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Evaluated thermoluminescence trapping parameters—What do they really mean?

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HIGHLIGHTS

- Double TL peak may look like a single peak.
- Simulated double peak analyzed by peak-shape methods and by deconvolution.
- Determination of effective activation energies and frequency factors.
- Effect of anomalous stability predicted.

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ABSTRACT

The main two trapping parameters in thermoluminescence (TL), the activation energy and the frequency factor, are often calculated and used for the evaluation of the stability of the TL signal at a given temperature. In several cases, "anomalous" values of these parameters, either very high or very low have been reported in the literature. In practically all of these cases, the values reported have been recognized to be effective values which resulted from some special circumstances related to the specific materials in hand. Obviously, these effective values are not associated directly with the real rate of thermal release of carriers from traps at the ambient temperature, prior to heating, and therefore, they do not indicate the real decay time of the TL signal or, in other words, the stability of the signal which may be used in TL dosimetry or dating of archaeological or geological samples. In the present paper, we discuss briefly some of these cases and add, in more detail, a rather elementary situation of very low effective activation energy and frequency factor. A model with two trapping states and one kind of recombination center is used and the simulation includes the numerical solution of the relevant sets of coupled differential equations in the three stages of the measurement, namely, excitation, relaxation and heating for a given set of the trapping parameters. The parameters are chosen in such a way that two overlapping TL peaks occur, which look together like a single first-order peak, but with anomalously low evaluated effective activation energy and frequency factor. Implications regarding the possible results in glow curve deconvolution are discussed.

1. Introduction

In the study of thermoluminescence (TL), one may be interested in the values of the relevant trapping parameters. These parameters and the relation between them are of importance in determining the temperatures of the TL peaks, their dose dependence as well as other properties, in particular their stability at ambient temperature. The main parameters mentioned in the literature are the activation energy, the escape frequency factor and the recombination and retrapping probability coefficients. The activation energy has to do with the energy required to release thermally a trapped electron into the conduction band. As for the frequency factor, according to Mott and Gurney (1948), the frequency factor s (s^{-1}) should be of the order of magnitude of the Debye frequency, which has to do with the number of times per second that the trapped electron interacts with the phonons. Also mentioned a lot

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in the literature is the order of kinetics of the peak; whereas first- and second-order kinetics have rather simple physical meaning, the intermediate order cases are always heuristic simplified presentations of more complex situations determined by all the relevant trapping parameters.

A number of methods for evaluating the basic trapping parameters from a TL peak are based on the peak-shape. A simple example (see Chen, 1969), yielding the activation energy for a first-order peak is

$$E = 2.52kT_m^2/\omega - 2kT_m, \quad (1)$$

where T_m is the temperature at the maximum and $\omega = T_2 - T_1$, the full width at half intensity and where T_1 and T_2 are, respectively, the low and high half-width temperatures and k (eV/K) is the Boltzmann constant. Note that the order of kinetics of a peak is usually determined by its symmetry factor, defined as

$$\mu_g = \delta/\omega, \quad (2)$$

where $\delta = T_2 - T_m$.

As shown by Randall and Wilkins (1945), once the activation energy of a first-order peak is determined, the frequency factor can be easily determined by using the maximum condition

$$s = \frac{\beta E}{kT_m^2}\exp(E/kT_m), \quad (3)$$

where β (K/s) is the constant heating rate. In the present work, we discuss some difficulties in the use of conventional peak-shape and curve fitting in evaluating the parameters, in particular in cases where two or more TL peaks occur in close vicinity to each other. Previously presented cases of very high apparent activation energy and non-physically high frequency factor, the models of which are based on the concept of competition, will briefly be mentioned (Chen and Hag-Yahya, 1996; Chen and Pagonis, 2014). The effect of anomalous fading has also been explained in the past by a similar model of competition (Chen and Hag-Yahya, 1997). In the present work, we demonstrate, using numerical simulations, that very low effective values of the activation energy and frequency factor may be evaluated due to the occurrence of two or more TL peaks in close vicinity to each other. When this situation takes place, an apparent anomalous stability may be deduced. Also will be discussed the possible implications on the results obtained when numerical deconvolution of a glow curve is used for separating individual glow peaks and determining their trapping parameters.

2. Previous work on anomalous effective activation energies and frequency factors

As pointed out above, according to Mott and Gurney (1948), the frequency factor s should be of the order of magnitude of the Debye frequency, which has to do with the number of times per second that the trapped electron interacts with the phonons. Indeed, many results reported by various authors over the years gave values of s in the range of 10^{10}–10^{13} s^{-1}. In some cases, anomalously high values of the frequency factor, accompanied by high values of the activation energy, were reported. Taylor and Lilley (1978) reported a frequency factor of 2×10^{20} s^{-1} and an activation energy of 2.06 eV of peak V of LiF:Mg, Ti (TLD-100). Even larger values were reported by Gorbics et al. (1967) and by Pohlit (1969). Fairchild et al. (1974) suggested that the kinetics of this peak and other peaks with unusually large s might be complicated and the apparent first-order behavior is an approximation of a more complex kinetics situation. One should note that peak V in LiF:Mg, Ti is part of a complex glow curve, usually separated by some kind of deconvolution.

Chen and Hag-Yahya (1996, 1997) presented a model of one trap and three recombination centers, one radiative and two non-radiative, to explain the possibility of high activation energy and very high frequency factor. They wrote the relevant sets of simultaneous differential equations for the excitation and heating stages and solved them numerically. As a result of the competition of the two radiationless centers, the apparent curve which simulates the measurable TL peak looks like a very narrow first-order peak. With regard to Eq. (1), this means that ω is very small and, as a result, the apparent activation energy is very high, around twice as large as the value inserted into the simulations. Once this high value is inserted into Eq. (3), the effective frequency factor is many orders of magnitude higher than the one used for the simulation. In an example given by Chen and Hag-Yahya (1996), the inserted parameters are $E = 1.2$ eV and $s = 2.5 \times 10^{11}$ s^{-1} and the evaluated parameters are $E_{eff} = 2.24$ eV and $s_{eff} = 9.3 \times 10^{21}$ s^{-1}. Mandowski (2006) has offered another possible explanation to the occurrence of very high frequency factors and high activation energies in first-order-shaped TL peaks, which is based on the concept of cascade detrapping (CD).

In the literature, there are also reports on very small frequency factors, accompanied by small activation energies. Haake (1957) reported results of activation energies and frequency factors of TL in ZnS•ZnO-Cu, Pb, Cl and ZnS-Cu, Cl, in which values of the frequency factor between 1 and 2×10^3 s^{-1} were found. He also mentions previously found values of the frequency factor of TL in ZnS determined by Hoogenstraaten and Klasens (1953) and Dropkin (1954), in which the frequency factor s was found to be between 300 and 5×10^4 s^{-1}, again non-physically low values. Hickmott (1972) studied a TL peak at ~380 °C in sputtered SiO_2 films and found an activation energy of $E = 0.66$ eV and a frequency factor of $s = 10^4$ s^{-1}. Unusually low values of the activation energy and frequency factor have been reported for the associated effect of thermally stimulated conductivity (TSC). Bräunlich (1967) and Sunta et al. (1999) pointed out that within the one-trap-one-recombination-center model (OTOR), if retrapping is strong and if the traps are filled to saturation, the standard initial-rise method as well as the peak-shape methods and glow peak fitting yield very low effective values of the activation energy. Bräunlich (1967) showed by numerical solution of the relevant set of differential equations that for saturated trap and A_n/A_m~1000 where A_n is the retrapping probability coefficient and A_m the recombination probability coefficient, the initial-rise method yields a value of ~0.43E where E is the real activation energy. Sunta et al. (1999) tested two models, OTOR and interactive multitrap system (IMTS) in which the occurrence of an additional thermally disconnected deeper trap (TDDT) is assumed. Using peak shape methods (similar to Eq. (1) above) as well as a best-fit method, they found for cases of saturated trap and high retrapping low values of the effective activation energy down to ~0.466E. These authors have not dealt with the effective frequency factor, but it is obvious that in this case, the effective frequency factor found by Eq. (3) would be several orders of magnitude lower than the "real" one. Also should be mentioned the work by Kierstead and Levy (1991) who simulated a series of rather closely located TL peaks, due to a series of activation energies, and analyzed them using the repeated initial-rise method. Their conclusion is that the first and sometimes last activation energies in the series could be accurately determined. As for the other peaks, the analysis yielded a continuum of activation energies, usually in the same range as the inserted discrete ones.