# STUDY OF UNIFIED MODEL FOR THERMALLY STIMULATED LUMINESCENT PHOSPHORS

**Tarun Kumar Dey[1] and Brahma Nand Jha[2]**

[1]Post Graduate Department of Physics, L. S. College, Muzaffarpur

Email: tkdeyphy@gmail.com

[2]Department of Physics, M.S.S.G College,Areraj,B.R.A Bihar University,Muzaffarpur – 842001

Email: bnjha1235@gmail.com

**ABSTRACT**

The thermally stimulated luminescence (TSL) glow curves arising simultaneously from localized, semi-localized and delocalized transitions have been investigated theoretically. It has been found that it is possible to explain the dose dependence of glow peak temperature Tm in case of localized transitions. In addition to this a comparative study among the localized and delocalized transitions model is also reported. It is expected that the model is capable of explaining the various experimental results observed in many TSL phosphors.

**INTRODUCTION:**

Due to the limited information available about the nature and the behavior of defects and their mutual influence over short as well as long range in various TSL phosphors, it is not possible to explain the TSL process from the first principle. In view of this, till today there is no theory to predict the exact behavior and properties of a TSL phosphor. Further it is impossible to predict and calculate the influence of dopant on host lattice as the amount of doping is small i .e. up to few mole % or parts per million (ppm). In view of these physical facts, the models of TSL based upon phenomenological approach are being used and are playing important role in the understanding of the TSL process and its applications in various fields.

Till today the models of TSL are based upon two type of independent assumptions i.e. the electrons emitted from the traps during heating may move to recombination centres via i) the conduction/delocalised band ii) the excited state of the trap/impurity (sub- conduction recombination) [I]. The first mode of recombination is called delocalised/conduction band recombination whereas second mode is called sub-conduction/locali sed recomb ination . In the first process the electrons are free to move through the whole crystal lattice whereas in the second process they are not free.

The models based on above assumptions are inadequate as there are large number of experimental results, which cannot be explained using any of the above models. Some of the experimental results are [2-3]:

1. In many phosphors, the TSL glow curves exhibit linear, sub-linear and supra linear behaviour i.e. dose vs. TSL response
2. Observance of TSC even in those phosphors in which it is suspected that TSL arises from localised recombination.
3. The TSL glow curves exhibit abnormal (>0.52) geometrical factor.
4. Observance of abnormal value of attempt to escape/frequency factor (vibrational frequency).
5. Glow peak temperature $T_m$ sometimes is independent of radiation dose upto certain value whereas after this value $T_m$ is function of dose.
6. Peak temperature Tm is function of dopant in some of the phosphors such as $CaS0_4$ doped with rare earths.

These experimental evidences have changed the earlier held notion of the theoretical modeling i.e. simple models of highly localized point defects or well separated trapping and recombination centres assuming complete delocalization of charge carriers are not adequate.

All these facts need to be incorporated in the theoretical models of TSL so that TSL behaviour of most of the TSL materials can be explained. In this paper, the localized, semi-localised and delocalized recombination processes are treated simultaneously and some of the above mentioned points have been explained.

**THE MODEL:**

In a material with a wide band gap, following possibilities can occur simultaneously during heating phase of the phosphor [4-5]:

1. The trapped electron is raised directly to the conduction band, where it is free to move and may be re-trapped or can recombin e with a trapped hole (delocalised recombination) .
2. The trapped electron is raised thermally from the ground state of the trap to an excited state below the conduction band, from where it may be re-trapped or recombine with a trapped hole, which are in its immediate vicinity. For simplicity it has been assumed that there is only one electron in the ground state of the trap (localised recombination).
3. Further during heating the electrons in the excited state of the trap may also move to the conduction band and may get re-trapped or recombine with a trapped hole (semi-localised recombination).

In the above model (as shown in Fig. 1) the possibility of transition of electrons from the ground state of the trap to the recombination centres (quantum mechanical tunneling) is ruled out.

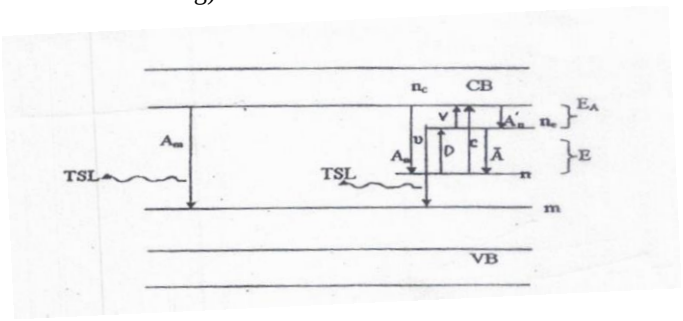


Fig. 1: Energy level scheme for unified model.

On the basis of these assumptions the equations of the unified model are

$$\begin{aligned}
\frac{dn}{dt} &= -ns\exp(-E/kT) + \bar{A}n_c - ns\exp(-(E+E_A)/kT) + A_n(N-n)n_c \\
\frac{dn_c}{dt} &= ns\exp(-E/kT) - \bar{A}n_c - n_e s^*\exp(-E_A/kT) + A'_n(N-n)n_c - vn_e \\
\frac{dn_c}{dt} &= -A_n(N-n)n_c - A'_n(N-n)n_c + n_e s^*\exp(-E_A/kT) - A_m m n_c + ns\exp(-(E+E_A)/kT) \\
\frac{dm}{dt} &= -vn_c - A_m m n_c
\end{aligned} \qquad (1.1)$$

where $n$ is the number density of the electrons in the ground state of the trap (m-3), $n_c$ is the number density of the electrons in the excited state of the trap ($m^{-3}$), $N$ is the total concentration of the available traps ($m^{-3}$), $n_c$is the number density of the electrons in the conduction band ($m^{-3}$), $m$ is the concentration of recombination centres ($m^{-3}$) &$m = n + n_e + n_c$. $D$, the excitation of trapped electrons to the excited state of the trap (detrapping). C, and $V$, excitation of electrons to the conduction band from ground and excited state of the trap. $A_n$ and $A_n'$ are re-trapping coefficients for the conduction band electrons to the ground and the excited state of the trap respectively ($m^3/s$). I n the set of equations 1.1, the retrapping rate from the excited state of the trap to the ground state of the trap is $\bar{A}\, n_e$. This means that the probability per second for retrapping transition is $\bar{A}$ (Hz) and $\bar{A}$ can have values over a widerange ($\bar{A}$ <s, $\bar{A}$ >s and $\bar{A}$ = s). $A_m$ is the recombination coefficient for the conduction band electrons (m3/s) undergoing delocalised recombination . $v$ is the transition probability per second for recombination via localised transitions (Hz) and can have values varying from 103-I 015sec-1• In fact $v$ represents intra-pair transitions between spatially correlated traps and recombination centres. $s$ is the frequency factor (Hz) for the electron in the ground state of the trap and is related to the vibrational frequency of the lattice, $s^*$ is the frequency factor in the excited state of the trap ($m^{-3}$), $k$ the Boltzman's constant (J/K) and $T$ the absolute temperature ( K). $E$, the energetic distance from the ground state of the trap to the excited state ofthe trap (activation energy, eV), $EA$ (eV) is the energetic distance from the excited state of the trap to the conduction band and $(E + EA)$ is the energy required to raise the trapped electron directly to the conduction band in single activation. The set of equations 1.1 represents localised, semi/extended localised and delocalised behaviour simultaneously. In this model , the TSL arises from both the processes namely localised, semi-localised and delocalised recombination and the resultant glow curves are the superposition of the TSL of both the processes. The individual contribution of both the processes is decided by the various retrapping and recombination parameters as well as by the radiation dose.The intensity $I$ of TSL is given by

$$I = -\frac{dm}{dt} = vn_e + A_m m n_c \qquad (1.2)$$

In the set of equations 1.2, the TSL intensity arising from localised recombination, $I_{Loc}$is $vn_c$ whereas the TSL intensity arising from delocalised recombination process $I_{Dloc}$ is $A_m\, mn_c$.

*The special cases of the set of equations 1.1*

i. *If it is assumed that during heating, the electrons from the ground state of the trap are not raised directly to the conduction band in single activation but they are first raised to an excited state below the conduction band and further from the excited state of the trap they may be raised to the conduction band. This is a two-step thermal activation. Under these assumptions the set of equations 1.1 can be written as*

$$\begin{aligned}
\frac{dn}{dt} &= A_n(N-n)n_c - s\exp\left(-\frac{E}{kT}\right)n + \bar{A}n_e \\
\frac{dn_e}{dt} &= s\exp\left(-\frac{E}{kT}\right)n - \bar{A}n_e - S^*\exp\left(-\frac{E_A}{kT}\right)n_e + A'_n(N-n)n_c - vn_e \qquad (1.3a) \\
\frac{dn_c}{dt} &= -A_n(N-n)n_c - A'_n(N-n)n_c + s^*\exp\left(-\frac{E_A}{kT}\right)n_e - A_m m n_c \\
\frac{dm}{dt} &= -vn_e - A_m m n_c
\end{aligned}$$

The set of equations l.3a represents the semi-localised transitions model.

ii. If the excitation of trapped electrons to the excited state below conduction band is not allowed i.e. ( $n_e$= 0), but they can be raised directly to the conduction band, then from the set of equations 1 .1, we have

$$\frac{dn}{dt} = -ns\exp\left(-\frac{E+E_A}{kT}\right) + A_n(N-n)n_c$$
$$\frac{dn_c}{dt} = -A_n(N-n)n_c - A_m m n_c + ns\exp\left(-\frac{E+E_A}{kT}\right) \quad (1.3b)$$
$$\frac{dm}{dt} = -A_m m n_c$$

which is delocalized / conduction band model of Halperin and Braner [1].

iii. If there is no excitation of trapped electrons to the conduction band either from the excited state of the trap or from the ground state of the trap, then from the set of equations 1 .1, we have

$$\frac{dm}{dt} = -vn_e$$
$$\frac{dn}{dt} = -ns\exp\left(-\frac{E}{kT}\right) + \bar{A}n_e \quad (1.3c)$$
$$\frac{dn_e}{dt} = \frac{dm}{dt} - \frac{dn}{dt}$$

which is localised transitions model of Chen and Halperin (assume $\bar{A}$= s) [1).

Hence all the models of TSL described earlier [1] by many researchers can be derived from the set of equations 1.1, implying that the set of equations 1.1 are more generalised when compared with other models.

**NUMERICAL STUDY:**

The set of equations 1.1 /1 .3a, which are stiff differential equations, is solved numerically for wide range of parameters. The parameters assumed theoretically unless otherwise mentioned are $E$ = 0.70 eV, $E_A$= 0.30 eV, $s$ = 1010 Hz, $s^*$ = s/10 Hz, $A_n=A_m=10^{-16}m^3/s$, $A_n=10^{-17}$ $m^3/s$, heating rate =1 k/s, $T_0$ =300k and $N = 10^{23}$ $m^{-3}$ the different parameters like $\bar{A}$, $A_m$, $N$ and $v$ can be normalized to a new dimensionless parameters $\mu_g = \bar{A}_m N/v$ and $r = \bar{A}/v$. The variation in the values of $\mu_g$ and $r$ for typical range of $A_m$ ($10^{-12}$-$10^{-20}$ m3/s) and $v$ ($10^3$-$10^{14}$ Hz) can be from $10^{-11}$

$10^{-8}$ and $10^{-11}$ -$11^{11}$respectively if it is assumed that the value of total number of available traps i.e. $N$ is nearly $10^{23}$ $m^{-3}$. The difference in the range of $\mu_g$ and $r$ by two three orders of magnitude is not ruled out.

**i. *TSL arising from mixture localised, semi-localised & delocalised recombination processes:***

To demonstrate the dose dependence of glow peak temperature $T_m$, the *TSL* glow curves arising from localised, delocalised and mixture of both the recombination Processes are obtained for three different doses i.e. $m_0 = n_0 = 10^{23}$, $10^{21}$, $10^{19}$ $m^{-3}$ and $n_{c0} = n_{c0} = 0$ The other parameters assumed theoretically are $\bar{A} = 10^{10}$ Hz, $v = 10^5$ Hz,i.e; $r = 10^5$.It is clear from Table-1 that the glow peak temperature $T_m$ is dose dependent implying that the order of kinetics is more than one and it is possible to have non-first order kinetics for the glow curves arising specially from localised recombination. Further if $v = 10^{10}$ Hz and $\bar{A} = 10^{10}$ Hz i.e; $r$ = 1, then it has been found that peak temperature $T_m$is independent of dose implying that order of kinetics is always one.

**ii.*TSL arising from semi-localised recombination processes:***

The set of equations 1.3a is solved numerically and the corresponding glow curves are obtained for $r=10^5$. Further the dose dependence of glow peak temperature $T_m$is also studied. The study implies that the glow peak temperatures of the TSL glow curves arising from localised recombination can exhibit dose dependence for higher values of $r$ (>>1) whereas for other values of $r$, the order of kinetics for the TSL glow curves arising from localised recombination is always one.

**LOCALISED AND SEMI LOCALIZED TRANSITIONS: A COMPARATRIVE STUDY**

*The basic properties of the TSL glow curves arising from pure localised recombination are:*

i. Glow peak temperature *Tm* is always independent of dose,
ii. The TSL glow curves are not accompanied with TSC,
iii. The order of kinetics is always one
iv. Isothermal decay is exponential and
v. TSL output vs. dose is linear but sub-linearity/saturation may occur at very high doses.

*Further the TSL glow curves arising for semi-localised recombination can have following properties:*

i. TSL glow curves are accompanied with TSC,
ii. Dose dependence of the glow peak temperature *Tm* can be observed,
iii. Non-first order kinetics can exist,
iv. TSL output vs. dose can be linear, sub-linear or supra-linear and saturation may also occur at very high doses and
v. The TSL glow curves arising from localised and delocalised transitions can have different spectral emissions i.e. possible to distinguish between local ised and delocalised components using spectrally resolved TSL.

**Table 1**

| Doso $m_0 = n_0$ | Localised Recombination | | | Delocalised Recombination | | | (Localised +Delocalised) Recombination | | |
|---|---|---|---|---|---|---|---|---|---|
| $m^{-3}$ | $T_m$ (K) | $I_m$(a.u.) | $\mu_g$ | $T_m$ (K) | $I_m$(a.u.) | $\mu_g$ | $T_m$ (K) | $I_m$(a.u.) | $\mu_g$ |
| $10^{23}$ | 458.81 | $6.99*10^{19}$ | 0.58 | 446.33 | $1.47*10^{21}$ | 0.50 | 446.33 | $1.54*10^{21}$ | 0.50 |
| $10^{21}$ | 525.06 | $7.66*10^{18}$ | 0.47 | 514.62 | $4.44*10^{18}$ | 0.46 | 520.38 | $1.19*10^{19}$ | 0.48 |
| $10^{19}$ | 538.00 | $1.15*10^{17}$ | 0.44 | 528.56 | $7.91*10^{14}$ | 0.43 | 538.00 | $1.15*10^{17}$ | 0.44 |

**CONCLUSION:**

The thermally stimulated luminescence (TSL) glow curves arising simultaneously from localised, semi-localised and delocalised transitions have been investigated theoretically. It has been found that it is possible to explain the dose dependence of glow peak temperature $T_m$ in case of localized transitions. In addition to this a comparative study among the localised and delocalised transitions model is also reported. It is expected that the model is capable of explaining the various experimental results observed in many TSL phosphors. Further detailed investigation in the presence of competing traps and recombination centres are required and the model needs to be tested in various TSL phosphors.

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