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Ultraweak Spectrally Resolved Thermoluminescence in Polymers

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Summary: Spectrally resolved thermoluminescence (TL) measurements provide a lot of information concerning trapping and recombination states in various dielectric materials. As long-lived luminescence is typically weak, this technique requires a very sensitive apparatus. This paper describes the measurement system that is used for studying spectrally resolved TL and phosphorescence decay in polymers. Exemplary investigations are presented for poly(*N*-vinylcarbazole) (PVK) thin films. The obtained spectra clearly indicate the influence of solvents (dioxane, chlorobenzene) and excitation wavelengths on TL in PVK samples.

Keywords: luminescence; phosphorescence; spectrally resolved thermoluminescence (TL); poly(N-vinylcarbazole) (PVK); thin films

Introduction

The thermoluminescence (TL) method was proposed by Urbach to study trapping processes in crystalline phosphors.[1] First theoretical explanation and a method of analysis of TL curves was proposed by Randall and Wilkins.[2] During TL measurement a sample at an appropriately low temperature is excited by a high-energy (e.g. UV or X-ray) radiation. When the sample is heated, the energy is released in the form of light. A series of peaks appearing on TL glow curve is usually attributed to trap levels characterised by different activation energies. Recently, many authors have pointed out the virtues of making spectral measurements during TL. The possibility to construct a three-dimensional representation of the intensity of emission as a function of wavelength and temperature adds materially to the ability to interpret the behaviour of the studied materials. The temperature peaks correspond to traps from which charge carriers are released whereas the emission bands carry information about the charge carrier recombination levels.

Much research has been done with poly(*N*-vinylcarbazole) (PVK, Figure 1).[3-5] It contains charge-transporting carbazole pendant groups. Though the polymer is not electrically

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conductive it has good photoconductivity properties with the emission peak located in the violet-blue region. In this paper we present some results of spectrally resolved TL measurements performed in PVK thin films. Particularly, the influence of excitation wavelength and the influence of solvents used for the preparation of PVK samples on TL features are presented.

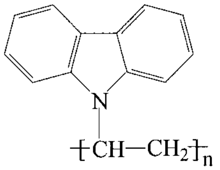

Figure 1. Poly(*N*-vinylcarbazole) (PVK).

Experiment

PVK (trade name Luvican, provided by BASF) was purified by dissolving in chloroform and reprecipitating into methanol six times. The powder was then redissolved in a solvent. Thus two kinds of samples were produced - PVKc (dissolved in chlorobenzene) and PVKd (dissolved in dioxane). Layers 50-100 μm thick were cast onto thick (0.3 mm) copper disk with diameter 20 mm. The samples were dried at room temperature for 24 h surrounded by vapour of the solvent.

The TL measurements were carried out in a cryostat that enabled sample temperature to be controlled between 78 K and 700 K. The sample was cooled with liquid nitrogen. A linear temperature rise, with respect to time, was provided by an autotuning temperature controller. The samples were excited with a 75 W xenon arc lamp installed in a high-intensity illumination system with a monochromator. The luminescence intensity was monitored using the spectrograph connected to a LN/CCD-1024E camera (chip format 1024 × 256, spectral range 190 - 1080 nm). The CCD camera was cooled with liquid nitrogen. It was connected to the temperature controller, which is necessary to stabilise working temperature of the camera (from 143 K to 203 K). A schematic diagram of this arrangement is shown in Figure 2. The sample was cooled down to 82 K and then excited with UV light at 323 nm or 363 nm. TL spectrum was recorded while heating the sample from 82 K to 300 K at a constant heating rate of 0.8 K/s. Temperature- and wavelength-resolved TL signals were obtained using custom-made software. The resolution of the system was varied from 10 to 20 nm depending on the of spectrograph grating, width of the spectrometer slit and the binding used for CCD camera chosen according to the intensities of the measured samples. The temperature resolution was about 3 K. The spectra were numerically calibrated with respect to wavelength and intensity.

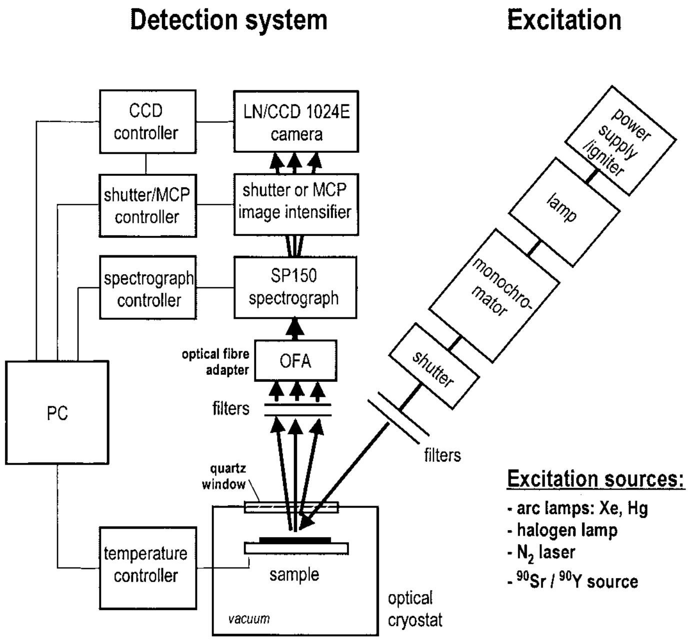

Figure 2. Block diagram of the measurement system.

Results

TL in PVK appears in the wavelength range 300-850 nm. Figures 3 and 4 demonstrate spectrally resolved TL spectra of PVKc excited at 323 nm (PVKc323) and 363 nm (PVKc363), respectively. Emission spectra of PVKc323 and PVKc363 are different. Figure 5 clearly shows the difference at the maximum intensity of TL in PVKc323 and PVKc363. When PVK was dissolved in dioxane, the TL spectra were the same for both excitations: 323 nm (PVKd323) and 363 nm (PVKd363) (Figure 6).

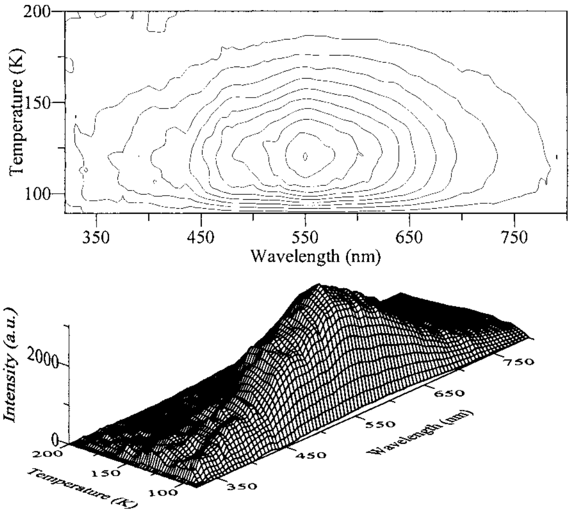

Figure 3. Isometric and contour plots of TL emission from PVKc323 sample. The spectra were recorded at 82 K - 300 K, after excitation at 323 nm.

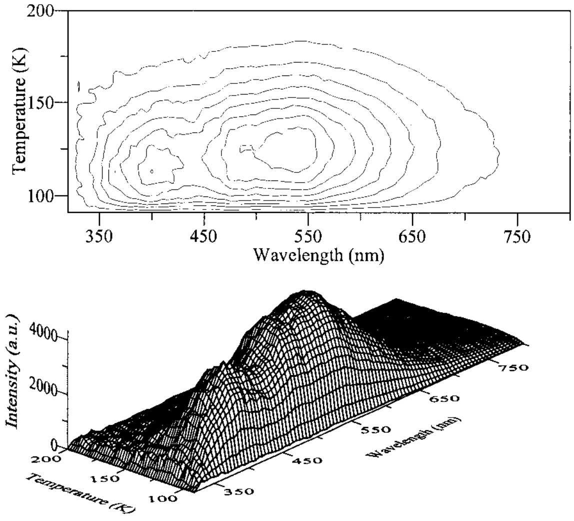

Figure 4. Isometric and contour plots of TL emission from PVKc363 sample. The spectra were recorded at 82 K – 300 K, after excitation at 363 nm.

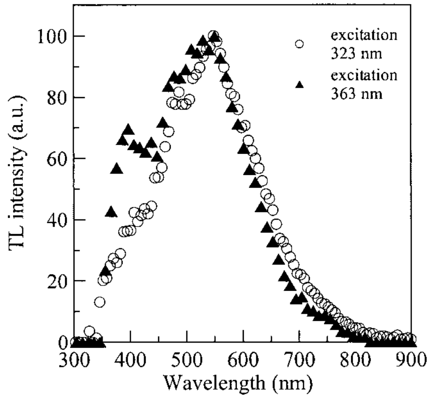

Figure 5. TL spectra of a PVKc thin film, at the maximum intensity of TL peak. Temperature range was 110 K-120 K (for PVKc323) and 123 K-133 K (for PVKc363).

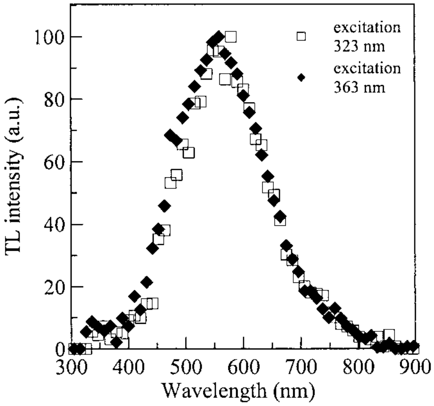

Figure 6. TL spectra of a PVKd thin film at the maximum intensity of TL peak. Temperature range was 110 K-120 K (for PVKd323) and 104 K-114 K (for PVKd363).

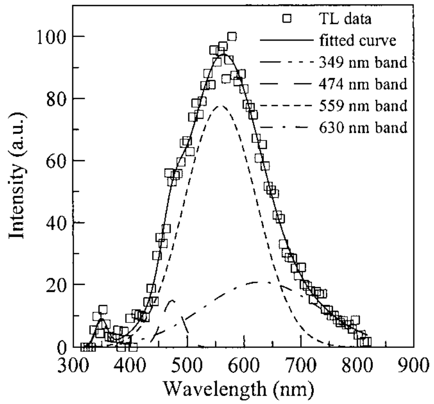

Figure 7. Deconvolution of TL emission spectrum in the temperature range 113-123 K (at the peak maximum) in PVKc363 to four bands.

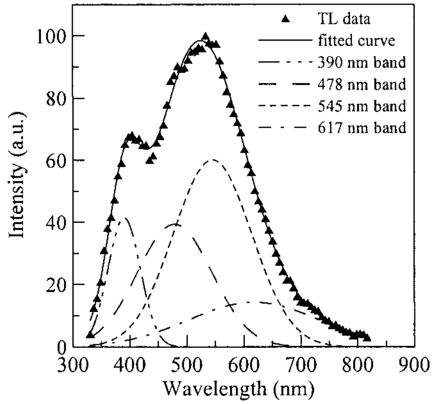

Figure 8. Deconvolution of TL emission spectrum in the temperature range 110-120 K (at the peak maximum) in PVKd323 to four bands.

As one can see, the TL spectra of PVKc323 and PVKd323 are not identical. The kind of the solvent used for preparation of the sample is also important. To characterise the emission spectra quantitatively, PVKc and PVKd were deconvoluted to several Gaussian bands. Figures 7 and 8 show fitting for PVKc363 and PVKd323, respectively. Table 1 presents detailed results of deconvolution for all samples.

Table 1. Emission spectra deconvoluted with four Gaussian bands in PVK at the maximum intensity (λ - wavelength, *I* - intensity of the emission spectra).

PVKc323		PVKc363		PVKd323		PVKd363	
λ (nm)	*I* (a.u.)	λ (nm)	*I* (a.u.)	λ (nm)	*I* (a.u.)	λ (nm)	*I* (a.u.)
382	13	390	47	352	9	371	6
490	49	462	35	477	19	473	17
570	41	538	72	558	80	552	88
622	33	619	18	636	25	648	16

Conclusions

Spectrally resolved thermoluminescence is a new powerful technique providing a lot of information relating to trap and recombination centres in dielectric solids. The measurements were made for PVK thin films to study the influence of a solvent on luminescence properties of this material. Emission spectra of PVK prepared in chlorobenzene and dioxane were deconvoluted for several nearly identical bands with significantly different intensities. This may suggest different structural arrangement of PVKc and PVKd. Due to various topological configuration some of the radiative transitions are more preferred but the other less. The same applies to luminescence quenching. Further studies are still required to explain physical basis of the reported phenomena.

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[1] F. Urbach, *Wien. Ber. II A* **1930**, *139*, 363.
[2] J. T. Randall, M. H. F. Wilkins, *Proc. R. Soc. A* **1945**, *184*, 366.
[3] J. Sanetra, D. Bogdał, S. Nizioł, P. Aramatys, J. Pielichowski, *Synth. Met.* **2001**, *121*, 1731.
[4] G. Z. Li, N. Minami, *Chem. Phys. Lett.* **2000**, *331*, 26.
[5] J. Sanetra, F. Bai, M. Zheng, G. Yu, D. Zhu, *Thin Solid Films* **2000**, *363*, 118.
[6] D. B. Romero, M. Schaer, M. Leclerc, D. Ades, A. Sioce, L. Zuppiroli, *Synth. Met.* **1996**, *80*, 271.