CHAPTER I
INTRODUCTION AND REVIEW OF LITERATURE

1.1 INTRODUCTION

Thermoluminescence (TL) is known\(^{(1)}\) to have been first observed by Robert Boyle in 1669. He reported to Royal Society in London about a feeble light emitted by a diamond piece when it is warmed in dark. Much work was not done on the TL phenomenon or its applications for quite long time later. It is only during the last two decades that the progress in TL research and its applications has accelerated\(^{(1-5)}\) phenomenally.

TL is exhibited by a host of minerals, organic crystals, glasses, ceramics, organic compounds and biochemicals. The most widely studied materials for their TL characteristics are CaF\(_2\), LiF, Mg\(_2\)SiO\(_4\), LiB\(_4\)O\(_7\), CaSO\(_4\), etc. TL of minerals like quartz, Al\(_2\)O\(_3\), Calcite, Zircon etc. is studied because of its importance in archaeological and geological applications.

1.1.1 THERMOLUMINESCENCE - DEFINITION AND MECHANISM

Thermoluminescence can be defined as the thermally stimulated release of stored energy in the form of light from a pre-excited material. The phenomenon of TL in inorganic di-electrics is explained with the aid of band theory of solids. The large forbidden energy gap (\(\sim 10 \text{ ev}\)) between the conduction and the valence bands is considered
to have many localised metastable energy levels because of the defects due to impurities present in the crystal lattice. It is these levels which are responsible for the emission of TL (Figure 1.1).

On interaction of ionizing radiations, the electrons from the Valence Band (VB) are released into the Conduction Band (CB) leaving a free Hole (H) behind. A number of these liberated charge carriers namely the Electrons (E) and the Holes recombine releasing energy in the form of light (called fluorescence). Some of these are however trapped at the localised energy levels called Traps (T).

If the traps are not deep enough, the charge carriers get released (de-trapped) by thermal agitation even at room temperature giving rise to the emission of light called phosphorescence or delayed emission. In the case of deeper traps larger stimulating energy is required to release the trapped carriers. In such a case when the crystal is heated, either the electrons or the holes (whichever is trapped with less trap-depth) will be ejected out to the traps. This in turn recombines with the charge carrier in the oppositely charged trap.
FIG. 11. SCHEMATIC REPRESENTATION OF THE MECHANISM OF THERMOLUMINESCENCE DURING IRRADIATION AND HEATING.
This recombination produces the emission called Thermoluminescence. The location of recombination usually contains an impurity which acts as the actual emission centre.

1.1.2 Glow Curve and Glow Peak:

The intensity of TL light (I) against the sample temperature is called TL glow curve. A typical glow curve of a natural quartz is shown in Figure 1.2. The individual peaks in the glow curve are called the TL glow peaks. The temperature at the maximum of the glow peak is the measure of the detrapping energy of the charge carrier (thermal activation energy) and the intensity is a function of the number of charge carriers.

Whenever a trapped charge carrier is released by thermal activation, the only available approach is to consider the probability of finding these in a particular potential energy arrangement with a Maxwellian distribution of energies at various temperatures. If we consider a trap with a trap depth $E$, the probability of finding the trapped charge carriers with these energy $E$ (for detrapping) increases exponentially by:
FIG-1.2. A TYPICAL GLOW CURVE OF NATURAL PINK QUARTZ

TEST EXPOSURE: $2.7 \times 10^4 R$
and thus the probability of escape (detrapping) is:

\[ p = s e^{-E/kT} \]  

(2)

where:

- \( p \) = probability of escape
- \( s \) = frequency factor of the trap (dimension: sec\(^{-1}\))
- \( E \) = Trap depth
- \( k \) = Boltzman's constant
- \( T \) = temperature \( \text{K} \)

It is reasonable to understand the probability as the inverse of the average life \( \tau \) of the charge carriers in the trap at a temperature \( T \), as:

\[ \frac{1}{\tau} = p = s e^{-E/kT} \]  

(3)

1.1.3 EFFECT OF ORDER OF KINETICS ON GLOW PEAKS

Randall and Wilkins\(^{(6)}\) provided the simplest derivation for Thermoluminescence. The basic assumptions they put forward were that once an electron escape from a trap there is no possibility for it to get re-trapped and that the luminescence intensity at any temperature is proportional to the rate of de-trapping.
If $n$ is the concentration of the filled trap at any time $t$ (at temperature $T$), then the intensity ($I$) of TL is given by:

$$I \propto \frac{dn}{dt} \quad \text{OR} \quad \cdots \quad \cdots (4)$$

$$I = -c \frac{dn}{dt} \quad \cdots \quad \cdots (5)$$

where $c$ is the proportionality factor which includes the radiative transmission probability and the minus sign indicate the decrease of $n$ with time.

Assuming a linear heating rate $q$,

$$T = T_0 + qt \quad \cdots \quad \cdots (6)$$

where $T_0$ is the initial temperature.

It can be shown that:

$$n = n_0 \exp \left[ - \int_{T_0}^T \frac{s}{q} e^{E/kT} \, dT' \right] \quad (7)$$

OR

$$I = n_0 s e^{-E/kT} \exp \left[ \int_{T_0}^T \frac{s}{q} e^{-E/kT'} \, dT' \right] \quad (8)$$

where $n_0$ is the initial number of trapped electrons at a fixed temperature $T_0$; $s e^{-E/kT}$ is a constant at any fixed temperature and if taken as $\Lambda$

$$\frac{dn}{n} = -\Lambda \, dt \quad \cdots \quad \cdots (9)$$

which on integration gives:

$$n = n_0 \ e^{-\Lambda t} \quad \cdots \quad \cdots (10)$$

from equation 5 and 9

$$I = -c \ \frac{dn}{dt} = -c n_0 \Lambda$$
From equation 10 and 11 we get a relation
\[ I = I_o e^{-\lambda t} \] \hspace{1cm} (12)

where \( I_o = A n_o \)

Thus at a fixed temperature \( T \), TL intensity decays exponentially and this TL process is said to be following the **FIRST ORDER** kinetics. The first order kinetic process of TL basically has the assumption that once an electron escapes from a trap, there is no significant probability of its returning to the same trap.

Garlik and Gibson\(^{69}\) considered the case where a free electron has equal probability for going to recombination (luminescence) centre and getting re-trapped. If \( N \) is the total number of traps per \( \text{cm}^3 \) of which \( n \) are occupied at time \( t \); the probability of the released electron going to the recombination centre is:

\[ \frac{n}{N-n+n} = \frac{n}{N} \]

Therefore

\[ I = c \frac{dn}{dt} \cdot \frac{n}{N} = -c s e^{-E/kT} \frac{n^2}{N} \] \hspace{1cm} (13)

By integrating the equation for a temperature range of \( T_0 \) to \( T \).
\[ I = \frac{n_0^2 \cdot s' \cdot e^{-E/kT}}{1 + s' \cdot n_0 \int_0^T \exp \left( -\frac{E}{kT'} \right) dT'}^2 \quad \text{...(14)} \]

where

\[ S' = \frac{s}{N} \]

called the pre-exponential constant

and has a unit cm\(^3\)/sec.

At a fixed temperature \( T \), equation for the TL intensity can be derived as:

\[ I = \frac{T_0}{(1 + A'_t n_0 t)^2} \quad \text{...(15)} \]

where

\[ A'_t = cs' \cdot e^{-E/kT} \]

This process of luminescence is called to follow second order kinetics.

In many cases the process follows neither the first order nor the second order kinetics. May and Partridge\(^{(72)}\) gave the following equation for \( I \) which follows any non-first order process.

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

\[ I = -cs'n \cdot \exp \left( -\frac{E}{kT} \right) \quad \text{..... (16)} \]

where \( l = \text{order of kinetics which can have any value.} \)

Solving the equation we get the value of \( I \) as:

\[ I = s' n_0^l c \exp \left( -\frac{E}{kT} \right) \left[ \left( \frac{(l-1)s'}{q} \right) \left( n_0 \right)^{l-1} \int_0^T \exp \left( -\frac{E}{kT'} \right) dT' + 1 \right]^{-1/(l-1)} \quad \text{...(17)} \]
\( \gamma \) has the dimension \( \text{sec}^{-1} \) and is similar to frequency factor \( s \) of first order kinetics. Therefore:

\[
I = C s n_o \exp \left( -\frac{E}{kT} \right) \left[ \frac{(l-1)s}{q} \int_T^\infty \exp \left( -\frac{E}{kT'} \right) dT' + 1 \right] -l(l-1) \quad \ldots \quad (18)
\]

This equation is not valid for \( l=1 \) but as \( l \) approaches 1, it becomes similar to the first order case.

1.2 REVIEW OF LITERATURE

1.2.1 Earlier Studies on Defect Centres in Quartz

Emission of TL is related to the bleaching of the colour centres. In this section the colour centre studies are therefore summarised.

The early studies on quartz includes the work of Cohen \( (25) \) and Holden \( (7-9) \). These studies mainly deal with colouration and its interpretation in quartz. Later, Forman \( (10) \) gave an explanation to the colouration induced by irradiation. According to him, what happens in \( \text{SiO}_2 \) is that when an ionizing radiation enters the crystal lattice, the host atoms are ionised and the electrons liberated may have sufficient energy to migrate through a small distance inside the crystal and get either trapped or recombined with parent type atom. It may take a permanent place in between the lattice molecules and produce a colour centre.
Even though there are different views about the origin of the colour of quartz the most prominent hypothesis is that the different colour centres in different natural quartz samples are due to different impurities (4, 11-16). The impurities are incorporated during the crystal growth e.g. Co$^{2+}$ in blue quartz (14). There is a correlation between the irradiation response and the temperature of formation since the latter factor influences the solid solubility of impurity in quartz (16). Quartz formed at low temperature especially at a non-aluminous environment shows a very weak irradiation response. Schnaat (17) explains the electronic structure of the trapped hole centre in smoky quartz. The formation of colour centres in this sample is explained to be due to the unpaired hole trapped at different types of oxygen ligands around the Al impurity. O'Brien (18), Weil (24) and Leitz (19) explain the colour centre formations in smoky quartz as due to Al impurity in the lattice. The role of interstitial alkali ions in the formation of colour centres is studied by Anderson (20), Wright (21) and Barry (22). Ichikawa (23) explains the mechanism as due to the disturbed net work in the vicinity of Li$^+$ and Na$^+$ impurity ions. Medlin (4, 11) and others tried to explain the mechanism by correlating the impurities with
creation of trapping centres. It was known\(^{(16)}\) that impurities can improve the TL output considerably. Our observation\(^{(5)}\) also showed the same.

1.2.2 Thermal Sensitisation

Heat treatment on the mineral quartz will change its structure\(^{(108)}\) to different polimorphs of quartz. These crystalline forms are created by the temperature of formation and its mode of cooling. The different polimorphs found in nature are low quartz (\(\alpha\text{-quartz}\)), high quartz (\(\beta\text{-quartz}\)), tridymite, cristobalite etc.

A major part of the naturally available quartz is low quartz. Its stability goes up to 573.4°C under normal pressure. It belongs to the trioganal system, point group 32. The three fold (optical) axis is called c-axis, the three two fold axes perpendicular to it are the a-axes. The unit cell contains three formula units, each Si is situated on one of the two fold axes and surrounded by an almost regular tetra hedron of oxygen. Each oxygen is shared by two silicon atoms. In addition to the silicon sites there are interstitial sites in the channels along the optical axis that may be occupied by impurity ions (Figure 1.3). Low quartz can convert itself to a high quartz on heating beyond 573.4°C. Similarly a high quartz can change over to a low quartz.
FIG 1.3 A DRAWING OF ALPHA QUARTZ STRUCTURE SHOWING HOW THE ATOMS ARE PACKED TOGETHER

○ Silicon ○ Oxygen
on cooling down. So this temperature at which the conversion takes place is usually termed as the "inversion point" of quartz.

The high-low inversion of quartz involves a change in bond angle and length. Si atom shifts its position in such a way as to destroy one set of two fold axis and to convert the six fold axis to three fold axis without breaking the Si-O-Si bonds. (Figure 1.4). The unit cell dimension decreases when a high quartz change over to low quartz. The changes are purely reversible if the temperature is brought down very slowly and none of the properties are permanently altered. 

The presence of duaphine twinning is usually seen in high quartz and it is suggested that this is produced at the inversion temperature.

The inversion temperature is considered to be a constant for a natural quartz. But it is known that the inversion temperature is sensitive to the impurities present in the crystal, particularly Al. A single crystal of quartz with different growth zones shows that the inversion points for each growth zone differs from each other. Analysis shows that the amount of Al impurities vary from zone to zone.
FIG 1.4 A DRAWING OF BETA QUARTZ STRUCTURE SHOWING HOW THE ATOMS ARE PACKED TOGETHER

• Silicon  ○ Oxygen
On further heating beyond 870°C the high quartz will change over to tridymite. This form of quartz have three different phases; low-middle and high forms of tridymite, depending upon its heating temperature.

There are many other high temperature forms of quartz namely, Crystobalite, Coesite, Keatite and Stishovite etc.

Even though there exist many forms of quartz, it is the only stable mineral found commonly in the nature.

Effects of thermal treatment on its TL characteristics are studied by many workers in the past. Ichikawa\(^2\) observed enhancement in TL output of 110°C peak on preheating of the sample. He observed a sudden change in sensitisation after heating around 573°C. He explains the effect as due to imperfections produced by effects of annealing.

Effect of preheating of the sample on TL sensitivity of all individual peaks are studied by Kaul\(^2\) et al. It is observed that the TL intensity of various peaks increases with heating temperature and maximum effect was observed in Peak no. 3 which appears around 240°C.

Kaul\(^2\) studied the effect of various parameters like heating rate, duration of heating etc. on glow
peaks of quartz. He observed the degree of variation in TL peaks inversely related to the glow peak temperature.

Thermal sensitisation of 100°C peak of a pink quartz is observed by McDougal(28) and maximum sensitisation was observed by treatment at 400°C before the exciting radiation exposure.

Even though earlier workers could show the effect of thermal treatments on individual peaks, the effect of heating on the integrated TL and its correlation with the phase transformations at 573°C and 870°C is not clearly described. Apart from showing the correlation on the effect of cooling rate, the effect of duration of heating is also studied in this thesis.

Effect of heating rate during pre-irradiation treatment on the TL intensity is shown by Kaul(27) on different TL peaks of quartz. He observed greater sensitisation by faster heating during the pre-irradiation treatment.

1.2.3 Radiation Effects:

It is known(16,58-61) that quartz is coloured when exposed to ionizing radiations and that it can be bleached(29) by heating or by exposing it to uv light.

It is possible to sensitise the TL output by pre-gamma ray irradiation. Ichikawa(26) observed this
phenomenon in a sample of natural quartz. He found a sensitisation of 300 times for a pre-dose of 6x10^6 R. He assumes that the impurities and lattice defects existing in natural sample play an important role in the formation of imperfection by multiple ionization of negative impurities and its subsequent displacement into interstitial positions and thus producing some rearrangements in the chemical bonds. The sensitisation phenomenon is attributed to creation of new trapping centres by Kaul et al, while Durrani et al explained it as due to the damage of Al/alkali recombination centres. The sensitisation phenomenon is used for heat resistant dosimetry by Fleming et al. They observed that there is no annealing procedure which can desensitise the radiation induced sensitisation. McDougall also found similar results. Present work shows that although the radiation induced sensitisation is highly resistant to temperature treatment, prolonged heating as well as uv exposure reverse the enhanced sensitivity towards the original level.

The sensitisation of the 100°C peak subsequent to an annealing treatment was observed by Zimmerman. She explains the phenomenon as due to the intrinsic change in the concentration of the luminescence centres.
She supported her hypothesis with TSEE observations. Fleming(35) used this phenomenon for dating of pottery samples. None of these studies seems to have arrived at the optimum heat treatment required for maximum sensitisation of the 100°C peak.

The change in the emission spectral pattern due to the gamma induced sensitisation as well as the additive nature of this type of sensitisation on the thermal sensitisation etc. are not studied by the previous workers.

1.2.4 Effect of Stress

The effect of stress and strain on different quartzite minerals including granite rocks are studied elaborately by Hara(37-39), Douglas(40) and others(41-43). Stress and strain caused by progressive loading will produce change in some solid state characteristics of the material. Although exact mechanism is not explained yet, McDougall(28) tried to explain the phenomenon as due to the variation in free energy of the crystal which in turn is related to the annihilation and formation of lattice dislocations. Douglas(40) explains the mechanism as due to the strain hardening developed by the dislocation nets produced by stress and strain in crystals.

Different possibilities of formation of defect centres are studied by McDougall(44). Effect of stress
and strain on peak parameters like thermal activation energy is studied elaborately by Manconi\textsuperscript{(42)} et al. They did not observe any systematic change in the activation energy with this treatment. The observed changes were irregular. It is to be noted that the effect on TL due to a prolonged stress is not reported. Prolonged stress is of importance in the geological context.

Disordering of the crystalline structure to a glassy state at a high impact of load of the order of 300 K bars is reported by Short\textsuperscript{(43)}.

1.2.5 Polarisation

The effect of electrolysis and hence of the electric field on the colouration of natural and synthetic quartz has been studied by Kreft\textsuperscript{(45)} who explained the colour centre formation in quartz in terms of Al impurity in substitution of Si. Kreft\textsuperscript{(45)} explained the effect as due to the charge compensation in the lattice by interstitial monovalent positive ions like Li, Na or Hydrogen. According to this model, irradiation can remove electrons from the tetrahedron leaving holes which are associated primarily with oxygen adjacent to Al. According to Skobel'st'syn\textsuperscript{(57)} an electric field can excite the crystals owing to the transfer of electrons from valence band and luminescence centre to the
So far no work has been reported on the effect of electric polarisation on TL of quartz.

1.2.6 Photo transfer

A previously irradiated phosphor when partially erased by heating, shows an appreciable TL signal at higher temperatures. This residual signal has been found\(^{(47)}\) to affect the TL sensitivity of the phosphor very much. Transfer of charge carriers from high temperature traps to low temperature traps in quartz was observed by Medlin\(^{(11)}\). But UV induced transfer from a residual peak and its relations were not studied. Photo-transfer is used for many applications. It is used\(^{(48)}\) for studying the anomalous fading of TL peaks in sample like feldspar and fluorite samples. Also, it is used\(^{(49,50)}\) as a tool in TL dating of ancient pottery. The radiation induced sensitisation of 100°C peak is known to be reversed\(^{(34,35)}\) by UV exposure. But a glow peak wise systematic work on the desensitisation of the sensitised quartz sample by UV bleaching is not reported yet.

1.2.7 Spectral Characteristics

The TL emission spectrum of natural quartz has not been studied in detail. It is known\(^{(16)}\) that TL of
quartz is blush-white in colour. Baliff\(^{(51)}\) also studied the spectral characteristics of quartz by introducing different filters. He observed the TL emission of quartz to peak at about 375 nm. The variations in the spectral characteristics due to different parameters like heat and irradiation has not been studied.

The absorption spectrum of natural and synthetic quartz has been well studied\(^{(12,46,52-55)}\) in the past. The absorption maxima are found between 400-500 nm in all the cases. The correlations of colour centres, TL and absorption spectra are studied by many workers\(^{(56-67)}\) in the past.

1.2.8 Peak Parameters

The peak parameters of different peaks of quartz are determined by Fuller\(^{(29)}\). A similar study was conducted by many workers\(^{(28,30,21)}\) in the past. But the order of kinetics for the different individual TL peaks are not determined.

Each TL peak in a sample represents a defect in the crystal structure. It is characterised by parameters like activation energy \(E\), order of kinetics \(n\), frequency factor \(s\) etc. These parameters in turn depend on glow peak temperature and its half width. A number of methods are available for determining the activation
energy \( E \) and frequency factor \( s \) and have been reviewed by Nicholas et al\(^{(62)}\), Braunlich\(^{(63)}\) and Halperin\(^{(68)}\). Most of the methods for determining \( E \& s \) require the knowledge of order of kinetics except in the case of that advocated by Garlick and Gibson\(^{(69)}\) which is known as the initial rise method.

The order of kinetics can be determined from the shape of the peaks\(^{(70,71)}\) and from the isothermal decay of TL peaks\(^{(72,73)}\). In quartz, activation energy and frequency factor have been determined by Fuller et al\(^{(56)}\) but the determination of the order of kinetics has not been carried out systematically. It has been arbitrarily assumed to be monomolecular. The experiments on these have lacked detailed investigations. Heating rate is an important factor for determining the peak temperature. The effect on TL yield by the rate of irradiation is reported by Groom et al\(^{(74)}\). They observed that with a high dose rate the radiation damage results in reduction in TL output. The dependence of temperature of irradiation is examined by Mc Keover et al\(^{(75)}\). Their observations have shown that the TL intensity falls as the temperature of irradiation decreases. He explains the phenomenon as due to the immobilisation of alkali
ions at very low temperature (much below room temperature). In the present work, irradiation temperature is chosen around the room temperature to examine the effect of its use in the geological and archaeological applications.

1.2.9 Applications of TL of quartz

Natural Brazilian quartz was used as a dosimeter and its properties were studied by Ichikawa (76). The peak appearing at 280°C is used as the dosimetry peak and linearity is reported up to $10^6$ R. Quartz is used as a heat resistant dosimeter by Fleming et al (32) and similar observations are reported by Mc Dougall (33). The properties of quartz and its potential as an accident TLD is examined by Mc Dougall (28).

In the present work we have reported the use of natural TL of quartz as an indicator of environmental radiations in the monazite bearing beaches.

Thermoluminescence of rocks (77, 78) and Minerals (79-81) has been studied by many workers in the past with a view to develop its application in Geological dating (82-85) and prospecting (86).

TL of quartz is used as a tool in determining the age of the ancient pottery samples. Valladas (31) examined the problems encountered during the dating using
inclusion quartz of the pottery. Self induced radiation of the quartz grains and the environmental contribution of radiation are studied by many workers and incorporated in the TL dating technique. Its use in authenticity testing of ancient ceramics is demonstrated by Zimmerman, Aitken, Mc Kerrell et al.

Thermoluminescence has been suggested as a tool for certain forensic investigations. Its potential application in the field is indicated by Ingham and Chandrasekaran.

Radioactive mineral prospecting is proposed by many workers in the past using thermoluminescence of quartz. But actual field results have not been reported.

1.3 **SCOPE AND OBJECT OF THE WORK INCLUDED IN THE THESIS**

Quartz is a major constituent of the earth's crust and is found almost everywhere in soil, sand and rocks. Its crystallography is very stable. It is found to be a good TL sensitive mineral. This property of quartz plays an important role in many fields like geology, archaeology, radiation dosimetry etc.

It is found that the TL of quartz is affected significantly by physical treatments like heat, radiation, stress and polarisation. These factors, unless taken care of properly, are likely to cause complications in
the various applications.

The present work deals with the effect of the physical treatments like heating, exposure to ionizing radiations, stress and polarisation on the TL properties of mineral quartz samples. The results are discussed with a view to derive information about the defect centres. Some new areas of field applications like estimating the natural radiation environment and dating of beach sediments are demonstrated.

New information is brought out in this thesis on order of kinetics and activation energy values for TL glow upto about 600°C. Similarly the modifying effects of heat, stress, pre-irradiation and uv exposure all provide new informations.
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