MODELLING AND THE INVERSE PROBLEM IN SPECTRALLY RESOLVED THERMOLUMINESCENCE

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ABSTRACT

Typical analysis of thermoluminescence (TL) 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. 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 some numerical methods for modelling (simulation) of spectrally resolved thermoluminescence as well as determination of parameters of traps and recombination centres from measured data. The latter case is more complex. For this purpose we put forward a new technique called surface fitting. Exemplary data for selected materials are presented.

INTRODUCTION

Thermoluminescence (TL) is one of the basic tools for the determination of traps and recombination centres in dielectrics. Typical analysis of 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 [1,2]. 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 [3,4]. Spectrally resolved thermoluminescence 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 numerical methods for modelling (simulation) of TL-3D kinetics as well as determination of parameters of traps and recombination centres from TL-3D data. The latter case is more complex. 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 the first/second order kinetics model and gaussian/lorentzian emission band profile. Exemplary data for selected polymers and other materials are presented.

BASIC EQUATIONS

The most acceptable model for the description of charge carriers kinetics during thermal stimulation is based on the following set of equations [2]:

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

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

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

where E_i stands for the activation energy, N_i, n_i, and m_s denote the concentrations of trap states, electrons trapped in 'active' traps and holes trapped in recombination centres (RC). 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 ν_i' is the frequency factor. Conductivity of the sample (TSC) is assumed to be proportional to 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.

Unfortunately, the model does not give us any information concerning spectral distribution of the emitted light. TL intensity defined above: $J^{(s)} \propto (-\dot{m}_s)$ is the total intensity emitted by the s-th recombination centre. In typical TL measurements the intensity was averaged over all RCs. TL-3D technique allows to differentiate among various types of RCs. Let us assume that the partial intensity coming from the i-th trap level is given by J_i. Thus, the process of charge carriers' flow from the i-th trap level to the s-th RC is given by the product $J_i G_s$ where G_s is a function describing light emission band profile. Hence, the total TL-3D surface will be given by

$$Z(T,\lambda) = \sum_{i=1}^{p} J_i(T) \sum_{s=1}^{q} G_s(\lambda) \qquad (2)$$

Therefore, the intensity is a product of kinetic and spectral parts. To calculate TL-3D surface one has to assume particular form of these two functions. In principle, $J_i(T)$ can be taken as a solution of eqs. (1). The simplest analytical solutions of (1) are known as the first and second order kinetic equations.

$$J_i(T, J_{0i}, E_i, \alpha_i) = \begin{cases} J_{0i}\exp\left(\frac{-E_i}{kT}\right)\exp\left[-\alpha_i\int_{T_0}^{T}\exp\left(\frac{-E_i}{kT'}\right)dT'\right], & \text{first order} \\ J_{0i}\exp\left(\frac{-E_i}{kT}\right)\left[1+\alpha_i\int_{T_0}^{T}\exp\left(\frac{-E}{kT'}\right)dT'\right]^{-2}, & \text{second order} \end{cases} \tag{3}$$

Spectral distribution is usually given by gaussian function

$$G_s(\lambda, G_{0s}, \lambda_{0s}, \sigma_s) = G_{0s}\exp\left[\frac{-(\lambda-\lambda_{0s})^2}{2\sigma_s^{\ 2}}\right] \tag{4}$$

NUMERICAL CALCULATIONS

Equations (3) and (4) allow to calculate TL-3D spectrum assuming appropriate trap and RC parameters and then substituting them into formula (2). Two examples of this kind are presented in Figs. 1 and 2.

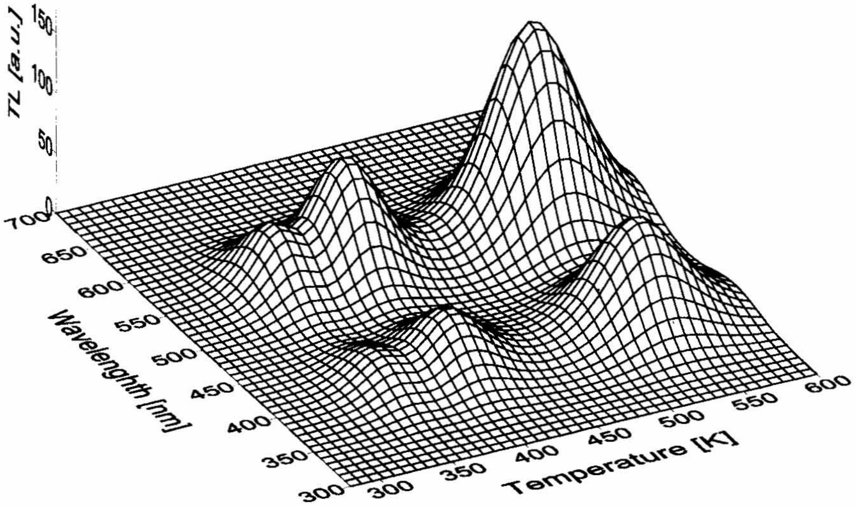


Figure 1. Computer generated spectrally resolved thermoluminescence spectrum. Six peaks visible on the diagram correspond to three trapping levels and two recombination centres.

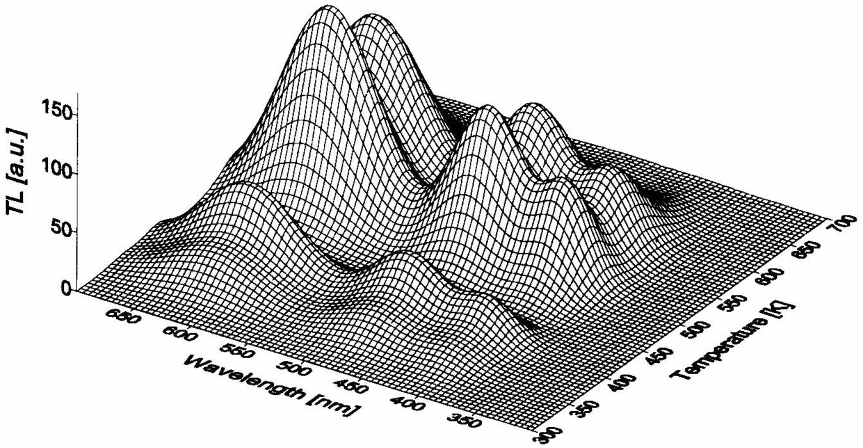
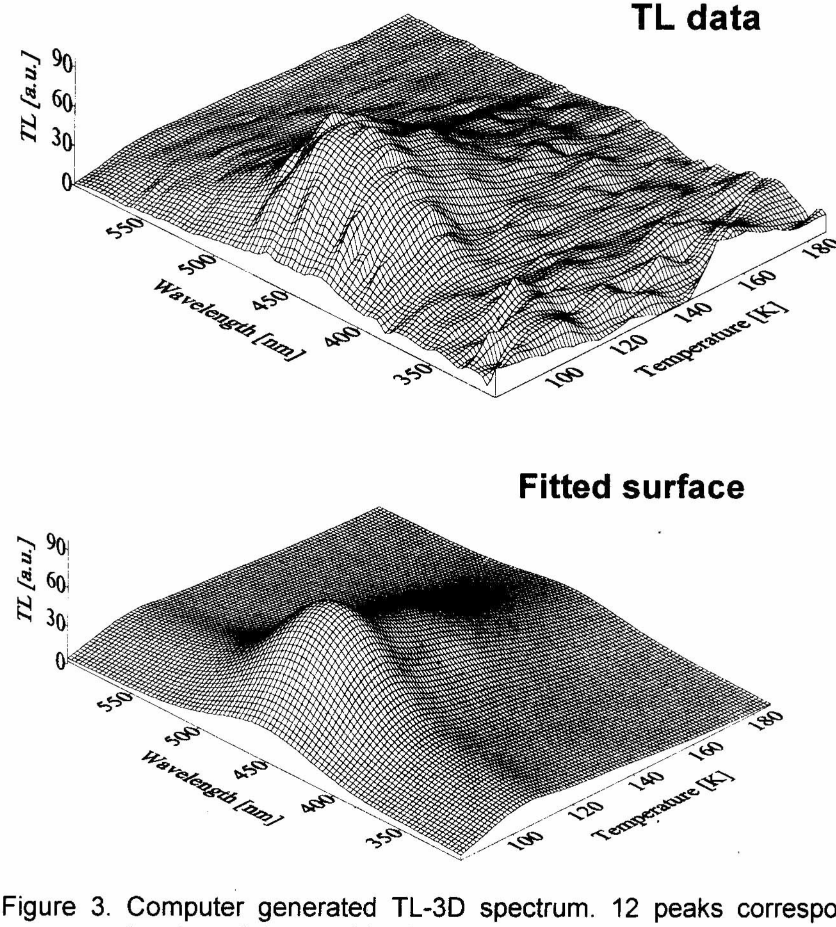


Figure 2. Computer generated TL-3D spectrum. 12 peaks correspond to 4 trap levels and 3 recombination centres.


TL data

Fitted surface

Figure 3. Computer generated TL-3D spectrum. 12 peaks correspond to 4 trap levels and 3 recombination centres.

The determination of trap parameters from measured TL-3D spectra is a more important and a complex task. For this purpose we put forward a new technique called surface fitting. Assuming mathematical form of TL-3D surface as given by eqs. (2,3,4) it is possible to determine particular parameters of traps and RCs. Function Z(T,λ) now has the form:

$$Z(T,\lambda)=\sum_{i=1}^{p} J_i(T,J_{0i},E_i,\alpha_i)\sum_{s=1}^{q} G_s(\lambda,G_{0s},\lambda_{0s},\sigma_s) \tag{5}$$

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

$$\sum_{\substack{\eta\in\Omega_T\\ \xi\in\Omega_\lambda}}[Z_D(T_\eta,\lambda_\xi)-Z(T_\eta,\lambda_\xi)]^2=\min \tag{6}$$

where Z_D denotes experimentally measured data, but η and ξ 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. $G_{01}=1$). In such case we observe pq three dimensional peaks. 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 an efficient. Average computing times were in the range of minutes on a personal computer.

The surface fitting method was applied to spectrally resolved thermoluminescence data in R10EPK epoxy resin. The resin was prepared by adding glycydyl derivative of carbazole - 9-(2,3-epoxypropyl)carbazole (EPK) to epoxy resin. In curing process we obtained a homogenous polymer with the carbazolyl group chemically bonded to the resin (REPK). The sample was prepared as a mixed composition, which contains 10 wt. % of EPK (R10EPK), using low molecular commercial epoxy resin – Ruetapox 0162 (Bakelite AG) [5]. The data and the fitted surface are presented in Fig. 3. Most reasonable fit was obtained for two traping centres and two recombination centres giving four elementary peaks. Four individual surface peaks are shown in Fig. 4. Calculated activation energies are 0.083 eV (first order peak with maximum at 102 K) and 0.053 eV (second order peak with maximum at 120 K). Emission bands are positioned at 452 nm (a sharp peak) and 428 nm (a broad one).

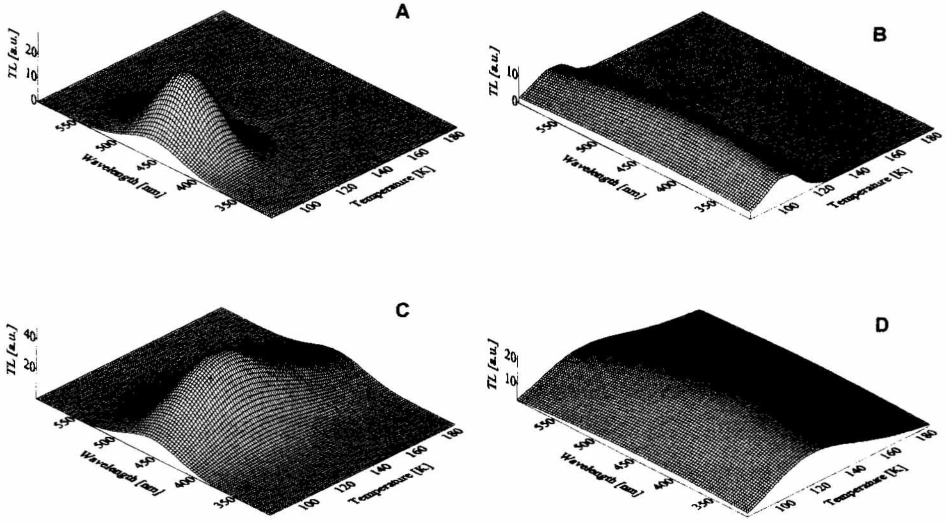


Figure 4. Individual surface peak of spectrally resolved thermoluminescence in R10EPK.

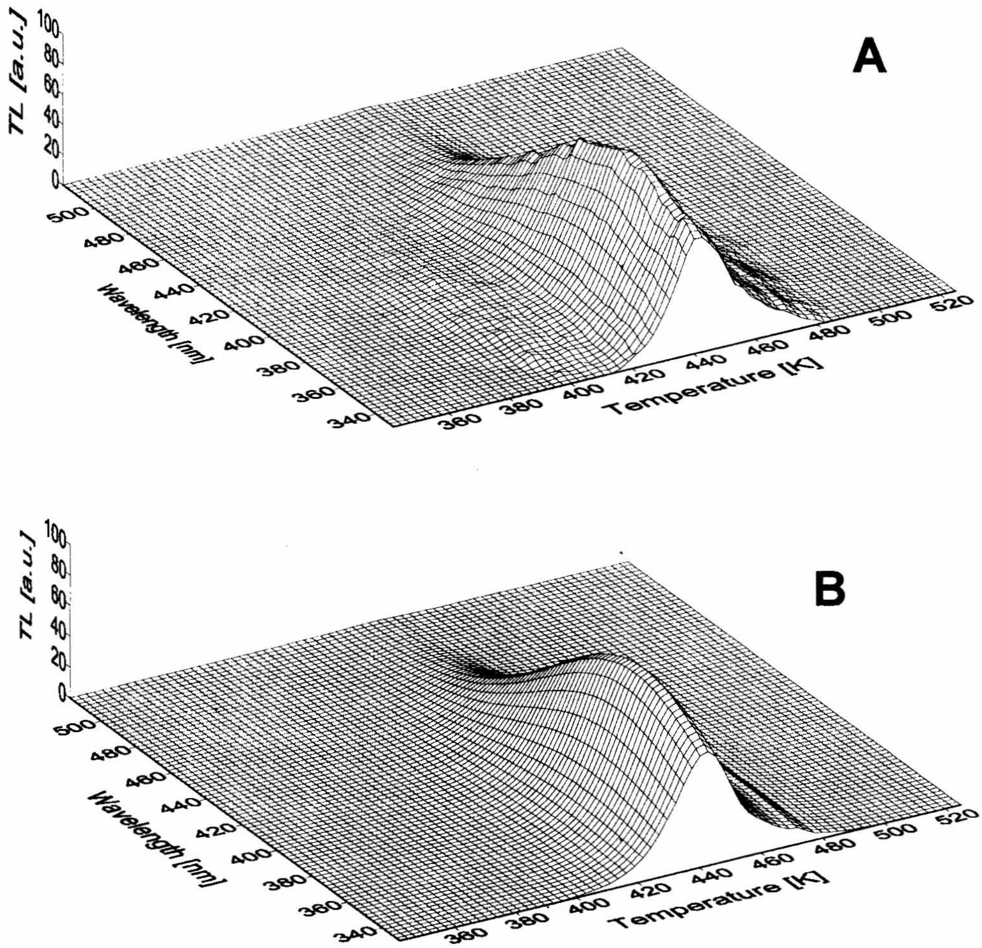


Figure 5. Spectrally resolved thermoluminescence experimental data (A) of LiF:Mg,Cu,Ti and the total fitted surface (B) by assuming 3 trapping levels and two recombination centres (i.e. 6 surface peaks).

The surface fitting technique was applied also to the analysis of spectrally resolved TL of some thermoluminescent detectors based on LiF:Mg luminophor: LiF:Mg,Ti and high-sensitive LiF:Mg,Cu,P. The samples were prepared at the Institute of Nuclear Physics (Kraków, Poland) [6]. The role of luminescence centres in these materials is usually attributed to defects connected with, respectively, titanium and phosphorus dopants. Therefore, in present study, luminescence of LiF detectors with various dopants was measured. In Fig. 5 TL-3D of LiF:Mg,Cu,Ti (MCT) sample is shown. The concentration of dopants was: Mg 0.2 %, Cu 0.05% and Ti 130ppm. Prior the measurements the sample was irradiated with a dose 8.75 Gy. The measurements were carried out in a vacuum cryostat that enables sample temperature to be controlled between 78 K and 700 K. Detailed numerical analysis indicates at least six peaks resulting from three trapping states and two recombination centres. The fitted spectrum and some of the fitted peaks are shown in figure 4. Calculated activation energies of trap levels are: 1.96 eV, 2.75 eV and 3.71 eV. Two broad emission bands are centered around 367 nm and 285 nm.

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 measured in experiment so, it allows for more precise and credible identification of trapping levels and recombination centres. Presently, this 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 broaden to include more general quasi-equilibrium approximation [7-10] and the TL theory for spatially correlated systems [11].

ACKNOWLEDGEMENTS

This work was supported by the Polish Committee for Scientific Research grant no. 4T11F00922

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