

New generation of organic scintillation materials

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Organic scintillation materials of the next generation have been designed and prepared, namely, organic polycrystals obtained from finely ground perfect single crystals by pressing and organic composite scintillators obtained by immersing crystalline grains into an optically transparent polymer matrix. The scintillation characteristics of proposed scintillation materials as detectors for short-range ionizing radiation and fast neutrons are discussed. This technology forms the base for production of large area detectors which can be used in devices for environmental radiation control, for security purposes (i.e. at customs to prevent the forbidden entry of fission materials), for various nuclear physical experiments, and in other branches of science and technology.

Разработаны органические сцинтилляционные материалы нового поколения — органические поликристаллы, полученные прессованием кристаллических зерен структурно-совершенного монокристалла, а также органические композиционные сцинтилляторы, изготовленные путем введения кристаллических зерен в оптически-прозрачную полимерную матрицу. Обсуждаются сцинтилляционные характеристики предложенных сцинтилляторов как детекторов короткопробежного излучения и быстрых нейтронов. Предложенная технология является основой дальнейшей разработки органических детекторов большого диаметра для решения актуальных задач мониторинга окружающей среды, таможенного досмотра, проведения различных ядерно-физических экспериментов.

Organic single crystals, liquids, and plastics were investigated as scintillator materials since 50ths or 60ths of the 20th century due to good luminescent characteristics thereof [1]. The materials included unitary, binary, and ternary solutions (solid and liquid) of organic luminescent molecules. While these molecular scintillation materials belong to different classes of organic substances, all of them are aromatic hydrocarbons consisting of condensed or bonded systems of benzene rings [1]. In the 70ths and 80ths, it became clear that to obtain a high quality scintillator, it is not sufficient just to have some solution with good pho-

toluminescence characteristic. Investigation of the scintillation mechanism have shown that in contrast to photoluminescence, the first excitation step is characterized by radioluminescence. This step can be even more important than the electron excitation energy transfer processes in the system [2–5]. In addition, for real practical applications, cheap scintillators of large volume were necessary which would allow the electronics to separate signals out of detected and background radiation. Therefore, the number of types of scintillators which have proven practical applications is not so large. It should be stated that plastic scintillators do

not allow pulse shape discrimination, while liquid scintillators are not always easy to use in field measurements.

Organic single crystals have the best spectrometry characteristics and light yield as compared to plastics and liquids but are more expensive and their diameters do not exceed 60–80 mm. In the 90^{ths}, it became clear that for practical applications, the only organic single crystals which could be produced and used as scintillators were stilbene (C₁₄H₁₂) and *p*-terphenyl (C₁₈H₁₄) activated with diphenyl butadiene [5]. Nevertheless, even for these crystals, which show superior properties than other organic crystals, the physical processes defining their growth still limited their structural perfection as well as their diameter (which plays the role of "input window" for thin crystals).

Improvement in the crystal growth technologies made it possible for us to produce organic single crystals with a controlled structural perfection, diameters up to 120 mm, and thickness of 100 mm; the light yields in these new crystals are 1.4 times higher than in similar organic crystals produced by standard technology [6, 7]. Nevertheless, crystalline organic scintillators with a greater detection area are still required for special applications. Therefore, we designed and prepared organic scintillation materials of the next generation, i.e. organic polycrystals obtained from finely ground perfect single crystals by pressing. The main idea of this approach is the following. The size of grains obtained by grinding a single crystal must have dimensions large enough to detect short-range particles or recoil nuclei. A set of grading sieves provides the selection of the grain fraction of necessary size L which has to be comparable with, or be larger than, the range of the ionizing particle. Polycrystals obtained in this way should provide a good light collection to obtain an appreciable scintillation signal from a short-range ionizing radiation under detection.

The organic composite scintillator is another novel type of large area organic detector. Those are made by grinding a stilbene crystal to different grain size fractions. These fractions are added to an optically transparent polymer base. Such a composite scintillator is encapsulated in a housing made from organic glass to improve the light collection and to raise the efficiency of fast neutron detection. This detector can be used for the detection of fast neutrons in devices for environmental radiation control,

for security purposes (i.e. to prevent the illegal transport of fission materials), for physical experiments, and in other branches of science and technology.

Organic single crystals. The main differences between our technique and traditional ones are the following [8]. An organic single crystal is grown from a melt that contains electron-seeking addition agents (ESAA). The charge-transfer complex-like structures consisting of a melt molecule and an ESAA molecule arise. The electrostatic field of such a complex initiates polarization of adjacent molecules, and forms oriented parts in the melt. These oriented parts promote the formation of crystallization centers in the growing crystal layer, which predetermines the crystal growth process [7]. Doping the melt with different amounts of ESAA molecules makes it possible to control the structural perfection of the grown single crystals. This results in a change of root-mean-square random orientation σ of the single crystal mosaic structure, and therefore, in a change in the concentration of deep traps for charge carriers and excitons [6]. It is assumed that the single crystal with minimal value of σ has the highest structure perfection. Annealing increases the radioluminescence intensity only by 10 %, while the radioluminescence intensity of a structurally perfect single crystals is 140–150 % as much as for ordinary organic single crystal obtained using the same material [5].

Organic polycrystal scintillators. A polycrystal scintillator is a cold-pressed or hot-pressed polycrystal based on grains (with grain size L) of stilbene or *p*-terphenyl. Grinding of a single crystal with high structural perfection at a low temperature followed by separation of the crystal grains obtained through sieves provides the raw material for such a polycrystal. The cold-pressed polycrystals were obtained by single-axial pressing (100–800 MPa) of the single crystal powder in a rigid mould at room temperature. The hot-pressed polycrystals were obtained during the annealing at the melting temperature and hydrostatic compaction at about 150 MPa. Thus, in the latter case, a solid-state recrystallization is an additional step in the crystal preparation [7, 8]. To consider in detail the correlation between the L -value range and the scintillation characteristics of polycrystals, we have used grains of a stilbene single crystal divided into 7 size ranges. The hot-pressed stilbene polycrystals had the following

Table. Scintillation characteristics of stilbene and doped *p*-terphenyl single crystals

Scintillation material	Scintillator dimensions, mm		Working temperature, K[11]	Light yield, photons/MeV	Energy resolution, %
	Diameter	Height			
Doped <i>p</i> -terphenyl	10 to 120	1 to 100	160 to 385	$2.8 \cdot 10^4$	<10
Stilbene	10 to 120	1 to 100	180 to 350	$1.4 \cdot 10^4$	<10

ranges of *L*-values: 1.0 to 1.2 mm, 1.2 to 1.5 mm, 1.5 to 1.7 mm, 1.7 to 2.0 mm, 2.0 to 2.2 mm, 2.2 to 2.5 mm, and 2.5 to 3.0 mm.

Composite organic scintillators. A composite scintillator contains the grains (with grain size *L*) of stilbene (or *p*-terphenyl) immersed into an optically transparent polymer. The current investigation includes 10 grain size ranges with *L*-values between 1 and 4.5 mm, namely, 1 to 1.3, 1.3 to 1.5, 1.5 to 1.7, 1.7 to 2.0, 2.0 to 2.2, 2.2 to 2.5, 2.5 to 3 mm, 3.0 to 3.5, 3.5 to 4.0, and 4.0 to 4.5 mm. It should be noted that the grains in this system are separated by the matrix. Therefore, the task of improvement of the structure perfection of a composite scintillator in contrast to the case of a polycrystal does not appear. For composite scintillators, it is important to choose the correct matrix base and to understand the optimal concentration and dimensions of crystal grains inside this matrix. Some aspects of the proposed technology has been recently described [9, 10].

The demands for optimal thickness of a neutron detector and the dimensions of crystal grains have to base on the following. Neutrons ionise indirectly the scintillator molecules by producing the secondary particles (recoil protons) which, in turn, ionise and excite the scintillator molecules. As to the scintillator thickness sufficient to make the generation process of recoil protons effective, it is necessary to take into account that the efficiency increases with scintillator thickness, but the energy resolution is worsening. To estimate the size of grains, it is to note that to detect the recoil proton of highest energy in the spectrum, it is necessary to take the grains with *L*-values equal to the path range of such a proton in the medium. At the same time, the light collection processes may influence considerably the scintillator light yield and the grain size influence on the light collection is rather significant. The only is clear that as the *L*-value decreases the number of scattering surfaces for scintillation light increases, therefore, light output of the scin-

tillation detector becomes reduced. Therefore, results can be obtained only in direct experiments.

Table presents the main scintillation characteristics of stilbene and *p*-terphenyl (doped with 0.1 % 1,4-diphenyl-1,3-butadiene) single crystals obtained by the technology described above, and shows the averaged values of light yield and energy resolution. The spread in the values obtained for different samples does not exceed 10 %. The results of measurements obtained in [11] allow us to extrapolate the average light yield value obtained at room temperature to the temperature ranges presented in Table.

For the light yield measurements in a series of $\text{Ø}30 \times 5 \text{ mm}^3$ hot-pressed stilbene polycrystals, we used 0.622 MeV conversion electrons from a ^{137}Cs source and 4.97 MeV alpha particles from ^{239}Pu placed in 2 mm collimator. The light yield of the reference stilbene single crystal $\text{Ø}30 \times 5 \text{ mm}^3$ was 1.2×10^4 photons per 1 MeV of gamma radiation energy.

Figs. 1 and 2 demonstrate the amplitude spectra of alpha- and beta-scintillations, respectively, for samples from a series of $\text{Ø}30 \times 5 \text{ mm}^3$ hot-pressed stilbene polycrystals. Using the results of those measurements, we have calculated the relative light yield *J* of stilbene composite scintillators. Fig. 3 shows the calculated *J* values vs grain size *L* of stilbene polycrystals. On the abscissa, the average *L* values for specific grain size ranges are presented. Both for alpha particle excitation and for conversion electron excitation, the light yield of the reference $\text{Ø}30 \times 5 \text{ mm}^3$ stilbene single crystal is taken as 100 %.

The hot-pressed polycrystal with *L* of 2.0 to 2.2 mm is seen to exhibit the optimal relative light yield. Scintillators obtained using the grains with *L* exceeding 1.5 mm have the light yield values differing within 10 %. So, the hot-pressed polycrystals as short-range detectors are close in the scintillation efficiency the single crystal and have to be more transparent for the emitted

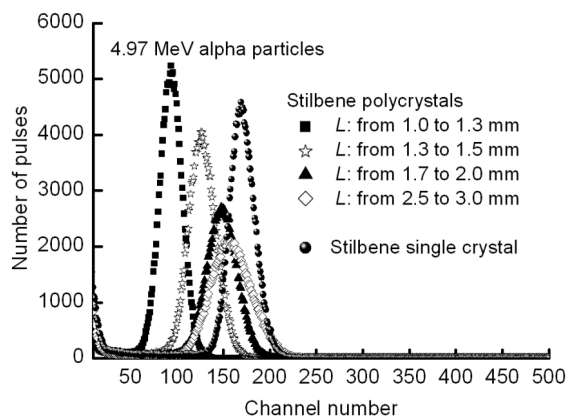


Fig. 1. Amplitude spectra of alpha scintillations for samples of a series of $\text{Ø}30 \times 5 \text{ mm}^3$ hot-pressed stilbene polycrystals with grain size L .

light. In contrast to single crystals, the preparation method using the polycrystals does not impose any physical limitations on their diameter, but in practice, that will be defined by the requirements to scintillation light collection (including the light detection system size), and to the operation conditions requirements (mechanical load, temperature, etc.).

We have studied a series of stilbene composite scintillators and a series of doped *p*-terphenyl composite scintillators as fast neutron detectors using a ^{239}Pu -Be source. To separate neutron (recoil proton) scintillations from background signal from gamma photons, we used a discrimination method based on the difference in scintillation pulse shapes obtained under different excitation types [12]. The neutron spectrum reconstruction procedure from the recoil proton spectrum has been described in detail in [13]. The neutron scintillation spectrum $\varphi(E_n)$ (1) can be reconstructed from a recoil proton spectrum $u(E_p)$ that was measured for $E_p \leq E_n$, i.e.

$$\varphi(E_n) = -\frac{E_n}{\varepsilon(E_n)} \times \left. \frac{du(E_p)}{dE_p} \right|_{E_p = E_n}, \quad (1)$$

where $\varepsilon(E_n)$ is the detection efficiency; E_n and E_p , the energies of neutrons and recoil protons, respectively.

Fig. 4 presents an example of the reconstructed neutron spectrum from a ^{239}Pu -Be source for a composite scintillator. This result was obtained for the $\text{Ø}30 \times 20 \text{ mm}^3$ composite *p*-terphenyl binary scintillator with L of 1.7 to 2.0 mm. Peaks 1 through 9 in Fig. 4

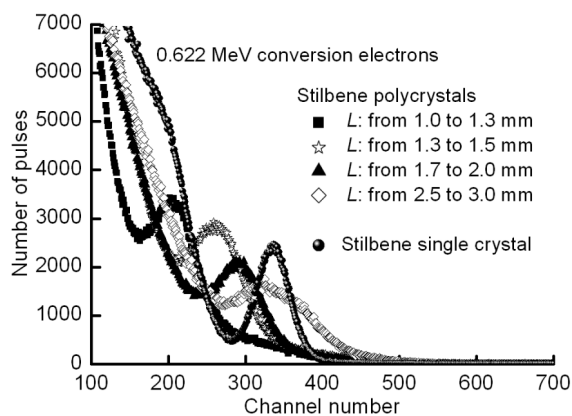


Fig. 2. Amplitude spectra of beta scintillations for samples of a series of $\text{Ø}30 \times 5 \text{ mm}^3$ hot-pressed stilbene polycrystals with grain size L .

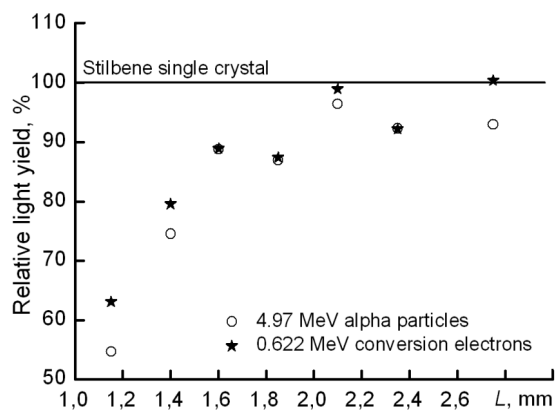


Fig. 3. J value vs grain size L dependences for hot-pressed stilbene polycrystals irradiated with 4.97 MeV alpha particles (circles) and 0.622 MeV conversion electrons (stars).

correspond to well-known neutron energies (3.1, 4.2, 4.9, 6.4, 6.7, 7.3, 7.9, 8.6, and 9.7 MeV, respectively [14–16]) emitted by a ^{239}Pu -Be source. It should be noted that such a spectrum is typical of all stilbene and *p*-terphenyl composite scintillators. The considerations of the reconstructed neutron spectra for a series of stilbene composite scintillators and for a series of doped *p*-terphenyl composite scintillators has shown that the energy resolution of peaks in neutron spectra for composite scintillators is not worse than for reference single crystals of stilbene and doped *p*-terphenyl, respectively.

The dependence of the fast neutron detection efficiency on neutron energy is among main characteristics of a scintillator as a neutron detector. The relative efficiency of neutron detection ε_{rel} as a function of neutron energy was calculated as

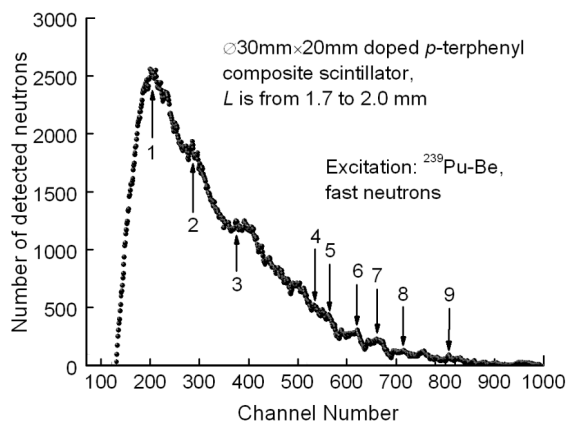


Fig. 4. The reconstructed neutron spectrum of a ^{239}Pu -Be source for a p -terphenyl composite scintillator with L values of 1.7 to 2.0 mm.

$$\varepsilon_{rel}(E_n) = \frac{N_{rel}^i(E_n)}{I_{rel}^i(E_n)}, \quad (2)$$

where $N_{rel}^i(E_n)$ is the relative number of pulses at the maximum of peak i of a reconstructed neutron spectrum (see Fig. 4); $I_{rel}^i(E_n)$, the relative number of neutrons of energy E_n generating the scintillation signal that corresponds to the peak i of reconstructed neutron spectrum. The $I_{rel}^i(E_n)$ values can be obtained from the calculated energy spectrum of the neutron source. For a ^{239}Pu -Be sources of fast neutrons, such information is available only for neutron energies $E_n \geq 3.1$ MeV [14–16]. The values of $N_{rel}^1(E_n)$ and $I_{rel}^1(E_n)$ for $E_n \sim 3.1$ MeV was taken as unity.

Fig. 5 summarizes the calculation results of the relative fast neutron detection efficiency ε_{rel} vs neutron energy E_n for a series of $\text{Ø}30 \times 20 \text{ mm}^3$ doped p -terphenyl composite scintillators with different grain size ranges L . No correlation between the relative efficiency ε_{rel} and the grain size range L was observed for composite scintillators excited by neutrons of the same energy E_n . In addition, Fig. 5 shows ε_{rel} values (2) for $\text{Ø}25 \times 15 \text{ mm}^3$ reference doped p -terphenyl single crystal and for liquid scintillator on the base of ditolyl methane and naphthalene. The fast neutron detection efficiency for composite p -terphenyl scintillators decreases more steeply with neutron energy E_n increase than for the reference p -terphenyl single crystals, but it is practically the same as for standard effective liquid scintillator. Such a result is also typical of

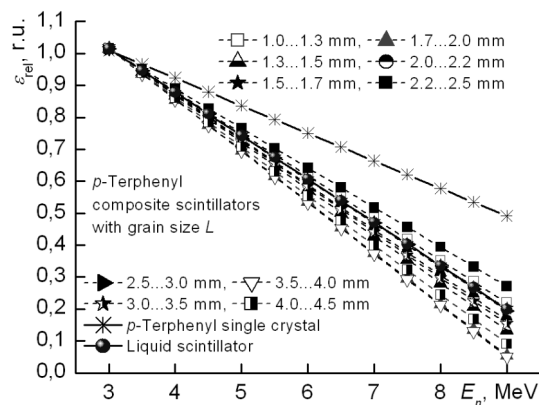


Fig. 5. The lines of formal linear approximations for the relative efficiency ε_{rel} of fast neutron detection vs neutron energy E_n for a series of $\text{Ø}30 \times 20 \text{ mm}^3$ doped p -terphenyl composite detectors with different grain size range L , for a $\text{Ø}25 \times 15 \text{ mm}^3$ reference doped p -terphenyl single crystal and for liquid scintillator on the base of ditolyl methane and naphthalene.

composite scintillators based on stilbene grains.

Thus, improvement in the crystal growth technologies has formed a basis to develop a new generation of effective organic scintillators. The proposed preparation technology of organic polycrystals and composite scintillators imposes no physical limitations on their diameter, but in practice, that will be defined by the requirements to scintillation light collection (including the light detection system size), and to operation conditions (mechanical load, temperature, etc.). The consideration of amplitude spectra of alpha particles from a ^{239}Pu isotope and conversion electrons from a ^{137}Cs isotope shows that the hot-pressed polycrystals with the grain size range of 2.0 to 2.2 mm provide the optimal relative light yield. For practical purposes, the optimal grain size is between 1.5 mm and 3 mm. The scintillation characteristics for this region of grain sizes do not change appreciably while the amount of raw material (single crystals) used decrease appreciably. The composite scintillators can be used to discriminate the scintillation signals from radiations with different specific energy losses as well as the organic single crystals (in contrast to plastic scintillators). The composite organic scintillators, like the liquid scintillators, can provide homogeneous isotropic large area scintillators taking the shape of housing where they have been prepared. Organic

composite scintillators on the base of stilbene and *p*-terphenyl doped with 4-diphenyl-1,3-butadiene in the neutron energy range of about few MeV provide high efficiency of neutron detection comparable with the efficiency for single crystals and effective liquid scintillators.

The proposed scintillators can be used to detect the fast neutrons and short-range ionizing particles in environmental radiation control, medical, and security applications (e.g. to prevent the forbidden entry of fission materials), as well as in experimental nuclear physics.

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Нове покоління органічних сцинтиляційних матеріалів

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Розроблено органічні сцинтиляційні матеріали нового покоління — органічні полікристали, отримані шляхом пресування зерен структурно-досконалого монокристала, а також органічні композиційні сцинтилятори, виготовлені шляхом введення кристалічних зерен в оптично-прозору полімерну матрицю. Обговорюються сцинтиляційні характеристики запропонованих сцинтиляторів як детекторів короткопробіжних випромінювань та швидких нейтронів. Запропоновано технологія є підґрунтям подальшої розробки органічних детекторів великої площі для вирішення актуальних проблем моніторингу навколишнього середовища, митного огляду, проведення різних ядерно-фізичних досліджень.