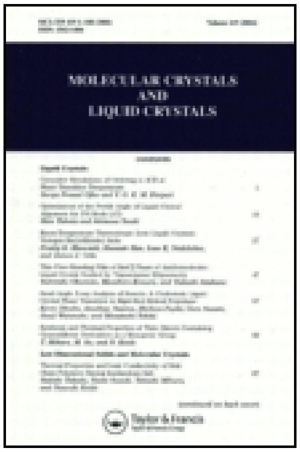

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Transport and Recombination of Charge States in Organic Single Crystalline and Polycrystalline Scintillators

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Studies of some aspects of the processes of transport and recombination of charge states in organic scintillation crystals which differ in theirs structural peculiarities are presented.

Keywords radioluminescence, polaron states, organic crystals.

INTRODUCTION

The action of ionizing radiation results in generation of charge states in organic media. A charge carrier during it motion produces electronic, vibronic and sometimes lattice polaron states due to polarization interaction of it molecular surrounding[1]. It defines the features of the radioluminescence (RL) pulse-shape formation because the molecular excitation is caused by recombination of such states[2]. Therefore, RL can be the alternative, not traditional approach to study structural features of organic materials as well as electronic processes in them.

The processes of transport and recombination of charge states in organic single crystals as well as in organic polycrystals are studied. The investigations are based on the results of the measurements of the parameters of RL pulse fast component performed by improved single-photon technique on the set-up with subnanosecond resolution[3].

Single crystals of stilbene with controlled structural perfection[4] and doped *p*-terphenyl are studied. Organic polycrystals were obtained by the cold pressing technique from fine-grained powder under pressures of $(1...8)\bullet 10^2$ MPa at the room temperature. The powder was obtained by grinding of the melt-grown activated and non-activated p-terphenyl single crystals grown from the melt [5]. Recrystallization process took place during annealing of a polycrystal at initial melting temperature and hydrostatic compression of 10...20 MPa as well. It allowed to obtain samples of polycrystals with good transparency and size of grains up to 3 mm.

EXPERIMENT

For all organic single crystals the RL pulse shape was described best of all as

$$i(t) = f_G(t) * \exp(-t/\tau) \equiv \int_0^t f_G(t-x) \bullet \exp(-x/\tau)dx, \quad (1)$$

$$f_G(t) = \left\{const/(\sqrt{2\pi}\sigma)\right\} \bullet \left\{\exp\left[-(t-\Delta)^2/2\sigma^2\right]\right\}, \quad (2)$$

where t is the time after excitation, τ is a decay time constant, σ is a time constant, $\Delta \approx 3\sigma$. Function $f_G(t)$ (2) describes the additional delay of the times of RL photon emission. The solution of kinetic equations with function of "excitation" which defers from δ-function [6] has shown that this delay is due only to the processes preceding the process of electron excitation energy transfer from donor to acceptor, namely to the processes of generation and recombination of charge states. Gaussian form of Eq.(2) is due to the plurality of acts of generation and recombination of charge-states, i.e. the processes result in the excitation of organic crystal molecules. Tables 1 and 2 show the values of τ and σ, as well as the values of relative light yield J measured for the single crystals studied. The σ_c - value is the root-mean-square random orientation of the crystal mosaic and C in Table 2 is the concentration of diphenylbutadiene molecules. Investigations of polycrystals of *p*-terphenyl confirmed the validity of pulse-shape fast RL description in form of (1) with

Eq.(2). Table 3 shows the results for polycrystals. In Table 3 C is the concentration of diphenylbutadiene molecules in the powder; but the value $J = 1$ is taken for the light yield of single crystal of *p*-terphenyl for which $\sigma = 490$ ps, $\tau = 3.0$ ns.

TABLE 1 Characteristics of RL pulse for stilbene single crystals

σ_c, minute of arc	σ, ns	τ, ns	J, rel.units
160	0.18	3.32	0.87
61	0.18	3.49	0.95
49	0.18	3.63	0.96
26	0.21	3.71	1.00

TABLE 2 Characteristics of RL pulse for *p*-terphenyl single crystals

C, %	σ, ns	τ, ns	J, rel. units
No doped	0.40	4.05	1.03
0.05	0.31	3.80	1.26
0.10	0.25	3.65	1.23
0.50	0.18	3.45	1.12

DISCUSSION

The deep structural traps formation intensifies with increase of σ_c - value (see Table 1) or luminescent molecule concentration, i.e. diphenylbutadiene molecules (see Table 2) [7]. It results in minor decrease of τ- and J- values, as well as too weak σ-σ_c dependence, i.e. the deep traps of charge carriers don't influence directly on the RL pulse rise of organic crystals. For doped single crystals the formation of shallow traps in surroundings of a solute molecule becomes more important factor. Due to charge carrier trapping it results in σ-value decrease with a diphenylbutadiene molecule concentration increase (see Table 2).

TABLE 3 Characteristics of RL pulse for *p*-terphenyl polycrystals

Grain size, mm	σ, ps	τ, ns	J, rel. units
	No doped		
< 0.5	494	2.4	63
0.5...1	464	2.4	77
1...2	493	2.6	83
	$C = 7\ 10^{-3}$ %		
< 0.5	680	3.3	91
0.5...1	630	2.8	109
1...2	660	3.4	93
	$C = 14\ 10^{-3}$ %		
< 0.5	660	3.2	94
0.5...1	610	2.8	117
1...2	710	2.6	122
	$C = 43\ 10^{-3}$ %		
< 0.5	610	3.0	109
0.5...1	580	3.7	86
1...2	510	3.6	93
	$C = 71\ 10^{-3}$ %		
< 0.5	550	3.4	122
0.5...1	550	3.4	106
1...2	600	3.7	125

The generation of the charge carriers by ionizing radiations results in formation of polaron states in two stage process. Firstly, the charge carrier can be captured by a trap with depth of

$$E_t' = kT\, ln(\tau_t \nu), \tag{3}$$

where k is the Boltzman constant, T is the temperature, ν is the attempt-to-escape frequency and τ_t is the time of localization. During the second stage due to the carrier interaction with dipoles induced on neighboring molecules the initial trap $E_t^{/}$ deeping on the value of δE. The characteristic value of δE is almost the same for a wide class of organic solid scintillators and is about 0.1 eV[1]. Therefore a trap depth will be equal to

$$E_t = E_t^{/} + \delta E. \qquad (4)$$

Taking $\tau_t \sim \Delta \sim 3\sigma$ (see Tables 1 and 2) one can obtained $E_t \leq 0.19$ eV. If $E_t^{/}$ - value is about kT then a polaron state can appear on every molecule due to temperature-activated process. In this case it is a dynamic traps of polarization origin. Polaron states move along the crystal and may be captured by different structural traps. When a charge carrier is captured by structural trap it can create a stable polarized environment. Such a charge state we can interpret as a polaron captured by structural trap.

Let us analyze the results of the studies for polycrystals. Change in the grain sizes for polycrystals of *p*-terphenyl didn't influence noticeably on the measured values (see Table 3). In comparison with initial single crystal for a pure polycrystal a weak decrease of τ-value was obtained due to formation of deep traps on the grain boundaries. To estimate an influence of shallow trap systems on the time parameters of the RL pulse we studied the problem of polaron states migration in a real organic crystals. It has been shown that the additional delay of the times of photon emission in pure polycrystals, as well as in initial single crystals of *p*-terphenyl is due to charge carriers capturing both by dynamic traps and structural traps of polarization origin formed in the vicinity of single low-angle grain boundaries of the crystal.

For organic polycrystal the effect of the solute luminescent molecules was more strong, and the σ-value increased as well (see Table 3). Let us assume that in addition to the shallow trap system with initial mean depth of $(E_t^{/})_1$ (which exists in pure polycrystal) the system with initial mean depth of $(E_t^{/})_2$ appears due to the presence of solute molecules, and therefore the difference between mean Δ - value for pure and doped polycrystals is caused by charge carrier localization on the second shallow trap system. In such a case the Δ- value in expression (2) will be equal to

$$\Delta = \eta_1\Delta_1 + \eta_2\Delta_2 \qquad (5)$$

where Δ_1 and Δ_2 are the Δ-values calculated for trap system 1 and 2, η_1 and η_2 are the probabilities of charge carrier localization on trap system 1 and 2, correspondingly. Table 4 shows the results of these calculations. The calculation of $(E_t')_2$-values (see Table 4) was based on assumption that $\eta_1 = \eta_2$ in equation (5). The χ is calculated as

$$\chi = \eta_2/\eta_1 \qquad (6)$$

for the case when $(E_t')_1 = 0.1$ eV and $(E_t')_2 = 0.2$ eV, i.e. for the real values of mean energies for the system of the traps formed by low-angle grain boundaries and medium-angle ones, respectively [1]. Table 4 shows that for the case of the former case the differences between $(E_t')_1$ and $(E_t')_2$- values are negligible, and for the second one calculated χ- values and thereby η_2-values are too small. These calculations show that for organic crystals with different structure perfection the process of polaron states recombination as well as the recombination of polaron states with charge-states formed in result of charge carrier localization on very shallow initial structural traps mainly influence on the prompt RL pulse formation.

TABLE 4 $(E_t')_1$ and $(E_t')_2$ - values calculated for polycrystals of *p*- terphenyl

C, 10^{-3} %	$(E_t')_1$, eV	$(E_t')_2$, eV	$(E_t')_2 - (E_t')_1$, eV	χ, rel. units
7	0.117	0.131	0.014	0.014
14	0.117	0.131	0.014	0.014
43	0.117	0.125	0.008	0.007
71	0.117	0.125	0.008	0.007

In Table 4 C is concentration of diphenylbutadiene, $(E_t^{/})_1$ is calculated according to Eqs.(3) and (4), $(E_t^{/})_2$ is calculated for the case when $\eta_1 = \eta_2$ in expression (5), χ is given by expression (6).

Thus the correlation between crystal structure and the features of it RL response allows to study the energy spectrum of local trapping centers, as well as the process of dynamic charge states transport in organic crystalline materials. Such a study is not traditional. The results have been adduced show that in contrast to photoluminescence process the RL one is caused by features of generation, transport and recombination of dynamic charge-states of polarization origin.

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