

## COMPOSITE SCINTILLATORS BASED ON ORGANIC GRAINS AND THEIR PULSE SHAPE DISCRIMINATION CAPABILITY

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Studies of photoluminescence, relative light output and optical transmission of organic single-layer composite scintillators with different grain sizes have been carried out. The paper presents the dependences of these values on the grain sizes for fractions <0.04; <0.06; 0.06...0.1; 0.1...0.3; 0.3...0.5; 0.5...1.0 mm. Possible physical mechanisms of such results are discussed.

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### INTRODUCTION

The issue of registration of the flow of ionizing particles in conditions where the flow intensity is extremely low is very important in modern medical, geological, environmental, biological problems, for the border patrol to preclude unauthorized transport of nuclear materials, during the liquidation of nuclear man-made disasters, and etc. Radiation with large specific losses  $dE/dx$  of particle energy  $E$  per unit length of its path  $x$  in the media are the most harmful to humans and other living creatures. The harm caused by ionizing radiation to a living organism can be described as the product of the absorbed dose and the so-called radiation-weight factor  $w_R$ , which characterizes the long-term effects of such radiation. For photons of gamma radiation  $w_R = 1$ , for alpha particles, fast neutrons with energies  $E_n \leq 2$  MeV and  $2$  MeV  $\leq E_n \leq 20$  MeV, the values  $w_R = 20$ , 20, and 10, respectively [1]. Therefore, even the device that can be used is capable to accurately count the number of recorded events but does not separate them by the "type" of radiation, the use of such information is dangerous and misleads the user.

For fast neutron spectrometry, it is important that the scintillation medium has a high hydrogen content, so organic scintillation materials are most relevant in this case. Moreover, in contrast with inorganic ones, they have negligible backscattering for charged particles, so it increases the efficiency of their registration. Organic scintillators in the form of single crystals and liquids efficiently separate high  $dE/dx$  radiation from low  $dE/dx$  background radiation as the slow component of the radioluminescence pulse. [2], which makes these materials most effective in creating systems for detecting radiation that is more harmful to living beings under background radiation conditions with a low  $dE/dx$  value. In particular, for organic molecular crystals, the ability to separate signals from radiation with different  $dE/dx$  as a consequence of the process of fusion of triplet molecular excitons is called the pulse shape discrimination capability (PSD) [2].

However, modern technology for obtaining organic single crystals limits their maximum size and shape,

besides being quite expensive. The solution to this problem can be a new type of scintillators – heterostructured organic scintillators, that is, media containing grains of organic scintillators. These grains are connected by sintering during hot pressing (polycrystals or the so-called van der Waals ceramics), or introduced into a transparent gel composition (composite scintillators) [2].

In the case of continuous media, the PSD capability, caused by the difference of the mechanisms of spin-selective processes for excited  $T$ -states, has been well studied, but for heterostructured materials, the results are still poorly presented. A similar study was initiated by the authors of the article. The PSD capability for such samples is currently considered simply as an experimental fact [3–5].

In addition, there are currently no data on PSD capabilities of heterostructured organic scintillators based on grains of different sizes. However, it is obvious that the size of an elementary cell (crystal grain), which limits the transport and recombination of  $T$ -states in such systems, must significantly affect this process. This, in turn, leads to a change in the formation of the slow component of the scintillation pulse and, as a consequence, determines the PSD capability of the scintillator.

The theoretical basis for such studies were presented by us in [6]. We note that in the case of this article, the probability of direct excitation to the  $T_l$  state was increased due to the high optical radiation density.

### 1. TECHNOLOGICAL ASPECTS OF OBTAINING OF EXPERIMENTAL SAMPLES

We have chosen *trans*-stilbene and *p*-terphenyl as the scintillation materials for the studies in this article because of their known scintillation properties.

The single-crystal samples were grown using the Bridgman-Stockbarger method. More details about samples preparation technologies can be found in [6].

#### 1.1. SOURCE MATERIALS

To obtain samples based on *p*-terphenyl, we used commercially available raw materials, which were

thoroughly purified. Unfortunately, *trans*-stilbene manufactured by leading companies does not allow obtaining scintillators with the required high characteristics [7]. Our preliminary studies (see, for example, [6]) have found impurities that limit the characteristics of the material. Therefore, for the production of samples based on *trans*-stilbene, we synthesized this substance of sufficient quality.

## 1.2. TECHNOLOGICAL FEATURES OF THE CREATION OF COMPOSITE SCINTILLATORS

Two series of composite scintillators have been created: based on *trans*-stilbene and *p*-terphenyl. In each series, the samples differed in the grain sizes.

To obtain single-layer composite scintillators crystalline grains obtained by cracking a polycrystalline ingot in nitrogen were separated (using a set of calibrated sieves) into fractions of different sizes. The selected fraction was applied to a layer of polysiloxane elastomer, which is not a luminescent material [8], in an amount of about 70...80% of the total sample volume. The sample size was chosen to be 15×15 mm for the convenience of the experiments. For the possibility of irradiation with alpha particles, one of the surfaces of the grains was not covered with an elastomer layer. The samples were left at 60 °C for 24 h to solidify.

## 2. EXPERIMENTAL RESEARCH METHODS

### 2.1. METHOD OF THE MEASURING OF THE LUMINESCENCE SPECTRA

Luminescence spectra were obtained on a Cary Eclipse Fluorescence Spectrometer. For each material, its own luminescence excitation wavelength ( $\lambda$ ) and wave-length range of the luminescence spectrum were selected. The excitation and emission slits were 1.5 nm and 2.5 nm, respectively. The luminescence intensity ( $I$ ) was taken as the number of readings in the luminescence spectrum.

### 2.2. METHOD OF THE MEASURING OF THE SPECTRA OF SCINTILLATION AMPLITUDES

The amount of light emitted by the scintillator is characterized by the magnitude of the luminous flux, i.e. the ratio of the number of photons arising in the scintillator to the energy lost in it by ionizing radiation. The essence of the method is to measure the electrical signal at the output of the photodetector, which fixes the glow of the scintillator. At the output of the photodetector, the electrical signals, caused by the photons of the scintillation pulse that have arisen in the scintillator, are summed. The value of this accumulated signal is proportional to the amplitude of the scintillation pulse [7, 9]. For organic scintillators, it is better to use photomultipliers as a photodetector. We used a 9208A photomultiplier manufactured by Electron Tubes Ltd., for which, according to the passport data, the dark current has a record low value of  $6.8 \cdot 10^{-11}$  A at an anode sensitivity of 50 A/Lm [10]. The original photomultiplier circuit had an electrical signal generation time  $\tau_{ap} = 2 \mu\text{s}$ .

More often, the light output is determined by the spectrum of scintillation amplitudes. For this task, an ADC was used, connected to a PC, where the accumulation and processing of the received data was carried out.

The relative light output can be calculated using the following formula:  $C = (J / J_{ref}) \cdot 100\%$ , where  $J$  is the value of the maximum amplitude of the spectrum of the test sample,  $J_{ref}$  is the value of the maximum amplitude of the spectrum of the reference scintillator. Recalculating the data obtained in relation to the value of the light output of the reference scintillators in photons per 1 MeV, we obtain the values of the light output of the studied samples. The error of this method is less than 5% [11]. The setup was calibrated using  $^{22}\text{Na}$ ,  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ , and  $^{152}\text{Eu}$  gamma sources.  $^{239}\text{Pu}$  was used as a source of alpha particles.

### 2.3. METHOD OF THE MEASURING OF THE OPTICAL TRANSMISSION

The optical transmission was measured using a Shimadzu UV-2450 spectrophotometer. The absolute error in determining the wavelength was 0.4 nm, and the error in measuring the spectral transmission coefficients was 0.6% [11]. An integrating sphere was used in the measurements, which made it possible to collect most of the scattered light on the photodetector of the spectrophotometer. The spectrophotometer has two channels. Before measurements, the device was calibrated, i.e. 100% was taken as the value when the same signal passed through both channels of the spectrophotometer. The sample was placed in the path of one of the beams and tightly pressed against the outer surface of the sphere with a clamp. Measurements were made relative to air (one channel remained unfilled). This value in the formula  $T = (\Phi / \Phi_0) \cdot 100\%$  was taken as  $\Phi_0 = 100\%$ .

## 3. RESULTS AND DISCUSSION

### 3.1. RESULTS OF THE MEASUREMENT OF THE LUMINESCENCE SPECTRA

The samples were excited in the “red” region of the spectrum (in the region of absorption of their molecular triplet excitons) when radiation was detected in the “blue” region, i.e. in the fluorescence region. In this way, only the light resulting from the fusion of triplet excitons can be detected.

The energies of the triplet levels for *trans*-stilbene and *p*-terphenyl are 2.2 and 2.5 eV, respectively [6]. Therefore, if light photons have a small amount of energy (2.37 eV for *trans*-stilbene), the intensity of delayed fluorescence increases. The same is true for other materials.

As an example, Fig. 1 shows the luminescence curves obtained for samples based on *trans*-stilbene when excited directly to the  $T_1$  state (i.e. without excess energy). The same measurements were made for higher energies (wavelength for *trans*-stilbene 523 nm) and showed the expectedly higher intensity. A similar set of measurements was carried out for *p*-terphenyl.

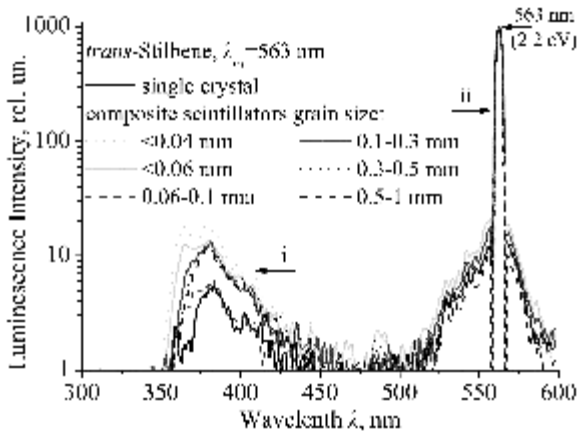


Fig. 1. Luminescence spectra of a single crystal and single-layer composite scintillators based on *trans*-stilbene grains upon excitation by the light with a wavelength of 563 nm

In the figure in the band 350...420 nm, we see the characteristic fluorescence of *trans*-stilbene, which has a low intensity due to indirect (through *T-T* annihilation) excitation of luminescence centres. Similar spectra were obtained for all scintillators in the framework of this article. Two groups of peaks can be distinguished: (i) delayed fluorescence (DF) peaks and (ii) reflected excitation light peak. When the excitation wavelength was changed, the peaks of the DF band did not change their position.

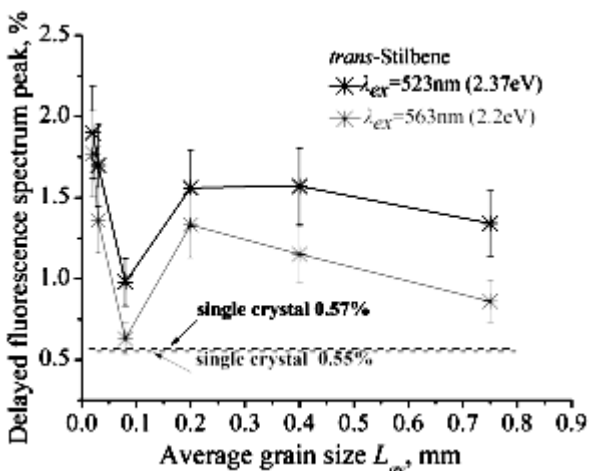


Fig. 2. Dependences of the relative intensity of the delayed fluorescence peak of composite scintillators on the average size of  $L_{av}$  of *trans*-stilbene grains compared to *trans*-stilbene single crystal, when excited by light with wavelengths of 523 and 563 nm

Based on the data in Fig. 1 and similar data for excitation at a wavelength of 523 nm, the curves in Fig. 2 were plotted. Here  $L_{av} = (L_{j+1} + L_j)/2$  is the average grain size, where  $L_{j+1}$  and  $L_j$  ( $L_{j+1} > L_j$ ) are the largest and smallest grains in the fraction.

Similar curves for *p*-terphenyl are shown in Fig. 3.

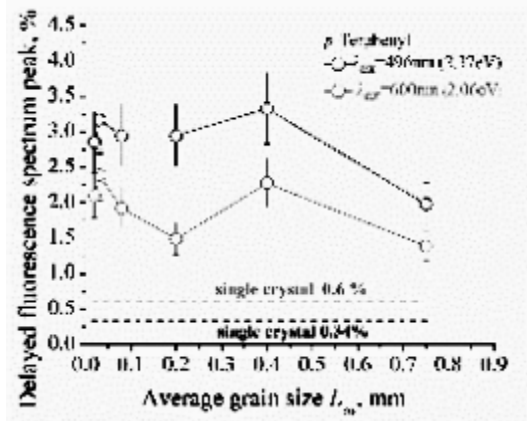


Fig. 3. Dependences of the relative intensity of the delayed fluorescence peak of composite scintillators on the average size of  $L_{av}$  of *p*-terphenyl grains compared to *p*-terphenyl single crystal, when excited by light with wavelengths of 496 and 600 nm

Similar curves for *p*-terphenyl activated by 0.1 wt.% 1,4-diphenyl-1,3-butadiene (DPB) are shown in Fig. 4.

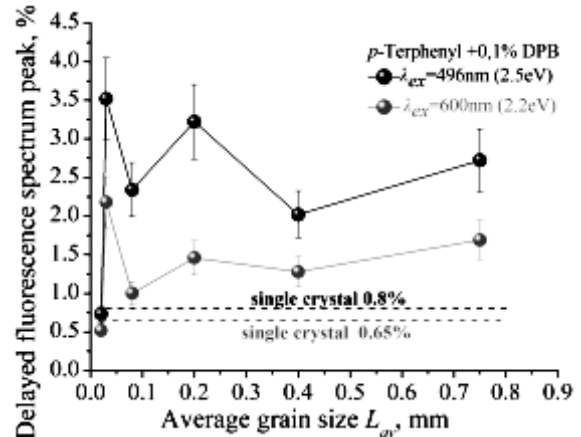


Fig. 4. Dependences of the relative intensity of the delayed fluorescence peak of composite scintillators on the average size of  $L_{av}$  of *p*-terphenyl activated by 0.1 wt.% DPB grains compared to *p*-terphenyl activated by 0.1 wt.% DPB single crystal, when excited by light with wavelengths of 496 and 600 nm

From Figs. 2–4, quite high DF values are observed for fine-grained scintillators. For scintillators with larger grains, as the grain size increased, the spread of DF intensity values exceeded their tendency to increase or decrease. As expected, the lowest value of the DF intensity was obtained for single crystals, which is most likely due to the almost unlimited possibility of  $T_1$  states to “run away” from their point of origin, while the grain size limits the movement of *T*-excitons. It should be remembered that that the lifetime of *T*-excitons in such media is on the order of  $10^{-3} \dots 10^{-2}$  s, so they can repeatedly bounce off grain boundaries, which increases the probability of *T-T* annihilation events. It is important to note that prof. Agranovich predicted this effect.

### 3.2. RESULTS OF MEASUREMENT OF SCINTILLATION AMPLITUDE SPECTRA

For the purposes of this article, we measured the scintillation amplitude spectra of single crystals and composite scintillators based on selected materials. As noted earlier, the excitation of the samples was carried out using a standard source of  $^{239}\text{Pu}$  alpha particles.

For the scintillation amplitude spectra, we will give as an example data for samples based on *p*-terphenyl (Fig. 5).

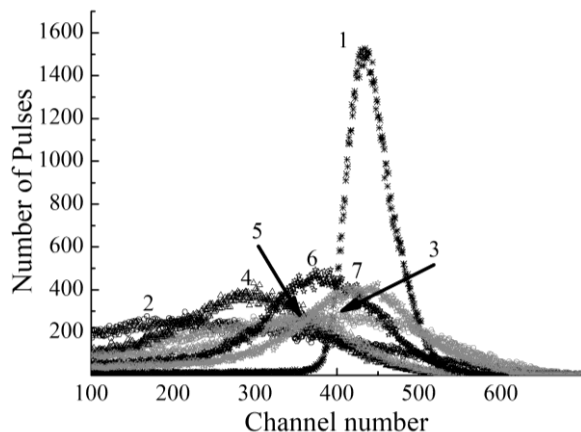


Fig. 5. Scintillation amplitude spectra of samples of composite scintillators based on *p*-terphenyl grains (curves 2–7) and *p*-terphenyl single crystal (curve 1). Curve 2 – grain size < 0.04 mm, curve 3 – < 0.06 mm, curve 4 – 0.06 – 0.1 mm, curve 5 – 0.1 – 0.3 mm, curve 6 – 0.3 – 0.5 mm, curve 7 – 0.5 – 1.0 mm

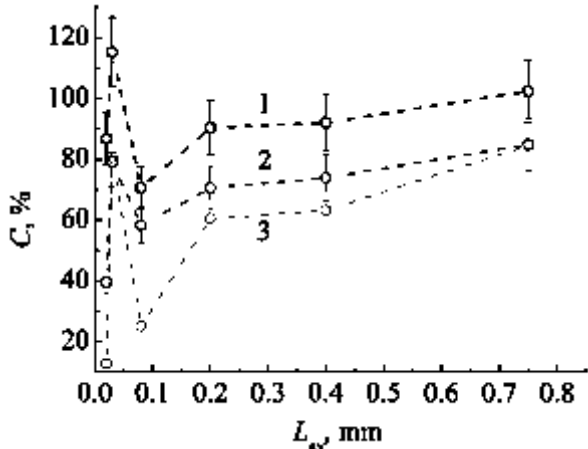


Fig. 6. Relative light output  $C$  for composite scintillators based on *trans*-stilbene (curve 1), *p*-terphenyl (curve 2) and *p*-terphenyl with 0,1% DPB (curve 3)

Based on the data shown in Fig. 5 and data for other materials used in this article, the curves shown in Fig. 6 were constructed.

As can be seen from the figure, there is a clear dependence on the grain sizes.

### 3.3. OPTICAL TRANSMITTANCE OF SINGLE-LAYER COMPOSITE SAMPLES

To complement the data in this article, optical transmission measurements of the previously mentioned materials were carried out in the wavelength range of

190...800 nm. Graphs for *trans*-stilbene are given as an example.

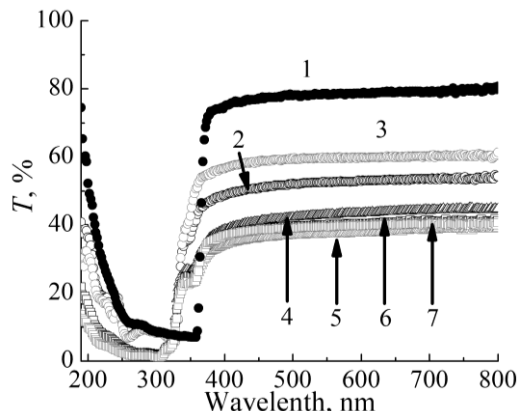


Fig. 7. Spectra of optical transmittance  $T$  of samples based on *trans*-stilbene. Designations as in Fig. 5

Fig. 7 shows that in the luminescence region of the scintillation materials studied in this article (>390 nm), the optical transmittance is quite high. Using the data in Fig. 7, the dependences of the optical transmission in the luminescence region on the average granule size were plotted. These curves are shown in Fig. 8.

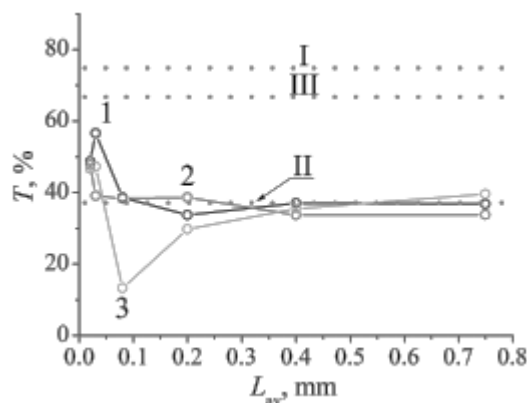


Fig. 8. Optical transmission of single-layer composite scintillators based on selected materials at 390 nm. Dashed lines I, II and III – optical transmission of single crystals of *trans*-stilbene, *p*-terphenyl and *p*-terphenyl, with 0.1% DPB, respectively. Other designations as in Fig. 6

### CONCLUSIONS

Based on the data presented in this article, the following conclusions can be drawn:

1. The dependence of the intensity of the glow on the size of the granules differed greatly under photoexcitation and excitation by ionizing radiation. This effect arises in connection with different mechanisms of the formation of instantaneous and delayed fluorescence in these cases.

2. When excited by alpha particles, there was a tendency for the signal to increase with increasing grain size to the level of single crystals. This is reminiscent of our previous results on excitation of these materials by light into the first singlet state [6]. However, for granules with a fraction <0.06 mm, there is a spike that requires further analysis.

3. Irradiation with light with a wavelength lying in the absorption region of triplet excitons of these materials, a fluorescence spectrum was observed, similar in spectral composition to the spectrum of instantaneous fluorescence. According to the experimental conditions, excitation can occur only due to the fusion of triplet excitons; accordingly, we observed a spectrum of delayed fluorescence. Since there is a multiplicity prohibition, the intensity of this spectrum reached only a few percent of the intensity of the excitation light. Note that the sample was excited not by individual light pulses, but in a continuous mode. In this case, the drop in the DF intensity due to the inhibition was compensated for by increasing the density of the photon flux that excites this material.

Single crystals had the lowest DP intensity, which is most likely due to the possibility of the  $T_1$ -states moving away from each other in such scintillators, since their volume for these states can be considered quasi-infinite. In this case, in composite scintillators, the effect of exciton reflection from the granule surface appears, which increases the probability of their recombination with a decrease in the granule size. Recall that the lifetime of  $T_1$ -states is about  $\sim 10^{-3} \dots 10^{-2}$  s.

It should also be noted that, upon excitation by light, the density of occurrence of  $T_1$ -states is orders of magnitude lower than the density of their occurrence in the track of an alpha particle.

#### ACKNOWLEDGEMENTS

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### КОМПОЗИЦІЙНІ СЦИНТИЛЯТОРИ НА ОСНОВІ ОРГАНІЧНИХ ГРАНУЛ ТА ЇХНЯ МОЖЛИВІСТЬ ДО РОЗДІЛЕННЯ ЗА ФОРМОЮ ІМПУЛЬСУ

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Проведено дослідження фотолумінесценції, відносного технічного світлового виходу та оптичного пропускання органічних одношарових композиційних сцинтиляторів з різними розмірами гранул. Наведено залежності цих значень від розмірів зерен для фракцій <0,04; <0,06; 0,06...0,1; 0,1...0,3; 0,3...0,5; 0,5...1,0 мм. Обговорюються можливі фізичні механізми таких результатів.