

Thermo Luminescence Stimulated by Different Technique

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Abstract

The movement of electrons from the conduction band to the deeper levels which provides the luminescence. The first order characteristic that T_m independent on n_0 . The heating rate β must change T_m in such a way that the equality still holds. The nonlinear heating function $T(t)$ dependent intensity. If the heating function is monotonically increasing then. Similarly for the second order kinetics. We discuss electron traps and hole recombination centers. The kinetics of the process in more general terms and to see how the simplified cases of first order, second order and more general case emerge in above equation. These are related to the relation between the concentration of electrons in the conduction band and in traps and to the rate of change of these concentrations namely. The TL peak of a first order or second order kinetics a number of attempts have been made to add a third parameter is that of general order kinetics. It is to be noted that this mixture is in the terms of the differential equation rather than in the first and second order solution as suggest empirically with the neutrality assumption one gets. The basic principle of laser stimulated TL is that the ionizing radiation generates electron-hole pairs. A fraction of this pairs recombine spontaneously, the radiative recombination results in fluorescence. The rest of them are captured at the trapping sites for electrons and holes. Some of these traps are thermally unstable and leak continuously giving rise to phosphorescence, while others are thermally stable at the storage temperature and do not significantly detrapping until stimulated externally. The phenomenon of thermally stimulated luminescence occurs when the detrapping take place due to heating of material and optically stimulated luminescence arises when the detrapping is caused by optical means i.e. The hole detrapping is also possible.

INTRODUCTION

When ionizing radiations (x-rays, α -rays, γ -rays, β particles and α particles) is incident upon an insulator or semiconductor and is heated, then the energy stored in the phosphor, as a result of irradiation process, liberates in the form of visible light in addition to the normal thermal radiation. The additional visible light emitted during first heating is called thermoluminescence. Reheating the phosphor, immediately after it gives rise to only normal thermal emission. When an irradiated coloured crystal is heated at a

rapid rate, carriers (holes or electrons) are set free from the traps (defect sites) and emission takes place when they recombine with a charge of opposite sign. The defect sites which release the carriers are known as traps. In contrast, the centers from which thermal transitions are not likely but a probability of capture of a charge of opposite sign is appreciable, are called "recombination centers". This emission is generally known as thermally stimulated luminescence or simply "thermoluminescence" abbreviated as TSL or TL.

The radiation dose absorbed by phosphor after the last heating of the sample is measured by the emitted TL. This dose can be estimated if the TL response to unit radiation dose (TL-sensitivity) is known. In most of the luminescence process, the exciting source is indicated by a prefix in the terminology, e.g., photoluminescence is excited by photons, but thermoluminescence is the misnomer because thermal energy is not the source for excitation. It is only a stimulant for material pre-excited by some other source of radiation to yield thermoluminescence. A theoretical basis to luminescence was given by [1-4]

Robert Boyle's observation of a strange "glimmering light" on warming a diamond in the dark led to the discovery of TL in 1663 and he reported to the Royal Society in London. 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 phosphors grown in the laboratory. Although considerable work 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 [5]. 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 to-day.

The kinetic process is applicable of the theory of thermoluminescence (TL) and it is neither a first order kinetics 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.

Thermoluminescence studies provide a new field of investigation of solid materials [6-9]. It can be a much more sensitive radiation detector than either a Geiger or Scintillation Counter. Its applications have engulfed a whole spectrum of disciplines such as Archaeology, Biology, Biochemistry, Forensic science, Geology, Radiation dosimetry, Radiation Physics, Solid State Physics, Space Science, Spectroscopic Analysis, TL Photography and so on. The most fundamental process in all these applications is the radiation dosimetry [10-14].

We have studied the thermoluminescence stimulated by different technique, primarily to get help to understand the mechanism and characteristics of ML. The present paper reports the TL stimulated by different technique and discusses the correlation between ML and TL.

THERMOLUMINESCENCE KINETICS

Although in most experimental situations the TL curve consists of a number of overlapping peaks, it is appropriate to start the discussion by dealing with a single peak so as to understand the basic processes. For most purposes, it is not really necessary to assume that the glow curve consists of only one peak. The analysis of a single peak may be just as valid if a series of peaks occurs, provided that the peak of interest is sufficiently separated from the others, either because it appears separately or because we have an efficient method to isolate it from the rest of the curve.

The first information from TL peaks was extracted by Urbach (1930) who found empirically that in KCl the relation between the activation energy E in electron volts and the peak's maximum T_m in k is approximately given by

$$E = \frac{T_m}{500}$$

This result was later used by other authors for other materials but was not found to be very accurate.

FIRST ORDER KINETICS

The first systematic account of TL peaks was given and it is based on the simple band model shown in Fig.1. They ascribed the occurrence of a TL peak to the thermal release of electrons from traps and their subsequent recombination with the holes trapped in recombination centers. The basic assumption they made are as follows :

- (i) No direct transitions take place from the defect to the recombination centre.
- (ii) The number of defect sites is small compared with the number of luminescent centres.
- (iii) The recombination lifetime in the conduction band is small.

- (iv) No retrapping or trapping into any other trap or recombination into any other recombination centre (except for the one postulated to be directly relevant to this particular TL peak) is allowed.

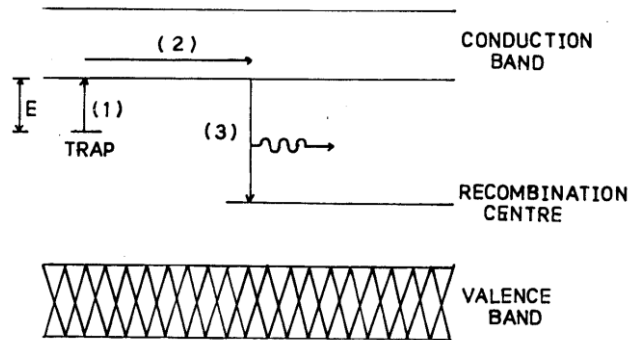


Fig.1: The processes involved in thermoluminescence: (1) thermal excitation, (2) electronic migration, and (3) luminescence

The rate of depopulation of the defect is given by

$$\frac{dn}{dt} = -n(N_c S v) \exp\left(-\frac{E}{kT}\right) + A n_c (N - n) \text{ -----(1)}$$

In the first term 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 possibility 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 a first simplification it is assumed that retrapping is negligible. This is a valid assumption if the concentration of traps is small compared with the concentration of recombination centres, Further, if the recombination lifetime τ is very short the electron concentration in the conduction band n_c will remain essentially constant. Loss takes place due to the recombination centres or the trapping levels, so in general

$$\frac{dn_c}{dt} = -\frac{n_c}{\tau} + \frac{dn}{dt} \text{ -----(2)}$$

When τ is short, $\frac{dn_c}{dt}$ is negligible compared with the other terms. We may also relate the time and temperature by $T = T_0 + \beta t$, if we raise the temperature at a constant rate β from the initial temperature T₀. So equation (2) becomes

$$\frac{n_c}{\tau} = \beta \frac{dn}{dT}$$

It is the movement of electrons from the conduction band to the deeper levels which provides the luminescence so $\frac{n_c}{\tau}$ is proportional to the light intensity I. In the case of no retrapping (A = 0), from equation (3.1), we get

$$\frac{dn}{dt} = -n(N_c S v) \exp\left(-\frac{E}{kT}\right) \quad \text{-----(4)}$$

$$\text{or} \quad \frac{dn}{dt} = -n S \exp\left(-\frac{E}{kT}\right) \quad \text{-----(5)}$$

where S = $M_c S v$ is called the “frequency factor” and has units of seconds⁻¹.

Integration of equation (5) gives

$$\int \frac{dn}{n} = - \int_{T_0}^T \frac{S}{\beta} \exp(-E/kT) dT + C$$

$$\text{or} \quad \log n = - \int_{T_0}^T \frac{S}{\beta} \exp(-E/kT) dT + C$$

where c is the constant of integration.

At T = T₀, n = n₀, therefore, we have

$$C = \log n_0$$

Now, the above equation may be written as

$$n = n_0 \exp\left[- \int_{T_0}^T \frac{S}{\beta} \exp\left(-\frac{E}{kT}\right) dt\right] \quad \text{-----(6)}$$

The light intensity may be given by

$$I = -\eta \frac{dn}{dt} = \eta S n \exp\left(\frac{-E}{kT}\right) \quad \text{-----(7)}$$

or

$$I = \eta n_0 S \exp\left(-\frac{E}{kT}\right) \exp\left[- \int_{T_0}^T \frac{S}{\beta} \exp\left(-\frac{E}{kT}\right) dT\right] \quad \text{-----(8)}$$

where η is the probability that recombination will occur radiatively.

It can be seen easily from equation (8) that the intensity builds up as T increases, reaches a minimum for particular value of T_m and then falls off for any further increased heating. By

setting $\frac{d}{dT}(\log I) = 0$, at T = T_m we obtain

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

$$\frac{d}{dT} \left[\log n_0 S c - \frac{E}{kT} - \int_{T_0}^T \frac{S}{\beta} \exp\left(-\frac{E}{kT}\right) dT \right]_{T=T_m} = 0$$

$$\text{or} \quad \frac{E}{kT_m^2} - \frac{S}{\beta} \exp\left(-\frac{E}{kT_m}\right) = 0$$

$$\text{or} \quad \frac{\beta E}{kT_m^2} = S \exp\left(-\frac{E}{kT_m}\right) \quad \text{-----(9)}$$

The fact that no does not appear in equation (9) immediately proves the first order characteristic that T_m not depend on n₀. Equation (9) can be written

$$\beta = \left(\frac{Sk}{E}\right) T_m^2 \exp\left(-\frac{E}{kT_m}\right) \quad \text{-----(10)}$$

Changing the heating rate β must change T_m in such a way that the equality still holds. The term $T_m^2 \exp(-E/kT_m^2)$ is monotonically increasing with T_m, therefore, increasing β will immediately cause T_m to increase.

Using equation (9) we get for the maximum intensity as

$$I_m = \eta S n_0 \exp\left(\frac{-E}{kT_m}\right) \exp\left[- \int_{T_0}^{T_m} \frac{E}{kT_m^2} dt\right]$$

$$\text{or} \quad I_m = \eta S n_0 \exp\left(\frac{-E}{kT_m}\right) \quad \text{-----(11)}$$

Randall and Wilkins obtained the following expression for the trap depth E,

$$E = 25kT_m \quad \text{-----(12)}$$

where T_m is the glow peak temperature.

There are quite a few interesting implications borne out of Randal- Wilkins formalism :

- (i) At a constant heating rate β , T_m shifts towards higher temperatures as E increases or S decreases. The area under the glow peak in each case is, however, strictly proportional to the concentration of the trapped electrons at the start of the experiment.
- (ii) For a given trap (i.e. constant E and s values), T_m shifts to higher temperatures as β increases.
- (iii) The temperature T* at which the probability of electron escape is 1 sec⁻¹ is some what higher than the

temperature T_m at which the glow maximum occurs. It can be easily shown that there exists a heating rate β^* for which T^* and T_m will coincide and the trap depth will be given by

$$E = \beta^* k(\log s)^2 \quad \text{-----(13)}$$

If the sample is maintained isothermal at temperature T, then solution of equation (7) is given by

$$I(T) = I_0 \exp[-S \exp(-E/kT)t] \quad \text{-----(14)}$$

The above equation shows that at constant temperature, TL intensity falls exponentially with time. Plot of the 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 (14), but these contributions are due to several exponentially decaying components.

Most workers use linear heating function (or actually, the best experimentally possible approximation). Some attention should be paid, however, to the possibility of using nonlinear heating functions. Reconsidering equation (7) with no particular assumption concerning the heating rate, we get instead of equation (8), the expression.

$$I(t) = \eta n_0 S \exp\left(\frac{-E}{kT}\right) \exp\left\{-S \int_{t_0}^t \exp\left(\frac{-E}{kT(t)}\right) dt\right\} \quad \text{---(15)}$$

where $T(t)$ is the heating function.

Assuming that the heating function is monotonically increasing i.e. $\frac{dT}{dt} = 0$: a change of variable yields.

$$I(T) = \eta n_0 S \exp\left(\frac{-E}{kT}\right) \exp\left[-S \int_{T_0}^T \left(\frac{dT}{dt}\right)^{-1} \exp\left(\frac{-E}{kT}\right) dT\right] \quad \text{---(16)}$$

Repeating the procedure of setting the derivative of the function describing the glow peak to zero, a generalized maximum condition is readily found in the following way

$$\beta_m \left[\frac{E}{kT_m^2} \right] = S \exp\left[-\frac{E}{kT_m} \right] \quad \text{---(17)}$$

where $\beta_m = (dT/dt)_{T_m}$ is the instantaneous heating rate at the maximum. Thus, as far as the maximum temperature is concerned, one does not have to maintain very accurate linear heating functions nor has one to resort a hyperbolic heating even though it does not have some mathematical advantage in the analysis of the whole glow curve. Thus, these various heating rate methods derived from the maximum condition

can be used just as well as with non-linear heating function provided β_m is used instead of β in the relevant expression.

SECOND ORDER KINETICS

Garlick and Gibsons (1948) modified the equation (5) 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 is 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 center is given by n/N . They found the kinetic equation

$$I = -\eta \frac{dn}{dt} = \eta \left(\frac{S}{N}\right) n^2 \exp\left(\frac{-E}{kT}\right) \quad \text{----- (18)}$$

$$\text{or } I = S' n^2 \exp\left(\frac{-E}{kT}\right) \quad \text{-----(19)}$$

where $S' = \frac{S}{N}$ is a constant having units of $m^3 \text{sec}^{-1}$.

Solving equation (18), we get

$$-\frac{dn}{dt} = S' n^2 \exp\left(\frac{-E}{kT}\right)$$

$$\text{or } -\frac{dn}{n^2} = \int_0^t S' \exp\left(\frac{-E}{kT}\right) dt$$

$$\text{or } \int \frac{-dn}{n^2} = \int_0^t S' \exp\left(\frac{-E}{kT}\right) dt + C_1$$

$$\text{or } \frac{1}{n} = \int_0^t S' \exp\left(\frac{-E}{kT}\right) dt + C_1 \quad \text{---(20)}$$

where C_1 is the constant of integration.

Taking again the linear function $T = T_0 + \beta t$ and changing the variable in equation (20), as $dt = 1/\beta dT$, we get

$$\frac{1}{n} = \int_{T_0}^T \frac{S'}{\beta} \exp\left(\frac{-E}{kT}\right) dT + C_1$$

Applying the condition that at $T=T_0$, $n = n_0$, we get

$$C_1 = \frac{1}{n_0}, \text{ and thus we get}$$

$$\frac{1}{n} = \int_{T_0}^T \frac{S'}{\beta} \exp\left(\frac{-E}{kT}\right) dT + \frac{1}{n_0}$$

or

$$\frac{1}{n} = \frac{1}{n_0} \left[\left(\frac{n_0 S'}{\beta} \right) \int_{T_0}^T \exp\left(\frac{-E}{kT}\right) dT + 1 \right]$$

or

$$n = n_0 \left[1 + \left(\frac{n_0 S'}{\beta} \right) \int_{T_0}^T \exp\left(\frac{-E}{kT}\right) dT \right]^{-1} \quad \text{---(21)}$$

Substituting this value of n into equation (19), we get

$$I(T) = \eta n_0^2 S' \exp\left(\frac{-E}{kT}\right) \left[1 + \left(\frac{n_0 S'}{\beta} \right) \int_{T_0}^T \exp\left(\frac{-E}{kT}\right) dT \right]^{-2} \quad \text{---(22)}$$

It is readily seen that the term dominating the temperature dependence in the initial rise is $\exp\left(\frac{-E}{kT}\right)$. At higher

temperatures the second decreasing function dominates so that the product function is decreasing. Somewhere between these two regions the glow curve, therefore reaches its maximum.

The condition for the maximum is found by setting the derivative of $\log I(T)$ to zero at $T=T_m$ and thus we have

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

or

$$\frac{E}{kT_m^2} - \frac{2 \left(-\frac{n_0 S'}{\beta} \right) \exp\left(\frac{-E}{kT_m}\right)}{\left[1 + \left(-\frac{n_0 S'}{\beta} \right) \int_{T_0}^{T_m} \exp\left(\frac{-E}{kT}\right) dT \right]} = 0$$

$$1 + \left(\frac{n_0 S'}{\beta} \right) \int_{T_0}^{T_m} \exp\left(\frac{-E}{kT}\right) dT = \left[\frac{2kT_m^2 n_0 S'}{\beta E} \right] \exp\left(\frac{-E}{kT_m}\right) \quad \text{---(23)}$$

It is obvious that as opposed to the first order case, n_0 appears in equation (23) and therefore we can expect that T_m will depend on n_0 . It can be shown numerically or analytically that increasing n_0 causes T_m to decrease.

Other aspects of dependence of the glow curve on the initial concentration n_0 are of paramount importance when we are interested in TL as a dosimetric tool. In many cases one associates the initial concentration with the imparted dose and then the dependence of different parts of the glow peak on n_0 is important. First, the dependence of the total area on n_0 is the interesting. In first order kinetics, since the intensity at each point is multiplied by the same factor while changing n_0 , the total area varies by the same amount so that the total area is

proportional to n_0 . Except for special cases this is a very general situation. It's occurrence in second order peaks can be illustrated by integrating equation (22) from T_0 to infinity. A

simpler way is to take from equation (18) $I = C \left(\frac{dn}{dt} \right)$ and integrate (with respect to time) from zero to infinity.

Thus, we get

$$\begin{aligned} \int_0^\infty I(t) dt &= -\eta \int_0^\infty \left(\frac{dn}{dt} \right) dt \\ &= -\eta \int_{n_0}^{n_\infty} dn = \eta (n_0 - n_\infty) \quad \text{--- (24)} \end{aligned}$$

Both in first and second order cases, n_∞ is zero and therefore the integral, which represents the area under the glow peak is proportional to n_0 . The cases where the area may not be proportional to n_0 are only those where $n_\infty \neq 0$.

For constant temperature T, the solution (23) reduces to

$$I = \frac{I_0}{(1 + I_0 P t)^2} \quad \text{---(25)}$$

where $P = S' \exp\left(\frac{-E}{kT}\right)$

Equation (25) represents the second order kinetics.

Now we shall consider the dependence of I on n_0 for a given temperature T. In the initial rise range i.e. T subsequently below T_m , equation (22) reduces to

$$I(T) \approx n_0^2 S' \exp\left(\frac{-E}{kT}\right) \quad \text{---(26)}$$

Since the second term in equation (22) is much smaller than unity, this shows immediately that for a given temperature in this range the dependence of I on n_0 is supralinear, namely

$I \propto n_0^2$. It is to be emphasized that this is true only in the initial rise range, as already shown that the total area is proportional to n_0 (and therefore in many cases, to the dose) and different dependences are expected in other portions of the curves as described in the following. Using equation (23)

and an approximation to $\int_{T_0}^T \exp\left(\frac{-E}{kT}\right) dT$, it can easily be shown that two terms in the brackets in equation (22) namely unity and $\left(\frac{n_0 S'}{\beta} \right) \int_{T_0}^T \exp\left(\frac{-E}{kT}\right) dT$ are more or less

equal at $T = T_m$. At higher temperature the latter term increases substantially and the unity can be neglected so that one obtains

$$I(T) \cong n_0^2 S' \exp\left(\frac{-E}{kT}\right) \left[\left(\frac{n_0 S'}{\beta} \right) \int_{T_0}^T \left(\frac{-E}{kT} \right) dT \right]^{-2} \quad \text{---(27)}$$

The main point for our present purpose is that the terms including n_0 cancel. This means that at the high temperature range the TL intensity is independent of n_0 for any temperature. Both the quadratic behaviour at low temperatures and the independence of n_0 are shown in

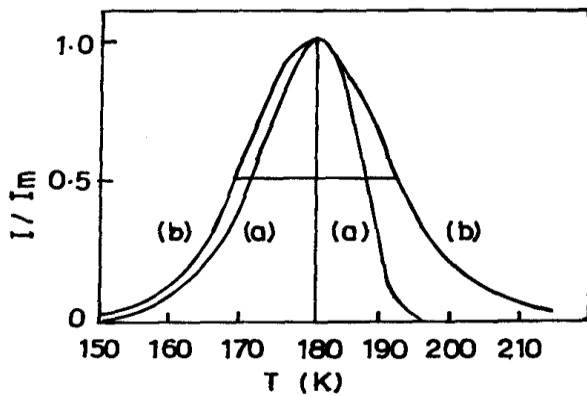


Fig. 2: Computed TL peaks of first-order (curve a) and second-order (curve b) kinetics. In the first-order peak. $E=0.4$ eV and $S=10^{10}$ sec $^{-1}$. In the second-order peak. $E = 0.4$ eV and $S = 10^{11}$ m sec $^{-1}$. n_0 is chosen in curve b so that the two maxima coincide. Both curves are normalized.

GENERAL ORDER KINETICS OF A SINGLE TL PEAK

As stated previously, a necessary condition for TL emission is the existence of atleast one trapping state and one kind of recombination centre in the forbidden gap of the material. In the discussion so far some simplifying assumptions were made regarding the parameters related to these imperfection states that lead to first and second-order kinetics. Limiting ourselves to only one trapping state and one recombination state, let us remove the other assumptions and consider a more general TL peak. We still assume that thermally stimulated carriers are raised into the conduction band. For the sake of simplicity we shall discuss electron traps and hole recombination centres.

The energy levels involved and the transitions are shown in Fig. 3. The concentration of trapping sites is denoted by $N(m^{-3})$, of which $n(t) (m^{-3})$ is occupied by electrons at time $t(s)$. These electrons can be thermally raised into the conduction band, climbing over an energy barrier of $E(eV)$ at a rate proportional to $\exp(-E/kT)$, thus, producing a

concentration $n_c(t)(m^{-3})$ of free electrons. Subsequently, these can be retrapped in a trap of same kind with a retrapping probability A_m , yielding a photon with energy $h\nu$ characteristic of the recombination centre. The equations governing this process are a set of three simultaneous differential equations. The one governing the recombination is

$$I(t) = \frac{-dm}{dt} = A_m m n_c \quad \text{---(28)}$$

This means that the emitted light is proportional to the rate of decrease of m which is the rate of recombination. The proportionality constant is arbitrarily set to unity, which sets the units of the emitted light. This rate of recombination is in turn, proportional to both the instantaneous concentration of free electrons n_c and holes in the centres m , the proportionality constant being $A_m (m^3 \text{sec}^{-1})$. This magnitude is usually interpreted as the product of the cross-section for recombination $\sigma_m (m^2)$ and the thermal velocity $v(m\text{-sec}^{-1})$.

The second equation deals with the traffic of electrons thermally raised from the trapping state. The rate of release of these electrons $-\frac{dn}{dt}$ is proportional to the concentration

$n(m^{-3})$ of the trapped electrons and to the Boltzmann function $\exp\left(\frac{-E}{kT}\right)$; the probability constant being $S(\text{sec}^{-1})$.

However, the actual rate of change of n is also related to the retrapping term. The rate of retrapping is proportional to the concentration of free electrons n_c and to unoccupied trapping states $(N-n)$, the proportionality factor being the recombination probability $A_n (m^3 \text{sec}^{-1})$. Thus, the combined equation is

$$\frac{dn}{dt} = S n \exp(-E/kT) - n_c (N - n) A_n \quad \text{---(29)}$$

The retrapping probability A_n is interpreted as the product of the cross-section for retrapping $\sigma_n (m^2)$ and the thermal velocity $V(m\text{sec}^{-1})$. The third equation is that of charge neutrality. In its simplest form it is given by $m = n + n_c$. In more realistic case the neutrality condition reads as $m + c_1 = n + n_c$, where c_1 is constant (m^{-3}) representing the net charge held by traps and centres that are inactive in the same temperature range. More precisely, c_1 represents the concentration in inactive centres less the concentration in inactive traps, so that it can be either a negative or a positive constant. Taking the first derivative with respect to time, the charge neutrality condition can be written as

$$\frac{dm}{dt} = \frac{dn}{dt} + \frac{dn_c}{dt} \quad \text{---(30)}$$

An equation equivalent to equation (30) keeping in mind the simultaneous occurrence of equations (28) and (29) has been given by for TL are as follows

$$\frac{dn_c}{dt} = S n \exp\left(\frac{-E}{kT}\right) - n_c [m A_m - (N - n) A_n]$$

The mechanism of TL on the basis of non-equilibrium thermodynamics and justified these kinetics equations (28) to (30) theoretically. A number of investigators studied the numerical solutions of equation (28) to (30). A technical difficulty which usually occurs is due to the fast variation with temperature, and therefore with time for a given heating function T(t) of the term $\exp(-E/kT)$.

The possibility of calculating the shape of a TL peak for a given set of trapping parameters is of great theoretical significance. However, the more interesting problem is the opposite one, namely, given an experimental TL peak and any additional information such as the simultaneously measured TL curve, to find the relevant trapping parameters. This is important from a purely physical point of view as well as from the applicative aspect of dosimetry and dating since both the stability of traps and centers and the dependence of their filling on the dose and dose rate are directly related to these magnitudes. It is appropriate, however, to first discuss the kinetics of the process in more general terms and to see how the simplified cases of first order, second order and more general cases emerge from equations (28) to (30). Two simplifying assumptions were first made by Adirovitch (1956). These are related to the relation between the concentrations of electrons in the conduction band and in traps and to the rates of change of these concentrations, namely

$$\left| \frac{dn_c}{dt} \right| \ll \left| \frac{dn}{dt} \right|, n_c \ll n \quad \text{---(31)}$$

Although there seems to be some connection between these two conditions, basically they are two separate relations and the occurrence of one does not necessarily imply the other. With these assumptions, found the expression.

$$I = -\eta \frac{dm}{dt} = \eta S n \exp\left(\frac{-E}{kT}\right) \frac{A_m m}{A_m m + A_n (N - n)} \quad \text{---(32)}$$

Since these equation contains the two unknown functions. n(t) and m(t), it cannot be solved without further assumptions. As mentioned above, wrote their first order equation assuming strong recombination. This can now be expressed in more specific terms. If we assume with relation to equation (32) that

$$A_m \cdot m \gg A_n \cdot (N - n) \quad \text{---(33)}$$

we readily get

$$I = -\eta \frac{dm}{dt} = \eta S n \exp(-E/kT) \quad \text{---(34)}$$

Using $|n_c| \ll |n|$ from (31) we get from equation (30)

$$\frac{dm}{dt} = \frac{dn}{dt}$$

which transforms equation (34) to the regular first-order equation. The condition (equation 33) is a relation between functions rather than parameters. It is, therefore, possible that at the low temperature range of a glow peak, the strong inequality holds and at higher temperatures, when m and n decrease, the inequality “weakens” or may even be inverted. This may result in a shift from first-to non first order behaviour within the same peak. The general solution of Randall Wilkins equation is

$$I(t) = \eta S n_o \exp\left(\frac{-E}{kT}\right) \exp\left\{-S \int_o^t \exp\left(\frac{-E}{kT}\right) dt\right\} \quad \text{---(35)}$$

The special case of a linear heating function $T = T_o + \beta t$.

Results in

$$I(t) = \eta S n_o \exp\left(\frac{-E}{kT}\right) \exp\left\{-\frac{S}{\beta} \int_{T_o}^T \exp\left(\frac{-E}{kT}\right) dT\right\} \quad \text{---(36)}$$

A number of investigators preferred to use hyperbolic heating function

$$T = \frac{T_o}{(1 + \beta' t)} \quad \text{---(37)}$$

Where β' is constant.

In this case, the integral on the right hand side of equation (35) becomes elementary with such a heating function.

The second order kinetics previously mentioned, results from different assumptions associated with equation (32). In one set of assumptions, one takes $n(t) = m(t)$ which is not very different from the parametric equality $n_o = m_o$. once the assumption $n_c \ll n$ is made. The assumption of equality of concentrations of trapped electrons and holes is rather restrictive since it implies that there really exists only one trapping state and one kind of recombination centres. In addition, we have to assert that retrapping dominates and thus we may take

$$A_n (N - n) > A_m \cdot m \quad \text{---(38)}$$

This, again, is a relation between functions. However, since both n(t) and m(t) decrease during the TL measurement the condition $A_n (N - n_o) \gg A_m m_o$ is sufficient for equation (38) to hold. We further assume that the trap is far from saturation, namely. $n \ll N$, to get

$$I = -\eta \frac{dn}{dt} = \eta \left(\frac{S A_m}{N A_n} \right) n^2 \exp\left(\frac{-E}{kT}\right) \quad \text{---(39)}$$

Alternatively, one can assume in addition to concentration equality, that $A_n = A_m$, which yields

$$I = -\eta \frac{dn}{dt} = \eta(S/N)n^2 \exp\left(\frac{-E}{kT}\right)$$

The solution to this equation is given by

$$I(t) = \eta n_0^2 S' \exp\left(\frac{-E}{kT}\right) \left[1 + \left(\frac{n_0 S'}{\beta} \right) \int_{T_0}^T \exp\left(\frac{-E}{kT}\right) dT \right]^{-2}$$

Where $S' = (S/N)$ for linear heating function.

It should be emphasized that the two cases discussed so far namely, first and second order kinetics, are only special cases, in a sense, extreme cases and the general case described by equation (29) to (36) may be of neither first nor second order. Even if the simplifying conditions (equation 32) are assumed to be general, the resulting equation (33) consists of very many intermediate cases that do not have a distinct order of kinetics. Although some researchers still attempt to determine for every TL peak a first order or second order kinetics, a number of attempts have been made to add a third parameter to the two “basic” ones, the activation energy E and preexponential constant S' (or S). It should be noted, however, that the addition of a third parameter is in principle only the step in the right direction since the general treatment should include eight parameter s ($E, S, A_m, A_n, N, n_0, m_0, n_{co}$) included in equations (29) to (31).

The best known way of including a third parameter is that of general order kinetics according to which one assumes that the glow peak is governed by

$$I = -\eta \frac{dn}{dt} = \eta S' n^b \exp\left(\frac{-E}{kT}\right)$$

where b is the order of kinetics. Usually b is assumed to be between 1 and 2 but sometime can exceed this range. The rational behind writing (42) is as follows. Considering Fig. 3, it is readily seen that a first order peak is asymmetric, whereas, a second order one is nearly symmetric.

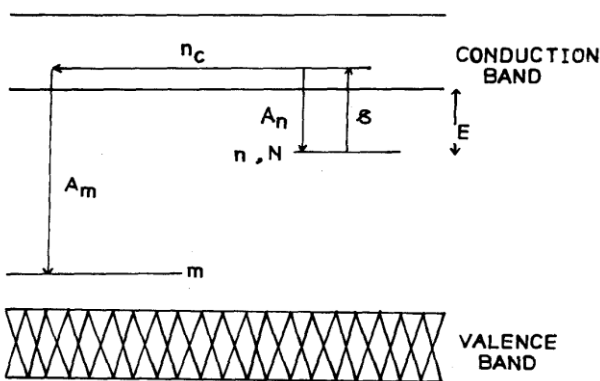


Fig. 3: Energy levels in the forbidden gap of a solid n, m and n_c are the concentrations of trapped electrons holes centers and free electrons respectively. A_m and A_n are the recombination and trapping probabilities.

We can define the symmetry factor μ_g as

$$\mu_g = \frac{\delta}{\omega} \quad \text{---(43)}$$

where $\delta = T_2 - T_m, \omega = T_2 - T_1$ and T_1 and T_2 are the low and high temperatures of half maximum intensity respectively. It has been shows that for first order kinetics, $\mu_g \approx 0.42$ and for second order $\mu_g \approx 0.52$. of course, intermediate symmetries represented by different values of μ_g are found and the simplest way to represent them is by taking $1 < b < 2$ in equation (42). Indeed, μ_g gradually changes from 0.42 to 0.52 while b increases from 1 to 2[15]. The solution of equation (42) for a linear heating with heating rate β is

$$I(t) = \eta s n_0 \exp(-E/kT) \left\{ \frac{(b-1)S}{\beta} \int_{T_0}^T \exp(-E/kT) dT + 1 \right\}^{-b/(b-1)} \quad \text{---(44)}$$

where S is defined by

$$S = S' n_0^{b-1} \quad \text{---(45)}$$

A few words of caution are in order with respect to this treatment, first, although equation (44) has been shown quite accurately, describe measured TL peaks, it is to be noted that in most cases it is only an empirical presentation and is not based on the three differential equations (29) to (31), which seems to have more physical significance. A set of physical assumptions which results in equation (42) with $b = 1.5$; at best, this attempt covers only very specific physical situations. The second difficulty with respect to equation (42) is related to the meaning of pre-exponential factor S' . The dimension of S' according to equation (42) should be $m^{3(b-1)} / \text{sec}^{-1}$, namely, the dimension changes with the order b . In order to by pass this difficulty the magnitude S has been defined in equation (45), which has dimension of sec^{-1} . It should be noted, however, that this frequency factor is a constant for a given sample and a given dose (i.e. given n_0), but would vary in the same sample when dose is varied. Still, the general order case is useful since intermediate cases can be dealt with it smoothly goes to the first and second order when $b \rightarrow 1$ and $b \rightarrow 2$ respectively.

Different approaches have been presented in the literatures for simplified descriptions of single TL peaks which are of neither first nor second order. [16] in an intirely empirical approach, assumed a weigted combination of first and second order solutions and used a curve fitting method to analyze glow peaks in rare earth doped CaF_2 crystals. [17] used only one of the assumptions leading from equation (33) to the second order case, namely $n = m$, and found the following differential equation in n

$$I(t) = -\eta \frac{dn}{dt} = \frac{\eta A_m n^2 S \exp\left(-\frac{E}{kT}\right)}{[(A_m - A_n)n + A_n N]} \quad \text{---(46)}$$

$m = n$ is not likely to occur, and since $n_c \ll n$ is usually the case, one can make use of the appropriate relation

$$m = n + c_1 \quad \text{---(47)}$$

where c_1 is a constant; positive or negative in a given temperature range. Proceeding with the assumption $A_m = A_n$, one gets

$$I(t) = -\eta \frac{dn}{dt} = \eta \left\{ \frac{S}{(c_1 - n_0)} \right\} n(n + c_1) \exp\left(\frac{-E}{kT}\right) \quad \text{---(48)}$$

Alternatively, one can assume strong retrapping $A_n (N-n) \gg A_m M$ along with the assertion $N \gg n$ which means that the trap is far from saturation and one gets

$$I(t) = -\eta \frac{dn}{dt} = \eta \left(\frac{S A_m}{N A_n} \right) n(n + c_1) \exp\left(\frac{-E}{kT}\right) \quad \text{---(49)}$$

Both equations (48) and (49) can be assumed up as

$$I(t) = -\eta \frac{dn}{dt} = \eta S' n(n + c_1) \exp\left(\frac{-E}{kT}\right) \quad \text{--- (50)}$$

where S' is a constant with dimension $m^3 \text{sec}^{-1}$. The advantage of this approach compared to general-order kinetics equation (42) is that one can make physical assumptions which, at least at the limit, bring about the occurrence of equation (50). Moreover, the parameter S' has more 'reasonable' dimension compared to the order-dependent parameter in equation (42). Similarly in equation (42), we can easily describe the conditions leading to first-and second-order. Very large values of c_1 bring about first-order kinetics whereas very small c_1 yields second-order. Equation (50) can be written as

$$I(t) = -\frac{dn}{dt} = S' n^2 \exp\left(\frac{-E}{kT}\right) + S' c_1 n \exp\left(\frac{-E}{kT}\right) \quad \text{--- (51)}$$

and is referred to as "mixed-order" kinetics. It is to be noted that this mixture is in the terms of the differential equation rather than in the first-and second-order solution as suggested empirically showed that with the neutrality assumption equation (47) alone, one gets.

$$I(t) = -\eta \frac{dn}{dt} = \eta S \exp\left(\frac{-E}{kT}\right) F(n) \quad \text{--- (52)}$$

$$\text{where } F(n) = \frac{S A_n n(n + c_1)}{\{A_m (n + c_1) + A_n (N - n)\}} \quad \text{---(53)}$$

Under appropriate conditions, $F(n)$ can be written as a power

series in the following way

$$F(n) = a_1 n + a_2 n^2 + a_3 n^3 \dots \dots \dots \quad \text{---(54)}$$

In the above case, no constant additive term is included, since $F(0) = 0$. In some cases (but not always), the first terms alone may give a reasonable approximation leading to an equation equivalent to equation (50) under assumptions which may be broader than those involved in equations (48) and (49). The disadvantage compared to general order kinetics is that the mathematical treatment is somewhat more complicated.

LASER STIMULATED LUMINESCENCE

The use of lasers gave a new dimension to the field of stimulated luminescence. Due to the wide varieties of available lasers, they can be used both for thermal as well as optical stimulation. High power and directionality are two major assets of a laser, which give a large amount of flexibility in an application. High power CO₂ laser, which emits at 10.6 μm, is a good candidate for thermal stimulation of a phosphor. Heating rates as high as 10⁴c/sec are achievable, which results in large signal to noise ratio, a very desirable feature in a device. It is also possible to choose an appropriate laser to optically stimulate a material without heating it. It has the advantage that material will not degrade unlike the case of thermal stimulation, where repeated cycle of heating and cooling may diffuse the dopants to change its initial characteristics. However, in optical stimulation, practical problem may arise in discriminating the bright stimulating laser from the low level signal. In personnel dosimetry, where low doses are to be evaluated, it is desirable that the stimulating laser may lie at a much different wavelength (say in infrared than the emission of the phosphor, which is in the visible (preferably in the blue-green region) for better detection by a photomultiplier tube. On the other hand, in radiography where doses of x-rays are involved this restriction is not very important.

BASIC PRINCIPLE

The basic principle of stimulated luminescence is depicted in Fig.4. The ionizing radiation generates electron-hole pairs (Fig.4). A fraction of these pairs recombine spontaneously, the radiative recombination results in fluorescence. The rest of them are captured at the trapping sites for electrons and holes. Some of these traps are thermally unstable and leak continuously giving rise to phosphorescence, while others are thermally stable at the storage temperature and do not significantly detrapp until stimulated externally (Fig.4b). The phenomenon of thermally stimulated luminescence occurs when the detrapping takes place due to heating of the material (Fig. 4c) and optically stimulated luminescence arises when the detrapping is caused by optical means (Fig. 4d). It may be mentioned here that it is not always true that only electron is mobile. The hole detrapping is also possible and indeed has been observed [18].

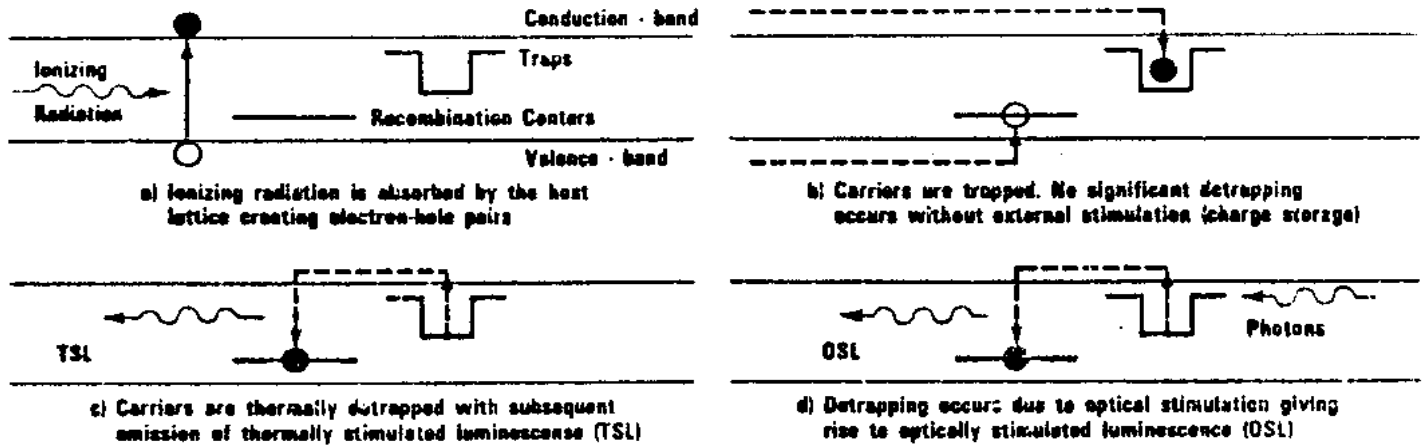


Fig. 4. Schematic of stimulated luminescence

The role of lasers in stimulated luminescence can be understood from the following :

Let n be the number of trapped charges. Under external stimulation, charges detrapp at the rate of dn/dt and a fraction of them eventually recombine to give out luminescence, the intensity of luminescence I is given by

$$I = -K \frac{dn}{dt} \quad \text{---(55)}$$

for thermal stimulation, rate of detrapping depends on the rate of heating β ($= \frac{dT}{dt}$), substituting in equation (55) we obtain

$$I = -K\beta \frac{dn}{dT} \quad \text{---(56)}$$

From equation (56), it is obvious that larger is the rate of heating (β), higher will be the instantaneous intensity of luminescence. Laser heating can achieve heating rates few orders of magnitude higher than the conventional heating. In a practical application, it amounts to obtaining a larger signal, in addition to fast readout.

Remembering that

$$-\frac{dn}{dt} = pn \quad \text{---(57)}$$

where p is the probability of detrapping.

For optical stimulation, p will depend upon σ , the cross-section of absorption as well as on I_s , the intensity of stimulating light. Thus, the intensity of stimulated luminescence is given by

$$I = -K \frac{dn}{dt} = -Knp = -K\sigma I_s n \quad \text{---(58)}$$

The use of laser can result in I_s being several orders of magnitude higher than the conventional sources and therefore a much higher signal can result.

In the thermal stimulation, the probability of detrapping p is temperature dependent and is given by

$$p = se^{-E/kT} \quad \text{---(58)}$$

where E is the trapdepth and s is the frequency of escape. This factor increases monotonically and rapidly with the rise of temperature. On the other hand, for optical stimulation according to equation (58). The probability p remains constant similar to an isothermal detrapping where the effective temperature T_{eff} is given by

$$p = \sigma I_s - s e^{-E/kT_{eff}} \quad \text{---(59)}$$

Thus, irradiation by laser for optical stimulation amounts to raising the temperature to T_{eff} instantaneously and thus heating it very fast and then let the traps decay characteristic of this temperature. Unless T_{eff} is comparable to the T_{max} of thermal stimulation, significant detrapping will not take place in a reasonable time.

To consider the effect of retrapping, the equation (57) can be rewritten

$$-\frac{dn}{dt} = pn - \beta n_c (N - n) \quad \text{---(60)}$$

where β is the retrapping coefficient, n_c is the number of conduction electron and N is the total number of traps. In optical stimulation, to obtain significant detrapping, $pn \gg \beta n_c (N - n)$. This knowledge is very important for a device based on the principle of optical stimulation. As optical stimulation can be achieved, both through CW as well as pulsed lasers, not only the intensity of the laser but the laser pulse length t_p also plays an important role. It has been argued that the pulse width of the stimulating laser should be larger than the recombination lifetime τ_R and the trapping lifetime

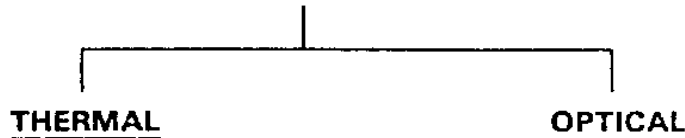
τ_T , otherwise, retrapping will complete with recombination and detrapping may not be complete despite very high photon flux.

It appears from the qualitative description given so far that for application such as personnel dosimetry, where very low doses are involved, the thermal stimulation by lasers may be desirable as it is likely to completely empty the traps in a reasonable time. However, for radiography, the optical

stimulation is suitable because it is fast although traps may not completely empty, but a signal proportional to the trapped charge is obtained. The device can then be heated or flooded with suitable light for reuse.

A brief summary of the salient features of thermally and optically stimulated luminescence is given in Table I.

LASER STIMULATION



<u>PHENOMENON</u>	PHOTON-PHONON INTERACTION	PHOTON-ELECTRON INTERACTION
<u>LASER</u>	CO ₂ LASER 10.6 μm (TYPICAL)	Nd:YAG 1.06 μm; DIODE 0.8-0.9 μm; He-Ne 0.63 μm
<u>MATERIAL</u>	CaSO ₄ : Tm/DY (TYPICAL)	BaFX:Eu (X = Cl, Br, I); ALKALINE EARTH SULFIDES DOUBLY DOPED WITH RARE EARTHS
<u>RESPONSE TIME</u>	≈ ms	< μs
<u>RESIDUAL MEMORY</u>	NEGLECTIBLE	APPRECIABLE
<u>APPLICATIONS</u>	DOSIMETRY, IMAGING	IMAGING, OPTICAL MEMORY

TABLE I

ADVANTAGE OF FAST DETRAPPING

It has been mentioned earlier that fast detrapping can result in higher signal. However, in certain applications such as dosimetry, where the stimulated signal is integrated over the total period of stimulation, the advantage of fast detrapping is not obvious. For example from equation (55) one can write

$$n = \frac{1}{K} \int_0^t I dt \quad \text{-----(61)}$$

and thus integrating the stimulated luminescence intensity over time should give us n and thus the dose received by the device.

In practice, however, the important factor is not the signal alone but the signal to noise ratio. The fast detrapping rate enhances the signal to noise ratio. To understand this point let us refer to Fig. 5. Fig.5 exhibits three thermally stimulated glow curves A, B and C obtained with three different rates of heating, such that $\beta_A < \beta_B < \beta_C$, for the same amount of trapped charge n.

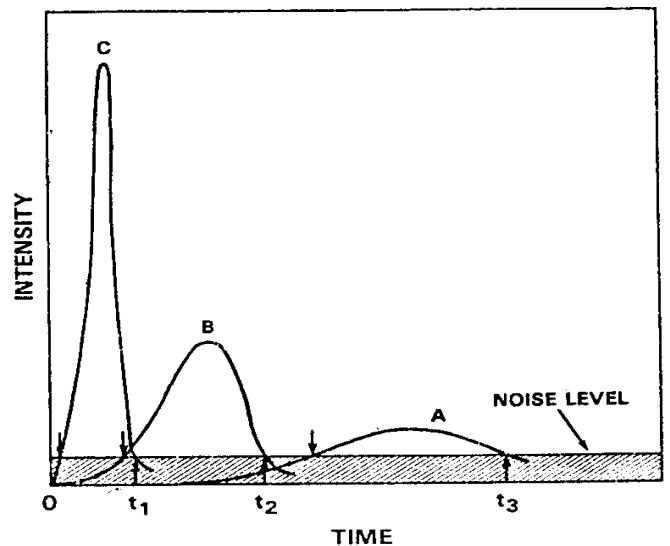


Fig. 5 Signal to noise ratio for different rates of heatings

It is expected from the equation (61) that the area under each curve A, B and C should be the same. However, the peak height increases with the rate of heating and the charge detrapping takes place in a shorter time depending on the rate of heating. In fact, the intensity at the maximum of thermally stimulated luminescence is given by

$$I_m = -n_0 s \exp(-E/kT_m) \exp \int_{T_0}^{T_m} S/\beta \exp(-E/kT) dT \quad \text{---(62)}$$

where T_m is the temperature of maximum intensity. It has been argued Randall et al (1945) that for the first order kinetics

$$\int_{T_0}^{T_m} \left(-\frac{S}{\beta} \exp(-E/kT) dT \approx 1 \right) \quad \text{---(63)}$$

and remembering that at the peak of TSL

$$\beta E / (kT_m)^2 = S \exp(-E/kT_m) \quad \text{---(64)}$$

This simple model yields an expression for the peak intensity as a function of heating rate as follows:

$$I_m = n_0 \beta E / (kT_m)^2 \quad \text{---(65)}$$

The equation (65) shows that the intensity of TSL maximum is linearly proportional to the rate of heating. In addition, the intensity is also proportional to initially trapped charge.

In Fig.5, a constant noise level is assumed, and it is obvious from the above considerations that increase in the rate of heating is very effective in enhancing the signal to noise ratio. On the other hand, if the area under the TSL curve is to be considered as the measure of signal, we see that for curve A, the noise is integrated for a much longer time i.e. t_3 sec unlike the case of curve C, where it is integrated for a much shorter time i.e. t_1 sec. In addition, for curve A, a significant fraction of the signal is buried under the noise, which is represented by the fraction of the curve under the noise level in the Fig. 5. Thus, an enhanced signal to noise ratio is expected with increase in the rate of heating whether the peak height or the area of the TSL curve is considered as the measure of the signal.

For optical stimulation similar consideration will apply. Of course, the rise of the OSL curve would be very fast because incident photon is absorbed by the trapped carrier and raised to an excited state from where it is free to recombine with the opposite charge in a very short time. However, the observed risetime of the signal is generally limited by the risetime of the detection system which is of the order of nanosecond. The decay of the OSL would be rather slow and shall depend upon the stimulating intensity.

THERMALLY VERSUS OPTICALLY STIMULATED LUMINESCENCE

Both TSL and OSL processes involve detrapping of the stored charge and subsequent recombination of the detrapped charge with a recombination center. However, our investigations in MgS phosphor doubly doped with rare earth ions reveal that

the charges released in two processes are of opposite kind. Of course, the destruction of TSL resulted in the disappearance of OSL. The description that follows, however, is phenomenological and application to other phosphor systems is yet to be established.

Some of the important results of our investigations in MgS doubly doped with rare earth ions are as follows: The TSL peaks (for MgS:Ce,Sm at 346 and 449K) can be optically bleached by near infra-red light, high temperature peak being affected more than the low temperature peak. The stimulation spectrum was unaffected by the anneal of low temperature peak and could also be bleached similar to the high temperature TSL peak. Moreover, after optical bleach or thermal anneal of the high temperature peak, the stimulation spectrum disappeared, indicating an intimate correlation between the TSL and OSL in these phosphors.

Fig.6 depicts the thermally stimulated emission spectrum of MgS:Ce,Sm and MgS:Eu,Sm [18]. In both cases, the emission spectrum consists of Sm^{3+} emission attributed to the transitions to ${}^6H_{5/2}$, ${}^6H_{7/2}$, and ${}^6H_{9/2}$ ground states, respectively. Fig.7 shows the laser stimulated optical emission spectra of these two phosphor system. In the case of MgS:Eu,Sm, the OSL spectrum is a broad band characteristic of Eu^{2+} ion, while it is characteristic Ce^{3+} doublet for MgS:Se,Sm. These results point to the fact that Sm^{3+} is the recombination center for TSL and the charge (hole) is trapped at Eu^{2+} or Ce^{3+} ions and for OSL the trapped charge is an electron, which recombines with a hole at Eu or Ce sites with a characteristic emission of Eu^{2+} or Ce^{3+} ions. A plausible scheme for the observed TSL and OSL in these two phosphors is shown in Fig. 3.8.

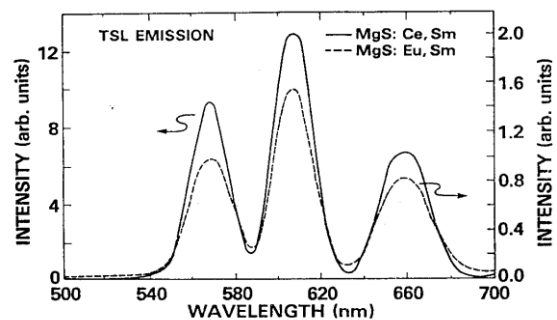


Fig 6. TSL emission.

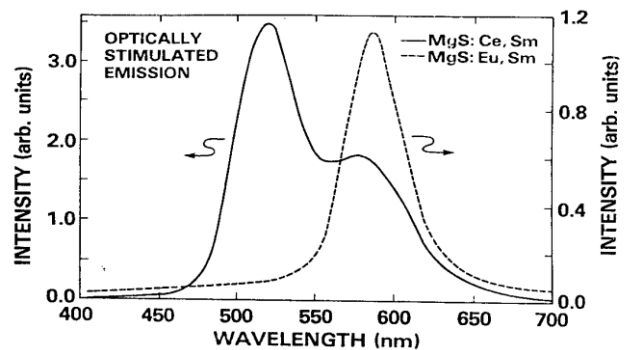


Fig. .7. OSL emission

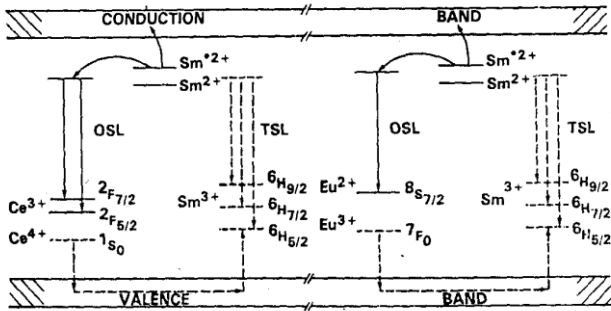


Fig. 8 Schematic of OSL and TSL emission

TUNNELLING AND STIMULATED LUMINESCENCE

Role of tunnelling in stimulated luminescence is not clear. However, it is possible in a real life situation that stimulated luminescence is assisted by tunnelling. The energy of the external stimulus (optical or thermal) may not be sufficient to raise the trapped charge to a delocalized level (conduction or valence band), but can raise the trapped carrier to an excited state from where it can tunnel to recombine with the opposite charge. Raising the trapped charge to an excited state amounts to lowering the energy barrier for tunnelling. Large amounts of experimental evidence has been gathered to indicate the presence of tunnelling in various materials. McKeever et al (1985) and Visocekas (1979).

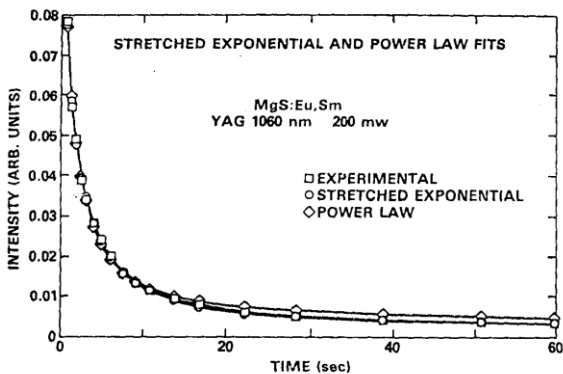


Fig. 6. OSL decay.

Fig. 9. optically stimulated luminescence as a function of time in MgS:Eu,Sm stimulated by 1.06μm Nd:YAG laser

The optically stimulated luminescence as a function of time in MgS:Eu,Sm stimulated by 1.06μm Nd:YAG laser is shown in Fig. 9 The experimental curve has been fitted with a theoretical expression derived which is as follows

$$I = I_0 (1 - e^{-W_0 t}) t \quad \text{-----(66)}$$

This expression has been derived on the basis of a tunnelling model between the pairs of traps and recombination centers separated by various distances.

A closer look at Fig. 9 reveals that the equation (66) does not fit the experimental data very well for longer time intervals.

Instead an expression, known as stretched exponential

$$I = I_0 \exp(-\alpha t^\beta) \quad \text{---(67)}$$

better fits the experimental data.

The shallow traps and the excited states of deep traps do not distinguish. Thus the rate of charge tunnelling from the trap to the recombination center is denoted by a term

$$W(R) = W_0 e^{-2R/a} \quad \text{---(68)}$$

which is typical of the ground state of an hydrogen-like system to which a simple trap can be compared. However, if one considers tunneling from an excited state of an hydrogen-like system (for example $n = 2, \ell = 1$), the radial eigenfunction is given by

$$R_{21} = \text{Const} \exp(-k/r) \cdot r \quad \text{---(69)}$$

and the rate of tunneling should, appropriately, be given by

$$W(R) = W_0 \exp(-2R/a) \cdot R/a \quad \text{---(70)}$$

This function decreases slowly as compared to the function given by equation (68) and has the potential of generating a stretched exponential dependence of OSL on time. Therefore, it is more appropriate for MgS:Eu,Sm to consider that OSL is probably caused by the tunnelling of the carriers which are optically raised to the excited state of deep traps [19].

Another interesting observation in MgS:Eu,Sm which supports tunneling can be understood the absorption spectrum of this material exhibits two prominent absorption bands around 480nm, 260nm, which are attribute to the transitions $^8S_{7/2} \Rightarrow ^2T_{2g}$ and $^8S_{7/2} \Rightarrow ^2E_g$ respectively, in Eu^{2+} ion. Previously heated phosphor, to empty all the trapped charges, when exposed to 500nm light, which is unable to cause band to band excitation, exhibits thermally as well as optically stimulated emission. This result can be interpreted as follows: 500nm light is able to excite an electron in the Eu^{2+} ion to the t_{2g} level from where it can tunnel to Sm^{3+} ion, and can remain trapped there leaving behind a trapped hole in Eu^{2+} . This situation is identical to the situation depicted in Fig. 8 and can result in thermally stimulated luminescence due to the release of hole from Eu ion and optically stimulated emission due to the release of electron from the Sm ion.

APPLICATIONS

A number of applications of laser stimulated luminescence are possible. Some of these have been already developed to the extent that a commercial device is either available or soon to be marketed. Few important ones are enumerated below:

1. Radiation Dosimetry - Both thermal and optical stimulated luminescence, by lasers, can be applied to radiation dosimetry. Thermally stimulated luminescence by using laser (popularly known as Laser Heated Thermoluminescence Dosimetry) has taken great strides in the recent past in this direction .
2. Computed Radiography - Both thermally and

optically stimulated luminescence has been successfully used for x-ray imaging. Typical material used for optical stimulation is BaFX:Eu (X=Cl, Br, I) and the stimulation was achieved through He-Ne laser Sonoda et al (1983). Imaging by thermal stimulation is achieved by heating CaSO₄:Dy phosphor by CO₂ laser.

- Optical Memory - Possibility of filling the deep traps in rare earth doped alkaline earth sulfides with visible light and detrapping with infra-red lasers has resulted in the development of 'Electronic Trapping Optical Memory' device. This device is expected to hold data up to one billion bytes per disk. Moreover, unlike the magneto-optic device, no heating of the disk surface is required when storing the information, which increases the longevity of the storing medium.
- Laser Discrimination - Some phosphors such as MgS:Se,Sm and pretreated MgO exhibit different colors under thermal and optical stimulation. It affords a means to discriminate between the laser causing the optical stimulation (generally the near infra-red laser) and the laser causing thermal stimulation (far infra-red laser such as 10.6μm CO₂ laser)

CONCLUSIONS

(1) According to first order kinetics of TL following equations are derived

$$I = \eta n_0 S \exp\left(-\frac{E}{kT}\right) \exp\left[-\int_{T_0}^T \frac{S}{\beta} \exp\left(-\frac{E}{kT}\right) dT\right]$$

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

$$I_m = \eta S n_0 \exp\left(\frac{-E}{kT_m}\right)$$

$$I(t) = \eta n_0 S \exp\left(\frac{-E}{kT}\right) \exp\left\{-S \int_{t_0}^t \exp\left(\frac{-E}{kT(t)}\right) dt\right\}$$

$$I(T) = \eta n_0 S \exp\left(\frac{-E}{kT}\right) \exp\left[-S \int_{T_0}^T \left(\frac{dT}{dt}\right)^{-1} \exp\left(\frac{-E}{kT}\right) dT\right]$$

(2) According to second order kinetics of TL following equations are derived

$$I = S' n^2 \exp\left(\frac{-E}{kT}\right)$$

In the initial rise range i.e. T substantially below T_m then we get

$$I(T) \approx n_0^2 S' \exp\left(\frac{-E}{kT}\right)$$

At higher temperature the latter term increases subsequently and the unity can be neglected so that one obtains.

$$I(T) \approx n_0^2 S' \exp\left(\frac{-E}{kT}\right) \left[\left(\frac{n_0 S'}{\beta} \right) \int_{T_0}^T \exp\left(\frac{-E}{kT}\right) dT \right]^{-2}$$

(3) According to general order kinetics of a single TL peak following equations are derived

$$I(t) = \eta S n_0 \exp\left(\frac{-E}{kT}\right) \exp\left\{-\frac{S}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{kT}\right) dT\right\}$$

$$I(T) = \eta n_0^2 S' \exp\left(\frac{-E}{kT}\right) \left[1 + \left(\frac{n_0 S'}{\beta} \right) \int_{T_0}^T \exp\left(\frac{-E}{kT}\right) dT \right]^{-2}$$

$$I(t) = \eta S n_0 \exp(-E/kT) \left\{ \frac{(b-1)S}{\beta} \int_{T_0}^T \exp(-E/kT) dT + 1 \right\}^{-b/(b-1)}$$

$$I(t) = -\eta \frac{dn}{dt} = \eta S \exp\left(\frac{-E}{kT}\right) F(n)$$

$$F(n) = \frac{S A_n n(n+c_1)}{\{A_m(n+c_1) + A_n(N-n)\}}$$

(4) Laser stimulated TL intensity are derived

$$I_m = -n_0 s \exp(-E/kT_m) \exp \int_{T_0}^{T_m} \frac{S}{\beta} \exp(-E/kT) dT$$

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