study of effect of plastic deformation on the TL of materials may be useful in criminology in the following way. During any accident materials get deformed. If the TL of deformed material will be checked it may give indication of the direction and strength of the shock occurred during the accident. The measurement of the TL of deformed material chosen from the accidental place may possess the stress and the direction in its memory which can be recorded from the TL measurement. It is expected that the systematic study may also indicate the time duration between the accident and the time of analysis.
Now a days TL is used in the dating of the archaeological objects. During the span of their life, the archaeological object might have received shocks due to earthquakes, volcanic eruptions etc. Thus, they might have suffered deformation bleaching and their age determined from TL technique may be faulty. If the deformation of the material is known and furthermore if there is a calibration chart regarding the dependence of TL intensity on the deformation of the crystal, the faulty age determined may be corrected.

The pre-irradiation deformation has general tendency to increase the TL intensity and post-irradiation deformation has general tendency to decrease the TL intensity. However, some of the TL peaks changes in an unpredicted manner. To date the science of the effect of plastic deformation on the TL of crystals is least understood. This needs a systematic and detailed investigation.

It is expected that from the successful study of effect of plastic deformation on the TL of materials, it will be possible to design a TL dosimeter whose response will be unaffected by the plastic deformation.
The successful study of effect of plastic deformation on the TL of materials may provide sufficient information regarding the deformation bleaching, deformation luminescence, isothermal decay of coloration in micro-crystalline powders, dislocation exo-electron emission etc.

The study of pre- and post-irradiation deformation effects on TL may be helpful in understanding the kinetics and mechanisms of TL.

The investigation shows that the TL intensity may get affected significantly by the mechanical or thermal deformation occurring prior to irradiation or after the irradiation. Therefore, it is desirable to search and use such dosimeter materials whose TL intensity is independent of deformation.

The influence of plastic deformation on the course of photo-chemical coloration (radiolysis) of alkali halides as well as the inverse interaction between radiation defects and moving dislocation has excited interest of many years (Clark and Crawford 1973, Moharil et al 1979a,b, Deshmukh et al 1983, 84). In this regard, the effect of deformation on the coloration process have primarily been used as tools for
investigating the interaction of dislocations with colour centres. The study of luminescence induced during plastic deformation of coloured alkali halide crystals has clearly indicated that the dislocation colour centre interaction is involved in causing this process (Metz et al 1957, Leider 1958, Butler 1966, Shmurak and Eliasberg 1967, Alzetta et al 1970 and Chandra 1996).

1.7 OBJECTIVES OF THE PRESENT INVESTIGATION

There have been done number of studies on the thermoluminescence (TL) of irradiated crystals for the last three decades. At present, the TL phenomenon of different materials is widely used in measurement of radiation doses and in dating of archaeological and geological materials.

The TL phenomenon was initially concerned with the studies on the effect of dopants, irradiation time, emission spectra on the sample of different materials. It is speculated that the studies on the effect of deformation on TL properties of materials may help in understanding the exact mechanism of TL.

In modern technology, we encounter with increasing frequency the situation when material experience ionizing radiations and are also subjected to mechanical stresses that cause their plastic deformation. This makes it necessary to investigate these effects simultaneously and estimate the
participation, in the radiation defect formation, of plastic deformation and also the influence of radiation defects on the elastic properties. Some preliminary investigations have been made in this direction and it is found that the mechanical bleaching effect in some TL materials may be as high as 40% which has direct bearing on certain applications. In the TL dating of Lunar and Terrestrial rock, this effect would introduce significant errors due to lack of knowledge of the strain history of material and accordingly it may cause error in accounting the radiation dose received by the materials on the dating calculation. It is also necessary to know the mechanical history of TL materials used in different fields, i.e., in environmental monitoring, personnel monitoring, in radiation therapy and in accidental dosimetry.

Although in normal use, dosimeter crystals are not deformed, however, rapid cooling following annealing can cause the generation of dislocation densities equivalent to several percent plastic strain. This needs that the dependence of TL intensity of the dosimeter materials on the plastic deformation should be well known.

The mechanical bleaching effect in γ-irradiated alkali halide was found to be as high as 40%, which has direct bearing on certain applications. In the TL dating of lunar and terrestrial rocks, this effect would introduce significant errors due to the lack of knowledge of the strain history of the material and accordingly the amount of bleaching of the
neutral radiations dose received by the materials on which
dating calculations are based. Similarly, it is necessary to
know the mechanical history of the materials used in
environmental dosimetry, personnel dosimetry and accidental
dosimetry.

It is expected that from the successful study of plastic
defformation on the TL of materials, it will be possible to
design a TL dosimeter whose response will be unaffected by the
plastic deformation. Furthermore, the study of pre- and
post-irradiation deformation effects on TL may be helpful in
understanding the kinetics and mechanism of TL.

Now a days, TL is useful in the dating of the
archaeological objects. During the span of their life, the
archaeological objects might have received shocks due to
earthquakes, volcanic eruptions etc. Thus, they might have
suffered deformation bleaching and their age determined from
TL technique may be faulty. If the deformation of the material
is known and furthermore if there is a calibration chart
regarding the dependence of TL intensity on the deformation of
the crystal, the faulty age determined may be corrected.

The effect of deformation in solid is connected with
structural and electronic excitation process. Any systematic
work on the effort of mechanical treatment on TL should be
studied on the extent of mechanical treatment done on the
samples. Such mechanical phenomena of shocking, rubbing etc.
has to be studied on different conditions. Such as studies on the thermoluminescence (TL) as a function of degree of mechanical treatment and pressure is important. The objective of the present investigation is to understand the effect of pre- and post-irradiation deformation on the thermoluminescence (TL) and TL spectra of KCl:KBr mixed crystals. The study has been made with respect to the following points:

(i) Growth and characterisation of KCl:KBr mixed crystals

(ii) To understand the mechanism of TL in KCl:KBr mixed crystals

(iii) Effect of pre-irradiation deformation on the TL of KCl:KBr mixed crystals

(iv) Effect of post-irradiation deformation on the TL of KCl:KBr mixed crystals

(v) Theoretical approach to the effect of pre- and post-irradiation deformation on the TL of KCl:KBr mixed crystals.