

Development of new composite scintillators based on organic single crystal grains

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The proposed organic composite scintillators contain crystalline grains of stilbene or *p*-terphenyl incorporated into a two-component non-scintillating polymer matrix. Discussed are the technological aspects of the making of such scintillators: the selection of the crystalline grain size, the optimum ratio of the scintillation material and the organosilicon matrix amounts, the search for optimum light collection conditions, etc. The proposed technology makes it possible to obtain large-diameter organic composite scintillators for detection of short-range ionizing radiation and spectrometry of low-activity fluxes of fast neutrons.

Предложенный органический композитный сцинтиллятор представляет собой кристаллические зерна стильбена или *п*-терфенила, введенные в полимерную двухкомпонентную несцинтиллирующую матрицу. Обсуждаются технологические аспекты получения композитных сцинтилляторов: подбор размера кристаллических зерен, оптимального соотношения количеств сцинтиллирующего материала и кремнийорганической матрицы, поиск оптимальных условий светосбора и т.п. Предложенная технология позволяет получать эффективные органические композитные сцинтилляторы большого диаметра для детектирования короткопробежных ионизирующих излучений и спектрометрии низких потоков быстрых нейтронов.

Due to low atomic mass and, consequently, low back scattering probability of particles to be registered, organic molecular scintillation materials are the best detectors of short-range radiation (α- and β-particles) extremely harmful for human organism. In hydrogen-containing organic materials, fast neutrons generate recoil protons with maximum energy equal to the neutron energy, therefore, organic scintillators and detectors based thereon are also used for fast neutron spectroscopy [1].

One of the most important problems in the detection of ionizing radiation, including fast neutrons, is the necessity to register radiation of very low activity. Therefore, such a detector may be rather thin, but its diameter is to be large enough to increase the solid angle of detection and, consequently, the detection efficiency.

To obtain efficient large-diameter organic scintillators, we have developed a new class of organic materials, namely, composite scintillators based on stilbene and *p*-terphenyl. The proposed material consists of crystalline stilbene or *p*-terphenyl grains incorporated into a two-component polymer matrix. The crystalline grains were produced by crushing stilbene and *p*-terphenyl perfect structure single crystals were grown from the melt; the crushing was performed in liquid nitrogen. The grains of different size were obtained by sifting the crushed crystals through sieves of different mesh sizes. The linear grain size L varied from 0.5 up to 4.5 mm. The prepared composite material was placed into optically transparent organic glass container.

Described below is the method we have developed to obtain crystalline grains of stilbene and *p*-terphenyl doped with 0.1 %

1,4-diphenyl-1,3-butadiene. At first, a single crystal of high structure perfection (with the root-mean-square misorientation of mosaic blocks not exceeding 30′) was grown from the melt [2]. Then the obtained single crystal was crushed in liquid nitrogen. Such a procedure minimizes the loads which influence negatively the structure perfection of the grains resulting in decreased transparency. The grains obtained were dried at room temperature in a dark room for at least 12 hours. Afterwards, the grains were sifted through a calibrating sieve which separates them into fractions of different size [3].

While selecting the crystalline grains for composite scintillators, in particular, for fast neutron detectors, it is necessary to proceed from the fact that the grain size must be comparable with the recoil proton free path in the material [4]. As established in the course of our studies, the grains of 0.5 to 2.5 mm linear size provide a high homogeneity of the detector sensitivity over the whole output window area due to the total light collection on the whole scintillator surface and, consequently, high light yield and efficiency of fast neutron detection. As the average linear grain size diminishes, the number of the grains per unit scintillator volume increases, so the number of reflecting surfaces per unit volume grows, thus hindering the light transmission through the scintillator. Increase in the size of the scintillator particles may reduce the efficiency of fast neutron registration by the proposed composite detector [3].

To establish the scintillator optimum composition, the composite scintillators were studied with different glue bases, concentrations of crystalline grains and organosilicon matrices. We have produced a series of composite stilbene scintillators with the linear grain size L varying from 1 to 2 mm. As a matrix, an organosilicon rubber was chosen possessing inertness, nonhygroscopicity and maximum transparency in the stilbene luminescence region. This material provides stability of the detector luminescence parameters during its operation, that complies with the requirements imposed on scintillators. The selected fraction of crystalline grains was incorporated into different organosilicon bases such as SKTN (the viscosity $\eta = 110$ poises), Sylgard-186 ($\eta = 1100$ poises), Sylgard-527 ($\eta = 230$ poises). The investigations have shown that the composite scintillator with L of 1–2 mm and the organosilicon base Sylgard-527 had the best relative efficiency of fast neutron detection. The repeated measurements results of the fast neutron registration efficiency and the detector light output performed in the course of 12 months have testified that the main physicochemical characteristics of the scintillators remained unchanged. Thus, in further studies, Sylgard-527 [3, 4] was used as a non-scintillating glue base.

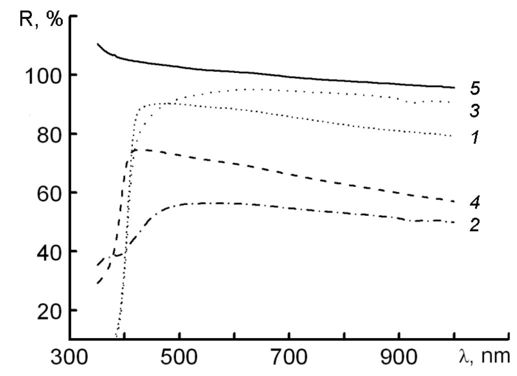

Fig. 1. Reflection factor R vs wavelength λ for different types of reflective coatings. (*1*) Sigmacaver 211, (*2*) Eccobond-45 Clear + MgO, (*3*) Eccobond-45 Clear + TiO_2, (*4*) VL-528 enamel, (5) Tetratek.

An additional series of composite stilbene scintillators with different content of stilbene grains incorporated into organosilicon base was produced and examined. The studies have shown that as the stilbene concentration increases from approximately 50 up to 75 %, the relative efficiency of fast neutron detection increases, too [3]. The experimental data have shown that the optimum content of stilbene grains in the immersion medium which provides high efficiency of fast neutron registration is at least 70 % of the matrix mass. A further increase of this content is not expedient, as it results in a worsened detector optical contact homogeneity and causes deterioration of the scintillation characteristics. A decrease of the stilbene content reduces the efficiency of fast neutron detection due to loose packing of the crystalline grains in the matrix [3, 4].

The reflective coating influence on the detector characteristics is considerable and depends on the pigment concentration in the polymer base as well as on the reflective layer thickness τ. In this connection, the study included a search for the most effective reflecting coating for the composite scintillators. We have examined a number of coatings, such as Sigmacaver 211, Eccobond-45 Clear + MgO, Eccobond-45 Clear

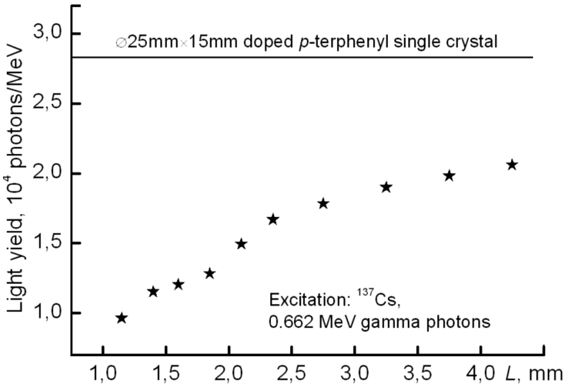

Fig. 2. Light yield of doped p-terphenyl composite scintillators with different grain size irradiated with 0.662 MeV gamma photons.

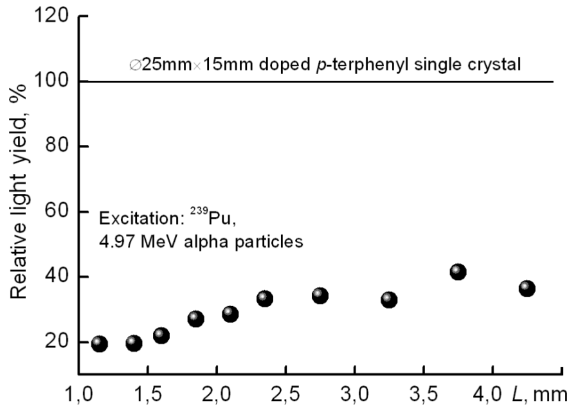

Fig. 3. Light yield of doped p-terphenyl composite scintillators with different grain size irradiated with 4.97 MeV alpha particles.

+ TiO_2, VL-528 enamel, and Tetratek, which were spread on the K-8 glass substrates. The reflecting coating thickness was varied from 0.18 to 0.63 mm. The reflection spectra were measured using a Hitachi 330 spectrometer in the wavelength region of 350–1000 nm. Fig. 1 presents the dependences of the reflection coefficient R on the wavelength for different reflector types. The obtained results testify that the diffuse reflector Tetratek possesses the best characteristics. Therefore, the containers for the composite scintillators were coated with two layers of said reflector at a 0.52–0.54 mm thickness.

When making the containers, the following requirements were taken into account. First, the scintillator height has to provide efficient detection of fast neutrons with few MeV energy (for instance, the calculated registration efficiency for 2 MeV neutrons for a 200 mm high stilbene single crystal is about 20 % [5]). Second, the scintillator should retain a sufficient transparency to self-emission. Such requirements are fulfilled for a 20 mm high container. The containers for the experimental composite scintillators of 30 mm diameter were made from structural organic glass. In our case, the container was also used as a light guide. Moreover, the container design was chosen so that it provided the use of the detector to register short-range α- and β-radiation. For this purpose, the container was furnished with additional covers which had through holes of 10 mm diameter.

We have produced and studied composite scintillators obtained from stilbene grains of 10 fractions with the following linear sizes L: 1.0–1.2 mm, 1.2–1.5 mm, 1.5–1.7 mm, 1.7–2.0 mm, 2.0–2.2 mm, 2.2–2.5 mm, 2.5–3.0 mm, 3.0–3.5 mm, 3.5–4.0 mm, 4.0–4.5 mm. The samples of similar composite scintillators were also made from the ground activated p-terphenyl single crystals. In the course of work, large diameter composite detectors were prepared, namely, ∅200 mm×20 mm composite detector based on stilbene grains and ∅200 mm×20 mm one based on activated p-terphenyl grains.

We have studied a series of 10 composite stilbene scintillators of ∅×30 mm×20 mm size obtained using stilbene grains of different fractions, and similar series of 10 composite scintillators based on p-terphenyl grains activated with 0.1 % 1,4-diphenyl-1,3-butadiene. In addition, there composite scintillators of 200 mm diameter based on the same materials were studied. Presented below are the experimental results which demonstrate the scintillation properties of the studied composite materials used as short-range α- and β-radiation detectors, as well as fast neutron detectors.

The calculated light yield values for a series of composite scintillators based on activated p-terphenyl grains excited with gamma photons from ^{137}Cs and α-particles from ^{239}Pu source are presented in Figs. 2 and 3, respectively. The source of α-particles was placed into 2 mm high collimator. For the measurements with gamma radiation (Fig. 2), the light yield values are given in absolute units, whereas for the measurements with short-range α-radiation (Fig. 3), these data are presented in percent; the light yield of standard activated p-terphenyl single crystal being taken as 100 %. The average values of the parame-

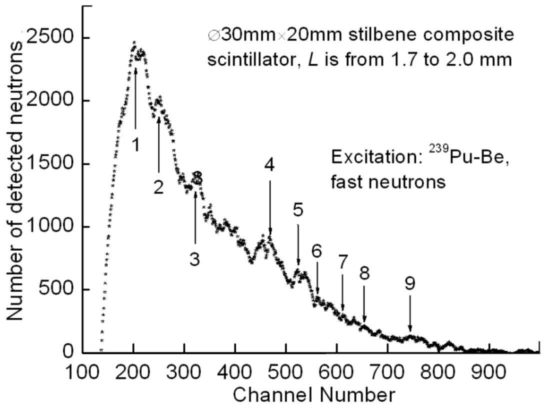

Fig. 4. Reconstructed neutron spectrum of ^{239}Pu–Be source for ∅30 mm×20 mm composite stilbene scintillator with grain size ranging from 1.7 to 2.0 mm.

ter L are given for each grain fraction. As seen from Figs. 2 and 3, the light yield reaches its maximum at L ~ 2.5 mm and remains practically unchanged at further increase of the average grain size [6].

When studying the composite scintillators based on stilbene and *p*-terphenyl with fast neutrons, a ^{239}Pu–Be source was used with 10^5 neutrons/s flux. The selective detection of fast neutrons against gamma background was realized in accordance with [7]. The reconstruction method of fast neutron energy spectra from scintillation amplitude spectra of recoil protons was described in our paper [6]. Presented as an example in Fig. 4 is a reconstructed neutron spectrum of the ^{239}Pu–Be source for the composite *stilbene scintillator with the linear grain size varying from 1.7 to 2.0 mm. In this Figure, only those* ^{239}Pu–Be energies are indicated which are reported in theoretical and experimental papers (see the references in [6]), namely 3.1, 4.2, 4.9, 6.4, 6.7, 7.3, 7.9, 8.6 and 9.7 MeV, arrows 1–9, respectively.

To estimate the degree of light yield inhomogeneity for the obtained large diameter composite scintillators, we measured the light yield irradiating different parts of the scintillators, in particular, the centers and four additional zones (see Fig. 5(b)). The latter were located at four opposite sides of the scintillator, the distance between the scintillator center and any of the additional zones being 70 mm. The light yield values were measured according to the standard procedure using a ^{137}Cs source.

We characterized the degree of light yield inhomogeneity by ΔLY parameter:

$$\Delta LY = \left| \frac{J_1 - J_i}{J_1 + J_i} \right| \quad (1)$$

where J_1 and J_i are the light yield values measured at the scintillator center and at a point i, respectively. For $i = 1$, the ΔLY was assumed to be 1. Fig. 5(a) presents the results of light yield measurements and the calculated ΔLY values for five ∅200 mm×20 mm composite scintillators obtained from crystalline stilbene grains. In this Figure, the dotted line shows the absolute light yield for reference stilbene single crystal. The open symbols correspond to the calculated light yield values at the measurement points; the half-closed ones are the calculated ΔLY values.

Consideration of these data testifies that the maximum scatter of the light yield val-

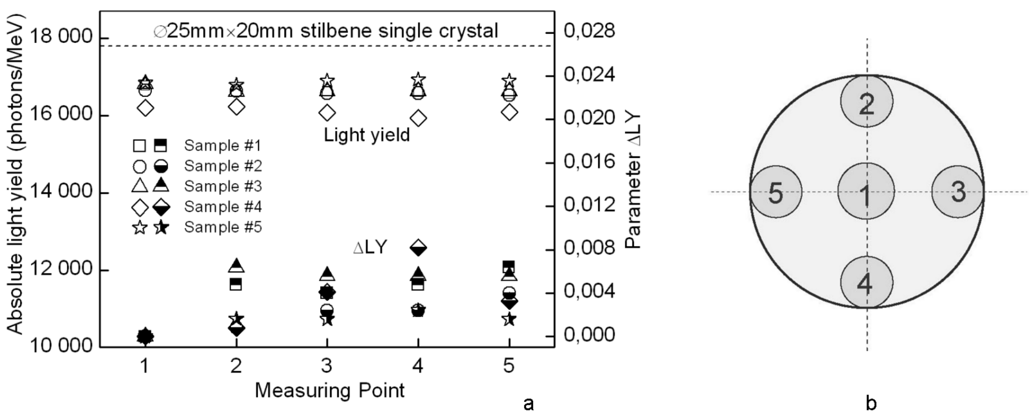

Fig. 5. Absolute light yield values measured at the points 1–5 for a series of ∅200 mm×20 mm composite stilbene scintillators (the upper family of opened symbols) and the corresponding calculated values of ΔLY parameter (1) (the lower family of half-closed symbols). Fig. 5(b) schematically presents the light yield measurement procedure for large-diameter scintillators.

ues measured for different parts of the large diameter scintillators does not exceed 5 %, i.e. the standard error of the light yield measurement method. Thus, it should be concluded that the proposed technique gives reproducible results and makes it possible to produce homogeneous large diameter composite detectors.

Thus, considering the production technology aspects of new organic composite scintillators based on crystalline stilbene or *p*-terphenyl grains incorporated into a polymer two-component matrix, as well as the results of studying their scintillation characteristics, the following conclusions can be drawn. An efficient starting material for the composite scintillator is crushed stilbene or *p*-terphenyl single crystal with high structure perfection. The use of Sylgard-527 organosilicon rubber as a glue provides the manufacturing of composite scintillators with high scintillation characteristics. The optimum content of crystalline stilbene and *p*-terphenyl grains in the immersion medium is of the order of 70 %. The diffuse reflector Tetratek of 0.52 0.54 mm thickness provides the highest optical characteristics for the organic composite scintillators enclosed in organic glass containers. The scintillation characteristics of the proposed composite scintillators are only a little worse than those of the standard single-crystal scintillators. In contrast to most efficient liquid solutions of organic luminophors, composite scintillators on the base of stilbene or *p*-terphenyl grains are non-toxic, do not cause fire hazard and may be used without container. The proposed technology yields reproducible results and provides the production of homogeneous composite detectors of large diameters and different geometric configurations.

The proposed approach may find wide application in radioecology, radiobiology and medicine. The developed detectors for registration and spectrometry of fast neutrons may be also used to raise the reliability of the control systems of various nuclear sets, increase the safety of nuclear power stations and improve their ecological environment.

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References

1. N.Z.Galunov, V.P.Semynozhenko, The Theory and Application of the Radioluminescence of Organic Condensed Media, Naukova Dumka, Kiev (1997) [in Russian].
2. I.P.Krainov, N.Z.Galunov, S.V.Budakovsky, *Cryst. Res. and Techn.*, **24**, 193 (1989).
3. Decision of Grant No.13558/1, Sept 16, 2008 (Application U2008 08206 filed June 17, 2008) for Declared Patent "Method for Preparation of Stilbene-based Organic Scintillator for Fast Neutron Registration" (N.L.Karavaeva, N.Z.Galunov, O.A.Tarasenko).
4. S.V.Budakovsky, N.Z.Galunov, B.V.Grinyov et al., *Radiat. Meas.*, **42**, 565 (2007).
5. V.I.Kukhtevich, L.A.Trykov, One-crystal Scintillation Spectrometer (with Organic Phosphor), Atomizdat, Moscow (1971) [in Russian].
6. S.V.Budakovsky, N.Z.Galunov, N.L.Karavaeva et al., *Trans. Nucl. Sci.*, **54**, 2734 (2007).
7. J.H.Baker, N.Z.Galunov, A.M.Stepanenko, O.A.Tarasenko, *Radiat. Meas.*, **38**, 817 (2004).

Створення нових композиційних сцинтиляторів на основі зерен органічних монокристалів

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Запропонований органічний композиційний сцинтилятор являє собою кристалічні зерна стильбену або *п*-терфенілу, введені у полімерну двокомпонентну несцинтилюючу матрицю. Обговорюються технологічні аспекти отримання композиційних сцинтиляторів: добір розміру кристалічних зерен, оптимальне співвідношення кількостей сцинтиляційного матеріалу та кремнійорганічної матриці, пошук оптимальних умов збору світла і т.ін. Запропонована технологія дозволяє отримувати ефективні органічні композиційні сцинтилятори великого діаметра для реєстрації короткопробіжних іонізуючих випромінювань та для спектрометрії низьких потоків швидких нейтронів.