

# Systematic errors in thermoluminescence

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## Abstract

Thermoluminescence measurements potentially are distorted by a variety of systematic errors. Major difficulties are encountered with temperature values as there are inevitable temperature gradients which become more severe at higher heating rates. Distorted temperature scales need not introduce problems in radiation dosimetry but must be corrected for kinetic analyses of the thermoluminescence processes. Additionally one must correct for changes in emission spectra with temperature and separate wavelength dependent glow curve processes. The various problems of such systematic errors are considered as well as their wider consequences in comparing the luminescence with other measurement techniques applied to the same materials.

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## 1. Introduction

Thermoluminescence (TL) is a superbly sensitive technique to record radiation history in insulators and it is consequently widely used in radiation dosimetry and archaeological dating, as well as for studies of crystalline defects [1–4] and more recently in detection of phase transitions [5–8]. The TL concept was first used more than 50 years ago and it has an immense literature. In principle, exposure to radiation liberates electrons and holes which become trapped within the lattice and subsequent heating releases these charges allowing them to recombine and produce luminescence. In principle, the intensity of the luminescence generated during sample heating is proportional to the radiation dosage. As for any such process which is controlled by imperfections and impurities, one must be cautious and confirm both the linearity of the response and reproducibility of the material, but for practical purposes TL is ideal as the basis for radiation dosimetry. Many tens of materials have been marketed as

the “ideal” insulator for dosimetry. There are numerous conflicts as to the details of the TL process and with time it has become accepted that charge trapping and/or recombination can be at extended defect complexes and the initial model of isolated traps with long-range charge transport may be rare. The various temperature related emissions define intensity peaks and the overall pattern of intensity change with temperature is termed a glow curve.

Excellent detection sensitivity exists when the emission is in the short wavelength region (e.g. near 400 nm) where photomultiplier tubes (PM) are most responsive. The PM quantum efficiency (the probability of electron emission per incident photon) is routinely ~20% in the blue for commercially used PM detector systems. The cathodes used are far less sensitive to green or longer wavelength light and for blue emitting dosimeters, but this can be a bonus as such cathodes have very low background dark currents and insensitivity to thermal emission from the TL dosimeter equipment whilst the sample is being heated. Such tubes are not state of the PM art and currently there are newer PM tubes, or detection conditions, with QE performance above 50% in the blue and good green responses, whilst maintaining a low dark current [9].

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In dosimetry equipment filters are included in the system to reject long wavelength thermal emission and these define a broad band spectral range for the luminescence detection. Overall a good choice of dosimeter material with blue emission and a linear intensity with dose response allows one to have sensitive and reliable TL dosimetry.

## 2. Potential problems

Whilst the intensity data from TL are well suited for radiation dosimetry the high sensitivity of the method, as well as the simplicity and low cost of the basic equipment, means that exactly the same methods are widely used in more demanding fundamental studies of minerals and other insulators. The glow curves are often analysed to define parameters such as the trapping energy ( $E$ ) and an escape frequency from the trap ( $Y$ ) [1–4,10]. Unfortunately, in numerous cases such analysis has led to a wide range of errors and misinterpretation of the data. Even more unfortunate is that, since the standard dosimetry systems tend to be similar, the same systematic errors in data collection, and interpretation, are made by many groups, and hence the warning signs are missed. Several main types of error occur and they may be listed as:

1. Broad band filtering which rejects and/or confuses wavelength sensitive glow curves.
2. Many of the attempts to record emission spectra during TL fail to adequately correct the wavelength dependence of the system and/or incorrectly transform wavelength data into photon energy views as needed for spectral analysis of the component emission bands.
3. High heating rates, which were beneficial in dosimetry as they improve signal to noise for weak signal detection, distort the glow curves and the apparent temperatures at which specific processes occur. The temperature errors introduce major difficulties when comparing the TL peaks with changes in other parameters, such as furnace anneals induced changes of optical absorption or EPR data. Even when making comparisons with spectrally resolved TL the same problems exist since such data are normally collected at a low heating rate.
4. Attempts to model the kinetic parameters of the TL peaks are seriously distorted by the use of incorrect temperatures in the analyses.

Consideration of these systematic errors is definitely not new, but despite the earlier discussions and reviews of the problems, for example the essential requirement of spectral analysis [11], and temperature errors and distortions of the glow curves during fast heating [5,12–18], it is clear that a very large number of research groups are still ignoring the problems and failing to recognise that, because these are systematic errors; agreement with other publications is not a validation of the results and analyses.

### 2.1. Wavelength dependence of the glow curve

If there is only one emission process then the glow curve is insensitive to wavelength and detection via a broad band optical filter and a wavelength dependent PM response does not perturb the shape of the glow curve. For many commercial dosimeters this is effectively true [3], and indeed if the spectral responses do not change with radiation dose then this is unimportant in dosimetry. However, for the majority of insulator systems, and particularly many minerals that include a range of impurity controlled emission sites, this is not the case. The spectrum is thus a mixture of intrinsic and impurity controlled processes which can define quite independent glow curves. Interpretation of such data viewed via a polychromatic broad band filter is highly suspect. It is essential to use spectrally resolved TL measurements and carefully correct the response for the wavelength dependent sensitivity of the spectrometer and detector system for defect analysis and separation of the various emission bands. One must also be cautious to transform the data from the typical collection mode of wavelength ( $\lambda$ ) dispersion with a fixed bandwidth ( $d\lambda$ ) (as results from diffraction grating spectrometers) to the physically more meaningful presentation in terms of photon energy ( $E$ ). Note that an intensity transformation from  $I(\lambda)d\lambda$  to  $I(E)dE$  is essential, as well as the change in axis from wavelength to energy.

The quantum efficiency (QE) curves of the PM tubes, the response of diffraction gratings with wide wavelength coverage and the transformations from  $I(\lambda)d\lambda$  to  $I(E)dE$ , all emphasise the short wavelength blue signals at the expense of those in the red. The overall spectral distortions can be very significant and, for example in one of the Sussex spectrometer systems the relative  $I(\lambda)d\lambda$  values for blue and red signals at 400 and 800 nm favoured the blue by a factor of  $\sim 200$ . With such enormous detection sensitivity bias in favour of the blue signals one also introduces the danger of misinterpretation in separation of true red signals (poorly detected) from the weak second-order diffraction of blue signals (which are efficiently detected). Hence second and third order filtering is necessary, but not always included in the measurements. Further, ignoring the energy transformation depresses the true significance of the red signals by another factor of four relative to those in the blue region.

Figs. 1 and 2 present an example of an isometric and contour plot for the TL emission of Er doped SrF<sub>2</sub> [19]. The data have been corrected for the wavelength dependence of the spectrometer. In this particular spectrometer system two different diffraction gratings are used to optimise the red performance, rather than attempt to use one grating over the entire spectral range. Nevertheless, the photocathode QE and grating effects still meant that the original signal near 550 nm was weaker than the 300 nm signal by a factor of about two and the 700 nm lines needed enhancement by  $\sim 5$  times. The example is instructive as the figures show that the various emission lines of Er as well as

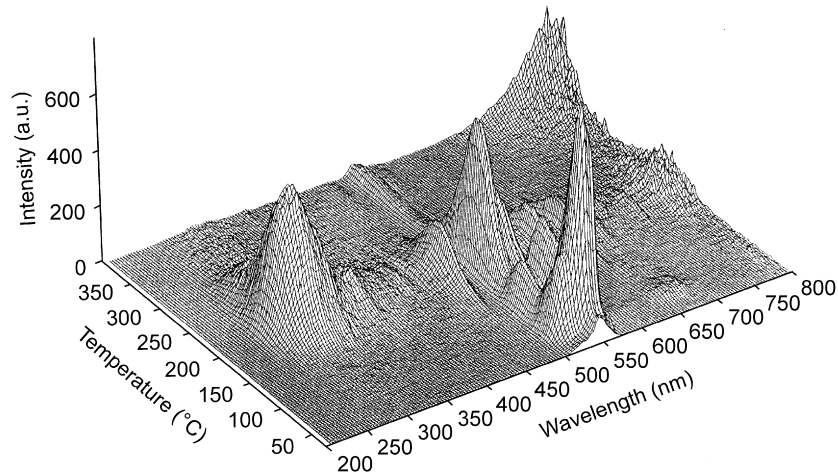


Fig. 1. An example of a spectrally resolved TL signal for Er doped SrF<sub>2</sub> [19]. The data were corrected for the response of the spectrometer system.

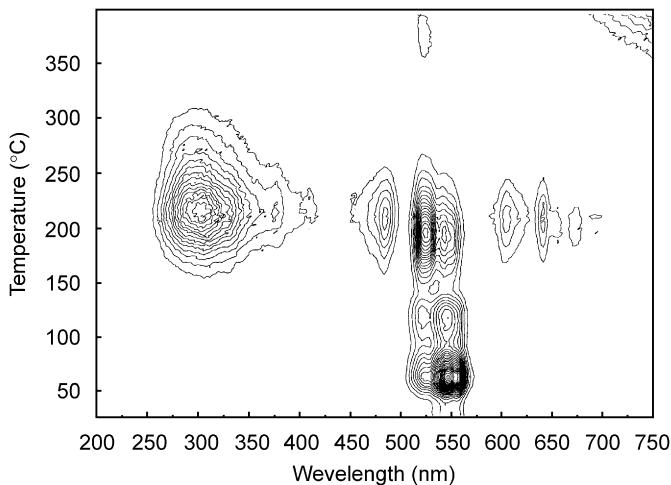


Fig. 2. A contour map of the data from Fig. 1.

the intrinsic UV band define different TL curves. There are also temperature shifts between the peak intensities. Near 800 nm one sees the onset of black body emission from the heater strip. In this example of a low heating rate (0.1 K/s) the sample and heater strip are at a similar temperature so it is possible to study long wavelength emission. On the wavelength plot the 300 and 550 nm signals are of comparable intensity but on an energy transformed view the 550 nm signals are thus enhanced by  $(550/300)^2$ , i.e. a factor of 3.4. Overall this has shifted their relative importance by  $\sim 6.8$  times compared with the initial measurements. A larger correction exists for the longer wavelength signals.

It is not uncommon that emission from impurity sites such as Mn, Fe or rare earth ions etc., defines totally different glow curves from those associated with intrinsic defects of the lattice. For example, for a mineral such as charoite there is a weak blue emission from intrinsic processes but intense signals around 590 nm from a range of Mn sites, and longer wavelength emission bands near 710 nm linked to the iron impurities. The three types of site

have unrelated glow curves [20]. TL glow curves recorded with dosimetry conditions of a blue filter and a blue sensitive PM tube intended for short wavelength detection would totally miss most of the major signals.

At low temperatures there are many examples which show broad band UV/blue emission from intrinsic processes, such as exciton relaxation, and an independent set of features linked to impurities. The events are most readily recognised with rare earth impurities since these have characteristic emission line spectra and detailed measurements have been made in the case of LaF<sub>3</sub> [21,22], BGO [23], CaSO<sub>4</sub> [24], etc. The impurity events often dominate the spectrum at temperatures above about 120 K as hole traps are often unstable at these temperatures and the excitons are mobile and can preferentially decay at the impurity sites. Fig. 2 demonstrates an example of such a wavelength dependent glow curve situation for rare earth transitions. Long-range lattice distortions are sensitive to the impurities, and their concentrations, and result in small temperature movements of the glow peaks (e.g. often on the scale of say 10 degrees). By contrast, large impurity concentrations can cause phase separation or defect clustering [22] and, in the case of zircon [25], different impurity precipitates have been considered to alter the glow peak temperature by more than 100 degrees.

It should be noted that the intrinsic processes linked to recombination of a relaxed exciton result in an emission process near 400 nm ( $\sim 3.1$  eV) but the transition energy is perturbed by the presence of impurities and the dielectric constants of the host. For quartz TL the main peak can vary from say 370 to 470 nm depending on the absence or presence of impurity sites such as H, Al or Ge. Further, a very similar emission band inevitably occurs in most silicates, and many other wide bandgap insulators. Hence, detection of blue emission in this spectral region is not *a priori* evidence for a specific host, as has been claimed by some authors, in, for example, attempts to separate feldspar and quartz inclusions within a mineral sample.

These brief examples underline that spectral resolution of TL is an essential requirement and the more normal approach of using a broad blue band filter is only of minor value for any detailed study of defect properties. Considering the very large number of research groups using TL it is surprising that so few laboratories have troubled to develop suitable wavelength resolved TL systems, especially as the data are extremely informative.

## 2.2. Temperature corrections with heating rate

The mathematical modelling of a single isolated glow peak has been discussed by many authors and in simple terms includes release from a trap of depth  $E$  (eV) and a vibrational frequency factor for attempting to escape  $s$  ( $s^{-1}$ ). For a heating rate of  $\beta$  (degrees per second) one can define a so-called “first order” equation as

$$I(T) = \phi n_0 s \exp\left(\frac{-E}{kT}\right) \exp\left[-\frac{s}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{k\theta}\right) d\theta\right], \quad (1)$$

where  $k$  is Boltzmann’s constant ( $8.616 \times 10^{-5}$  eV/K),  $\phi$  is the luminescence efficiency,  $n_0$  is the original population of filled electron traps and  $T = T_0 + \beta t$ .  $\theta$  is a dummy variable representing temperature.  $E$  is the activation energy and  $s$  is the frequency factor which is related to the local lattice vibration frequency. The peak position ( $T_m$ ) moves with heating rate as defined by

$$\frac{kT_m^2}{\beta E} = \frac{1}{s} \exp\left(\frac{E}{kT_m}\right). \quad (2)$$

So in principle one can obtain  $E$  and  $s$  by noting  $T_m$  values as a function of  $\beta$ .

The idealised TL model needs refinement for real materials and considerable effort has been made in developing more sophistication for this equation to allow for charge retrapping, inclusion of alternative traps and non-luminescence decay routes, etc. Nevertheless, if one is to extract the key parameters for the process ( $E$  and  $s$ ) one must be able to compare the theory with accurate experimental data. It is this step which poses a very major problem as a result of systematic errors. The temperature control systems use thermocouples welded on to the heater plate to define a linear temperature rise with time and one thus records a temperature from a single point on the heater strip. Unfortunately, there are small temperature gradients beneath the sample along the heater and this is not the temperature of the emissive surface of the sample. As was modelled and demonstrated in detail in earlier work [12,13] there are temperature gradients along the heater; there are problems of thermal contact between the heater and sample, and temperature gradients across the sample. In automated TL readers the sample is placed on the heater without the benefit of tight thermal coupling that might be achievable in a research system. Background gas offers some thermal coupling and so an inert gas is often included in the chamber. However, the sample, an insulator,

inevitably develops a thermal gradient between the heater strip and the emissive front face of the sample. The problems are exacerbated by higher heating rates (as preferred for commercial TL readers). The problem is not confined to heater plate methods but is equally apparent in hot gas control systems and extreme examples have been cited with a 100 degree error between measured and sample temperature [14–17], as well as considerable distortions in the shape of the glow curve.

Separation of changes in peak temperature caused by thermal lag from “true” temperature shifts defined by Eq. (2) is non-trivial. Therefore an experiment was made to assess the apparent temperature of a phase transition [5]. The phase transition changes were in good agreement with the earlier modelling. They indicated that for a phase transition which should appear at 138 °C at a heating rate of 1 degree per second there was a lag of >20 degrees with a long uniform heater strip, but this was larger at ~30 degrees for data from a TL dosimeter system. This is a direct measure of the temperature lag in the system and is in addition to the movement of the predicted shifts in glow peak temperature with heating rate. Note that in dosimetry systems heating rates of up to 30 or 50 degrees per second are used, implying temperature lags of perhaps 100 degrees.

The use of Eq. (2) to assess the activation energy is therefore invalid as the measured data do not describe a linear plot. Adjustment of the data was possible where the temperature lags had been accurately calculated [12,13] and this provided linearity of the data that indicated a slightly higher activation energy than might have been claimed from the lowest heating rates of the original data. Such detailed information is not normally available and an empirical approach was proposed by Kitis and Tuyn [14,15]. They assume that the error is small for the lowest heating rates and then predict the “correct”  $T_{\max}$  for each of the higher heating rates. This defines an empirical correction function where  $T_{\max}(j) = T_{\max}(i) - c \ln(\beta i / \beta j)$ , for different heating rates  $j$  and  $i$ , and  $c$  is a constant. This can generate a reasonably linear plot. As an example we recorded a set of glow curves taken at different heating rates for a dosimeter material  $\text{MgB}_4\text{O}_7:\text{Tm,Na}$  irradiated each time for 1 min with a  $^{90}\text{Sr}$  source. Data were taken with typical dosimetry heating rates from 1 to 40 degrees per second. Fig. 3 shows examples of the glow curves and Fig. 4 includes both the plot of Eq. (2) for the measured data and the generation of a “linear” data set by using the empirical correction factor. The adjusted data define an activation energy near 1.21 eV with an  $s$  value of  $1.24 \times 10^{12} \text{ s}^{-1}$ . The energy is inevitably similar to that indicated by the values from the lowest heating rates. However, the earlier calculations and lower heating rate experiments showed that the systematic errors were clearly apparent down to rates as low as 0.1 K/s. Thus the value is still slightly less than the fully corrected value.

In the example of Fig. 4 the thermal lag is at least 50 degrees at the highest heating rate compared with that at 1 K/s, but ~150 degrees higher than the event recorded at

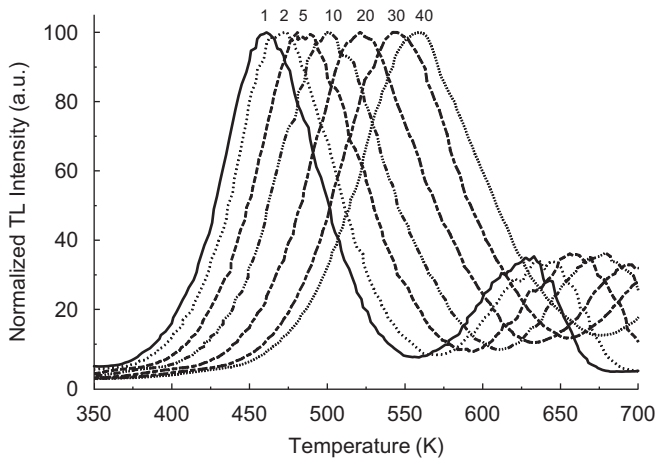


Fig. 3. Glow curves of  $\text{MgB}_4\text{O}_7:\text{Tm,Na}$  irradiated 1 min with  $^{90}\text{Sr}$   $\beta$  source recorded at 1, 2, 5, 10, 20 and 40  $\text{K s}^{-1}$ .

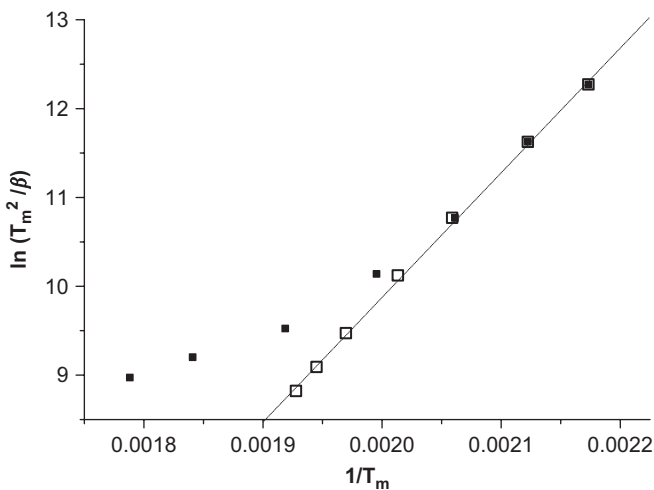


Fig. 4. Attempted analysis of the activation energy using TL peak temperatures (solid points), as measured and after applying an empirical correction factor to minimise the temperature lag errors (open squares).

0.1 K/s. The example indicates the difficulty in discussing a glow peak in terms of the measured peak temperature. In this case one could ignore the systematic errors for an informal discussion with other TL groups and call the main signal the 550 K feature ( $\sim 277^\circ\text{C}$ ). However, for comparisons with other work in the literature, such as data on emission spectra of the TL, EPR, optical absorption or thermal annealing, this same event would appear near 390 K ( $\sim 117^\circ\text{C}$ ). The problem is that the exponents of the different techniques fail to correctly associate the different types of data.

Note that, as pointed out by all the authors who have considered this problem, the form of the glow curve is seriously distorted at the higher heating rates and so any assessment of the activation energy from a full curve fitting is unreliable. This is unfortunate as many detailed theoretical models of TL discuss more complex models with “second order” kinetics which require knowledge of the full curve shape.

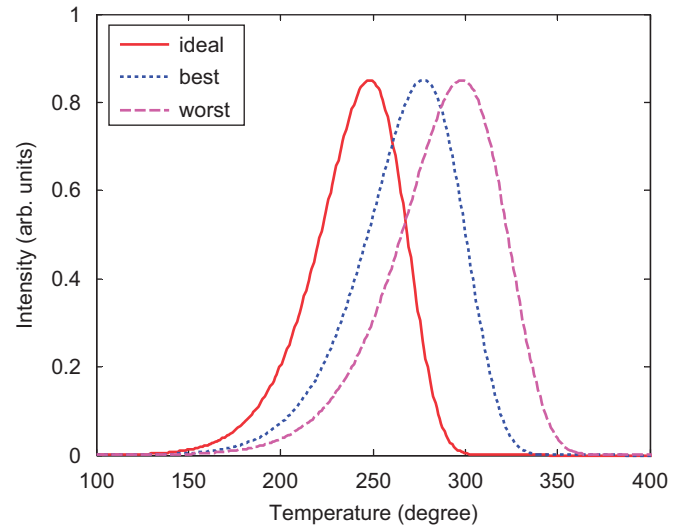


Fig. 5. Theoretical glow curves predicted with parameters of a 50 K/min heating rate,  $E = 1.0\text{ eV}$  and  $s = 1 \times 10^{10}\text{ s}^{-1}$ , note that ‘ideal’ stands for glow curve without any temperature error and ‘best’ and ‘worst’ are based on the experimental temperature lag of Ref. [5].

### 2.3. Temperature errors and activation analyses

One may use Eqs. (1) and (2) to predict the ideal peak temperatures and form of the glow curves at different heating rates. If one then introduces realistic experimental temperature lag data one can predict the probable experimental values of the displaced and distorted glow curve. In order to see what such uncorrected data would provide in an analysis one can then match the form of this shifted curve to new values for the activation energy in Eq. (1). An example of this approach is modelled in Fig. 5 in which the correct peak temperature shifts between 30 and 50 degrees. We have considered the case for  $E$  and  $s$  values of 1.0 eV and  $10^{10}\text{ s}^{-1}$  and a modest heating rate of  $\sim 1\text{ K/s}$  (i.e. high for emission spectra TL but low for dosimetry). Using the experimental lag data from Ref. [5] the apparent activation energy increases from 1 eV to between 1.13 and 1.22 eV. At the higher dosimetry heating rates the apparent energy can reach at least 1.3 eV. Such differences, of up to 30%, are sufficiently great that both modelling and detailed analysis are seriously impaired. The example thus underlines the fact that it is absolutely essential to correct for the systematic errors before making any discussion or analysis of glow curves.

### 3. Conclusions

Systematic temperature errors are inevitable in high heating rate measurements of thermoluminescence. They need not introduce problems in radiation dosimetry as identical errors exist during calibration of the sensitivity of the dosimeter. However, on using TL in defect studies one must correct for changes in emission spectra with temperature and separate wavelength dependent glow curve processes. Significant distortions of the glow curves

are introduced by thermal lags between the thermocouple on the heater and the emitting surface of the insulator. Failure to make corrections for these factors leads to erroneous estimates of the dominant TL processes as well as errors in activation energy and frequency factor analysis. Whilst it is convenient to cite the apparent TL peak temperature in conversation it is essential to introduce corrections in publications, not least as this will offer easier comparisons with events recorded by other measurement techniques.

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