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COMPOSITE SCINTILLATORS AND SOME FEATURES OF THEIR RADIATION RESISTANCE

Nowadays, composite scintillators find applications in a growing number of tasks dealing with the detection of ionizing radiation. They have several advantages in comparison with other scintillation materials. With the emergence of a new generation of accelerators, the radiation load on detectors is significantly increased. Therefore, the development of materials with high radiation resistance for radiation detectors becomes an important task. We propose to apply composite scintillators as radiation-resistant materials. The most important factor is that irradiation can significantly modify the characteristics of a scintillation material. The aim of this work was to study the specific features of possible radiation-induced damages and transformations in composite scintillators under the action of ionizing radiation. A comparative analysis of the relative light yield, transmittance, and luminescence spectra, as well as their dependences on the accumulated dose, is carried out for various composite scintillators containing grains of organic or inorganic single crystals, such as $Gd_2SiO_5:Ce$, $Gd_2Si_2O_7:Ce$, $Al_2O_3:Ti$, $Y_2SiO_5:Ce$, *and* $Y_3Al_5O_{12}:Ce$. *Probable mechanisms of radiation-induced changes occurring in scintillators under irradiation are proposed, and the influence of those processes on the radiation resistance of composite scintillators is analyzed.*

Keywords: composite scintillators, radiation resistance.

1. Introduction

The development and creation of new scintillation materials is a challenging task both in Ukraine and throughout the world. The idea to create a new type of organic scintillation materials not in the form of a continuous medium, but as an inhomogeneous material containing chaotically oriented scintillation single-crystalline grains, was proved by us to be promising as long ago as in 1998–2003 [1–3]. Unlike organic single crystals, plastics, and liquids, those materials are not homogeneous, but heterogeneous ones, whose microscopic inhomogeneities govern their macroscopic parameters.

Materials of this type can be manufactured by linking grains with one another with the help of the hot pressing, when the grains become sintered together, or by inserting the grains into a transparent gel-composition (in order to fix the grains as nuts in a piece of chocolate). We called the materials of the first type (van der Waals ceramics) as organic polycrystals, and those of the second type as composite scintillators. The community started to study those ideas more actively after 2011, when it was proved that the unique properties are inherent to composite scintillators containing not only organic-scintillator grains, but also grains of inorganic scintillation crystals [3–11]. After our first publications, our colleagues from the Niederlands, the Republic of Korea (the South

Korea), Poland, and the Russian Federation started to actively develop this problem. These mainly were our mutual works with foreign scientists from the mentioned countries, except those from the Russian Federation [3–5, 7, 9, 10, 12].

Composite scintillators have a number of advantages in comparison with other scintillation materials.

1. A composite scintillator is cheaper and simpler in manufacture than single crystals. In some cases, the expensive stage of single-crystal growing can be omitted, or a waste material obtained, when treating single crystals, can be used. In the latter case, the main loss of a scintillation material, which could take place during its treatment, is absent, because the treatment itself is not required.

2. The creation of large, almost infinite areas is possible. A specially prepared gel-composition can link separate parts of the scintillator into a single specimen [13]. There are no technological restrictions on the number of such links.

3. Not only the specimen size, but also the dimensions of grains grains can be varied. This possibility enhances the control the material properties and affects the detection selectivity with respect to ionizing radiation [7, 8].

A technology of creation of new types of organic scintillation materials for the efficient registration of fast and thermal neutrons has been proposed earlier. It made possible to create detectors with no restrictions on the area and shape of an input window [5, 7]. The obtained scintillation materials and detectors on their basis are universal, simple in application, and can be used in a wide spectrum of tasks associated with the detection and identification of ionizing radiation.

Recently, we got interested in a new application of those objects, which are unique by their properties. After the appearance of a new generation of accelerators, the radiation load on the detectors in those accelerators is substantially increased. For example, in experiments on the Large Hadron Collider (LHC), the radiation dose for the scintillation detectors can reach 10–100 Mrad and, in accordance with the plans of an LHC modernization, it is intended to be made even higher in the future (see, e.g., work [14]). Such factors determine a special importance of searching for new radiation-resistant scintillation materials.

After the irradiation, the scintillation material can reveal a degradation of its parameters. Therefore, we should specify what we mean under the term "radiation-resistant material". The radiation resistance is not a constant criterion for a specific irradiation dose D. There is a complicated system of relationships for the parameters before ($D = 0$) and after the irradiation to every separate dose D and for each material in the framework of that or another problem. In our case, following the classical definition given by Birks, we will consider a scintillator to be radiation-resistant to the irradiation dose D, if the ratio between the value of a certain key parameter corresponding to this dose, A_D, and its value before irradiation, A_0, changes by a factor less than two [15], i.e. if

$$A_{\rm rel} = A_D/A_0 \geq 0.5. \qquad (1)$$

Criterion (1) will be used for the values of the relative light yield $L_{\rm rel}$ and the relative optical transmittance $T_{\rm rel}$. These quantities were calculated according to Eq. (1) on the basis of experimental data obtained for the corresponding exposure doses D and for $D = 0$.

Therefore, in this work, we will analyze and discuss the features in the manifestation of the radiation resistance of composite scintillators and the probable mechanisms of radiation-induced destructions and transformations in scintillators under the action of ionizing radiation. The analysis is based on the results obtained in our previous works.

2. Experimental Part

The samples to be studied were fabricated by crushing crystals (wastes of the single-crystal manufacture) and inserting the obtained grains into a gel-composition. Afterward, the latter was held till its complete polymerization. Irradiation was performed, by using 10-MeV electrons on a linear accelerator at the National Science Center Kharkiv Institute of Physics and Technology.

The light yield was determined from the results of measurements of scintillation amplitude spectra. The corresponding error amounted to 5%. The amplitude scale linearity was verified, by using the radionuclide sources ^{241}Am (17 keV), ^{137}Cs (32.7 keV), ^{152}Eu (41 keV), ^{241}Am (59.6 keV), ^{152}Eu (77.9 keV), and ^{152}Eu (122.0 keV). The value of the relative light yield was obtained as the ratio between the scintillation amplitudes for the examined and reference samples subjected to the irradiation with gamma quanta emitted by ^{137}Cs, alpha particles emitted by ^{239}Pu, and photons emitted by ^{241}Am. As a reference specimen, a single crystal with the same chemical composition as in grains of the composite scintillator was chosen.

The optical transmittance was measured on a two-channel spectrophotometer Shimadzu-2450. The comparison channel remained empty, so that the optical transmittance was measured with respect to air. The measurement error amounted to 0.5%. Luminescence spectra were registered on a spectrofluorimeter Varian Cary Eclipse.

3. Choice of the Composite Scintillator Matrix and Researches of Its Radiation Resistance

In work [16], scintillators on the basis of polydimethyl-co-diphenylsiloxane and polymethylphenyl-co-methylhydrosiloxane were studied. The researches showed that those systems activated by molecules of some organic luminophores possess a higher radiation resistance (to 30 Mrad) than plastic scintillators on the basis of standard matrices, like polystyrene.

One of the shortcomings inherent in such systems is the presence of benzene rings, because the latter have a tendency to be easily destroyed under irradiation, whereas the probability of their self-restoration is low. However, the main point in this issue concerns the damage and restoration of the centers that can directly affect the luminescence of the scintillator matrix. This influence may worsen the optical properties of the matrix, whereas the latter has to be resistant to the action of high ionizing radiation fluxes.

Unlike other scintillators, the matrix of composite scintillators must not scintillate. Radioluminescence arises in scintillation grains located in the nonluminescent matrix material. Owing to this feature of composite scintillators, we obtained an opportunity to make the most important step to the manufacture of radiation-resistant scintillators. We changed from matrices containing benzene rings to polysiloxanes, which do not contain them. Since the matrix of our composite scintillators is not luminescent, it can affect the luminescence of a composite scintillator only by varying its transparency in the luminescence band of grains.

In the experiments that will be analyzed below, we chose the dielectric gel-composition Sylgard-184 on the basis of polymethylsiloxane. It is radiation-resistant in the whole interval of doses, $D \leq 90$ Mrad, which were used in the experiments aimed at the selection of gel-compositions [17]. The transparency of this gel-composition to light with the wavelengths $\lambda \geq 390 \div 400$ nm (this is the luminescence band of experimental grains) decreased from 90% to 87%, i.e. only by 3%, under irradiation to all D ($D \leq 90$ Mrad). For longer light wavelengths, this difference remains the same or becomes even smaller. A more detailed research and a substantiation of our choice of the dielectric gel-compositions can be found in work [17].

4. Radiation Resistance of Organic Materials

4.1. Organic crystals, polycrystals, composite and plastic scintillators

Composite scintillators on the basis of grains of organic single crystals are efficient for the registration of alpha-particles and fast neutrons. They are also used in combined neutron detectors for the separate detection of fast and thermal neutrons against the gamma-radiation background [7, 18]. Those materials are rather promising for the tasks of radioecology.

However, the researches of the radiation resistance of organic single crystals and polycrystalline and composite scintillators (Fig. 1) on the basis of grains of molecular single crystals showed that those scintillators are not radiation-resistant even at a dose of about 0.5 Mrad [13]. In Fig. 1, the relative light yields of composite scintillators on the basis of single-crystalline grains are depicted. Curves *1* and *2* composite scintillators with granule dimensions of 0.5–1 and 2–2.5 mm, respectively; and curve *3* to a polycrystal obtained by the hot pressing of thin (narrower than 1 mm) flakes grown up from a solution.

In the standard plastic scintillators, the scintillation signal diminishes by more than twice, if the radiation dose is lower than 10 Mrad [13]. This result completely agrees with the data obtained in works [16, 19].

4.2. Organic luminophores at ultralow concentrations

Since the composite scintillators containing grains of organic crystals are not radiation-resistant, we de-

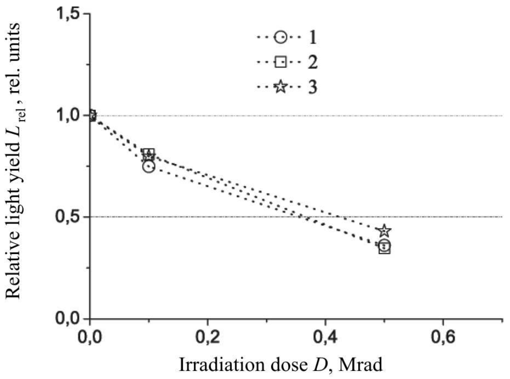

Fig. 1. Dependence of the relative light yield $L_{\rm rel}$ on the accumulated dose D for organic scintillators

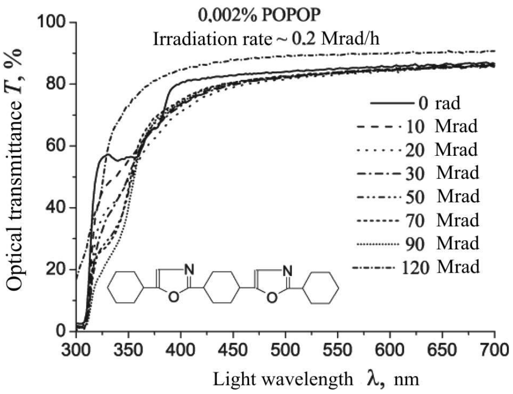

Fig. 2. Dependences of the optical transmittance T on the wavelength λ for samples obtained by introducing POPOP (1,4-di-[2-(5-phenyloxazolyl)]benzene) molecules in a concentration of 0.002% into Sylgard-184 at various irradiation doses D

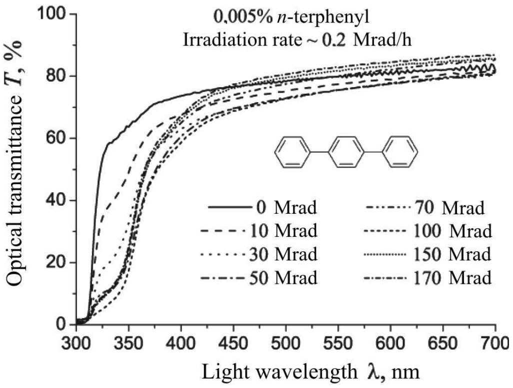

Fig. 3. Dependences of the optical transmittance T on the wavelength λ for samples obtained by introducing p-terphenyl molecules in a concentration of 0.005% into Sylgard-184 at various irradiation doses D

cided to introduce molecules of organic luminophores with ultralow concentrations into the gel-composition and to study the obtained systems with respect to their radiation resistance. In this case, the probability for ionizing radiation to directly interact with luminophore molecules is extremely low, so that the radiation resistance is determined by the parameters of the dominating (by its content) substance. In the way, such systems can be used as light guides. The values of optical transmittance for such systems are shown in Figs. 2 and 3.

Figures 2 and 3 demonstrate that the systems concerned are rather radiation-resistant with respect to their optical transmittance, because the optical transmission coefficient does not fall even by two times within the luminescence interval of those luminophores. One can also see that the optical transmittance decreases in the short-wave region, which is associated with the absorption band of luminophore molecules introduced into the gel-composition. Proceeding from those measurements, we may assert that the systems with p-terphenyl luminophore molecules are radiation-resistant to doses not lower than 170 Mrad, and with introduced 1,4-di-[2-(5-phenyloxazolyl)]benzene (POPOP) molecules to doses of 120 Mrad. The luminescence spectra of those systems are depicted in Figs. 4 and 5.

From Figs. 4 and 5, one can see that the growth of the accumulated dose D gives rise to the appearance of a new structureless luminescence band in the longer-wave spectral section. According to our hypothesis, this shift can be observed due to the formation of chemical dimers between the molecules of luminophores and the matrix. In the case of benzene-ring destruction or detachment, a hypochromic shift would have been observed. However, in our case, the opposite displacement – namely, the bathochromic one – is observed, which can also testify to the formation of dimers. In work [16], it was proved that polysiloxanes have a tendency to form dimers with luminophore molecules, the so-called exciplexes, under the action of ionizing radiation.

The results obtained for the materials, which can be used as optical shifting light guides (the impurity concentration is very low, so that reabsorption is infinitesimally small), testify that POPOP is radiation-resistant to doses of 105–110 Mrad, and p-terphenyl to doses not lower than 170 Mrad.

5. Radiation Resistance of Inorganic Composite Scintillators

As was indicated above, the organic scintillators are not radiation-resistant materials under irradiation even to the dose $D \approx 10$ Mrad. Therefore, we decided to study the composite scintillators on the basis of grains of inorganic single crystals $Gd_2SiO_5:Ce$ (GSO), $Gd_2Si_2O_7:Ce$ (GPS), $Al_2O_3:Ti$, $Y_2SiO_5:Ce$ (YSO), and $Y_3Al_5O_{12}:Ce$ (YAG).

5.1. GSO- and GPS-based composite scintillators

The light yield of GSO single crystals is conventionally estimated as 8000–12000 photon/MeV (the light yield ratio between GSO and NaI(Tl) single crystals falls within the limits from 0.2 to 0.25). The light yield of GPS single crystals equals 30000–40000 photon/MeV [8]. The light yield of the composite scintillators on the basis of GSO and GPS grains with respect to that of single crystals with the same chemical composition amounts to about 90% and 60%, respectively. The decay time for the composite scintillators amounts to 40–45 ns [20]. According to the results obtained by M. Tanaka *et al.* in work [21], GSO single crystals can be activated. The activation of GSO and GPS is a very interesting problem. Nevertheless, this is not an uneasy problem. It consists of several parts, depending on the type of irradiation (charged particles, neutrons), concentrations of Ce, which can be activated by charged particles, and so forth. Hence, this problem has to be studied separately and carefully.

Luminescence excitation maxima for the composite scintillators on the basis of GSO and GPS grains are located in the intervals $\lambda \approx 360\div390$ nm and $\lambda \approx 360\div380$ nm, respectively. The wavelengths of luminescence maxima for GSO and GPS crystals amount to 440 and 395 nm, respectively [22]. The photoluminescence spectra for the composite scintillators containing GSO or GPS grains did not vary before and after the irradiation. This result testifies that, unlike the composite scintillators on the basis of organic grains [13], new luminescence centers do not appear in the scintillators on the basis of GSO and GPS grains after the irradiation.

Figure 6 demonstrates, as an example, the optical transmittance spectra obtained for the composite scintillators 4 mm in thickness on the basis of GSO grains and measured before and after their ir-

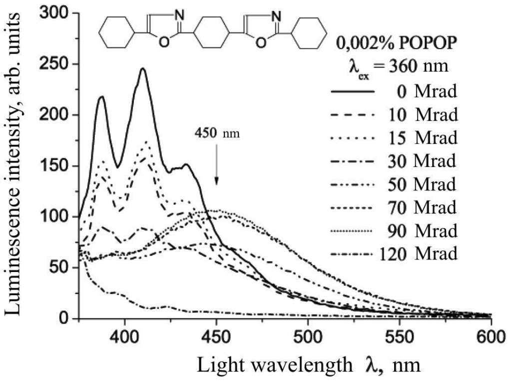

Fig. 4. Luminescence spectra of samples obtained by introducing POPOP molecules in a concentration of 0.002% into Sylgard-184 and subjected to various irradiation doses D. Excitation was carried out at a light wavelength of 360 nm

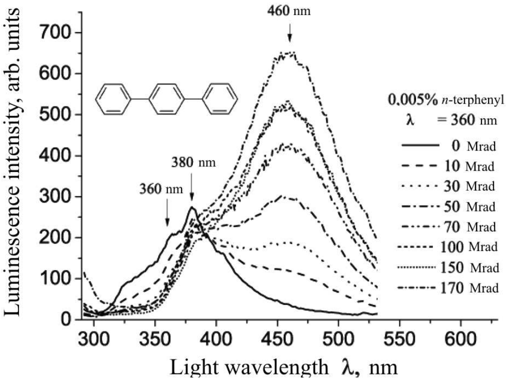

Fig. 5. Luminescence spectra of samples obtained by introducing p-terphenyl molecules in a concentration of 0.005% into Sylgard-184 and subjected to various irradiation doses D. Excitation was carried out at a light wavelength of 280 nm

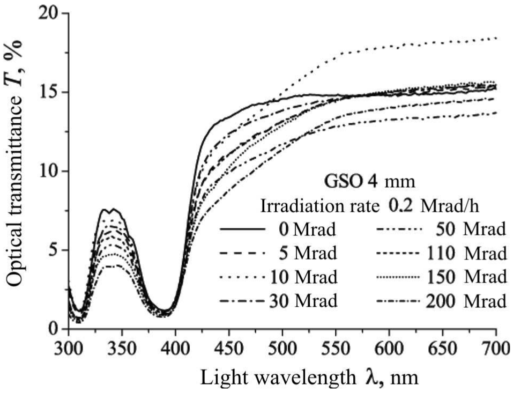

Fig. 6. Optical transmission coefficient T for a composite scintillator 17 mm in diameter and 4 mm in height containing GSO grains before ($D = 0$) and after the irradiation at a dose rate of 0.2 Mrad/h

radiation. The $T(\lambda)$ dependences at $\lambda < 440$ nm (GSO) or $\lambda < 395$ nm (GPS) practically reproduce the shape of the same dependence for the pure gel-composition. Those values correspond to the low-transparency band of the gel-composition, in which the value of T grows with λ until the saturation. For the transmission band of the pure gel-composition ($\lambda \geq 390$ nm), the value of T is close to 80–90% [17]. However, the transmittance dependences have not only one minimum of T at $\lambda \approx 310$ nm (this is the absorption maximum of the gel-composition [17]), but also minima in a vicinity of $\lambda \approx 360 \div 380$ nm (absorption for GPS grains) or $\lambda \approx 360 \div 390$ nm (absorption for GSO grains). Scintillation light mainly propagates within the wavelength interval near $\lambda \approx 440$ nm (GSO) or $\lambda \approx 395$ nm (GPS), where, as was said above, the matrix has an optical transmittance of about 80–90%.

At a dose rate of 0.2 Mrad/h and the light wavelengths $\lambda \geq 440$ nm (for GSO) or $\lambda \geq 395$ nm (for GPS), the optical transmission coefficient T decreases less than twice even after the irradiation to the dose $D = 200$ Mrad. For example, at $\lambda = 500$ nm, which corresponds to the transmission band of pure gel-compositions, the T-values for a single-layer scintillator and a scintillator 4 mm in thickness, which both contain GSO grains, equal 33–51% and 11–15% or, equivalently, $42 \pm 9\%$ and $13 \pm 2\%$, respectively. For GSO and at an dose rate of 1500 Mrad/h, the values of T at $\lambda = 500$ nm for a single-layer scintillator and a scintillators 4 mm in height equal 30–48% and 11–15% or $39 \pm 9\%$ and $13 \pm 2\%$, respectively. At the same time, for the scintillators containing GPS grains and irradiated at a rate of 0.2 Mrad/h, the values of T (also at $\lambda = 500$ nm) for a single-layer scintillator and a scintillator 4 mm in height equal 39–52% and 11–17% or, equivalently, $45.5 \pm 6.5\%$ and $15 \pm 4\%$, respectively.

Table 1. **Relative light yield L_{rel} for the composite scintillators on the basis of GSO grains at the dose D (Mrad) after the irradiation at a dose rate of 1500 Mrad/h**

D	L_{rel1}	Δ_1	L_{rel2}	Δ_2
0	1.00	0.05	1.00	0.05
5	1.00	0.05	0.79	0.04
10	1.03	0.05	0.8	0.04
15	1.03	0.05	–	–
20	1.00	0.05	–	–
30	0.98	0.05	0.62	0.03
50	1.00	0.05	0.67	0.03
70	1.03	0.05	0.62	0.03
90	0.97	0.05	0.65	0.03
100	0.97	0.05	0.66	0.03
110	0.94	0.05	0.66	0.03
130	0.92	0.05	0.63	0.03
150	0.88	0.04	0.65	0.03
160	0.88	0.04	0.62	0.03
170	0.90	0.05	0.61	0.03
200	0.92	0.05	0.55	0.03
225	0.92	0.05	0.60	0.03
250	0.94	0.05	0.46	0.02

L_{rel1} and L_{rel2} are the relative light yields of a single-layer composite, scintillator, and a composite scintillator 4 mm in height, respectively, on the basis of GSO grains GSO grains (in rel. units); Δ_1 and Δ_2 are errors for L_{rel1} and L_{rel2}, respectively (in %).

The measurement results obtained for the relative light yield L_{rel} of the composite scintillators on the basis of GSO and GPS grains grains before and after the irradiation are quoted in Tables 1 and 2. The value of the light yield before the irradiation was selected as a reference.

According to the data in Tables 1 and 2, the value of L_{rel} is not changed substantially with the dose growth up to $D = 200$ Mrad. This fact testifies to a high radiation resistance of the composite scintillators on the basis of GSO and GPS grains.

The values measured for the relative light yield L_{rel} and quoted in Tables 1 and 2 demonstrate that the composite scintillators on the basis of GSO and GPS grains are radiation-resistant to doses not less than 250 and 200 Mrad, respectively, at dose rate of 1500 and 0.2 Mrad/h, respectively.

Tables 1 and 2 also show that, after the irradiation at a rate of 1500 or 0.2 Mrad/h, the relative light yield $L_{\mathrm{rel}} > 0.5$. According to Table 1, the average value of L_{rel} has a weak tendency to decrease with an increase of the exposure dose D for the composite scintillators with GSO and GPS grains. This circumstance proves that, as the dose D grows, the effect of irreversible damage to luminescence centers becomes more and more important, and L_{rel} can be lower than 0.5 for higher doses ($D > 250$ Mrad). Table 2 shows that the data obtained for a dose rate of 0.2 Mrad/h have a wider spread of L_{rel}-values than for a dose rate of 1500 Mrad/h. Therefore, the composite scintillators on the basis of GSO or GPS grains are radiation-resistant. Our results prove this statement for $D \geq 200$ Mrad (at a dose rate of 0.2 Mrad/h) and $D \geq 250$ Mrad (at a dose rate of 1500 Mrad/h), respectively.

From Tables 1 and 2, one can see that the values of the relative light yield L_{rel} may fluctuate with the growth of the dose D. This behavior correlates with the results obtained for the optical transmittance T and described above. Such fluctuations may arise because the radioluminescence of a scintillator, whose luminescence centers are damaged by the irradiation, cannot be described by a monotonically decreasing function, since the properties of a scintillation material after its irradiation are changed not only owing to the irreversible destruction of its matrix substance, but also under the influence of other factors emerging as a result of the irradiation. Proceeding from the importance of this issue for the understanding of the mechanisms governing the radiation resistance of scintillators, we will consider it separately in Section 6 devoted to a comparative analysis of the characteristics of the composite scintillators containing grains of various single crystals.

5.2. Al_2O_3:Ti-based composite scintillators

Crystals on the basis of Al_2O_3 doped with Ce, Pb, Ca, Tl, Ti, and so forth are widely used, as modern laser materials, in thermoluminescent researches and radiation protection dosimetry; they were also proposed to be used in methods aimed at revealing the Dark Matter; and so on [23–33]. The light yield of a Ti-activated crystal approximately amounts to 0.3 times the light yield of a CsI:Tl single crystal. The decay time of the luminescence in Ti-activated crystals equals about 3.4 μs [30].

According to the results of work [33], $Al_2O_3:Ti$ crystals have a wide absorption band with a maximum at $\lambda = 490$ nm and a strong absorption in the UV interval near 300 nm with a shoulder of 240 nm, which is associated with Ti^{3+}-Ti^{4+} pairs (see below). The authors of work [33] reported that the light excitation at the wavelength $\lambda_{\mathrm{ex}} = 232$ nm (or 266 nm) stimulates the photoluminescence in the spectral interval $\lambda = 400 \div 410$ nm. The maxima in the spectra of this photoluminescence may correspond to the light wavelengths $\lambda_{\max} = 420$ [23,26,29], 425 [24, 25], and 430 nm [27, 28, 31]. This luminescence is generated by the centers containing Ti^{4+} ions, i.e. when a Ti^{3+} Ti gives up one (the Ti^{4+}-F^+ center) or two (the Ti^{4+}-F center) electrons to an oxygen vacancy. The luminescence associated with defects in $Al_2O_3:Ti$ crystals is often called "blue-band luminescence" [29, 31]. Ti^{3+} ions provide the near-infra-red (IR) luminescence in a spectral interval of 650–800 nm with a maximum close to 750 nm [23–25,30–33]. As a rule, this is a result of the ${}^2E_2 \rightarrow {}^2T_2$ transition [31,33].

The excitation of the composite scintillators on the basis of $Al_2O_3:Ti$ grains by light with $\lambda_{\mathrm{ex}} \approx$ ≈ 490 nm stimulates the luminescence at the wavelength $\lambda_{\max} = 725$ nm (luminescence of Ti^{3+} ions) [34]. The irradiation of the composite scintillators containing $Al_2O_3:Ti$ grains on a linear accelerator did not result in a variation of photoluminescence spectra in a band of 725 nm. At the same time, a substantial change of photoluminescence spectra in the blue band (310–600 nm) was observed at the excitation by light with a wavelength of 230 or 260 nm. Let us consider this case in more details.

Table 2. **Relative light yield L_{rel} for the composite scintillators on the basis of GSO and GPS grains at the dose D (Mrad) after the irradiation at a dose rate of 0.2 Mrad/h**

D	L_{rel1}	Δ_1	L_{rel2}	Δ_2	L_{rel3}	Δ_3	L_{rel4}	Δ_4
0	1.00	0.05	1.00	0.05	1.00	0.05	1.00	0.05
5	1.00	0.05	1.01	0.05	0.75	0.04	0.78	0.04
10	0.94	0.05	1.05	0.05	0.63	0.03	0.92	0.05
15	1.00	0.05	1.00	0.05	0.53	0.03	0.67	0.03
20	0.94	0.05	1.04	0.05	0.48	0.02	0.63	0.03
30	1.02	0.05	0.82	0.04	0.88	0.04	0.78	0.04
35	0.92	0.05	0.87	0.04	0.78	0.04	0.74	0.04
50	1.31	0.07	0.8	0.04	1.05	0.05	0.76	0.04
75	1.10	0.06	0.96	0.05	0.91	0.05	0.73	0.04
90	–	–	0.95	0.05	0.95	0.05	0.67	0.03
110	1.16	0.06	0.83	0.04	0.95	0.05	0.73	0.04
130	–	–	0.83	0.04	0.92	0.05	0.92	0.05
150	1.00	0.05	0.97	0.05	0.80	0.04	0.84	0.04
175	–	–	0.69	0.04	0.83	0.04	0.46	0.02
200	0.96	0.05	0.51	0.03	0.80	0.04	0.52	0.03

L_{rel1} and L_{rel2} are the relative light yields of a single-layer composite, scintillator, and a composite scintillator 4 mm in height, respectively, on the basis of GSO grains (in rel. units); L_{rel3} and L_{rel4} are the relative light yields of a single-layer composite scintillator and a composite scintillator 4 mm in height, respectively, on the basis of GPS grains (in rel. units); Δ_1, Δ_2, Δ_3, and Δ_4 are the relative errors for L_{rel1}, L_{rel2}, L_{rel3}, and L_{rel4}, respectively (in %).

The luminescence peak at $\lambda = 425$ nm, which can be observed in the spectra of $Al_2O_3:Ti$ single crystal, is absent for the composite scintillators. The luminescence with a maximum at $\lambda = 425$ nm is usually associated with the luminescence of Ti^{4+} ions [23, 29, 31, 33]. Therefore, this fact may mean that, when the single crystal is crushed and, hence, deformed, a transition from Ti^{4+} to Ti^{3+} can take place.

For the scintillators irradiated at a dose rate of 1500 Mrad/h, the following results were obtained. In a spectral interval of 310–350 nm, when the irradiation dose D grows, the luminescence intensity increases, if $D \leq 350$ Mrad, decreases, if 350 Mrad $\leq$ $\leq D \leq 450$ Mrad, and increases again, if 450 Mrad $\leq$ $\leq D \leq 550$ Mrad.

In a spectral interval of 380–500 nm, the situation is changed. At $D \leq 350$ Mrad, the intensity of the composite scintillator luminescence considerably increases with D and reaches the luminescence level of a single crystal. For doses 350 Mrad $\leq D \leq$ ≤ 550 Mrad, the luminescence intensity decreases with the growth of D to the luminescence intensity for a non-irradiated specimen.

In a spectral range of 500–600 nm, the luminescence intensity decreases (at $D \leq 350$ Mrad) and then increases (at 350 Mrad $\leq D \leq 550$ Mrad) with the growth of D. In the IR interval, the luminescence intensity first increases with the growth of D to $D = 450$ Mrad and then falls down.

At the irradiation of scintillators at a dose rate of 0.2 Mrad/h, the following results were obtained. The luminescence intensity within an interval of 310–350 nm was found to fluctuate with the growth of D. In an interval of 380–500 nm ($\lambda_{\max} = 455$ nm), the luminescence intensity increases by several times, as the accumulated dose D grows, and approaches the luminescence intensity of a single crystal. In the 500–600-nm and IR-intervals, the luminescence intensity decreases with the growth of D.

Hence, no monotonic dependence on the accumulated dose D is observed in a spectral interval of 300–800 nm at an dose rate of 1500 or 0.2 Mrad/h. The following fact is a common feature of the dependences for both radiation doses. The luminescence intensity in the blue luminescence band drastically increases firstly, as the dose D grows, but afterward, it ceases to grow or even considerably decreases. This luminescence is associated with centers containing Ti^{4+} ions. With the growth of D, the luminescence intensity in the IR interval firstly falls down and afterward insignificantly increases. The luminescence is provided by Ti^{3+} ions.

The only plausible explanation for all that is as follows. At low D-values, the formation of centers containing Ti^{4+} ions that arise at the ionization of Ti^{3+} ones dominates. As a result, the concentration of those centers increases, and the probability of a direct irradiation action on them also increases. In other words, the growth of the dose D gives rise not only to an increase of the ionization probability for Ti^{3+} ions, but also to an increase of the destruction probability for the centers containing Ti^{4+} ions. The irradiation can stimulate the transition between Ti^{3+} and Ti^{4+} ions and, at large irradiation doses, also the reverse transition from Ti^{4+} to Ti^{3+}.

In the interval $\lambda \geq 400$ nm corresponding to the transparency interval of a gel-composition and the luminescence interval of $Al_2O_3:Ti$, the value of the optical light transmittance T was not changed more than twice, even after the irradiation to a dose of 550 Mrad. The optical transmittance for the composite scintillators containing $Al_2O_3:Ti$ grains, as well as for scintillators on the basis of GSO and GPS grains, reveals stochastic fluctuations caused by modifications in the properties of a scintillation material under the irradiation. For instance, in the radioluminescence interval $\lambda = 725$ nm, the optical transmittance of a single-layer scintillator $Al_2O_3:Ti$ at dose rates of 1500 and 0.2 Mrad/h amounts to 46–63% and 45–60%, respectively or, equivalently, $54.5\pm8.5\%$ and $52.5 \pm 7.5\%$, respectively.

The dependence $T(\lambda)$ at $\lambda < 390$ nm is similar to that typical of the gel-composition with a minimum at $\lambda \approx 310$ nm. However, this minimum is not unique for this dependence; there is also a minimum in a band of 480–500 nm, which emerges owing to the absorption of Ti^{3+} ions in the crystals or $Al_2O_3:Ti$ grains.

In work [34], the light yield of an $Al_2O_3:Ti$ single crystal 1.5 mm in thickness, which we used as a reference scintillator, amounted to about 900 photon/MeV. For the composite scintillators containing $Al_2O_3:Ti$ grains 0.3–0.5, 0.5–1.0, and 1.5–2.0 mm in size, the light yields amounted to 670, 690, and 620 photon/MeV, respectively, before the irradiation.

The results of measurements of the relative light yield $L_{\rm rel}$ for the composite scintillators on the basis of $Al_2O_3:Ti$ grains obtained before and after the irradiation at dose rates of 1500 and 0.2 Mrad/h are quoted in Tables 3 and 4, respectively. According to the tabulated data, the composite scintillators satisfy the requirements to radiation-resistant scintillators, because their relative light yield $L_{\rm rel}$ is not changed substantially ($L_{\rm rel} > 0.5$) with the growth of D to $D = 550$ and 125 Mrad at dose rates of 1500 and 0.2 Mrad/h, respectively. The tables also demonstrate that the average value of $L_{\rm rel}$ has a weak tendency to decreasing with the growth of the accumulated dose D for the composite scintillators with $\mathrm{Al_2O_3:Ti}$ grains. The decrease of $L_{\rm rel}$ with the increase of D testifies that the damaging effect to luminescence centers in grains increases under the irradiation. Table 3 definitely shows that $L_{\rm rel}$ can be lower than 0.5 at higher doses ($D > 550$ Mrad). In Table 4, it is shown that the data obtained at a dose rate of 0.2 Mrad/h demonstrate a faster reduction of the $L_{\rm rel}$-value in comparison with the data obtained at a dose rate of 1500 Mrad/h.

Table 3. **Relative light yield $L_{\rm rel}$ for the composite scintillators on the basis of grains at the dose D (Mrad) after the irradiation at a dose rate of irradiation at a dose rate of 1500 Mrad/h**

D	$L_{\rm rel1}$	Δ_1	$L_{\rm rel2}$	Δ_2	$L_{\rm rel3}$	Δ_3
0	1.00	0.05	1.00	0.05	1.00	0.05
5	1.00	0.05	1.01	0.05	1.00	0.05
10	0.95	0.05	0.97	0.05	0.96	0.05
20	1.02	0.05	0.97	0.05	1.08	0.05
30	0.96	0.05	0.97	0.05	0.99	0.05
70	0.71	0.04	0.79	0.04	0.71	0.04
100	0.88	0.04	0.87	0.04	0.94	0.05
110	0.91	0.05	0.95	0.05	0.94	0.05
120	1.01	0.05	0.88	0.04	0.77	0.04
140	0.81	0.04	0.83	0.04	1.05	0.05
170	0.77	0.04	0.80	0.04	0.90	0.05
180	0.99	0.05	0.83	0.04	0.73	0.04
190	0.51	0.03	0.76	0.04	0.82	0.04
200	0.74	0.04	0.75	0.04	0.72	0.04
230	0.74	0.04	0.77	0.04	0.73	0.04
250	0.70	0.04	0.70	0.04	0.84	0.04
280	0.91	0.05	0.80	0.04	0.67	0.03
300	0.70	0.04	0.76	0.04	0.76	0.04
350	0.73	0.04	0.72	0.04	0.74	0.04
400	0.71	0.04	0.70	0.04	0.74	0.04
450	0.67	0.03	0.49	0.02	0.64	0.03
500	0.57	0.03	0.52	0.03	0.51	0.03
550	0.50	0.03	0.52	0.03	0.59	0.03

$L_{\rm rel1}$, $L_{\rm rel2}$, and $L_{\rm rel3}$ are the relative light yields of a single-layer composite scintillator on the basis of $\mathrm{Al_2O_3:Ti}$ grains 0.3–0.5, 0.5–1.0, and 1.5–2.0 mm in size, respectively (in rel. units); Δ_1, Δ_2, and Δ_3 are the relative errors for $L_{\rm rel1}$, $L_{\rm rel2}$, and $L_{\rm rel3}$ (in %).

The research results quoted in Tables 3 and 4 show that the relative light yield $L_{\rm rel}$ can fluctuate with the growth of D. Those results reproduce the results obtained for the scintillators on the basis of GSO and GPS grains. Processes which can be responsible for this effect will be considered in Section 6.

5.3. YSO- and YAG-based composite scintillators

The light yield of an YSO single crystal is taken to equal 9200–10000 photon/MeV. The decay time for YSO single crystals amounts to 42 ns [35]. The light yield of an YAG single crystal is taken to equal 9000–11000 photon/MeV. The decay time for YAG single crystals amounts to 120 ns [36].

Luminescence excitation maxima for the composite scintillators on the basis of YSO and YAG grains are located in wavelength intervals of 340–360 and 440–460 nm, respectively. The wavelengths at the luminescence maximum for the YSO and YAG composite scintillators amount to 415 and 535 nm, respectively [37]. Photoluminescence spectra for the composite scintillators containing YSO or YAG grains did not change their shape before and after the irradiation. The result obtained testifies that no new luminescence centers appeared under the irradiation.

Table 4. **Relative light yield $L_{\rm rel}$ for the composite scintillators on the basis of grains at the dose D (Mrad) after the irradiation at a dose rate of irradiation at a dose rate of 0.2 Mrad/h**

D	$L_{\rm rel1}$	Δ_1	$L_{\rm rel2}$	Δ_2	$L_{\rm rel3}$	Δ_3
0	1.00	0.05	1.00	0.05	1.00	0.05
5	0.70	0.04	0.64	0.03	0.68	0.03
10	0.49	0.02	1.05	0.05	1.21	0.06
15	0.96	0.05	1.05	0.05	1.15	0.06
50	0.51	0.03	0.53	0.03	0.55	0.03
70	0.62	0.03	0.60	0.03	0.65	0.03
100	0.51	0.03	0.56	0.03	0.63	0.03
125	0.60	0.03	0.60	0.03	0.69	0.03

$L_{\rm rel1}$, $L_{\rm rel2}$, and $L_{\rm rel3}$ are the relative light yields of a single-layer composite scintillator on the basis of $\mathrm{Al_2O_3:Ti}$ grains 0.3–0.5, 0.5–1.0, and 1.5–2.0 mm in size, respectively (in rel. units); Δ_1, Δ_2, and Δ_3 are the relative errors for $L_{\rm rel1}$, $L_{\rm rel2}$, and $L_{\rm rel3}$ (in %).

The optical transmission coefficient for the composite scintillators on the basis of YSO and YAG grains at least 4 mm in height, for doses up to $D = 150$ Mrad and at a dose rate of 1500 Mrad/h, amounts to 9–13% (i.e. 11 ± 2%) for YSO in its luminescence interval $\lambda = 415$ nm and to 11–13% (i.e. 12 ± 1%) for YAG in its luminescence interval $\lambda = 535$ nm.

In Table 5, the results of measurements of the relative light yield L_{rel} obtained for the composite scintillators on the basis of YSO and YAG grains before and after the irradiation at a dose rate of 1500 Mrad/h are quoted. One can see that L_{rel} changes by less than two times with the growth of the accumulated dose D. This fact makes it possible to claim about a high radiation stability of the composite scintillators on the basis of Y_2SiO_5:Ce and $Y_3Al_5O_{12}$:Ce grains. These composite scintillators are radiation-resistant to doses not lower than 150 Mrad at a dose rate of 1500 Mrad/h. Similarly to the composite scintillators considered above, no monotonic dependence of L_{rel} on the accumulated dose D was observed.

6. Possible Mechanisms of Radiation-Induced Damage to Scintillators

As one can see from Tables 1 to 5, the values of the relative light yield L_{rel} can fluctuate with the growth of D. These fluctuations have a stochastic component and mimic the behavior of the optical transmittance T. Such fluctuations can emerge owing to the fact that radioluminescence of a scintillator, whose luminescence centers are damaged by the irradiation, cannot be described by a monotonically decreasing function, because the parameters of a scintillation material after the irradiation change not only as a result to an irreversible damage to its matrix, but also under the influence of secondary factors arising due to the irradiation.

Table 5. **Relative light yield L_{rel} for the composite scintillators on the basis of YSO and YAG grains at the dose D (Mrad) after the irradiation at a dose rate of 1500 Mrad/h**

D	L_{rel1}	Δ_1	L_{rel2}	Δ_2
0	1.00	0.05	1.00	0.05
50	1.06	0.05	0.87	0.04
100	1.15	0.06	0.86	0.04
150	1.11	0.06	0.85	0.04

L_{rel1} and L_{rel2} are the relative light yields for the composite scintillator on the basis of YSO and YAG grains, respectively, (rel. un.); Δ_1 and Δ_2 are the absolute values of errors for L_{rel1} and L_{rel2}, respectively, in percents of the relative light yield.

Therefore, each of the dependences of the relative light yield L_{rel}, the optical transmittance T, and others on the irradiation dose D has to include a stochastic component. Such stochastic components may originate from the material activation, modification of luminescence centers, change of the decay efficiency of impurity centers and ions, and short-term damage of luminescence centers in grains with their further quick restoration. Certainly, the ability of the material to restore its parameters after the irradiation will permanently decrease, as the dose D increases, because the restoration will not always keep pace with the damage of luminescence centers in grains, when the dose becomes more considerable. This means that, for a true radiation-resistant scintillator with very rapid efficient restoration at higher doses D, the relative light yield L_{rel} and the light transmittance T must slowly decrease with the growth of the accumulated dose D.

Let us consider two possible processes. In the first case, all scintillation materials contain defects, impurity ions, molecules, and others, which can create levels in the crystal energy spectrum that correspond to decay centers. The irradiation destroys and changes not only the matrix, but the decay centers as well. As a result, the luminescence intensity may grow for a while because of a decrease in the luminescence decay efficiency in grains. A characteristic feature of this process consists in that, so long as the scintillator is luminescent, the luminescence spectrum is not changed irrespective of the D-value, because new luminescence centers do not appear.

The alternative process has a different origin. Let molecules, ions, and so forth belonging to primary luminescence centers of type A are damaged by the irradiation, so that centers of type B emerge. If the latter are new luminescence centers with a light yield higher than that for A-centers, the luminescence intensity of the scintillator grows after the irradiation during the B-center existence time and should decrease afterward [13]. The processes of this type include those, for which both direct and reverse irradiation-induced transitions between the main centers and the radiation-induced ones are possible.

Hence, there are two possible scenarios for the development of processes after the irradiation, which can be responsible for the stochastic component of luminescence intensity fluctuations. In the first case, the luminescence spectrum of a scintillator does not change its shape for various doses D, because new luminescence centers are absent. The alternative process is governed by a change of luminescence centers under the irradiation and should give rise to the variation of luminescence spectral characteristics.

In the examples presented above, only one of those processes was observed under the action of ionizing radiation, and this process is characteristic of a specific material. For organic scintillators, changes in their luminescence spectra are observed, and those systems are relatively not radiation-resistant (to 0.5 Mrad for organic crystals [13], 10 Mrad for plastic scintillators [13, 16, 19], and 30 Mrad for scintillators on the basis polydimethyl-co-diphenylsiloxane and polymethylphenyl-co-methylhydrosiloxane [16]). However, if ultralow concentrations of organic luminophore molecules are introduced into those materials, their radiation resistance increases; in particular, in the case of POPOP, to 105–110 Mrad and, in the case of p-terphenyl, to not lower than 170 Mrad). At the same time, for inorganic scintillators, the variation of their luminescence spectra can be either observed ($Al_2O_3:Ti$) or not (GSO, GPS, YSO, YAG). Let us consider each case separately.

In organic scintillators, the luminescence spectrum can be shifted, because those systems contain benzene rings (they are responsible for the luminescence). Under the ionizing radiation, those rings are destroyed. The probability of their restoration is low. This process worsens the optical properties of the matrix. At the same time, however, a new organic molecule luminescent in another spectral interval can be formed.

Under the irradiation, the composite scintillators on the basis of inorganic $Al_2O_3:Ti$ grains change the shape of their luminescence spectra. At a dose rate of 1500 or 0.2 Mrad/h, no monotonic dependence on the accumulated dose D is observed in the luminescence spectral interval (300–800 nm). At the same time, in the blue luminescence band, the luminescence intensity firstly drastically increases with D and, afterward, saturates or even considerably decreases. This luminescence is associated with centers containing Ti^{4+} ions. As the dose D increases, the luminescence intensity in the IR interval (this luminescence is associated with centers containing Ti^{3+} ions) firstly decreases and, afterward, either slightly increases or its reduction is slowed down.

Those facts bring us to a conclusion that, at low D-values, the formation of centers containing Ti^{4+} ions, which arise at the ionization of Ti^{3+} ones, is a dominating process. Thus, the concentration of centers containing Ti^{4+} ions grows, and the probability of a direct action of the irradiation on those centers increases. Higher D-doses increase the probability of the Ti^{3+} ionization. The probability of the destruction for the centers containing Ti^{4+} ions also increases. Under the irradiation, the latter process can give rise to the reverse transition from Ti^{4+} to Ti^{3+}.

For $Al_2O_3:Ti$-based composite scintillators under the ionizing radiation, not only a modification of the spectral characteristics, but also other processes associated with the destruction of luminescence centers can be observed.

For the composite scintillators on the basis of inorganic GSO, GPS, YSO, and YAG grains, the other scenario is realized. The luminescence spectrum of those systems is not changed with D. The luminescence grows, only if the decay centers are regenerated. As a result, after this time interval, the luminescence intensity should diminish through the restoration of the decay efficiency. The energy levels of those centers are located in the forbidden gap of the energy spectrum of single-crystalline grains. Hence, it is those centers that mainly affect the transmission coefficient T. The modification of luminescence parameters is caused by a radiation-induced damage to grains of a scintillation material. However, the self-restoration accompanies all processes. As a result, we obtain a complicated variation of scintillator properties.

Hence, as was marked above, the variation of the relative light yield L_{rel} that arises at the irradiation to various doses D should have a stochastic component. This component emerges as a result of changes in the decay efficiency for impurity centers and ions, as well as due to the temporary damage to the luminescence centers in grains with their further rapid restoration. At higher doses, when the parameter D grows, the radiation resistance of the material will gradually decrease against the background of stochastic fluctuations associated with secondary processes, until the damage effect for luminescence centers becomes a restrictive factor, and the processes of granule restoration cannot save the situation any more.

The composite scintillators on the basis ofs GSO and GPS granule demonstrate that, after the irradiation at dose rates of 1500 and 0.2 Mrad/h, the relative light yield $L_{\mathrm{rel}} > 0.5$. The corresponding average L_{rel}-value has a weak tendency to decrease with the growth of the dose D for the composite scintillators with both GSO and GPS grains. This fact proves that, with the growth of D, the damage effect to luminescence centers becomes more and more important, and, at higher doses ($D > 250$ Mrad), L_{rel} can be lower than 0.5. The data obtained at a dose rate of 0.2 Mrad/h have a larger spread of L_{rel}-values than for a dose rate of 1500 Mrad/h. Hence, the composite scintillators on the basis of GSO or GPS grains are radiation-resistant. The results obtained for $D \geq 200$ Mrad (at a dose rate of 0.2 Mrad/h) and $D \geq 250$ Mrad (at a dose rate of 1500 Mrad/h) confirm this statement.

Proceeding from the aforesaid, it is impossible to determine at once, which of the mechanisms will be observed in that or another scintillator. This issue has to be analyzed in every separate case. At the same time, the criterion associated with modifications in the luminescence spectrum shape or its invariance with the growth of D can be taken as proved.

7. Conclusions

To summarize, the following results have been obtained, while studying the radiation resistance of composite scintillators:

- the on the basis of grains of organic single crystals are not not radiation-resistant to a dose of 1 Mrad;
- the scintillators on the basis of GSO: Ce and GPS: Ce grains are are radiation-resistant to doses not lower than 250 Mrad;
- the scintillators on the basis of $Al_2O_3:Ti$ grains are grains are radiation-resistant to doses not lower than 550 Mrad;
- the scintillators on the basis of YSO: Ce and YAG: Ce grains are are radiation-resistant to doses not lower than 150 Mrad.

The introduction of POPOP and *p*-terphenyl in ultralow concentrations into Sylgard-184 showed that it is possible to obtain radiation-resistant materials with a shift of the luminescence spectrum in gel-compositions. Those materials can be used for the creation of light guides. They are radiation-resistant to doses not lower than 110–170 Mrad.

Possible processes of radiation-induced changes arising in scintillators under the irradiation and their mechanisms are proposed and studied. The influence of those processes on the radiation resistance is analyzed. All crystalline scintillation materials contain defects, which can play the role of either luminescence or decay centers. The irradiation destroys and changes not only the matrix, but those centers as well. As a result, the luminescence intensity can grow for a while. In this case, the luminescence spectrum of a scintillator does not change its shape under various doses D, because no new luminescence centers are generated. Another process is associated with the change of luminescence centers. It should result in a modification of the luminescence spectral characteristics.

For organic scintillators, the irradiation-induced changes manifest themselves in a modification of the luminescence spectral parameters. In the composite scintillators containing grains of inorganic crystals, the variation of luminescence spectral characteristics either can ($Al_2O_3:Ti$) or cannot (GSO : Ce, GPS : Ce, YSO : Ce, and YAG : Ce) take place. Therefore, in order to identify the possible processes giving rise to radiation-induced changes in scintillators, it makes sense to carry out such spectral researches before and after the irradiation.

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КОМПОЗИЦІЙНІ СЦИНТИЛЯТОРИ ТА ОСОБЛИВОСТІ ЇХ РАДІАЦІЙНОЇ СТІЙКОСТІ

Резюме

У даний час композиційні сцинтилятори знаходять застосування для вирішення все більш широкого кола задач детектування іонізуючих випромінювань, адже композиційні сцинтилятори мають низку переваг у порівнянні з іншими сцинтиляційними матеріалами. З виникненням нової генерації прискорювачів, радіаційні навантаження на детектори в цих прискорювачах суттєво збільшились. Це зумовлює особливу важливість пошуку нових радіаційно-стійких сцинтиляційних матеріалів. Нами було запропоновано використовувати композиційні сцинтилятори, як радіаційностійкі матеріали. Найбільш важливим є те, що після опромінення характеристики сцинтиляційного матеріалу можуть суттєво змінюватися. Метою цієї роботи було вивчення особливостей можливих радіаційних руйнувань та перетворень у композиційних сцинтиляторах під дією іонізуючого випромінювання. Проведено порівняльний аналіз відносного світлового виходу, прозорості і спектрів люмінесценції в залежності від накопиченої дози для композиційних сцинтиляторів, що містять гранули органічних або неорганічних монокристалів (Gd_2SiO_5 : Ce (GSO), $Gd_2Si_2O_7$: Ce (GPS), Al_2O_3 : Ti, Y_2SiO_5 : Ce (YSO) та $Y_3Al_5O_{12}$: Ce (YAG)). В роботі було досліджено та запропоновано можливі механізми і процеси радіаційних змін, які виникають в сцинтиляторах внаслідок опромінення, оскільки вони впливають на радіаційну стійкість композиційних сцинтиляторів.