

Radiation Resistance of Composite Scintillators Based on Grains of Oxide Single Crystals

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A large number of experiments carried out at charged particle accelerators indicate that the radiation dose accumulated by the scintillation materials contained in detectors is significant. For example, in experiments at the Large Hadron Collider, the radiation dose in scintillation detectors can reach 10 Mrad and will increase in the future. In this connection, the search for new radiation-resistant scintillation materials is especially important. Irradiation can significantly alter the characteristics of the scintillator material. The aim of this work was to study the features of possible radiation damage and transformations in composite scintillators under the action of ionizing radiation. We focused on composite scintillators, which are transparent non-luminescent gel-compositions containing grains of scintillation oxide single crystals. A comparative analysis of the spectra of the relative light yield, transmission, and luminescence, as well as their dependence on the accumulated dose for various composite scintillators, has been carried out. Possible mechanisms of radiation changes occurring in scintillators under irradiation are proposed and the influence of these processes on the radiation resistant of composite scintillators is analyzed. In this work, as in previous works in this series, we irradiated composite scintillators on a linear electron accelerator. The electron energy was 10 MeV. We irradiated with a low (0.2 Mrad/h) and a high (1500 Mrad/h) dose rate. At low dose rate, cracking occurs at lower radiation dose values (about 100–200 Mrad) than under irradiation at a high dose rate (up to 500 Mrad). The luminescent characteristics of the scintillator changed insignificantly until the gel composition fixing single-crystal grains cracked. After destruction of the gel composition, an abrupt deterioration in the properties of the sample took place.

topics: oxide composite scintillation materials, radiation resistance

1. Introduction

It is no secret that radiation-resistant detectors are needed in many areas of physics. This need is especially acute in the rapidly developing high-energy physics. Experiments on particle accelerators have shown that the radiation dose D accumulated by the detectors and in the incoming scintillation materials is significant. For example, according to modernization plans (see, e.g. [1]) in experiments at the Large Hadron Collider (LHC), the dose of radiation in the scintillator detectors can reach 100 Mrad. Therefore, a search for new radiation-resistant scintillation materials is becomes actual.

Our experiments with organic single crystals, polycrystalline and composite scintillators, based on large grains of molecular single crystals have shown

that such scintillators are not radiation resistant even for doses of about 1 Mrad. Plastic scintillators reduce their signals by more than two times when the dose of irradiation is less than 10 Mrad [2]. It agrees with the data presented in [3, 4]. In our experiments, electrons and photons of braking radiation with initial energies up to 10 MeV [2] irradiate the samples.

In [4], Alberto Quaranta and his co-authors investigated scintillators on the base of mixing vinyl terminated polydimethyl-co-diphenylsiloxane with hydride terminated polymethylphenyl-co-methylhydrosiloxane. They have shown that such systems activated by molecules of some organic luminophors have higher radiation resistant than plastic scintillators based on standard matrices, such as polyvinyltoluene or polystyrene.

Perhaps the main possible drawback of the systems is the presence of benzene rings that tend to break when exposed to irradiation but have low possibility of self-recovery after that. This impairs the optical properties of the base material, while a base of a scintillator has to withstand the influence of large fluxes of ionizing radiation.

A base of a composite scintillator, unlike other scintillators, must not be a luminesce material. Radioluminescence takes place in scintillation grains which are inside this non-luminescent material. Due to this specificity of composite scintillators, we get a chance to make the first basic move towards the production of radiation-resistant scintillators. We supersede polysiloxanes containing benzene rings with polydimethylsiloxane which does not contain them. Since the base of our composite scintillators is non-luminescent, a change in its transparency can only influence the luminescence of the composite scintillator.

Composite scintillators have a number of advantages over other scintillation materials:

- A composite scintillation material is cheaper and easier in production than a single crystal. In a number of cases it is possible to pass a costly stage of a single crystal growth or to use up waste from the processing of single crystals. The major loss of the scintillation material that appears during machining is absent because machining is absent.
- It is possible to create an almost infinite area of scintillator. A specially prepared gel composition can agglutinate separate parts of the composition scintillator in one uniform sample [2].
- It is possible to vary both the size of grains and the thickness of a sample, therefore one can enhance the detection selectivity [5, 6].

We will use the classical definition of “radiation-resistant” scintillator by J. Birks [7]. Let $I(0)$ and $I(D_{\max})$ be the amplitudes of the scintillation signals before and after irradiation, respectively. A scintillator is considered radiation resistant up to a dose of D_{\max} if the following inequality holds

$$\frac{I(D_{\max})}{I(0)} \geq \frac{1}{2}. \quad (1)$$

Recently, we have developed a new type of scintillation material, namely composite and polycrystal. The first type of material is a non-scintillating gel composition containing grains of inorganic or organic single crystals. The latter type is polycrystalline organic scintillators hot-pressed sintered, i.e., Van der Waals ceramics. Unlike single crystals, plastics, and liquids, these materials are not continuous media but heterostructured ones.

This work is devoted to the development of radiation-resistant composite scintillators containing oxide crystal grains. Later in this paper, the results of measurements of the radiation resistant of some scintillators will be presented.

Composite scintillators containing oxide scintillation grains have higher D_{\max} values than other scintillation analogues. Later in this paper we will consider the features of the scintillation process in these objects and the mechanisms limiting D_{\max} .

2. Irradiation of samples

As in previous works [8–13], electrons with an energy of 10 MeV from the linear electron accelerator of the NSC “Kharkiv Institute of Physics and Technology” irradiated scintillators at room temperature. The degree of inhomogeneity of the dose rate over the sample surface did not exceed 5%. Plastic dosimeters Harwell Perpex 4034 and radiochromic film dosimeters FWT-60-00 determined the dose rate (for more details, see [14]). The measurement error was $\pm 5\%$. The dosimeters were limited to the maximum dose. We used a set of identical dosimeters. A single dosimeter accumulated a relatively small dose interval. By summing up the results of such successive measurements, we determined the integral dose D that the scintillator receives during irradiation. We irradiated scintillators with two dose rates, namely 0.2 ± 0.01 Mrad/h (mainly bremsstrahlung photons) and 1500 ± 5 Mrad/h (the electron beam directly scans the sample surface).

It is important to note that all D values considered refer to the absorbed radiation dose in the water equivalent of the irradiated material.

The process of irradiation of composite scintillators takes place in the surrounding atmosphere. As noted above, we irradiated scintillators with either a low (0.2 ± 0.01 Mrad/h) or high (1500 ± 5 Mrad/h) dose rate. In the first case, it was a flux, mainly of bremsstrahlung photons. In the latter case, the electron beam directly scanned the sample surface.

At a low dose rate, the accumulated dose D reached 100 Mrad in 500 h, i.e., in 20 days and 20 h. At a high dose rate, the accumulated dose D was 500 Mrad as a result of irradiation for 0.34 h (i.e., 20 min). At a high irradiation rate, the samples were on a conveyor belt that moved with a constant speed. The conveyor periodically moved the scintillators to the region of the electron beam. In one pass in front of the electron beam, which lasts 12 s, the sample received the dose of about 5 Mrad. In this case, the sample was heated quickly. One pass of the conveyor with return to the same point lasted about 40–50 min. During this pass, the sample was cooled. Repetition of this process led to the accumulation of the required dose D . At the irradiation with the low dose rate, the samples were located in the experimental hall of the accelerator at a distance from the direct beam. The sample and the surrounding atmosphere were continuously irradiated with both electrons and bremsstrahlung radiation. In this case, the scintillators were always in the irradiation zone until they received the required dose D [8–11, 15].

3. Results and discussion

3.1. Features of the scintillation process in composite scintillators containing grains of oxide crystals

Previously [8–13, 15] we investigated the composite scintillators based on single crystal grains as radiation-resistant materials. To obtain composite scintillators, the grains are introduced inside the base component of scintillator, which is the non-luminescent transparent silicone elastomer Sylgard-184. The technology of production of such the composite scintillators we described in detail in [8–13, 15]. The transmittance of Sylgard-184 in the wavelength range $\lambda > 360$ nm was not lower than 90% [16]. Radiation resistant of silicone elastomer Sylgard-184 was more than 100 Mrad.

Table I demonstrates results of comparing the highest cumulative doses D of radiation for which the scintillator is still resistant [17–26]. Table I also shows the radiation resistant of known scintillators. It is obvious that the radiation resistant of the developed composite scintillators is higher than those that were massively used in real experiments in high-energy physics (for example, SCSN-81 plastic scintillators) before our studies.

The values of the relative light output can fluctuate with the increase of dose D (it was shown

in previous works [8–13, 15]). As a result, the radioluminescence of scintillators cannot be described only by a monotonically decreasing function, which is determined by irreversible destruction of its luminescent centres under the action of ionizing radiation. Therefore, when analysing the features of the radiation resistant of the composite scintillators, we considered possible mechanisms both of radiation damage and of restoring those originating in composite scintillators under the action of ionizing radiation.

3.2. The effect of large doses of radiation on the radioluminescence spectrum

Changes in the luminescence spectra of composite scintillators either take place (e.g. in grains of organic crystals or $\text{Al}_2\text{O}_3:\text{Ti}$) or do not occur (in e.g. grains GSO, GPS, YSO, YAG). Let us consider these cases separately.

3.3. Radioluminescence does not change its spectral composition under the influence of radiation

The luminescence spectrum of composite scintillators containing GSO, GPS, YSO, YAG grains does not change its shape under the influence of radiation [8, 10].

Comparison of radiation resistant of some scintillators.

TABLE I

	Material	Limiting dose D_{\max} [Mrad]	Fluorescence decay time [ns]	Remarks	
the known scintillators	organic single crystals and polycrystals	< 1	~ 3		
	plastic scintillator SCSN-81	10–15	~ 3	popular as the most radiation resistant	
	polysiloxane scintillators	~ 30			
	Inorganic single crystals				
	GSO:Na*	100 1000	40–45	Ref. [17–20] Ref. [18]	
	YSO:Na* or YAG:Na*	10	42 120	Ref. [21–24]	
	YAG:Na*	> 1000	120	Ref. [24]	
	$\text{Al}_2\text{O}_3:\text{Ti}^*$	> 1000	3400	Ref. [25, 26]	
composite scintillators of our design containing single-crystal grains	$\text{Al}_2\text{O}_3:\text{Ti}$	> 125 (dose rate 0.2 Mrad/h) > 550 (dose rate 1500 Mrad/h)	3400	cracking	
	Gd ₂ SiO ₅ :Ce (GSO:Ce) (gadolinium orthosilicate), Gd ₂ Si ₂ O ₇ :Ce (GPS:Na) (gadolinium pyrosilicate)	> 200 (dose rate 0.2 Mrad/h) > 250 (dose rate 1500 Mrad/h)	40–45	cracking	
	Y ₂ SiO ₅ :Ce (YSO:Ce) (yttrium orthosilicate)	> 150	42	radiation resistant	
	Y ₃ Al ₅ O ₁₂ :Ce (YAG:Ce) (yttrium aluminium garnet)	> 150	120	radiation resistant	
	Y ₃ (Al _{0.25} Ga _{0.75}) ₅ O ₁₂ :Ce (YAGG:Ce) (yttrium aluminium–gallium garnet)	> 100	28–37	radiation resistant	
	YAGG:(Ce,Ca)	> 100	7–21	radiation resistant	

*We found only references to the study of the characteristics of these crystals, and not references to their use in real conditions of experiments in high energy physics.

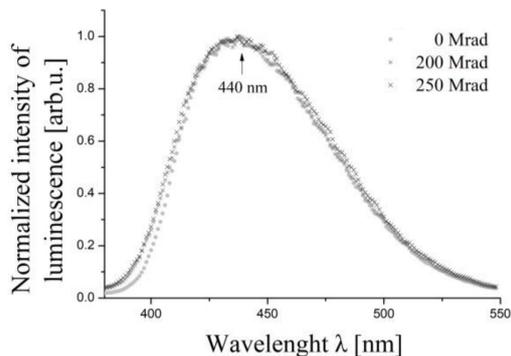


Fig. 1. Normalized luminescence spectra of 4 mm composite scintillator containing grains GSO. The wavelength of excitation $\lambda = 340$ nm. The dose rate is 1500 Mrad/h. Details in text.

Figure 1 shows an example of photoluminescence spectra for the composite scintillator containing GSO grains before ($D = 0$) and after irradiation during the time of B-centres existence and after that decreases [2]. According to the results demonstrated in Fig. 1 it is not our case when new luminescent centres do not appear after irradiation.

Figure 1 shows a typical example of luminescence spectra obtained for the composite scintillators based on GSO and GPS grains after irradiation with different D . This proves that the luminescence spectra of composite scintillators do not change their shape, and no new peaks appear in such a spectrum when the dose D increases. This result is very important for future discussion because it means that, unlike the composite scintillators based on organic grains [2], no new luminescent centres of different nature appear after the irradiation for scintillators based on GSO and GPS grains.

In Fig. 2, the L_{rel} value does not change significantly as D increases up to $D = 200$ Mrad. It indicates high radiation resistant of composite scintillators based on GSO and GPS grains.

Figure 2 show that the values of relative light output L_{rel} can fluctuate as D increases. This reminds results obtained for T value. Why such fluctuations are possible? To answer this question, we have to take into account that the radioluminescence of a scintillator, whose luminescent centres are damaged by radiation, cannot be described by a monotonic decreasing function, because the modification of the scintillation material after irradiation is caused not only by irreversible damage to its main substance. It turns out that second-order activity arises as the result of irradiation and complexifies the process.

Let us analyse two possible description of such a process. Suppose that molecules, ions etc. of kind A are damaged by radiation and centres of a B-type appear. If B-type centres are new

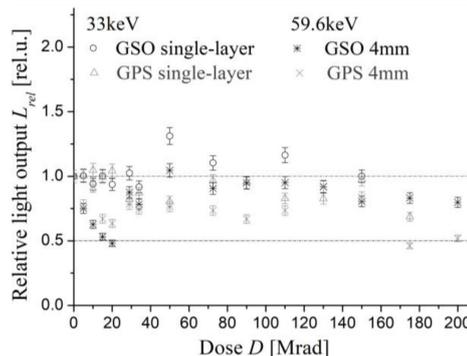


Fig. 2. Relative light output L_{rel} of a composite scintillator containing grains of GSO and GPS versus D . The dose rate is 0.2 Mrad/h.

additional luminescent centres with higher quantum yield than the A-type centres, the luminescence intensity of the scintillator grows after irradiation during the time of B-centres existence and after that decreases [2]. According to the results demonstrated in Fig. 1 it is not our case when new luminescent centres do not appear after irradiation.

The other possibility is the following. All scintillation materials contain quenching centres. Irradiation destroys and modifies not only the main substance but also the quenching centres. This may result in a temporary increase of the luminescence intensity due to a decrease in the quenching efficiency of the luminescence appearing inside the grains. In this case, the luminescence spectrum of the scintillator does not change its shape for different doses D because no new luminescence centres appear. This result is in a good agreement with the results demonstrated in Fig. 1. Of course, such an increase of luminescence takes place only during the regeneration period of quenching centres. Therefore, at this time period, the intensity of luminescence has to decrease due to restoration of quenching efficiency. The energy levels of such centres are in the energy gap of the grain energy diagram. Therefore, these centres mainly influence the optical transmittance T for λ values equal to the energy gap of the energy diagram of the grains. The change of luminescent characteristics caused by radiation damage of the scintillation material and its self-regeneration accompanies all these processes, which results in a complex variation of the luminescence properties. Therefore, the change in the relative light output L_{rel} , T value etc. that appears as a result of irradiation with different doses D has to have a random component. The effects of material activation, a change in the quenching efficiency of the impurity centres and ions, a temporary damage of the luminescent centres of the grains, and then their fast recovery cause this random component. The radiation resistant of the material will continuously decrease when the effect of the luminescent centres damage of the grains, not followed by their fast recovery, becomes of primary importance. This

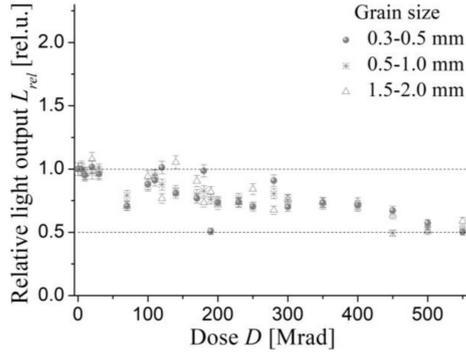


Fig. 3. Relative light output L_{rel} of the composite scintillators containing grains $\text{Al}_2\text{O}_3:\text{Ti}$ versus D . The dose rate is 1500 Mrad/h.

is possible for higher D , because for the actually radiation-resistant material with very fast recovery, the average values of the relative light output L_{rel} , the light transmittance T must slowly decrease with increasing D . Therefore, for the actually radiation-resistant material the random component of the process can determine the total change of the above-mentioned values if D value is not too high.

Our results obtained for composite scintillators based on the grains of GSO are in a good agreement with results and explanations described by M. Tanaka, and his co-authors [17] for GSO single crystals. They analyzed the effect of the fluctuation of light output for GSO single crystals, and gave the following explanation. When GSO absorbs the energy of the incident particle, the excitation of Gd^{3+} takes place. This energy has to be transferred to Ce^{3+} ions, which are the luminescence centres of GSO crystals. Due to impurities and host ions, a certain number of intermediate energy levels exist in the energy gap. They can absorb some fraction of the energy. In such case, the excited electrons relax to the intermediate levels and after that undergo radiationless transitions to the ground level. Therefore, they do not contribute to scintillation. In the GSO crystals, the concentration of the impurities is high enough and the probability of energy transfer from Gd^{3+} to such an impurity centre may be high. It can result in quenching of GSO luminescence. If these intermediate levels are occupied under the action of radiation, the energy transfer efficiency from Gd^{3+} to Ce^{3+} increases. This results in an increase in light output because such impurity centre after trapping electron is no longer able to quench the luminescence of the crystal. The lifetime of the intermediate levels can have a large spread. According to [17], for the most stable of them, this value can reach even several months. This explanation is in good agreement with our results obtained for composite scintillators based on the grains of GSO, because the grains are little single crystal of the same symmetry and chemical composition as the corresponding crystal.

Even for a radiation-resistant material with very fast recovery, the average value of the relative light output (L_{rel}) would decrease as D increases. Therefore, for the radiation-resistant material, the random component of the process can determine the total change of the above-mentioned values if the D value is not too high.

The same results were observed for composite scintillators based on GPS:Ce, YSO:Ce and YAG:Ce crystal grains.

3.4. The spectral composition of radioluminescence changes under the influence of radiation

Composite scintillators containing grains of organic single crystals have lowest radiation resistant. Radiation damages the benzene rings of their grains. The probability of recovery of such grains is extremely low. As a result of the destruction of the original organic molecules, new organic molecules luminescent in a different spectral range can appear.

In Fig. 3, the relative light output (L_{rel}) does not change significantly ($L_{rel} > 0.5$) with increasing D up to $D = 550$ Mrad and $D = 125$ Mrad for dose rate of 1500 Mrad/h and 0.2 Mrad/h, respectively. This indicates a high radiation resistant of the composite scintillators based on $\text{Al}_2\text{O}_3:\text{Ti}$ grains for such doses and dose rates. Figure 3 shows that the average value of L_{rel} has a weak tendency to decrease with increase of D value for the composite scintillators with grains of $\text{Al}_2\text{O}_3:\text{Ti}$. The trend of decrease in L_{rel} with D indicates that the effect of damage to the luminescent centres of the grains by radiation should increase with increasing D . Figure 3 clearly shows that for higher doses ($D > 550$ Mrad) the L_{rel} can be lower than 0.5.

Figure 3 demonstrate that the values of relative light output L_{rel} can fluctuate as D increases. To explain this we have to take into account that the radioluminescence of a scintillator, whose luminescent centres are damaged by radiation, could not be described by monotonic decreasing function, because the modification of the scintillation material after irradiation does not caused only by an irreversible damage of its main substance. The second-order activity arises as the result of irradiation and complicates the process. Composite scintillators containing inorganic grains $\text{Al}_2\text{O}_3:\text{Ti}$ demonstrate the highest radiation resistant.

Figure 4 indicate the changes in the luminescence spectra during irradiation of the composite scintillator containing grains of $\text{Al}_2\text{O}_3:\text{Ti}$ for various accumulated doses D when light with $\lambda_{ex} = 230$ nm excited the luminescence. In Fig. 4 the luminescence spectra of the samples are measured after irradiation with the dose rate of 1500 Mrad/h. For comparative analyzes it should be noted that the results show the spectra of the composite scintillator and the single crystal before irradiation

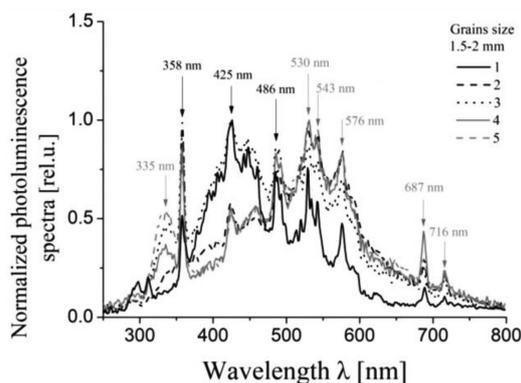


Fig. 4. Photoluminescence spectra of the non-irradiated single crystal of $\text{Al}_2\text{O}_3:\text{Ti}$ (curve 1) and the composite scintillators containing grains of $\text{Al}_2\text{O}_3:\text{Ti}$ (curves 2–5) excited by light with $\lambda_{\text{ex}} = 230 \text{ nm}$. Dose rate is 1500 Mrad/h. Details are in the text.

($D = 0$). Curves 1 and 2 (Fig. 4) show the photoluminescence spectra of the non-irradiated single crystal and the non-irradiated composite scintillator, respectively. Of course, Fig. 4 show spectra obtained after irradiation only with such doses of D for which the typical significant changes in the luminescence spectra take place. It is impossible to demonstrate all luminescence spectra obtained for all doses D , as it done in Fig. 3 for light output, because in such case, these spectra become indistinguishable.

Scintillation materials based on grains of single crystal $\text{Al}_2\text{O}_3:\text{Ti}$ also change the spectrum of their luminescence under the action of radiation. In the blue luminescence band, with the growth of accumulated dose D , we see the following. The luminescence intensity first sharply increases. Then the luminescence intensity stops increasing or even decreases. Note that this luminescence is associated with centres containing Ti^{4+} ions [10]. With increasing D the intensity of luminescence in the infrared (IR) band initially decreases and then slightly increases. This luminescence band is associated with centres containing Ti^{3+} ions. The formation of centres containing Ti^{4+} ions occurs as the result of the ionization of Ti^{3+} ions.

For $D \leq 350 \text{ Mrad}$, with growing D , the luminescence intensity increases in the spectral region 310–350 nm. For $D \leq 450 \text{ Mrad}$, the luminescence intensity decreases with increasing D . Then, its growth stops and begins to fall. This luminescence is associated with the generation of centres containing Ti^{4+} ions. With increasing D , the luminescence intensity in the IR band first decreases and then slightly increases. The Ti^{3+} ions give rise to IR luminescence [10].

It brings us to the only possible explanation. At low D values, the basic process is the generation of the centres containing Ti^{4+} ions that are formed during the ionization of Ti^{3+} ions. Consequently,

the concentration of centres containing Ti^{4+} ions increases, and the probability of direct exposure to radiation of these centres increases. With an increase in D , the probabilities of both ionization of Ti^{3+} ions and destruction of centres containing Ti^{4+} ions increase. The last of the mentioned processes can lead to the reverse transition between Ti^{3+} and Ti^{4+} ions under irradiation.

In other words, with an increase in the accumulated dose D , there is a redistribution of intensities between the blue and IR luminescence bands. This is somewhat similar to a pendulum.

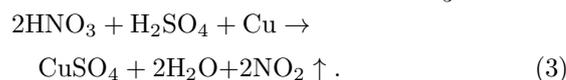
3.5. Cracking

After prolonged irradiation at a small irradiation rate (0.2 Mrad/h), a liquid is gradually formed on the surfaces and around the composite scintillators. Monitoring the pH using a universal indicator shows that this liquid has pH about 1, i.e., it is a strong-acid solution. At a high irradiation rate, we did not observe liquid around the samples. It is most likely due to both weak manifestation of the effect itself and high temperature of scintillators as they pass through the beam of charged particles. The latter could well have contributed to the evaporation of the resulting liquid.

To exclude the presence of a solution of sulfuric acid after irradiation, we performed a qualitative analysis for the SO_4^- washout of this liquid using the following reaction



In our case, the formation of BaSO_4 precipitate did not occur, i.e., acid H_2SO_4 in the test solution was absent. To confirm the presence of nitric acid appearing in the solution after irradiation, we carried out a qualitative analysis for the NO_3^- ions, i.e.,



During this reaction, we observed appearance of brown gas (NO_2). Thus, the presence of a solution of nitric acid, which appears during irradiation, can be considered proven.

To test the effect of acids on the cracking of composite scintillators we carry out a series of experiments. It should be said that we considered only the visible effects without additional quantitative measurements. Because we did not measure the elasticity of the samples after each series of irradiation until we saw that the samples were destroyed.

We have chosen the following acids: sulphuric (H_2SO_4), hydrochloric (HCl), orthophosphoric (H_3PO_4) and nitric acid (HNO_3). We placed the samples of composite scintillators or Sylgard-184 gel composition (Fig. 5) in concentrated aqueous solutions of these acids.

Dissolution of the polymer base of composite scintillators without cracking was observed in sulphuric acid (H_2SO_4). The first signs that the sample was dissolving appeared within an hour. After 72 h, the

TABLE II

Comparison of estimated D_{calc} values with experimental D_{exp} dose values.

Stage	Effect description	T_{chem} [h]	D_{calc} [Mrad]	D_{exp} [Mrad]
1	slight reduction in elasticity	120	24	50
2	surface cracking during bending, without fracture of the sample	240	48	100
3	appearance of fragility (breaks under a slight impact)	480	96	150
4	samples crack spontaneously	720	144	200–250

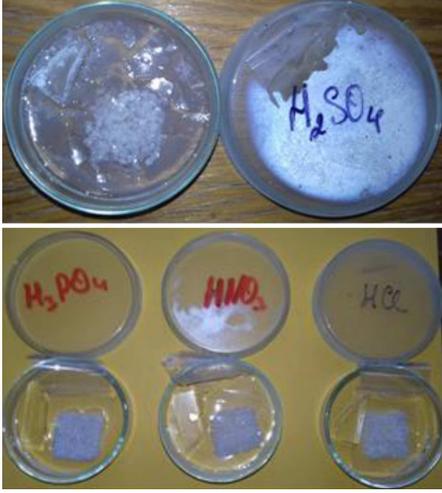


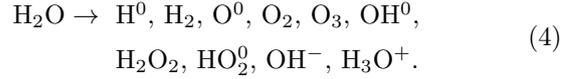
Fig. 5. Photographs of Sylgard-184 composite scintillators (with grains of Al_2O_3) and gel compositions placed in H_2SO_4 , HCl , H_3PO_4 and HNO_3 acids. We took the photos 60 min after we immersed the samples in acids.

degree of dissolution reached 90%. In solutions of hydrochloric acid (HCl) and orthophosphoric acid (H_3PO_4), we observed no visible effects of the action of acid on the composite scintillator. The gel and composite scintillators remained flexible even after several months.

Cracking of composite scintillators occurred when they were placed in nitric acid. This process took place in several stages. Table II demonstrates these stages. Table II also presents the estimated values of the accumulated dose D_{cal} , which could have been accumulated in a similar time at a slow rate of irradiation. Table II shows the experimentally obtained values of radiation doses D_{exp} at a small rate at which the corresponding effect was observed.

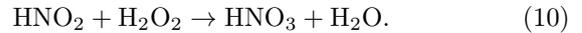
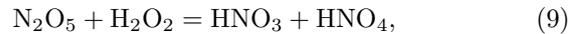
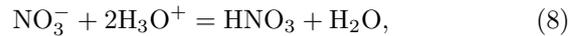
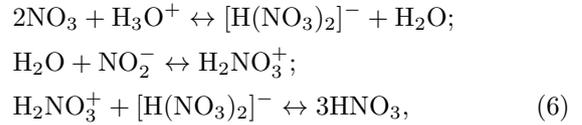
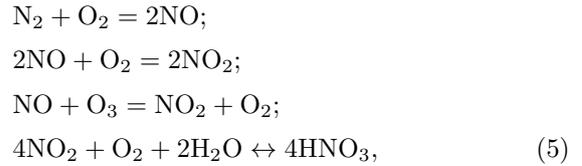
The process of irradiation of composite scintillators takes place in the surrounding atmosphere, which initially contains 78 vol.% nitrogen, 21 vol.% oxygen and 1 vol.% of other gases (water vapor, CO_2 etc.). Therefore, ionizing radiation affects not only the composite scintillator, but also compounds that are in the air. In other words, not only compounds from air, but also products of radiochemical reactions involving these substances can cause cracking of composite scintillators during

irradiation. For example, under the action of ionizing radiation on water vapor its radiolysis leads to the appearance of the following main products



The most active of them are I_3 , I_2I_2 , HO_2 , II^- and I_3I^+ [27]. Under the action of radiation, ionization of substances occurs, leading to formation of radicals and ions.

As shown above, nitric acid forms during irradiation of composite scintillators. Due to the fact that the nitrogen content in the atmosphere is 78 vol.%, and oxygen — 21 vol.%, the following reactions are possible in the presence of water vapour



These reactions are only examples of possible pathways for the formation of nitric acid and intermediates. Under the influence of ionizing radiation, reactions can also occur with the formation of other intermediate compounds. In this regard, it is important that the chemical activity of intermediate compounds, such as NO_2 , N_2O_5 , is quite high (see, e.g., [28]). From the experiment with acids it follows that it is the intermediate compounds and nitric acid vapours that interact with composite scintillators during irradiation.

According to [29], chemical destruction can occur in a polymer base under the action of acids. Actively acting chemical agents are oxidizing acids (chromic, concentrated nitric and sulfuric acids), which cause destruction of polymers (sometimes

TABLE III

Comparison of the observed effects for composite scintillators from the accumulated dose D when irradiation occurs in the air or in vacuum.

D [Mrad]	Description of changes that occur with composite scintillators after irradiation	
	In air	In vacuum
25	no visible effects	no visible effects
50	slight reduction in elasticity	no visible effects
75	cracks on the surface during bending appears, without the sample destruction	no visible effects
100	appearance of fragility (sample breaks under a slight impact)	slight reduction in elasticity
125	spontaneous cracking of a sample begins	slight reduction in elasticity
150	complete cracking of a sample	slight reduction in elasticity

within a few min). For example, under the action of concentrated nitric acid on polymers, oxidation (formation of carbonyl groups) and nitration (formation of nitro groups) occur simultaneously. Mineral acids (hydrofluoric, hydrochloric, dilute nitric and sulfuric, phosphoric, etc.) are less reactive with respect to polymers in comparison with oxidizing media. They practically do not affect polymers [29].

This confirms our experimental results that hydrochloric and phosphoric acids did not react with the polymer base of the composite scintillator, sulfuric acid began to dissolve it within an hour, and treatment with nitric acid led to cracking.

At the same time, the results of the effect of nitric acid obtained without irradiation (under laboratory conditions) and upon irradiation (on a linear electron accelerator) are somewhat different. Most likely, this is due to several factors. Firstly, under radiation conditions, nitric acid and its accompanying compounds cannot affect the basis of the composite scintillator constantly, since ionizing radiation not only contributes to the creation of such compounds, but may also destroy them. Another factor relates to the effect of ionizing radiation itself on the polymer base [30]. Deep chemical changes occur in polymers under the influence of ionizing radiation. Such radiation can cause bond breaks in the polymer chain. However, this is not always due to redistribution and dispersal of energy. For example, during the irradiation of polyethylene, only about 5% of the absorbed energy causes chemical reactions, and 95% turns into heat [30–32]. Under the action of high-energy radiation, not only destruction but also crosslinking of polymer chains occurs [30]. The crosslinking process of the polymer base can lead to the restoration of the integrity of the polymer chain and thereby increases the time before cracking.

To determine the degree of influence of the atmosphere in the radiation zone on the scintillator, we carried out the irradiation both in air and in a vacuum cell (Table III) [13].

As can be seen from Table III, the samples of composite scintillators irradiated in the presence of air decreased their elasticity with increasing irradiation dose D . This eventually led to their cracking. This is in good agreement with the results that we obtained in previous works. A different result

is observed for samples irradiated in vacuum. For them, at doses over 100 Mrad, only a slight decrease in elasticity was observed. This confirms that cracking of composite scintillators at a low accumulation of dose rate is determined by the products of radiochemical reactions in the atmosphere.

It should be noted that the relative light output L_{rel} of composite scintillators containing inorganic grains before their cracking was more than 0.5 [13]. After cracking, light output could not be measured.

One more remark: both inorganic single crystals and grains in composite scintillators were not mechanically damaged by nitric acid.

4. Conclusions

We can conclude that:

1. Composite scintillators have undeniable advantages. They do not require machining, which is the main source of crystalline material loss. Their manufacturing technology does not impose restrictions on the area and shape of the entrance window. They can be applied directly to another material in a compound detector or used separately. To output light from them, one can make a light guide of the same gel composition as the base of the scintillator. Thus, an optical contact appears between the scintillator and the fibre with the same refractive indices.
2. We studied the radiation resistant of composite scintillators containing grains of oxide crystals. The luminescence spectrum of the composite scintillator can either remain unchanged or change under irradiation. The peculiarities of the mechanism of radiation transformations in grains determine this effect.
3. We irradiated composite scintillators for a low (0.2 Mrad/h) and a high dose rate (1500 Mrad/h). For low dose rate, cracking occurs at lower D values (about 100–200 Mrad) than under irradiation with a high dose rate (up to 500 Mrad). Cracking of the scintillator in an aggressive environment of the irradiated zone limits these values.

4. Additional studies have allowed us to show that nitrogen compounds, including nitric acid, can appear in the irradiation zone under the influence of radiation. The scintillator in the irradiation zone can either begin to expand under the influence of heating or (and) to crack when exposed to aggressive atmospheric components.
5. At a low irradiation rate, the sample that has accumulated the dose D remains in the radiation zone longer than at a high one. At low dose rates, nitrogen-containing compounds forming in the radiation zone have a decisive influence on the effect of scintillator cracking. At high dose rates, cracking of scintillators occurs mainly due to their heating by radiation.

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