

## KINETIC ANALYSIS OF MONOCHROMATIC TL CURVES

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### ABSTRACT

In the kinetic analysis of thermoluminescence, 'monochromatic' curves are more useful and give more reliable information than the polychromatic glow curve. This is demonstrated for two specific cases. In one case (TL of albite) the kinetic analysis of monochromatic curves did not enable us to determine whether the red and blue emissions involved one recombination process or two independent processes. In the second case (TL of zircon) the prominent 110°C peak was found to involve three independent recombination processes.

### 1. GENERAL

In thermoluminescence (TL) as in other thermally stimulated processes (TSP) a signal is recorded as function of time (or temperature) while the sample under study is heated up in a controlled manner. The TL signal is the intensity of the light produced by radiative recombinations of mobile and trapped charge carriers. In contrast to most other TSPs, the TL output is 'two dimensional' in the sense that not only the intensity, but also the spectral composition of the emitted light might change with increasing temperature. In order to get the complete information from a TL run, the emission spectrum should be continuously recorded, along with the intensity. Ideally, the data should be stored as an  $I(\lambda, T)$  matrix which presents the TL intensity as function of the wavelength and the temperature. The results can be exhibited in a 'three dimensional' plot, such as the one shown in Fig. 1. Cuts parallel to the temperature axis give 'monochromatic' TL curves, while cuts along the wavelength axis depict the emission spectrum at various temperatures.

The kinetic analysis of TL is aimed at expressing the experimental curve as a superposition of several 'peaks'. It is usually assumed that each peak results from a single recombination process in which the depletion of a specific trap is

involved. The thermal release of charge carriers from traps is often governed by the following kinetic equation [1]

$$I = -dn/dt = sn^b \exp(-E/kT), \quad (1)$$

where I is the TL intensity, n is the concentration of the trapped charge carriers, E is the activation energy or depth of the trap from which the mobile charge carriers are released, b is called the kinetic order (usually  $1 \leq b \leq 2$ ), and s is called the pre-exponential factor.

The total light output is frequently used in TL kinetic analysis rather than monochromatic TL curves, especially when the TL intensity is weak. This should introduce no error when the emission spectrum does not change throughout a single peak. If, however, the spectrum does change with the temperature, the polychromatic TL curve is likely to give a distorted picture, and its analysis might yield erroneous results.

The advantages of monochromatic TL curves over the polychromatic curve are most important when several distinct recombination processes, having different emission spectra, occur simultaneously. In this case the polychromatic curve may contain several overlapping peaks, which might appear separately in the monochromatic curves. The merits and limitations of the 'monochromatic analysis' of TL will now be demonstrated by discussing two specific examples, concerning the TL of the minerals albite and zircon. Only a summary of the results is given here. A detailed account of the kinetic analysis can be found elsewhere for both the albite [2,3] and the zircon samples [7].

## 2. ALBITE

Figure 1 describes the TL of albite ( $\text{NaAlSi}_3\text{O}_8$ ), following a 200 krad X-irradiation at room temperature. The broad and complex TL curve exhibits two distinct spectral bands, in the blue and in the red. The '3D' plot is shown here prior to applying the correction factors which take into account the wavelength sensitivity of the system. In the corrected plot, the red band is ~70 times more intense than the blue one.

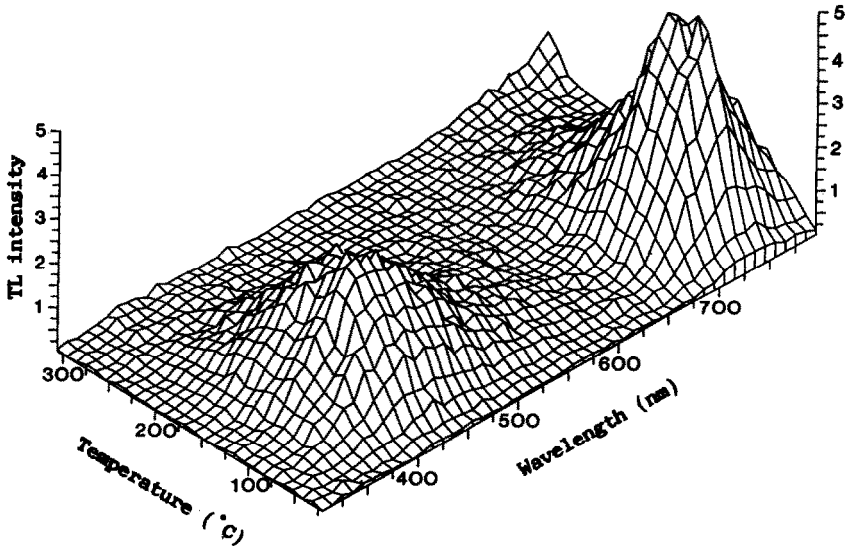
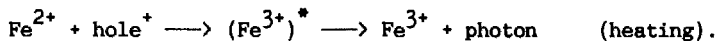
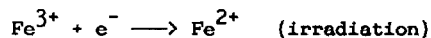


Figure 1: A 3-D plot of the uncorrected emission spectrum of albite.

Several studies have indicated that the blue emission is due to radiative recombinations of thermally released electrons with various hole centres, while the red band is attributed to the excitation of  $\text{Fe}^{3+}$  ions, probably substituting in tetrahedral  $\text{Al}^{3+}$  sites [2-6].

The excitation of the red emission might be explained by one of two alternative models. The first model can be described by the following equations



The irradiation reduces some of the  $\text{Fe}^{3+}$  ions to  $\text{Fe}^{2+}$  and in addition creates hole centres. It is equivalent to saying that the irradiation produces electron-hole pairs and that some of these electrons are trapped at  $\text{Fe}^{3+}$  ions while some of the holes are trapped at hole centres (e.g.  $\text{O}^{2-}$  near the  $\text{Fe}^{3+}$  ion). The holes are thermally released during the heating, become mobile and recombine with the  $\text{Fe}^{2+}$  ions. These recombinations result in  $\text{Fe}^{3+}$  ions in excited energy states which, upon relaxation to the ground state, emit the observed red TL.

The second model assumes energy transfer from electron-hole recombinations in various hole centres, to the  $\text{Fe}^{3+}$  ions, without any change in the valence of the Fe ions. The red band is thus explained as "secondary emission" due to blue photons which are absorbed by the  $\text{Fe}^{3+}$  ions, to be re-emitted as red light.

In the first model the two spectral bands involve two independent processes, while in the second model they stem from the same basic process. We tried to evaluate the kinetic parameters of the monochromatic TL curves, in order to determine which of the two models is correct. Indeed, it was found that the glow curves could be explained in terms of eight peaks, which seem to dominate the TL over the whole spectral region [2]. Their activation energies were: 0.60, 0.70, 0.82, 0.90, 1.05, 1.17, 1.24, and 1.39 eV. However, due to the strong overlapping, the results were not conclusive, and do not rule out the possibility that the red and blue bands involved different traps, which happened to have similar activation energies.

### 3. ZIRCON

The TL of zircon ( $\text{ZrSiO}_4$ ) single crystals, after x-irradiation at RT, was found to consist of an intense peak at  $109^\circ\text{C}$ , and a broad structure between  $180^\circ$  and  $400^\circ\text{C}$ . Two monochromatic TL curves are shown in Fig. 2. Cuts along the wavelength axis reveal two types of emission spectra: a broad band centred at 385 nm which is attributed to the excitation of the  $\text{SiO}_4^{4-}$  group [7-9] and a line spectrum which can be easily identified as transitions between energy levels of  $\text{Dy}^{3+}$  (a common impurity in natural and synthetic zircon [8-10]). Figure 3 depicts the TL emission spectrum at two temperatures; curve A is characteristic of the temperature range  $20$ - $180^\circ\text{C}$  while B typifies the emission spectrum between  $180^\circ$  and  $420^\circ\text{C}$ .

The kinetic analysis of monochromatic TL curves revealed that the broad peak between  $180^\circ$  and  $400^\circ\text{C}$  consists of seven partly overlapping peaks, with activation energies between 0.82 and 1.60 eV, and emission spectra typical of the  $\text{Dy}^{3+}$  ion [7]. These peaks can be explained by a 'charge conversion' model, similar to the one assumed in Sec. 2 for the  $\text{Fe}^{3+}$  emission in albite. According to this model, some of the  $\text{Dy}^{3+}$  ions reduce during the irradiation to  $\text{Dy}^{2+}$  by capturing electrons. The holes produced by this process are trapped in various types of hole traps. When the temperature is raised, holes are thermally released from their traps and become mobile. Consequently, recombinations of

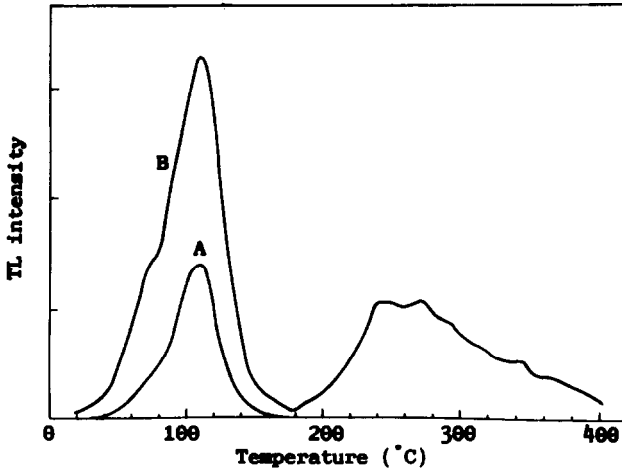


Figure 2: Monochromatic TL curves of zircon, recorded at 385 nm (A) and at 485 nm (B).

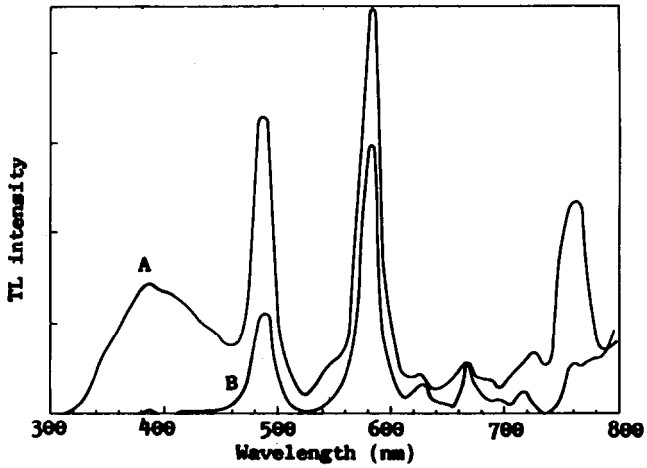


Figure 3: TL emission spectra at 100°C (A) and at 240°C (B).

holes with divalent Dy ions occur, which produce trivalent Dy ions in excited energy states. The photons emitted upon the relaxation of these ions to the ground state are the observed TL. The different activation energies are due to the existence of several types of hole traps, while the common emission spectrum (which consists of Dy<sup>3+</sup> lines) indicates that the recombination centre in all those TL peaks is the rare-earth ion.

The monochromatic analysis of the intense peak at 109°C revealed a complex structure. At wavelengths longer than 450 nm (the Dy<sup>3+</sup> spectrum) this peak was found to be much weaker at 72°C. Figure 4 depicts the fit between the experimental results and the theoretical expression at 485 nm. The kinetic parameters of the two peaks are presented in Table 1 (peaks 1a and 2a). Applying the same kinetic analysis to the monochromatic TL curve at 385 nm (curve A in Fig. 2) also revealed two peaks, the parameters of which appear in Table 1 (1b and 2b). Here the weaker peak appears at 77.5°C.

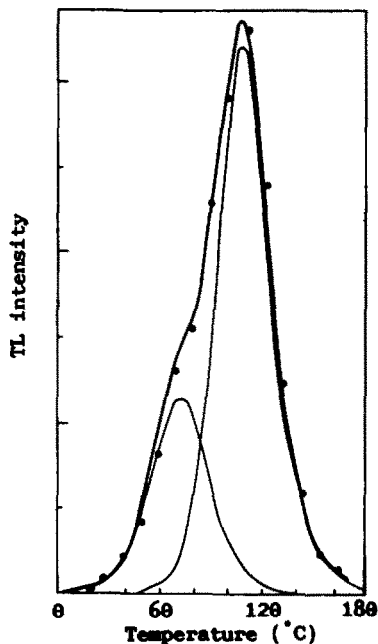
Table 1. The kinetic parameters of the low temperature TL peaks of zircon, at 485 nm (1a and 2a) and at 385 nm (1b and 2b). E is the activation energy, s the frequency factor and b the kinetic order.

Peak	T(°C)	E(eV)	s(s <sup>-1</sup> )	b
1a	72	0.82	2.4×10 <sup>10</sup>	1.8
2a	109	1.18	1.1×10 <sup>14</sup>	1.8-2
1b	77.5	0.89	1.6×10 <sup>11</sup>	1.9
2b	109	1.18	1.1×10 <sup>14</sup>	1.8

By comparing the kinetic parameters one can see that peaks 2a and 2b are practically the same. This is not the case with peaks 1a and 1b. The 385 nm peak occurs at 77.5°C with an activation energy of 0.89 eV while the peak with the Dy<sup>3+</sup> emission spectra occurs at 72°C with an activation energy of 0.82 eV.

Thus, at about 75°C, the TL consists of two separate processes, one with an activation energy of 0.82 eV and an emission spectrum typical of Dy<sup>3+</sup>, and the other with an activation energy of 0.89 eV and emission spectrum typical of the host lattice SiO<sub>4</sub><sup>4-</sup> group. The activation energy of the 77.5°C peak (0.89 eV) is in very good agreement with the theoretical value of 0.87 eV, calculated for the thermally assisted recombination of an electron and a hole trapped at adjacent Si<sup>4+</sup> and O<sup>2-</sup> ions respectively [9]. One can assume that free electrons and holes are produced by the irradiation and some of them are trapped on Si<sup>4+</sup>

**Figure 4** :The best fit of the low temperature peaks, recorded at 485 nm, to the theoretical expressions of general-order TL peaks. The full circles represent the experimental results, the thin curves are the evaluated peaks and the bold curve is their sum.



and adjacent  $O^{2-}$  ions respectively. When the crystal is heated up, electrons are thermally released and recombinations occur, accompanied by the emission of the observed UV band. The  $72^{\circ}C$  peak, which contains only  $Dy^{3+}$  lines, can be explained as a recombination of holes with  $Dy^{2+}$  ions, similar to the peaks in the range  $180^{\circ}-400^{\circ}C$ .

The  $109^{\circ}C$  peak was found to contain both the 385 nm band and the  $Dy^{3+}$  lines. (Since the kinetic parameters are the same for both types of emission, peaks 2a and 2b seem to stem from a single process.) It should be noted that a prominent peak at about  $110^{\circ}C$  has been reported by many researchers who studied the TL of zircon [8-10]. It always contains both the 385 nm band and lines typical to trivalent rare-earth ions (usually  $Dy^{3+}$  or  $Tb^{3+}$ ) and it seems to be independent of the specific activator or impurity and of the type of excitation (X, UV,  $\gamma$ -rays or  $\beta$ -radiation). One can therefore assume that the  $109^{\circ}C$  peak is associated with an intrinsic trapping centre rather than some specific impurity. The most simple possibility would be a lattice  $O^{2-}$  near a  $RE^{3+}$ . The four nearest  $O^{2-}$  ions which lie around the  $Zr^{4+}$  at a distance of 0.215 nm, as well as the

four second-nearest  $O^{2-}$  ions at 0.229 nm, should move a little farther when the  $Zr^{4+}$  is replaced by a  $RE^{3+}$  ion, because of the smaller electric charge. This distortion of the lattice would become even larger if an electron is transferred during the irradiation, from one of the  $O^{2-}$  ions to the  $RE^{3+}$ . The thermal release of this electron, and the ensuing recombination and relaxation of the lattice to its previous position, might excite both the host lattice and the  $RE^{3+}$  ion, resulting in the appearance of the two types of spectra.

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