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Determination of TL Kinetic parameters of a phosphor

Ravi Shrivastava, Vikas Dubey and Jagjeet Kaur Saluja

Govt. VYT PG Autonomous college, Durg (C.G.), India.

Abstract
Present paper reports the methods of evaluating the kinetic parameters like trap depth, frequency factor etc. by using the Glow Curve of a phosphor. Peak shape method is found to be suitable amongst all reported methods. This method provides the nearest possible values of all studied kinetic parameters which are discussed in details. MS -Excel sheet is prepared for calculation.

Keywords: Phosphor, kinetic parameters, glow curve, TL

INTRODUCTION

Mechanoluminescence (ML) is a type of luminescence induced by any mechanical action on solids. The light emission

Thermoluminescence (TL) is defined as the emission of light from a semiconductor or an insulator when it is heated, due to the previous absorption of energy from irradiation. The graph of the amount of light emitted during the TL process as a function of the sample temperature is known as a "TL Glow Curve".

The simplest model which describes the TL is OTOR Model (One Trap One Recombination Center Model).

Let
N = total concentration of the traps in the crystal (m^{-3}).
n (t) = the concentration of filled traps in the crystal (m^{-3}) at time t.
n_h(t) = concentration of trapped holes in the recombination center.
N_0 = concentration of filled traps at time t = 0
β = heating rate

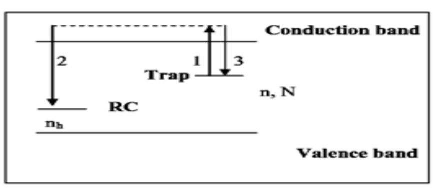

Figure - 1

In a simple Thermoluminescence model, when temperatures increases, electrons of the trap level goes into the conduction band (transition 1) and then it may follow two path of transition either 2 or 3 as shown in the figure1. When electrons after transition 3 reaches the Recombination level, holes available there recombines with the electron reaching which releases the energy, which is the cause of Thermoluminescence.

Following are the equations governing different order of kinetics:-

$$\frac{\beta E}{T_M^2} = s \exp\left(-\frac{E}{kT_m}\right) \text{ I Order Kinetics}$$

$$\frac{\beta E}{T_M^2} = s \exp\left(-\frac{E}{kT_m}\right)\left[1 + \left(\frac{2kT_m}{E}\right)\right] \text{ II Order Kinetics}$$

$$\frac{\beta E}{T_M^2} = s \exp\left(-\frac{E}{kT_m}\right)\left[1 + (b-1)\left(\frac{2kT_m}{E}\right)\right] \text{ General Order Kinetics}$$

METHODS FOR EVALUATION OF THERMOLUMINESCENCE

There can be many methods to evaluate the kinetic parameters of phosphors out of which few are listed below:-

1) Initial Rise Method
2) Peak position method
3) Different Heating Rate method
4) Peak Shape Method

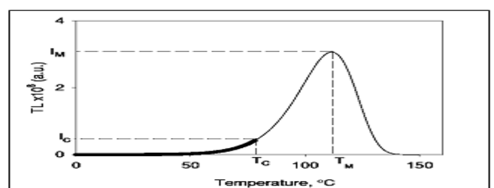

Figure - 1 Figure - 2

Initial Rise Method

This method is based on the analysis of the low temperature interval of peak. The initial rise method was first suggested by Garlick and Gibson.

The amount of trapped electrons in the low temperature tail of a TL glow peak can be assumed to be approximately constant, since the dependence of n (T) on temperature T is negligible in that temperature region. In fact the temperature increases, the first exponential in equation (1) increases, whereas the value of second term remains close to unity. This remains true for temperatures up to a cutoff temperature T_c, corresponding to a TL intensity I_c smaller that about 15% of the maximum TL I_M. A further increase in temperature ($T>T_c$) makes the second term in equation (1) decrease; the competition between two terms in equation (1) results in the peak shape of the TL glow curve.

By using this assumption of constant n (T), the thermoluminescence emission can be described by

$$I(T) \; \alpha \; \exp\left(-\frac{E}{kT}\right)$$

Following figure shows the initial rise part of a single TL glow peak. In applying the initial rise method, a graph of ln (I) is made, and a straight line is obtained. From the slop –E of the line, the activation energy E is evaluated without any knowledge of frequency factor s

Different Heating rate method

For calculating the trap depth from above mentioned method, we need to take two different glow curves of the same sample giving two different heating rates as 1 and 2. The following equation can be utilized:-

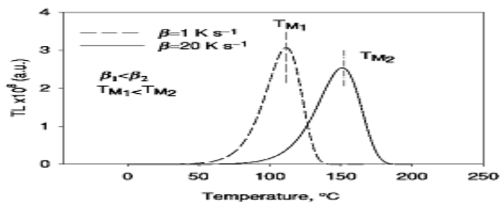

Figure - 3

Peak position method

Following equation is given for calculating the trap depth using only the peak position of a glow curve:

$E = 25kT_m$ OR $E = \frac{T_m}{500} = 23kT_m$

Peak shape method

The most accurate method for measuring kinetic parameters is peak shape method. The following factors are to be calculated using the geometrical properties of the glow curve:

T_m is the peak temperature at the maximum.

T_1 and T_2 are, respectively the temperatures on either side of T_m, corresponding to half intensity.

$\tau = T_m - T_1$ is the half-width at the low temperature side of the peak.

$\delta = T_2 - T_m$ is the half-width at the high temperature side of the peak.

$\omega = T_2 - T_1$ is the total half – width.

$\mu = \delta/\omega$ is so-called geometrical shape of symmetry factor.

Trap depth can be calculated by using τ, δ and ω in the following way:- $E_\alpha = c_\alpha \left(\frac{kT_m^2}{\alpha} \right) - b_\alpha (2kT_m)$

Where α is τ, δ and ω. The values of c_α and b_α are summarized as below:-

$c_\tau = 1.510 + 3.0\ (\mu - 0.42)$ $b_\tau = 1.58 + 4.2\ (\mu - 0.42)$

$c_\delta = 0.976 + 7.3\ (\mu - 0.42)$ $b_\delta = 0$

$c_\omega = 2.52 + 10.2\ (\mu - 0.42)$ $b_\omega = 1$

With $\mu = 0.42$ for the case of first order TL peaks and $\mu = 0.52$ for the case of second order peaks.

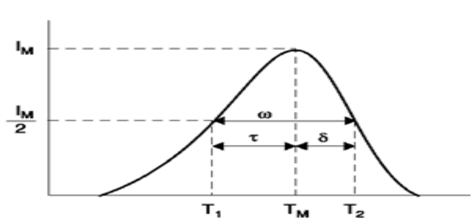

Figure - 4

Evaluatng kinetic parameters (using glow curve data)

A glow curve for a sample phosphor for different UV exposure time is shown below

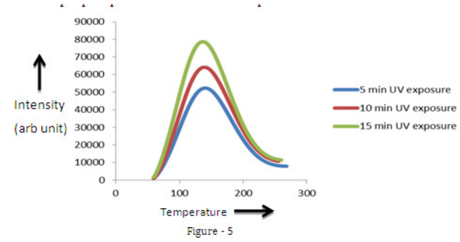

Figure - 5

Table 1. Shape factors (m). Activation Energy E and Order of Kinetics of UV irradiated sample phosphor

"Sample phosphor" Calculation Data									
UV	T1	Tm	T2	τ	δ	ω	μ = δ / ω	Activation energy	Frequency factor
5	98.6	138	190	39.4	52	91.4	0.569	0.568	1X10⁸
10	99.59	143	196	43.41	53	96.41	0.55	0.524	2X10⁷
15	99.85	144	197	44.15	53	97.15	0.546	0.516	2X10⁷

Table 2. The trap depth for the prominent glow peaks of the studied sample phosphors

Methods	5 min UV	10 min UV	15 min UV
$E_\omega = C_\omega \frac{KT_m^2}{\omega} - b_\omega(2KT_m)$	0.57	0.52	0.57
$E_\tau = C_\tau \frac{KT_m^2}{\tau} - b_\tau(2KT_m)$	0.57	0.47	0.57
$E_\delta = C_\delta \frac{KT_m^2}{\delta} - b_\delta(2KT_m)$	0.58	0.54	0.58

SAMPLE PHOSPHOR CALCULATION DATA													
UV Min	HTR	T1	Tm	T2	τ	δ	ω	μ = δ / ω	Activation energy	E/kTm	βe/(KTm*Tm)	e (E/Tm)	Frequency factor
5	276	98.6	138	190	39.4	52	91.4	0.56893	0.56819	16.04337	10.77365	9279981	99979262
10	276	99.59	143	196	43.41	53	96.41	0.54974	0.523778	14.6116	9.694237	2216862	21490783
15	276	99.85	144	197	44.15	53	97.15	0.54555	0.516457	14.37283	9.51295	1745980	16609423

UV Exposure Time (5 Minutes)													
Temperatures				half widths		Constants				Trap Depth		Shape Factor	
T_1 (in °C)	98.6	T_1 (in K)	371.6	τ	39.4	C_δ	2.071	b_δ	0	E_ω	0.579	μ	0.57
T_2 (in °C)	190	T_2 (in K)	463	δ	52	C_ω	4.05	b_ω	1	E_δ	0.585		
T_m (in °C)	138	T_m (in K)	411	ω	91.4	C_τ	1.96	b_τ	2.21	E_τ	0.572		

RESULTS

Peak Shape Method gives the nearest value of Kinetic parameter. The trap depth measured for a sample phosphor is found to be in the range of 0.47 eV to 0.58 eV. The frequency factors varies from $1x10^8$ to $2x10^7$ and the peak seems to be of second order kinetics.

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