

## Thermoluminescence glow curve involving any extent of retrapping or any order of kinetics

JAI PRAKASH

Department of Applied Science & Humanities, Buddha Institute of Technology,  
CL 1, GIDA, Gorakhpur 273 209, India

Previously at the Department of Physics, D.D.U. Gorakhpur University, Gorakhpur 273 009, India

E-mail: jpgkp.2010@rediffmail.com

MS received 3 October 2012; revised 25 April 2013; accepted 11 June 2013

**Abstract.** Adirovitch set of equations has been modified to explain the mechanisms involved in thermoluminescence (TL) glow curve. A simple model is proposed which explains the occurrence of TL glow curve involving any extent of retrapping or any order of kinetics. It has been observed that the extents of recombination and simultaneous rewrapping decide the order of kinetics involved. TL decay parameters, order of kinetics and initial concentration of trapped electrons per unit volume are evaluated easily and conveniently. It has been observed that retrapping increases with increasing order of kinetics.

**Keywords.** Thermoluminescence; Adirovitch set of equations; thermally stimulated processes; ionic thermocurrent.

**PACS Nos** 77.22.Ej; 78.60.Kn

### 1. Introduction

An electron excited from the valance band to the conduction band may either recombine quickly with an oppositely charged centre (fluorescence) or gets trapped at the trap centre [1]. Once it is trapped at the trap centre, it needs an external energy for it to excite again to the conduction band wherefrom it may recombine with an oppositely charged centre emitting a photon (luminescence). If the external energy is thermal, it is known as thermoluminescence (TL). Direct transition from trap centre to recombination centre is, however, forbidden. In an attempt to explain the TL glow curve, Adirovitch [2] proposed a set of three equations, which controls the traffic of electrons from the trap centre to the recombination centre via conduction band as

$$I = - \left( \frac{dm}{dt} \right) = mn_c A_m, \quad (1)$$

$$- \left( \frac{dn}{dt} \right) = ns \exp \left( \frac{-E_a}{kT} \right) - n_c (N - n) A_n \quad (2)$$

and

$$m = n + n_c, \quad (3)$$

where  $I$  is the intensity of the TL glow curve,  $m$  and  $n$  are the densities of holes and electrons in the respective recombination and trap centres,  $n_c$  is the density of electrons in the conduction band,  $A_m$  is the transition probability from the conduction band to the recombination centre,  $A_n$  is the transition probability from the conduction band to the trap centre,  $E_a$  is the activation energy or trap depth,  $s$  is the pre-exponential factor or escape frequency factor,  $k$  is the Boltzmann's constant,  $T$  is the absolute temperature,  $t$  is the time corresponding to  $T$  and  $N$  is the density of the total trap centre. Equations (1)–(3) are considered to be the basic equations which have been used by various workers to explain the occurrence of TL glow curve [3]. Mechanisms inherent in systems involving first-order kinetics or monomolecular kinetics are supposed to be recombination dominant with negligible or zero retrapping. Intensity ( $I_1$ ) of the TL glow curve at the temperature  $T$  involving first-order kinetics is represented by [4]

$$I_1 = n_0 s_1 \exp \left[ - \left( \frac{E_a}{kT} \right) - \left( \frac{s_1}{b} \right) \int_{T_0}^T \exp \left( \frac{-E_a}{kT'} \right) dT' \right], \quad (4)$$

where  $n_0$  is the initial concentration of the trapped electrons per unit volume at  $T_0$  corresponding to  $t = 0$ ,  $T_0$  is the initial temperature wherefrom the TL glow curve starts to appear,  $b$  is the constant linear heating rate and  $T'$  is an arbitrary temperature in the range  $T_0$  to  $T$ . Suffix 1 represents the parameters of first-order kinetics. It has been reported that probabilities of recombination and retrapping are equal in systems involving second-order kinetics [5]. The intensity ( $I_2$ ) of the TL glow curve involving second-order kinetics is given by

$$I_2 = n_0^2 s_2 \exp \left[ - \left( \frac{E_a}{kT} \right) \right] \left[ 1 + \left( \frac{n_0 s_2}{b} \right) \int_{T_0}^T \exp \left( \frac{-E_a}{kT'} \right) dT' \right]^{-2}. \quad (5)$$

The escape frequency factor  $s_2$  for second-order kinetics is a constant quantity with the dimension  $\text{m}^3 \text{s}^{-1}$ . Parameters  $s_1$  and  $s_2$  are related as

$$s_1 = N s_2. \quad (6)$$

Further, the intensities of second- and higher-order TL glow curves are represented by [6]

$$I_\ell = n_0^\ell s_\ell \exp \left[ - \left( \frac{E_a}{kT} \right) \right] \times \left[ 1 + \left( \frac{n_0^{(\ell-1)} s_\ell (\ell-1)}{b} \right) \int_{T_0}^T \exp \left( \frac{-E_a}{kT'} \right) dT' \right]^{-\ell / (\ell-1)}, \quad (7)$$

where  $\ell$  represents the order of kinetics involved. Equation (7) changes to eq. (5) for  $\ell = 2$ . Parameters  $s_1$  and  $s_\ell$  are related through the equation

$$s_1 = s_\ell N^{(\ell-1)}, \quad (8)$$

where  $s_\ell$  has the dimension  $\text{m}^{3(\ell-1)} \text{s}^{-1}$ . One gets eq. (6) from eq. (8) for  $\ell = 2$ . When all the available electron traps are filled initially, i.e. when  $N = n_0$ , eq. (7) changes to

$$I_\ell = n_0 s_1 \exp\left[-\left(\frac{E_a}{kT}\right)\right] \times \left[1 + \left(s_1 \left(\frac{\ell-1}{b}\right)\right) \int_{T_0}^T \exp\left(\frac{-E_a}{kT'}\right) dT'\right]^{-\ell/(\ell-1)}. \quad (9)$$

It is obvious that the intensity of the TL glow curve involving first-order kinetics represented by eq. (4) cannot be obtained from eq. (9), whereas the intensities of TL glow curves involving second- and higher-order kinetics can be obtained from it.

Chen and Winer [6] reported that the peak of a general order TL glow curve involving the  $\ell$ th order of kinetics appears at  $T_{m\ell}$  controlled by

$$\left[1 + \left(s_1 \left(\frac{\ell-1}{b}\right)\right) \int_{T_0}^{T_{m\ell}} \exp\left(\frac{-E_a}{kT}\right) dT\right] = \left\{\frac{\ell s_1 k T_{m\ell}^2}{b E_a}\right\} \exp\left(\frac{-E_a}{k T_{m\ell}}\right). \quad (10)$$

Equation (10) decides the location of the TL glow peak in cases involving first- and higher-order kinetics. Anomalies associated with eqs (9) and (10) led us to reinvestigate the mechanisms inherent in the TL process. Many attempts have been made [7–14] in the quest of proposing responsible mechanisms, but none of them has been found to be satisfactory. For developing a suitable model, the following points have to be taken into considerations:

- (1) Inability of eq. (9).
- (2) Ability of eq. (10).
- (3) Imposing the condition  $N = n_0$  while developing eq. (9).
- (4) Although  $A_m$  decides the transition probability, it has no direct role in the derivation of expression for the intensity of TL glow curve. It is the extent of recombination and simultaneous retrapping which decide the order of kinetics involved.
- (5) Same is the case with  $A_n$  in eq. (2).
- (6) Garlick and Gibson [5] have proposed that second-order kinetics is a case of strong retrapping probability or a case of fast retrapping process [15,16]. In actual practice, recombination and retrapping probabilities are, however, supposed to be 50% each in systems involving second-order kinetics.
- (7)  $s_\ell$  has the dimension  $\text{m}^{3(\ell-1)} \text{s}^{-1}$  which contradicts Arrhenius relation [17].
- (8) The relationship between  $s_\ell$  and  $s_1$  has no relevance and is not justified as they belong to systems involving different orders of kinetics.
- (9) In eq. (3), one gets  $n_c$  as a result of excitation of electrons from the trap centre. So,  $m = n + n_c$  represented by eq. (3) is misleading and illogical.
- (10) Dropping  $n_c$ , assuming  $n_c \ll n$ , is not valid in general.
- (11) The dependence of  $T_{m\ell}$  on  $n_0$  in systems involving second- and higher-order kinetics does not seem to be a realistic and reasonable proposition.

In view of the above observations, a model has been proposed which is found to be capable of explaining the occurrence of the TL glow curve successfully and is free from

anomalies mentioned above. The values of the TL decay parameters, order of kinetics and initial concentration of trapped electrons per unit volume are obtained easily and conveniently.

## 2. Proposed model

In a sample,  $m$  and  $n$  are equal leading to the assumption that sample as a whole is neutral. So, charge neutrality condition requires

$$m = n. \quad (11)$$

After excitation from the trap centre, one gets  $n_c$  in the conduction band. During this process,  $n$  decreases by the same amount. Thus, the charge neutrality equation can be represented as

$$m = (n - n_c) + n_c.$$

This relation obviously leads to eq. (11), and hence,  $n_c$  should not come in picture in charge neutrality equation as proposed by Adirovitch in eq. (3).

When the specimen is heated, trapped electrons are excited to the conduction band vide

$$-\left(\frac{dn}{dt}\right) = ns \exp\left(-\frac{E_a}{kT}\right) = \frac{n}{\tau}, \quad (12)$$

where  $\tau$  is the relaxation time at  $T$  which is represented with the help of Arrhenius relation [17] as

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right), \quad (13)$$

where  $\tau_0$  is the fundamental relaxation time or the relaxation time at infinite temperature.  $\tau_0$  and  $s$  are related to each other through the equation

$$\tau_0 = \frac{1}{s}. \quad (14)$$

Out of the excited electrons in the conduction band, some are retrapped and the remaining get recombined, and hence, effective rate of decrease of  $n$  or effective rate of excitation is expressed as

$$-\left(\frac{dn}{dt}\right) = ns \exp\left(\frac{-E_a}{kT}\right) - xns \exp\left(\frac{-E_a}{kT}\right), \quad (15)$$

where the second term on the right-hand side represents the electrons which are retrapped and  $x$  represents the fraction or part of the excited electrons which are retrapped such that  $0 \leq x \leq 1$ . It would be justified to mention that  $x$  depends on experimental conditions and also on the transition probabilities  $A_m$  and  $A_n$ . For  $x = 0$ , retrapping is zero corresponding to the first-order kinetics and for  $x = 0.5$ , retrapping is 50% corresponding to the second-order kinetics and so on. Equation (15) is further expressed as

$$-\left(\frac{dn}{dt}\right) = (1 - x)ns \exp\left(\frac{-E_a}{kT}\right). \quad (16)$$

The remaining electrons in the conduction band represented by the right-hand side of eq. (16) recombine with oppositely charged centres present at the recombination centre. Thus, the rate of recombination and hence the intensity of the TL glow curve will be represented as

$$I = - \left( \frac{dm}{dt} \right) = (1 - x)ns \exp\left(\frac{-E_a}{kT}\right). \quad (17)$$

The negative sign in eq. (17) is due to the decrease in  $m$  as a result of recombination. With the help of eqs (15) and (17), it can be shown, just for the sake of justification, that the excited electrons become equal to the sum of retrapped and recombined electrons as expected. It is obvious from eqs (16) and (17) that

$$\left( \frac{dm}{dt} \right) = \left( \frac{dn}{dt} \right). \quad (18)$$

This relationship suggested by eq. (18) is also obtained through eq. (11) justifying the validity of the ideas suggested in the proposed model. Further, it is not necessary to assume either  $N = n_0$  or  $n_c \ll n$  for developing the basic equations. Equations (11), (16) and (17) represent the modified Adirovitch set of equations.

### 2.1 TL intensity

Equation (16) can be solved to give

$$n = n_0 \exp\left[-(st(1-x)) \exp\left(\frac{-E_a}{kT}\right)\right]. \quad (19)$$

Non-isothermal form of eq. (19) is expressed as

$$n = n_0 \exp\left[-(s(1-x)) \int_0^t \exp\left(\frac{-E_a}{kT}\right) dt\right]. \quad (20)$$

With this value of  $n$ , eq. (17) results in

$$I = (1-x)n_0s \exp\left[-\left(\frac{E_a}{kT}\right) - \left(s\left(\frac{1-x}{b}\right)\right) \int_{T_0}^T \exp\left(\frac{-E_a}{kT'}\right) dT'\right]. \quad (21)$$

Intensity of a TL glow curve involving retrapping to the extent of  $x$  is represented by eq. (21).

### 2.2 TL peak

Equation (17) with the help of eq. (12) can be rearranged as

$$I = \left( \frac{(1-x)n}{\tau} \right). \quad (22)$$

Differentiation of eq. (22) with time and using eqs (17) and (18), one gets

$$T_m^2 = \left( \frac{bE_a\tau_m}{(1-x)k} \right), \quad (23)$$

where  $\tau_m$  is the relaxation time at  $T_m$ . Equation (23) gives the location of the TL peak in systems involving retrapping to the extent of  $x$ . It is obvious that  $T_m$  is independent of  $n_0$  as expected. For monomolecular or first-order kinetics, eq. (23) with  $x = 0$  results in

$$T_m^2 = \left( \frac{bE_a\tau_m}{k} \right). \quad (24)$$

Equation (24) is also obtained from eq. (10) after substituting its corresponding value of  $\ell$ . This clearly indicates about the generality of eq. (23). With changing  $b$ , the rate of recombination changes resulting in the changed value of  $T_m$ . Change in  $n_0$  only influences the intensity of the TL glow curve. It is worth mentioning that eq. (24) is also valid for ionic thermocurrent (ITC) measurements [18].

### 2.3 TL decay parameters

From eq. (17) one gets with the help of eq. (18)

$$\int_{n_0}^0 dn = - \int_0^\infty I dt \quad (25)$$

which gives

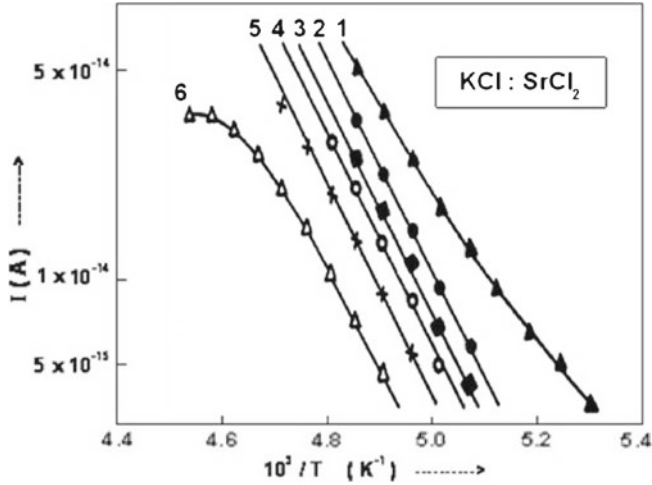
$$n_0 = \left( \frac{1}{b} \right) \int_{T_0}^\infty I(T') dT'. \quad (26)$$

Also, eq. (25) in the limits  $T$  to  $\infty$  gives

$$n = \left( \frac{1}{b} \right) = \int_T^\infty I(T') dT'. \quad (27)$$

Before developing equations for evaluating the TL decay parameters, mechanisms inherent in the TL decay process have to be taken into consideration. Retrapping of some of the electrons after excitation decreases the number of available electrons in the conduction band. Consequently, the intensity of the TL glow curve decreases. Also, the area enclosed in the TL glow curve decreases due to less number of electrons available for recombination. This argument is supported by eq. (26). Decreased value of  $n_0$  means that a specimen of the same system with lesser concentration has been considered. Obviously, TL glow curves recorded in these specimens shall give the same values of  $E_a$  and  $s$  as they belong to the same system. Similar findings have been recorded in many TL glow curves and ITC spectra. If the concentration is low and the relaxation is Debye type, one cannot see any dependence of dielectric relaxation parameters on the concentration of impurity vacancy (IV) dipoles [18]. In the initial rise method suggested by Bucci *et al* [18],  $\ln[I]$  plotted against  $[1/T]$  in KCl:Sr<sup>2+</sup> system results in a number of parallel straight lines corresponding to different concentration of IV dipoles as shown in figure 1, suggesting unchanged value of  $E_a$ . The intercept changes because of the change in the number of IV dipoles keeping  $s$  unchanged. This conclusion supports TL data also because ITC spectrum is very much similar to the TL glow curve involving monomolecular or first-order kinetics [18] (see §2.4).

Based on the discussions of the preceding paragraph, it is obvious that  $E_a$  and  $s$  of the system do not change due to different extents of retrapping. The evaluated values of  $E_a$



**Figure 1.** Plot of  $\ln(I)$  vs.  $(1/T)$  for six successive discharges recorded in  $\text{KCl}:\text{Sr}^{2+}$  single crystals [18]. The system has been polarized and then depolarized successively for recording the ITC data.

and  $s$  may correspond to a case of zero retrapping in the system. Thus, the values of  $E_a$  and  $s$  can be obtained after substituting  $x = 0$  in the relevant equations. In such condition eq. (17) for  $x = 0$  becomes

$$I = ns \exp\left(\frac{-E_a}{kT}\right)$$

which can be rearranged as

$$\ln\left(\frac{n}{I}\right) = \ln\left(\frac{1}{s}\right) + \left(\frac{E_a}{kT}\right). \quad (28)$$

It is obvious that one gets a straight line when  $\ln(n/I)$  is plotted against  $(1/T)$  in accordance with eq. (28). The slope of the line gives the value of  $E_a$  and from the intercept one gets the value of  $s$ . It is observed that these values of  $E_a$  and  $s$  do not satisfy eq. (24). Consequently, the value of  $x$  has been evaluated using eq. (23). It would be worth mentioning that eq. (28) has been used by many workers engaged in TL studies for evaluating TL decay parameters without caring whether eq. (24) is satisfied or not. Thus, the proposal of  $x$  finds a justification and the values of  $E_a$ ,  $s$  and  $x$  can be obtained using eqs (28) and (23), respectively.

#### 2.4 Similarity in TL glow curves and ITC spectra

Bucci *et al* [18] have mentioned that ITC spectrum is very much similar to the TL glow curve involving monomolecular or first-order kinetics. To establish this similarity for higher-order kinetics, it will be fruitful to compare the corresponding expressions of these processes. The intensity of a TL glow curve involving retrapping to the extent of  $x$  and expression for its corresponding peak are represented by eqs (21) and (23), respectively.

Depolarization current  $I$  in an ITC spectrum involving  $\ell$ th-order of kinetics is represented by [19]

$$I = \left( \frac{Q_0}{\ell \tau_0} \right) \exp \left[ \left( \frac{-E_a}{kT} \right) - \left\{ \frac{1}{b\ell \tau_0} \right\} \int_{T_0}^T \exp \left( \frac{-E_a}{kT'} \right) dT' \right] \quad (29)$$

whereas the peak position of ITC spectrum is expressed by [19]

$$T_m^2 = \left\{ \frac{\ell b E_a \tau_m}{k} \right\}. \quad (30)$$

After comparing eqs (21) and (29) for  $I$ , one finds a relationship between  $x$  and  $\ell$  as

$$\ell = \frac{1}{(1-x)}. \quad (31)$$

Thus, retrapping to the extent of  $x$  is equivalent to the involvement of  $\ell$ th order of kinetics both in TL as well as in dipolar relaxation processes. The same relation is also obtained between  $x$  and  $\ell$  when one compares eqs (23) and (30) for  $T_m$ . This obviously establishes a similarity between TL and ITC processes involving any extent of retrapping or any order of kinetics. Further, the method of evaluation of TL decay parameters  $E_a$  and  $s$  using eq. (28) is identical to the evaluation procedure of dielectric relaxation parameters  $E_a$  and  $\tau_0$  expressed by [19]

$$\ln \left( \frac{Q}{I} \right) = \ln(\tau_0) + \left( \frac{E_a}{kT} \right). \quad (32)$$

Moreover, expressions for  $n$  and  $n_0$  of the TL process are also similar to those of  $Q$  and  $Q_0$  of ITC process [19]. Further, initial rise method is equally valid for both these processes.

Probabilities of recombination and simultaneous retrapping corresponding to different orders of kinetics evaluated using eq. (31) are presented in table 1. It is worth mentioning that values presented in table 1 are in agreement with the ideas proposed by Randall and Wilkins [4], and Garlick and Gibson [5]. It is obvious from the table that probability of

**Table 1.** Probabilities of recombination and simultaneous retrapping as a function of order of kinetics involved in TL glow curves.

Order of kinetics ( $\ell$ )	Probability of recombination ( $1-x$ ) (%)	Probability of retrapping ( $x$ ) (%)
1	100	0
2	50	50
3	33.3	66.7
4	25	75
5	20	80
.	.	.
.	.	.
.	.	.
$\ell$ th	$(100/\ell)$	$[100(\ell-1)/\ell]$



retrapping increases with increasing  $\ell$ . It can be evaluated from eq. (31) that for  $x = 0.60$ , i.e. for 60% retrapping and 40% simultaneous recombination, the order of kinetics involved is 2.5.

It is observed that the evaluated values of the TL decay parameters  $E_a$  and  $s$  do not satisfy eq. (24). Similar observation has also been noticed by the author in a number of systems while dealing with the ITC data reported in the literature in connection with establishing a characteristic relaxation time for a given lattice:dopant system [20]. The same could not be reported by the author at that time probably due to lack of insight, explanation and vision. Some of the representative data reported in the literature are presented in table 2. Column 5 of table 2 presents the values of either  $s$  for the TL data or  $\tau_0$  for the ITC data. It is obvious from the table that  $T_m^2$  is different from  $bE_a\tau_m/k$  both in TL as well as in ITC cases, which should have been equal as per eq. (24). This justifies

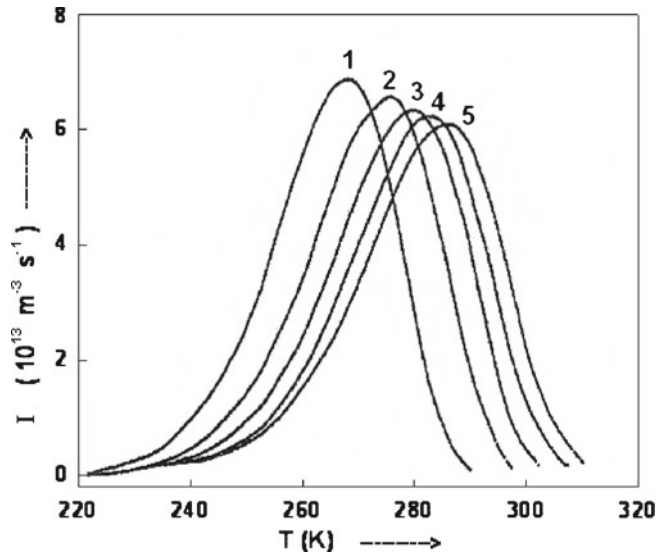
**Table 2.** Values of  $x$  or  $\ell$  for some representative systems supposedly involving first-order kinetics or 0% retrapping.

System	$b$ (K s <sup>-1</sup> )	$T_m$ (K)	$E_a$ (eV)	$s$ or $\tau_0$ (s <sup>-1</sup> ) or (s)	$x$	$\ell$	Reference
(a) TL Data							
NaCl:I	1.5	473	1.145	$2.00 \times 10^{11}$	0.30	1.42	[31]
Quartz	2	393	0.796	$2.10 \times 10^9$	0.08	1.09	[32]
Kyanite	2	389.42	0.91	$8.36 \times 10^{10}$	0.00	1.00	[33]
Kyanite (preheated)	2	407.79	0.96	$1.05 \times 10^{11}$	0.07	1.07	[33]
Aluminium oxide (irradiated)	5	638	1.52	$2.68 \times 10^{11}$	0.18	1.22	[34]
BaS:Bi	2	626	1.2	$1.38 \times 10^9$	0.76	4.24	[35]
BaSO <sub>4</sub> :U <sup>6+</sup>	2	488	1.3	$4.30 \times 10^{12}$	0.21	1.27	[36]
Synthetic quartz	4	363	0.85	$1.90 \times 10^{11}$	0.00	1.00	[37]
(b) ITC Data							
NaCl:Mn <sup>2+</sup>	0.1	214.3	0.67	$9.10 \times 10^{-15}$	0.11	1.12	[38]
NaCl:Mg <sup>2+</sup>	0.067	206	0.49	$8.80 \times 10^{-11}$	0.22	1.29	[39]
NaCl:NCO <sup>-</sup>	0.012	65	0.192	$2.00 \times 10^{-13}$	0.01	1.01	[40]
NaCl:NO <sup>2-</sup>	0.022	18.9	0.04	$7.00 \times 10^{-10}$	0.07	1.07	[41]
KCl:Mg <sup>2+</sup>	0.1	189	0.49	$3.85 \times 10^{-12}$	0.28	1.39	[42]
KCl:Mn <sup>2+</sup>	0.1	192	0.49	$6.20 \times 10^{-12}$	0.30	1.42	[42]
KCl:Yb <sup>2+</sup>	0.1	215	0.67	$1.10 \times 10^{-14}$	0.05	1.05	[42]
KCl:AsO <sup>2-</sup>	0.1	58.3	0.161	$1.60 \times 10^{-13}$	0.26	1.36	[43]
KBr:AsO <sup>2-</sup>	0.01	60	0.169	$2.40 \times 10^{-13}$	0.79	4.81	[43]
KBr:Sr <sup>2+</sup>	0.05	215	0.66	$4.0 \times 10^{-14}$	0.01	1.01	[44]
KBr:Se <sup>2-</sup>	0.05	230	0.72	$2.0 \times 10^{-14}$	0.04	1.04	[45]
KBr:NCO <sup>-</sup>	0.014	41	0.119	$2.0 \times 10^{-13}$	0.01	1.01	[40]
KBr:Cu <sup>+</sup>	0.184	70.2	0.196	$1.0 \times 10^{-13}$	0.00	1.00	[46]
KI:Pb <sup>2+</sup>	0.059	201.2	0.61	$4.50 \times 10^{-14}$	0.11	1.12	[39]
KI:Se <sup>2-</sup>	0.046	215	0.64	$13.00 \times 10^{-14}$	0.02	1.02	[47]
KI:AsO <sup>2-</sup>	0.016	60.5	0.172	$3.50 \times 10^{-13}$	0.34	1.52	[43]
KI:Te <sup>2-</sup>	0.066	217	0.62	$4.00 \times 10^{-14}$	0.90	9.75	[48,49]

the appearance of the factor  $1/(1 - x)$  in eq. (23) or the presence of  $\ell$  in eq. (30). Thus, eq. (23) enables one to determine the value of  $x$ . Likewise  $\ell$  can be obtained from eq. (30). In this way the values of  $E_a$ ,  $s$  and  $x$  or  $\ell$  can be determined conveniently and easily. In addition,  $n_0$  is also obtained using eq. (26). The model can be applied to analyse the TL and the ITC data equally effectively.

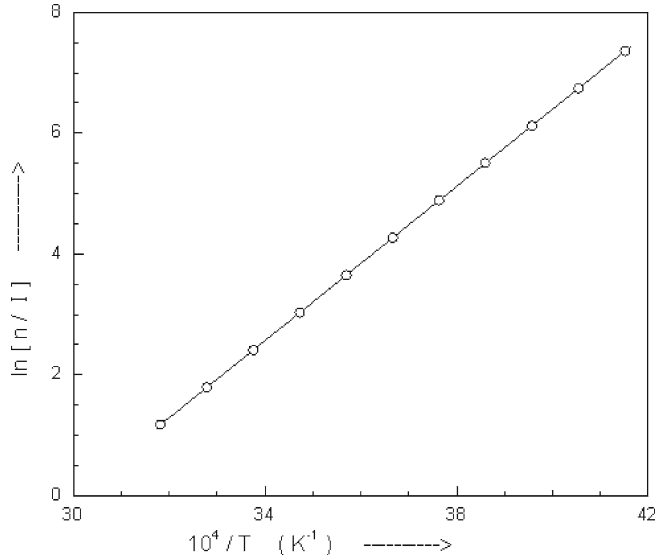
### 3. Results and discussion

The TL glow curves for hypothetical systems, with same values of  $E_a$ ,  $s$  and  $n_0$  but different values of  $\ell$  constructed with the help of eqs (21) and (31) following the same value of constant linear heating rate  $b$  are shown in figure 2. It is obvious that  $T_m$  shifts towards higher temperature with increasing value of  $\ell$ . Sharp fall-off of the TL glow curve at the high temperature end is due to the second exponential term. It is obvious from the figure that the intensity  $I_m$  of the TL peak at  $T_m$  decreases with increasing value of  $\ell$ . For the evaluation of TL decay parameters,  $\ln(n/I)$  for the glow curves of figure 2 are plotted against  $(1/T)$  in figure 3. It is obvious that one gets a straight line in accordance with eq. (28). The slope gives the value of  $E_a$  whereas the value of  $s$  is obtained from the intercept.  $x$  is evaluated with the help of eq. (23) and the corresponding value of  $\ell$  is obtained using eq. (31). The value of  $n_0$  is obtained using eq. (26). Evaluated values of  $E_a$ ,  $s$ ,  $x$  or  $\ell$  and  $n_0$  corresponding to curves 1 to 5 of figure 2 are presented in table 3. It is obvious that the evaluated values are in good agreement with the chosen values of the hypothetical systems. It would be worth mentioning that for  $\ell = 1$  of the hypothetical system of figure 2, retrapping to the extent of 10% is observed and the



**Figure 2.** TL glow curves for hypothetical systems having same parameters  $E_a = 0.55$  eV,  $s = 2 \times 10^8$  s $^{-1}$ ,  $n_0 = 2 \times 10^{16}$  m $^{-3}$  and  $b = 0.1$  K s $^{-1}$  for different orders of kinetics. The number on the curves indicates the involved order of kinetics.

*Thermoluminescence glow curve*



**Figure 3.** Plot of  $\ln(n/I)$  vs.  $(1/T)$  for the TL glow curves of figure 2.

corresponding value of  $\ell$  is found to be 1.11. This suggests an inaccuracy of  $\pm 10\%$  in the magnitude of retrapping and simultaneous recombination, and  $\pm 0.1$  in the order of kinetics, respectively. Thus, first-order kinetics with zero retrapping seems to correspond to an ideal case. Order of kinetics more than 1 has been reported in natural barite sample [21] and  $\text{CaF}_2\text{:Pr}$  single crystals [22]. It has also been observed that the location of TL peak in natural barite samples is independent of the extent of the irradiation dose, i.e. independent of  $n_0$  which is in accordance with the results of the proposed model. Similar observation has also been recorded in Pr-doped  $\text{CaF}_2$  single crystals. The intensity of TL peak in both these cases has, however, been found to change with  $n_0$  as expected. Order of kinetics, other than 1 or 2, has also been reported in [23–30]. TL peak in MgO single crystals [26] involves second-order kinetics at low concentration of iron impurity which

**Table 3.** Evaluated values of TL decay parameters and order of kinetics for hypothetical systems of figure 2.

Curve no.	Evaluated with the help of eq.				
	(28)	(23)	(31)	(26)	
	$E_a \text{ (eV)}$	$s \times 10^{-8} \text{ (s}^{-1}\text{)}$	$x$	$\ell$	$n_0 \times 10^{-16} \text{ (m}^{-3}\text{)}$
1	0.55	2	0.10	1.11	2
2	0.55	2	0.49	1.96	2
3	0.55	2	0.67	3.03	2
4	0.55	2	0.75	4.00	2
5	0.55	2	0.81	5.26	2

gradually changes to about 1.3 at high concentration. It has been reported by May and Partridge [29], and by Partridge and May [30] that the TL glow curve in  $\alpha$ -irradiated alkali halides involves an order of kinetics of 1.5. Thus, the findings of the proposed model are also supported by the experimental observations reported in the literature.

#### 4. Conclusion

A simple model has been proposed which explains the mechanisms involved in the occurrence of the TL glow curve. Among the electrons excited to the conduction band, some are retrapped and the remaining are recombined in such a way that the sum of the retrapped and the recombined electrons is equal to the electrons excited to the conduction band. Based on this fact, an expression for the intensity of the TL glow curve involving any extent of retrapping or any order of kinetics has been developed. No assumption has been incorporated in developing the generalized expression. Intensity of TL peak is found to depend on the initial concentration of trapped electrons as expected. TL decay parameters  $E_a$  and  $s$  along with  $x$  or  $\ell$  and  $n_0$  are evaluated conveniently and easily. The proposed model is also applicable to the ITC data equally effectively.

#### Acknowledgements

The author is thankful to Mr Devendra Prasad and Ms V Gupta for their help in computer graphics. Thanks are also due to Dr R A Agrawal, Chairman, BIT, for providing the necessary facilities.

#### References

- [1] A Jablonski, *Z. Phys.* **94**, 38 (1935)
- [2] E I Adirovitch, *J. Phys. Rad.* **17**, 705 (1956)
- [3] R Chen and Y Kirsh, *Analysis of thermally stimulated processes* (Pergamon Press, Oxford, England, 1981)
- [4] J T Randall and M H F Wilkins, *Proc. R. Soc. A* **184**, 366 (1945)
- [5] G F J Garlick and A F Gibson, *Proc. R. Soc.* **60**, 574 (1948)
- [6] R Chen and S A A Winer, *J. Appl. Phys.* **41**, 5227 (1970)
- [7] P S Majumdar, S J Singh and R K Gartia, *J. Phys. D: Appl. Phys.* **21**, 815 (1988)
- [8] Y Kirsh, *Phys. Status Solidi A* **129**, 15 (1992)
- [9] J Prakash, *Solid State Commun.* **85**, 647 (1993)
- [10] J Prakash and D Prasad, *Phys. Status Solidi A* **142**, 281 (1994)
- [11] P K Singh, *Behaviour of impurity–vacancy dipoles in alkali halides*, Ph.D. thesis (DDU Gorakhpur University, Gorakhpur, 2002)
- [12] J Prakash, S K Rai, P K Singh and H O Gupta, *Indian J. Pure Appl. Phys.* **42**, 565 (2004)
- [13] D K Dwivedi, *On the analysis of thermally stimulated processes*, Ph.D. thesis (DDU Gorakhpur University, Gorakhpur, 2006)
- [14] J Prakash, P K Singh and D K Dwivedi, *Indian J. Pure Appl. Phys.* **44**, 532 (2006)
- [15] S W S Mckeever, *Thermoluminescence of solids* (Cambridge University Press, 1988)
- [16] R Chen and S W S Mckeever, *Theory of thermoluminescence and related phenomenon* (World Scientific, Singapore, 1997)
- [17] S Z Arrhenius, *Phys. Chem.* 226 (1889)

- [18] C Bucci, R Fieschi and G Guidi, *Phys. Rev.* **148**, 816 (1966)
- [19] J Prakash, *Pramana – J. Phys.* **80**, 143 (2013)
- [20] J Prakash and A K Nishad, *Jpn J. Appl. Phys.* **27**, 2247 (1988)
- [21] M Prokić, *J. Phys. Chem. Solids* **18**, 611 (1977)
- [22] R K Sinha and M I Mukherjee, *Phys. Status Solidi B* **105**, 69 (1981)
- [23] C Muntoni, A Rucci and P Serpi, *Ricerca Sci.* **38**, 762 (1968)
- [24] R Chen, *J. Appl. Phys.* **40**, 570 (1969); *J. Electrochem. Soc.* **116**, 1254 (1969); *J. Phys. D* **2**, 371 (1969)
- [25] R W Ward and P W Whippley, *Canad. J. Phys.* **50**, 1409 (1971)
- [26] V Ausin and J L Alvarez-Rivas, *J. Phys. C* **5**, 82 (1972)
- [27] P M Serpi, A Rucci and A Serpi, *J. Lumin.* **9**, 488 (1975)
- [28] N Takeuchi, K Inabe and H Nanto, *Solid State Commun.* **17**, 1267 (1975)
- [29] C E May and J A Partridge, *J. Chem. Phys.* **40**, 1401 (1964)
- [30] J A Partridge and C E May, *J. Chem. Phys.* **42**, 979 (1965)
- [31] S D Singh, P S Mazumdar, R K Gartia and N C Deb, *J. Phys. D: Appl. Phys.* **31**, 231 (1998)
- [32] K A Rao, S K P Niyaz, N V P Rao and K V R Murthy, *Arch. Phys. Res.* **2**, 89 (2011)
- [33] G Wary and J M Kalita, *Indian J. Pure Appl. Phys.* **50**, 566 (2012)
- [34] K R Nagabhushana, B N Lakhminarasappa, D Revannasiddaiah and F Singh, *Bull. Mater. Sci.* **31**, 669 (2008)
- [35] S Singh, A Vij, S P Lochab, R Kumar and N Singh, *Bull. Mater. Sci.* **34**, 683 (2011)
- [36] M K Bhide, T K Seshagiri, S Ojha, S Murali and S V Godbole, *Int. Conf. Lumin., Applic. (ICLA)* (Hyderabad, Feb. 7–10, 2012)
- [37] G Kitis, V Pagonis, H Carty and E Tatsis, *Rad. Prot. Dos.* **100**, 225 (2002)
- [38] P Dansas, *J. Phys. Chem. Solids* **32**, 2699 (1971)
- [39] F Cusso and F Jaque, *J. Phys. C* **15**, 2875 (1982)
- [40] A Wilbrand, *Thermisch stimulierte depolarisation von zyanat-zentren in alkalihalogenidkristallen*, Diplomarbeit (Physikalisches Institut der Universität, Münster, FRG, 1979)
- [41] G Nierste, *Thermisch stimulierte depolarisation von NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> und PO<sub>2</sub><sup>-</sup>-zentren in einigen alkalihalogenidkristallen*, Diplomarbeit (Physikalisches Institut der Universität, Münster, FRG, 1981)
- [42] A Brun and P Dansas, *J. Phys. C* **7**, 2593 (1974)
- [43] J Prakash, *Phys. Status Solidi B* **135**, 741 (1986)
- [44] R Muccillo and J Rolfe, *Phys. Status Solidi B* **61**, 579 (1974)
- [45] J Prakash, *J. Phys. C* **12**, L577 (1979)
- [46] M Siu Li, M de Souza and F Lüty, *Phys. Rev. B* **7**, 4677 (1973)
- [47] J Prakash, *Phys. Status Solidi B* **121**, 127 (1984)
- [48] Ch Kokott, *Dielektrische relaxationen von chalkogen-luecken-zentren in kaliumhalogenidkristallen*, Dissertation (Physikalisches Institut der Universität, Münster, FRG, 1975)
- [49] Ch Kokott and F Fischer, *Phys. Status Solidi B* **106**, 141 (1981)