On the Appearance of a Thermoluminescence Glow Curve

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Abstract - **A model has been proposed which explains the mechanisms responsible for the appearance of a thermoluminescence (TL) glow curve. Adirovitch set of equations has been modified. A generalized equation has been developed which is found to be capable of explaining TL intensities of different order of kinetics including first order.**

1.INTRODUCTION

An electron excited to the conduction band from the valence band returns to the valence band again. However, if the electron is trapped in the met stable state (or trap level), it needs energy to be raised to the conduction band. When the system is heated, electrons are thermally released from their respective trap centers. Such released electrons may quickly recombine with an oppositely charged centre resulting in the appearance of a TL glow curve. Let us suppose that m and n represent the density of holes and electrons in the respective recombination and trap centers at the time t. Recombination is the process through which m decreases. Thus the TL intensity, will be given by

$$i = -dm/dt = m\, n_c\, A_m \tag{1}$$

where n_c is the density of electrons in the conduction band and A_m the probability. Rate of decreaseof n i.e. $(-dn/dt)$ will depend on the excitation of electrons into the conduction band and also on their retrapping. Thus

$$-dn/dt = n\, s_1 \exp(-E_a/kT) - (N-n)\, n_c\, A_n \tag{2}$$

The first term on the right-hand side of Eq.(2) represents obviously the rate of release of electrons from their respective traps and the second term represents the rate of retrapping. Apart from Eqs.(1) and (2), charge neutrality requires

$$m = n + n_c \tag{3}$$

Eqs. (1), (2) and (3) are known as Adirovitch set of equations describing the mechanisms responsible for the appearance of a TL glow curve.

To have some meaningful information's from Adirovitch set of equations, following two basic assumptions have been introduced

$$n_c \ll n \quad \text{and} \quad dn_c/dt \ll dn/dt \tag{4}$$

In view of these assumptions, Eq. (3) gives

$$m = n \quad \text{and} \quad dm/dt = dn/dt \tag{5}$$

Combination of Eqs. (1), (2) and (5) results into

$$i = -(dn/dt) = -(dm/dt)$$

or $i = n\, s_1 \exp(-E_a/kT).[\, mA_m / \{m\, A_m(N-n)A_n\}] \tag{6}$

This is the equation which has been used by various workers to prove into the mechanisms inherent in the TL processes.

Randall and Wilkins proposed that first order kinetics is a case of recombination dominant process with negligible retrapping. With reference to Eq. (6) it means that

$$mA_m \gg (N-n)A_n \tag{7}$$

In view of Eqs.(5) and (7), one gets from Eq. (6)

$$i = -(dm/dt) = -(dn/dt) = n\, s_1 \exp(-E_a/kT) \tag{8}$$

When the experiment is recorded following a linear heating rate b according to

$$T = T_0 + bt \tag{9}$$

One gets for the intensity of a first order TL glow curve

$$i_1 = n_o\, s_1 \exp[\,(-E_a/kT) - (s_1/b) \int_{T_0}^{T} \exp(-E_a/kT')dT'\,] \tag{10}$$

Garlick and Gibson proposed that second order kinetics is a case of strong retrapping probability. In view of Eq. (6), a retrapping dominated process leads to

$$(N-n)A_n \gg m\, A_m \tag{11}$$

Eq. (11) means that electrons which are excited, retrap several times before recombining into the centre. If it is assumed that trap is far from saturation i.e. $n \ll N$ and the probabilities of recombination and retrapping are equal, Eq. (6) in combination with Eqs. (5) and (11) gives.

$i_2 = n^2 s_2 \exp(- E_a/ kT)$ (12)

When the experimental run is recorded following a linear heating rate, the intensity of second order TL glow curve is given by

$$i_2 = n_o^2 s_2 \exp(-E_a/kT).[1 +(n_o s_2/b) \int_{T_0}^{T} \exp(-E_a/kT') dT']^{-2}$$ (13)

For a general order TL glow curve it has been shown by Chen that Eq. (6) for TL intensity is expressed as

$i_\iota = n^\iota s_\iota \exp(- E_a / kT)$ (14)

where s_ι is the pre-exponential constant having the dimensions $m^{3(\iota - 1)} s^{-1}$. The parameters s_1 and s_ι are related through the expression…

$s_1 = s_\iota N^{(\iota - 1)}$ (15)

It is obvious that for $\iota = 2$, parameters s_1 and s_2 are found to be related as

$s_1 = N s_2$ (16)

Thus, the mechanisms responsible for the occurrence of a general order TL glow curve are controlled by Eq. (14). When the experiment is recorded following a linear heating rate, intensity of a general order TL glow curve is represented by

$$i_\iota = (n_o/N)^{(\iota - \iota)} n_o s_1 \exp[(-E_a/kT)] [1+(n_o/N)^{(\iota - 1)}\{s_1(\iota-1)/b)\int_{T_0}^{T}\exp(-E_a/kT') dT']^{[-\iota]/(\iota-1)}\}$$ (17)

In the cases when all the available electron traps are filled initially i.e. when $N = n_o$, Eq.(17) changes to

$$i_\iota = n_o s_1 \exp[- E_{a\iota}/ kT] [1 +\{ s_1(\iota - 1)/ b) \int_{T_0}^{T}\exp(- E_a / kT') dT']^{\{-\iota/(\iota - 1)\}}$$ (18)

It has been reported by Chen and Winer that the peak of a general order TL glow curve appears at T_M such that

$$[1+\{s_1(\iota-1)/b)\}] \int_{T_0}^{T}\exp(-E_a/kT)dT = (\iota s_\iota k T_M^2/ bEa)\exp(-E_a/k T_M)$$ (19)

Eq.(19) decides the location of the TL glow peaks in the cases involving second and higher order kinetics including first order. Eqn.(19) suggests that the location of T_M is independent of N in first order kinetics as expected. However, T_M is found to be dependent on N in systems involving second and higher order kinetics.

Failure of Eqn.(18) to represent the intensity of first order TL glow curve and ability of Eqn.(19) to represent the position of the peak of general order TL glow curve led us to reinvestigate the mechanisms inherent in the TL processes. Further, the dependence of T_M on N in systems involving second and higher order kinetics seems to be unrealistic. In view of these facts, mechanism responsible for the appearance of a TL glow curve is reconsidered in this article with an aim to establish a generalized approach.

2. SUGGESTED MECHANISMS OF THERMOLUMINESCENCE

It is obvious that the order of kinetics involved in the system should either be a function of the constitution of the specimen under investigation or it should depend on the mechanisms inherent in the TL processes. If the first order kinetics is a recombination dominant process and if in the second order kinetics the probabilities of recombination and retrapping are equal, it obviously leads to the fact that the rate of recombination decreases with increasing order of kinetics. Thus, the first equation of the Adirovitch set of equations in the light of these arguments can be written as

$i=- (dm/dt) = (1/\iota) m n_c A_m$ (20)

It is obvious from Eqn.(20) that the rate of recombination decreases with the increasing order of kinetics.

While deriving expression for TL intensity for first order it is assumed that first order kinetics is a recombination dominant process i.e. $(N - n) A_n = 0$. It can be possible when either $A_n = 0$ or $(N - n) = 0$. The first term A_n cannot be zero and the second term $N = n$ can only be possible just at the start of the experiment when all the available electron traps are filled initially. As soon as an electron is released from the trap, $(N - n)$ will have some finite value and hence $(N - n)$ cannot be equal to zero during an experimental run. Hence, $(N - n) A_n$ can be set equal to zero for first order kinetics by expressing it as $((\iota - 1)/ \iota)(N - n) A_n$. In view of this argument, the second equation of Adirovitch set of equations can be expressed as

$-(dn / dt) = n s \exp(-Ea /kT)-((\iota-1)/ \iota) (N - n) n_c A_n$ (21)

It is obvious from eqn.(21) that the rate of retrapping increases with the increasing order of kinetics as wanted

The order of kinetics involved should depend on the constitution of the system. The neighborhood and environment, the trap and recombination centers will

essentially decide the order of kinetics involved. Thus, in view of this, the charge neutrality requirement is expressed as

$$\iota m = n + n_c \qquad (22)$$

Eqns.(20) to (22) are known as modified Adirovitch set of equations describing the mechanisms responsible for the appearance of a TL glow curve. In view of two basic assumption introduced through Eqn(4), one gets from eqns.(20), (21) and (22)

$$i = (1/\iota)\, ns\, \exp(-Ea/kT)\,[\iota m\, A_m /(\iota m\, A_m +(\iota -1)(N-n)A_n)] \qquad (23)$$

From eqn.(23) information about TL intensities of different order of kinetics can be obtained.

3. EXPRESSION FOR THE INTENSITY OF A GENERAL ORDER TL GLOW CURVE

It is now established mechanisms that first order kinetics is recombination dominant process whereas rate of recombination and retrapping are equal in second order kinetics. For a TL glow curve involving ιth order of kinetics rate of recombination and retrapping are related as

$$(\iota -1)\,(1/\iota)\, m\, n_c\, A_m = ((\iota -1)/\iota)(N-n)\, n_c\, A_n \qquad (24)$$

Obviously for ιth order of kinetics, $(\iota -1)$ x rate of recombination = rate of retrapping. Eq. (23), in the light of Eq. (24) results into

$$i = \{1/(2\iota -1)\}\,(n/\tau) \qquad (25)$$

Where τ is the mean life time or the relaxation time at the temperature T expressed as…..

$$\tau = (1/s)\, \exp[Ea/kT] \qquad (26)$$

Eqn.(25) can be solved to give

$$n = n_o\, \exp\left[\,(-\iota/(2\iota -1))\,(t/\tau)\,\right] \qquad (27)$$

Non-isothermal form of eqn.(27) can be written

$$n = no\, \exp\left[(-\iota/(2\iota -1))\int_0^t (dt/\tau)\right] \qquad (28)$$

Combination of eqns.(25) and (28) gives

$$i = [1/(2\iota -1)](n_o/\tau)\,\exp\left[(-\iota/(2\iota -1))\int_0^t (dt/\tau)\right] \qquad (29)$$

If the system is heated following a constant linear heating rate b as per eqn (9),one gets from eqn.(29)

$$i = [1/(2\iota -1)]n_o s\, \exp\left[(-Ea/kT)-\{\iota s/b(2\iota -1)\}\int_{T_o}^{T}(\exp(-Ea/kT')\,dT'\right] \qquad (30)$$

Eqn.(30) is the generalized equation for expressing the intensity of general order TL glow curve. Expressions for the TL intensity of different order of kinetics can be obtained from Eqn.(30) after substituting the corresponding values of ι as 1, 2, 3, 4 ...etc. It is obvious that Eqn.(30) results into Eqn.(10) for ι =1. Thus Eqn.(30) is entitled to be named as a generalized equation for expressing the intensity of a general order TL glow curve.

4. DISCUSSION

In the proposed model, all the anomalies mentioned in section 2 and 3 are removed. The location of the peak of a general order TL glow curve can be ascertained with the help of Eqn.(30). It is found that Tm depends on b, ι, E_a and s through relation

$$T_M^2 = ((2\iota -1)/\iota)\,[b\, E_a\, \tau_M /k] \qquad (31)$$

where T_M is the temperature at which maximum intensity I_M of the TL glow curve appears and τ_M is the corresponding relaxation time at T_M. It is obvious that T_M is independent of n_o as expected. The earlier finding that T_M is a function of n_o for second and higher order kinetics is also remedied through the suggested model. Further **s** of different order kinetics is found to be independent of each other as expected. Also the unit of pre-exponential factor is found to s^{-1} as per the requirement of the Arrhenius relation, whereas in the previous relation the unit of pre-exponential factor is $m^{3(\iota -1)}\, s^{-1}$, which is in contradiction to the Arrhenius relation. A system will obviously involve a particular order of kinetics and correspondingly it will have its own value of ι, E_a and s. The value of s in different order of kinetics other than the one involved by the system under investigation has no meaning. Obviously, the shortcomings of the earlier suggested model are removed through the proposed model. Thus eqn.(30) seems to be the right expression to represent the intensity of a general order TL glow curve.

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