

Surface fitting—new tool for spectrally resolved thermoluminescence analysis

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Abstract

Numerical deconvolution and curve-fitting algorithms are routinely used for the analysis of complex thermoluminescence (TL) data. This approach is generally not suitable for advanced TL measurements utilizing simultaneous detection of wavelength and intensity of the emitted light. In this paper we present new 'surface fitting' algorithm. Spectrally resolved TL surface is numerically deconvoluted for individual surface peaks corresponding to trap levels and recombination centres. This technique allows simultaneous determination of activation energies of traps and the emission bands associated with recombination centres utilizing all measured data points. To demonstrate possibilities of the method we applied the algorithm to numerical deconvolution of spectrally resolved TL data measured for high-sensitive LiF:Mg,Cu,P thermoluminescent detector.

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1. Introduction

Typical analysis of thermoluminescence (TL) data is based on various curve-fitting algorithms. Older methods used merely several characteristic points of TL curves as the peak position, inflection points or peak width (McKeever, 1985; Chen and McKeever, 1997). This approach is generally not suitable for advanced TL measurements utilizing simultaneous detection of wavelength and intensity of the emitted light. The possibility to construct a three-dimensional representation of the intensity of emission (TL-3D) as a function of wavelength and the temperature adds materially to the ability to interpret the behaviour of the materials being studied (Luff and Townsend 1992; PETERS et al., 1993). Spectrally resolved TL contains much more information concerning both trapping and recombination

states. This new technique requires a novel theoretical approach for extracting from experimental data as much information as possible.

In this paper we discuss some basic properties of spectrally resolved TL kinetics and numerical methods for determination of parameters of traps and recombination centres from TL-3D data. For this purpose we put forward a new technique that we call the *surface fitting*. TL-3D surface is numerically deconvoluted for individual peaks corresponding to trap levels and recombination centres. This technique allows simultaneous determination of activation energies and the emission bands based on various kinetic models. Here, we applied the technique assuming the first/second-order kinetics models and Gaussian emission band profiles. Exemplary data for LiF:Mg,Cu,P are presented.

2. Kinetic model

The most widely used one carrier model for the description of charge carrier kinetics during thermal stimulation is based on the following set of equations (Chen and

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McKeever, 1997):

$$-\dot{n}_i = n_i v_i \exp\left(\frac{-E_i}{kT}\right) - n_c A_i (N_i - n_i), \quad i = 1 \dots p, \quad (1a)$$

$$-\dot{m}_s = B_s m_s n_c, \quad s = 1 \dots q, \quad (1b)$$

$$\sum_{s=1}^k m_s = \sum_{i=1}^p n_i + n_c + M, \quad (1c)$$

where E_i stands for the activation energy, N_i , n_i and m_s denote the concentrations of trap states, electrons trapped in the ‘active’ traps and holes trapped in the recombination centres (RC), respectively. M stands for the number of electrons in the thermally disconnected traps (deep traps), i.e. traps that are not emptied during the experiment. A_i and B_s stand for the trapping and recombination probabilities, respectively, and v_i is the frequency factor. Conductivity of the sample (thermally stimulated, TSC) is assumed to be proportional to the concentration of carriers in the conduction band n_c and luminescence (TL) is proportional to $(-\dot{m}_s)$. TSC or TL spectrum usually consists of a series of peaks attributed to different trap levels in the material under study. During the TL readout a sample is usually heated with a constant rate β , therefore the temperature is a linear function of time, i.e. $T = T_0 + \beta t$. Any information concerning the spectral distribution of the emitted light is not explicitly included in the set of equations (1). Therefore, partial TL intensity defined as

$$J^{(s)} \propto (-\dot{m}_s) \quad (2)$$

is the total intensity emitted from the s th recombination centre. In typical TL measurements the intensity is averaged over all RCs. TL-3D technique allows to differentiate among various types of RCs. An idealized computer-generated TL-3D spectrum constructed by first-order, Gaussian-band-shape peaks is shown in Fig. 1. In general, the system consisting of p trap levels and q recombination centres could produce pq surface peaks. One may think of them as entities representing elementary TL processes in the material, i.e. charge carriers flow from the i th trap level to the s recombination centre.

To describe the kinetics quantitatively we have to construct an equation representing the entire TL-3D surface $Z(T, \lambda)$. Considering any set of kinetic equations (e.g. given by Eq. (1)) we can represent the TL partial intensity $J^{(s)}$ as a sum of peaks related to all trap levels:

$$J^{(s)}(T) = \sum_{i=1}^p J_{si}(T). \quad (3)$$

Thus, the process of the charge-carrier flow from the i th trap level to the s RC is given by the product $J_{si} G_s$, where G_s is a function describing the emission-band profile. In principle G_s depends on temperature only weakly, so it is reasonable

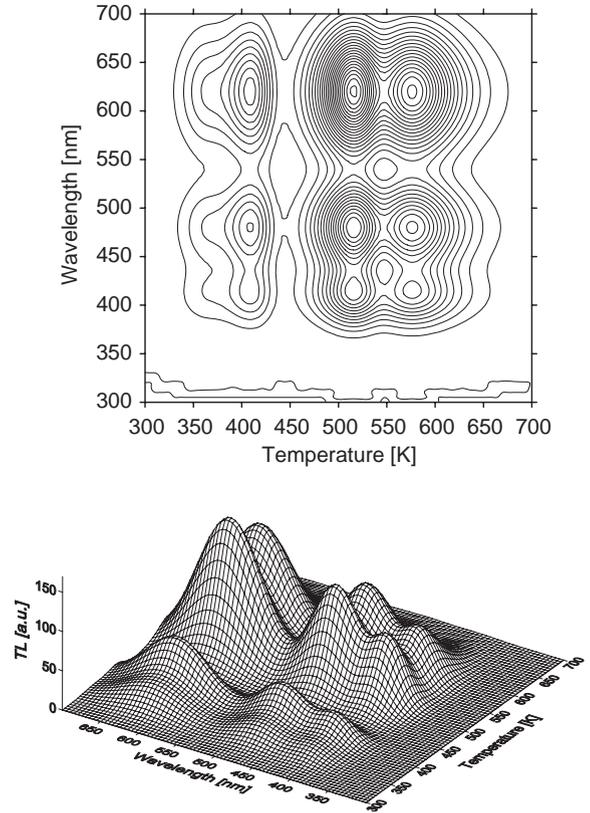


Fig. 1. Computer generated spectrally resolved thermoluminescence (TL-3D) spectrum. 12 peaks correspond to 4 trap levels and 3 recombination centres.

to neglect this dependence. Hence, the total TL-3D surface will be given by

$$Z_1(T, \lambda) = \sum_{i=1}^p \sum_{s=1}^q J_{si}(T) G_s(\lambda). \quad (4)$$

When the total relative decrease of charge carriers is small in all RCs during the release of carriers from the i th trap level, the peaks corresponding to different RCs are proportional to each other and occur at the same temperature. It can be expressed as $J_{si}(T) = \mu_{si} J_i(T)$, or even stronger assumption $J_{si}(T) = \mu_s J_i(T)$, where μ_{si} and μ_s are constants and $J_i(T)$ is the common i th peak intensity. These assumptions lead to the following simplified models:

$$Z_2(T, \lambda) = \sum_{i=1}^p J_i(T) \sum_{s=1}^q \mu_{si} G_s(\lambda) \quad (5)$$

and

$$Z_3(T, \lambda) = \sum_{i=1}^p J_i(T) \sum_{s=1}^q G_s(\lambda). \quad (6)$$

In the latter case μ_s were included as proportionality coefficients into G_s functions. $Z_3(T, \lambda)$, representing TL-3D

intensity, is a product of the kinetic and spectral parts. The three functions (4–6) contain different number of free parameters that have to be fitted to experimental data. If one assumes that each kinetic peak depends on n_J free parameters and each emission band depends on n_G free parameters, the total number of fitting parameters for Z_1 , Z_2 and Z_3 is $(n_J p q + n_G q - q)$, $(n_J p + n_G q + p q - p - q)$ and $(n_J p + n_G q - 1)$, respectively. However, in the first case (Z_1) it still could be reduced assuming e.g. the same activation energies for all “s” subscripts. The details depend on the particular kinetic model applied.

3. Numerical calculations

To apply the TL-3D kinetic models defined by Eqs. (4) and (6) one has to assume a particular form of J and G functions. The simplest, physically acceptable analytical kinetic solutions are known as the first and second order kinetic equations $J_i(T, J_{0i}, E_i, \alpha_i)$ (Chen and McKeever, 1997). Spectral distribution is usually given by the Gaussian function $G_s(\lambda, G_{0s}, \lambda_{0s}, \sigma_s)$. Assuming a mathematical form of TL-3D surface as given by Eq. (6) one can determine particular parameters of traps and RCs. To minimize the number of fitting parameters due to low intensity of measured data we apply the function $Z_3(T, \lambda)$ which now has the form

$$Z_3(T, \lambda) = \sum_{i=1}^p J_i(T, J_{0i}, E_i, \alpha_i) \sum_{s=1}^q G_s(\lambda, G_{0s}, \lambda_{0s}, \sigma_s). \quad (7)$$

Our goal is to find the set of unknown parameters $\{J_{0i}, E_i, \alpha_i, G_{0s}, \lambda_{0s}, \sigma_s\}$ by minimizing the sum of square deviations

$$\sum_{\substack{\eta \in \Omega_T \\ \zeta \in \Omega_\lambda}} [Z_D(T_\eta, \lambda_\zeta) - Z_3(T_\eta, \lambda_\zeta)]^2 = \min, \quad (8)$$

where Z_D denotes experimentally measured data, and η , ζ number points of two-dimensional grid $\Omega_T \times \Omega_\lambda$. For p trapping levels and q recombination centres the total number of fitting parameters is $3(p + q) - 1$, because one of the parameters $\{J_{0i}, G_{0s}\}$ could be assumed to be a constant (e.g. $G_{01} = 1$). The minimizing algorithm was written in *Pascal* and it was based on the modified Gauss–Seidel/Powell method. Even in the case of multiple peaks it turned out to be stable and efficient. Average computing time was in the range of minutes to 1 h on a personal computer.

The surface fitting technique was applied to an analysis of the spectrally resolved TL of high-sensitive LiF:Mg,Cu,P thermoluminescent detector. Samples were prepared at the Institute of Nuclear Physics (Kraków, Poland) (Bilski, 2002; Mandowska et al., 2002). Prior to the measurements the sample was irradiated with a dose of 0.688 Gy at room temperature. The measurements were carried out in a vacuum cryostat enabling to control the sample temperature between 78 and 700 K (Mandowski et al., 2003). TL-3D spectrum

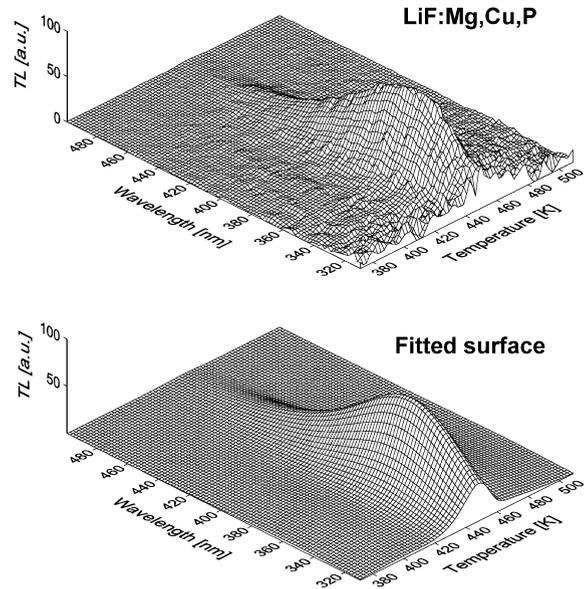


Fig. 2. Spectrally resolved thermoluminescence data and the fitted surface for LiF:Mg,Cu,P.

is shown in Fig. 2. Due to low resolution of the measured data we had to limit the analysis to six peaks resulting from three trapping states and two recombination centres. We denote these traps and RCs as T_1 , T_2 , T_3 and R_1 , R_2 , respectively. The fitted spectrum and the fitted peaks are shown in Figs. 2 and 3, respectively. Calculated activation energies of trap levels are: 0.85, 2.1 and 1.3 eV. T_1 and T_2 were fitted with first-order kinetics and T_3 with the second order. Two broad emission bands R_1 and R_2 are centered around 349 and 376 nm, respectively.

4. Conclusions

New numerical techniques for modelling and analysis of spectrally resolved thermoluminescence were shown. The *surface fitting* method could be successfully applied for determination of trap parameters from TL-3D. This technique utilizes all points obtained by experiment, that is why it allows for more precise and credible identification of trapping levels and recombination centres. Exemplary results were shown for the LiF:Mg,Cu,P sample. Obtained results for the trapping state T_2 and determined emission bands R_1 and R_2 are in a good agreement with previously published results (Bilski, 2002; Meijvogel et al., 1995). The trapping state T_1 probably represents a set of smaller peaks. To determine more precisely their activation energies from TL-3D spectra it is necessary to perform higher resolution measurements (e.g. using higher excitation doses). It should be stressed that the calculations were

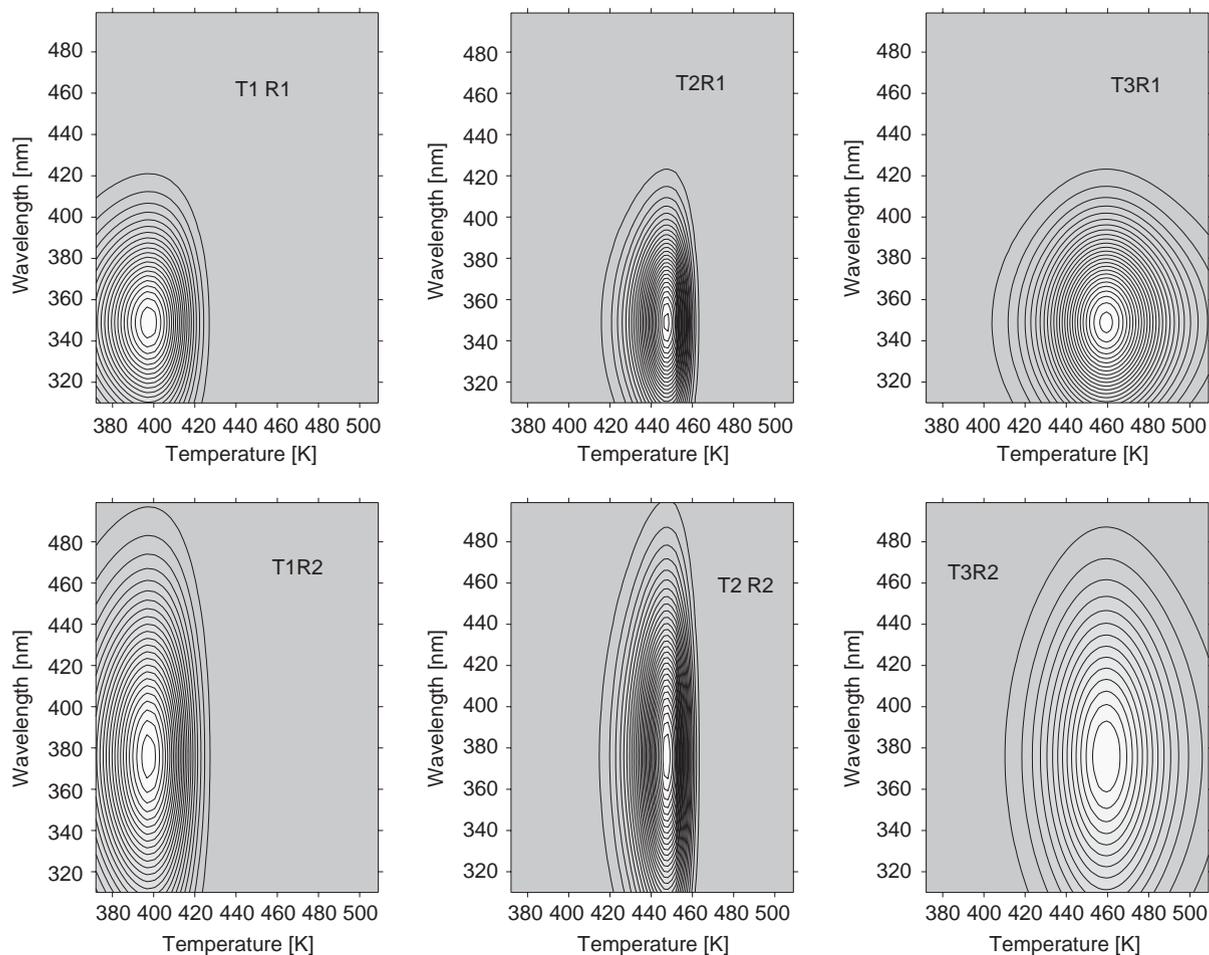


Fig. 3. Elementary TL peaks corresponding to charge carriers transitions from three trapping levels to two recombination centres.

performed under several simplifying assumptions leading to Eq. (7).

Presently, the surface fitting technique was adopted for the first- and second-order kinetics approximations. These simple, however, physically justified models, do not cover a wide variety of possible physical situations. Therefore it should be broadened also to include more general kinetic models—e.g. the quasi-equilibrium approximation (Mandowski and Świątek, 1999; Opanowicz and Przybyszewski, 1995; Sunta et al., 1999) and the TL theory for spatially correlated systems (Mandowski, 2002). In some cases it may be necessary to include also temperature dependence of the emission spectrum.

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References

- Bilski, P., 2002. Lithium fluoride: from LiF:Mg, Ti to LiF:Mg, Cu,P. *Radiat. Prot. Dosimetry* 100, 199–206.
- Chen, R., McKeever, S.W.S., 1997. *Theory of Thermoluminescence and Related Phenomena*. World Scientific, Singapore.
- Luff, B.J., Townsend, P.D., 1992. High sensitivity thermoluminescence spectrometer. *Meas. Sci. Technol.* 3, 65–71.
- Mandowska, E., Bilski, P., Ochab, E., Świątek, J., Mandowski, A., 2002. TL emission spectra from differently doped LiF:Mg detectors. *Radiat. Prot. Dosimetry* 100, 451–454.
- Mandowski, A., 2002. The theory of thermoluminescence with an arbitrary spatial distribution of traps. *Radiat. Prot. Dosimetry* 100, 115–118.
- Mandowski, A., Świątek, J., 1999. New fitting algorithm for the determination of trap parameters from TL curves. *Radiat. Prot. Dosimetry* 84, 123–126.
- Mandowski, A., Mandowska, E., Czub, P., Mazela, W., Świątek, J., Pielichowski, J., 2003. Kinetic analysis of long-lived luminescence in modified epoxy resins. *Proc. SPIE* 5136, 280–287.

- McKeever, S.W.S., 1985. *Thermoluminescence of Solids*. Cambridge University Press, Cambridge.
- Meijvogel, K., Bos, A.J.J., Bilski, P., Olko, P., 1995. Thermoluminescence emission characteristics of LiF(Mg,Cu,P) with different dopant concentrations. *Radiat. Meas.* 24, 411–416.
- Opanowicz, A., Przybyszewski, K., 1995. Is the quasi-equilibrium approximation in description of thermally stimulated luminescence and conductivity valid? *Proc. SPIE 2373*, 236–240.
- Piters, T.M., Muelemans, M., Bos, A.J.J., 1993. An automated research facility for measuring thermoluminescence emission spectra. *Rev. Sci. Instrum.* 69, 109–117.
- Sunta, C.M., Feria Ayta, W.E., Kulkarni, R.N., Chubaci, J.F.D., Watanabe, S., 1999. The quasi-equilibrium approximation and its validity for the thermoluminescence of inorganic phosphors. *J. Phys. D: Appl. Phys.* 32, 717–725.