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Gaussian approximation of thermoluminescence (TL) peaks: A common misconception for analysis of TL of persistent luminescent materials

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A B S T R A C T

Whenever one over simplifies a physical phenomenon or even any concept, misconceptions are bound to occur. This seems to be true in the case of use of thermoluminescence (TL) in the study of materials by non-specialists. The fact that most semiconducting/insulating materials exhibit TL has led to many publications that ignore the basic rules of use of TL in determining the two key intrinsic trapping parameters, the trap-depth (E) and the frequency factor (s) that control the phenomenon. Manipulation of the value of E and s in a system by suitable activator and co-activator leads to the optimization for specific use of materials. In this work we discuss a common misconception that has been continuously propagated. It is the deconvolution of complex glow curves using Gaussian function and using the component of TL peaks to calculate trap depth (E) by peak shape method. This assumption is questionable and can yield parameters that are physically unrealistic. To prove our point, we consider as many as four phosphors namely ZnS:Cu^{+} Co^{2+}, $Ca_xSr_{1-x}S$:Eu, $Sr_2MgSi_2O_7$:$Eu^{2+}Dy^{3+}$ and $BaZrSi_3O_9$:Eu^{2+}.

1. Introduction

1.1. General

In the last two decades or so scientists, other than the hard core solid state physicist have done extensive work on development of persistent luminescence materials that continue to emit light visible to human eye for hours even after ceasing of the optical excitation [1,2]. Persistent luminescent materials that are popularly known as “Glow-in-the-Dark” pigments have common applications in areas like safety indication, emergency illustration, road sign, bill boards, toys etc. Their potential applications in novel areas like diagnostics and imaging have excited material scientists as a whole [3,4]. Obviously this has led to development of large number of new phosphors [5,6]. Gartia and Chandrasekhar [1] have highlighted the fact that it is natural that all persistent luminescent materials exhibit excellent TL. Thus, it is quite common in most papers published on persistent luminescent materials to find some data on TL of the materials developed wherein speculations have been made about the trap-depth (E), the most important trapping parameter that decide the location of the peak temperature (T_m) for a fixed heating rate (β) [7–14]. The speculation is often based on the famous Urbach's relation (Chen and Kirsh [15])

$$E = \frac{T_m(K)}{500} \quad or \quad E = 23kT_m \tag{1}$$

where $E =$ Trap-depth.

$T_m =$ temperature at the maximum intensity.
$k =$ Boltzmann's constant.

Workers using eq. (1) for evaluation of the value of trap-depth (E) of the TL peak assigned to the phenomenon of persistent luminescence need to note that it is true only for the materials where the value of the frequency factor (s) is $10^9 s^{-1}$ [16]. Since the frequency factor can lie anywhere in between 10^7-10^{14} s^{-1} [15] the coefficient will change accordingly. As for example it has been shown to be 27–30 for quartz [17,18] $CaAlO_4$:Eu^{2+},RE^{3+} [19] and for LSO: Ce [20].

In another level of misconception which forms the basis of the present work, a number of workers have deconvoluted their TL data assuming the constituent TL peaks to be Gaussian [21–28]. This may be acceptable in certain cases like finding the number of TL

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peaks and their peak maxima (T_m) for using in dating and dosimetry [29]. However, in the framework of solid state physics, it must be rejected.

A Gaussian function is characterized by only two parameters, the mean (λ) and variance σ^2 where as in the simplest description TL in the framework, Randall- Wilkins first order kinetics [30], Garlick and Gibson's [31] second order kinetics or the often used general order kinetics equation of Chen [32] requires three parameters namely the trap depth (E), the frequency factor (s) and that order of kinetics (b). Thus deconvolution of TL data by Gaussian functions and subjecting the signals to Chen's general order kinetics equation [32] as done by numbers of workers is a misconception that needs to be taken care of. Analysis of TL with cautionary guideline for possible error has been done comprehensively and discussed in two classic texts [15,33].

In this paper we have presented the results of deconvolution of TL curves of $ZnS:Cu^+$, Co^{2+}, $Ca_xSr_{1-x}S:Eu$, $Sr_2MgSi_2O_7;Eu^{2+}Dy^{3+}$ and $BaZrSi_3O_9:Eu^{2+}$ using general order kinetics equation of Chen [32] and compared it with that performed by deconvolution with Gaussian functions. The consequences of use of Gaussian function in deconvolution of TL curve are examined and discussed.

1.2. Analysis of TL: some observation

The fact that TL has already been accepted by developers of persistent luminescent materials as a technique has its own pit falls. The phenomenon is pretty complex governed by three simultaneous differential equations [15].

$$I = -\frac{dm}{dt} = A_m m n_c \tag{2}$$

$$-\frac{dn}{dt} = sn\,exp(-E/kT) - n_c(N-n)A_n \tag{3}$$

$$-\frac{dn_c}{dt} = sn\,exp(-E/kT) - n_c[mA_m + (N-n)A + n] \tag{4}$$

where E – activation energy (eV).

s - the frequency factor (sec^{-1}).
A_m- the recombination probability ($cm^3 sec^{-1}$).
A_n-the retrapping probability ($cm^3 sec^{-1}$).
N- the concentration of the given trap (cm-^{3}).
n_0 – initial concentration of electrons in traps (cm-^{3}).
m_0 – initial concentration of holes in traps (cm-^{3}).
n_{c0}- – initial concentration of electrons in the conduction band (cm^{-3}).

Out of these eight parameters the first four are the intrinsic parameters that are characteristic of the specific imperfection whose thermal annealing manifests in the form of a single TL peak.

It is possible to determine the four intrinsic parameters however, because of practical reasons in most cases it is not practiced. Rather E and s are evaluated along with the order of kinetics (b) in the frame work of kinetics description of TL [15,34]. A direct correlation between b, A_m and A_n is not possible. The complexity of the problem is the main reason of many misconceptions. The Gaussian approximation of TL peak being one. Therefore, the misconception by no means is a lack of awareness but rather the usual trend that one expects in new areas of development of materials where functionality is good enough.

1.3. Computerized Glow Curve Deconvolution (CGCG): origin and its implication

Analysis of thermoluminescenec is a major subject in its own right and several review [35–37] and books [15,33,38] exist in the literature. The different methods of analysis are summarized and put in a tabular form with proper references and comments that need to be studied by practitioner of TL for evaluation of trapping parameters in the book of Mckeever [33]. Each technique has its own merits and demerits as well. However, in the last few decades Computerized Glow Curve Deconvolution (CGCD) has emerged as most preferred one for various reason [34,39]. These are.

(i) Unlike other methods full equations of first order (b = 1), second order (b = 2) or general order (b≠ 1 or 2) is used to decode the experimental data.
(ii) Though needs access to computer program it yields more reliable key trapping parameters (E and s).
(iii) User friendly deconvolution programmes are available [40–43].

CGCD is essentially is a curve fitting techniques where one fits the entire TL curve to definite set of E, s, and b. In this process small signals that are generally hidden are easily identified. This is not possible in other methods of analysis. Rather such signals introduce significant error ignored in many works.

2. Theoretical and experimental techniques

2.1. Theoretical techniques

The numerical technique used for CGCD in this work is already given in our earlier papers [17,44]. Briefly speaking,

(i) Simulation and comparison of first order [30], second order [31] and general order [45] TL peaks is performed using the program given in the book of Chen and Kirsh [15]. However, in our programme we estimated the number of TL peak using the second order derivative plot of TL curve. In addition, the programme automatically selects the best peak temperature within the range ±2°C of the given input T_m.
(ii) The programme enables one to select any TL peak and range of the TL peak under consideration.
(iii) The output gives the best fit TL peak with E, s and b. If the value of 's' comes out to be beyond the zone $10^6 \le s \le 10^{14}$ one can make some other choice.
(iv) In our case we restrict the value to $1 \le b \le 2$. It is to be remember that the parameter b has physical meaning only for b = 1 and 2.
(v) The goodness of fit is tested by the value of Figure Of Merit (FOM) [34,39]. Use of FOM for testing the criteria of goodness of fit in TL analysis is quite common. FOM is defined as

$$\mathrm{FOM} = \left[\sum_i \frac{|O(I_i) - I_i|}{A}\right] \times 100 \quad i = 1 \ldots N \tag{5}$$

where $O(I_i)$ is the observed or experimental data, I_i is value of the fitting function and A is the integral area of the fitted curve and N is the number of the experimental points along experimental measured curve. In the literature of TL value of FOM of the range 0.0–2.5% is considered to be good fit. If the range is 2.5–3.5%, the fitting is fair and if > 3.5 the fitting is bad.

The general order (b≠1 or 2) equation is given by