LIGHT GUIDES ON THE BASE OF DIELECTRIC GEL COMPOSITIONS

***N. Z. Galunov*[1]*, *N. L. Karavaeva*[1], *S. U. Khabuseva*[2], *A. V. Krech*[1], *L. G. Levchuk*[3], *V. F. Popov*[3], *A. D. Samokhin*[1], *P. V. Sorokin*[3]**

[1] *Institute for Scintillation Materials, National Academy of Sciences of Ukraine, 60 Lenin Avenue, 61001, Kharkov, Ukraine;*

[2] *State Scientific Institution "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Avenue, 61001, Kharkov, Ukraine;*

[3] *National Science Center "Kharkov Institute of Physics and Technology", 1 Akademicheskaya Str., 61108, Kharkov, Ukraine*

(Received May 16, 2014)

Light guides those have to shift the light of scintillator in a longer-wavelength region and collect this light on a photodetector are developed on the base of radiation resistant gel composition Sylgard-527. The luminescent molecules of POPOP(1, 4-bis-(2 (5-phenyloxazole))-benzene), PB (1, 4-diphenyl-1, 3-butadiene), or TP (p-terphenyl) were introduced in the composition. We study the total number of accounts S in the range of the spectrum, it relative value S_R, the light transmittance T before and after irradiation. The best results were obtained with POPOP and TP.

PACS: 42.88.+h, 81.05.Zx, 81.40.Wx

1. INTRODUCTION

Experiments which are planned or being carried out at the new-generation high-luminosity particle and heavy-ion accelerators (such as the LHC at CERN) are featured by the exposure of the detectors and subdetectors (trackers, calorimeters, etc.) to a high level of radiation doses. E.g. the hadron calorimeter (HCAL) of the CMS detector has a sampling structure with thin (4 mm thick plates of plastic scintillator) being sandwiched between thick brass layers. For the first 10 years of LHC operation, the most "critical" (closest to the interaction point) zones of the CMS endcap HCAL (HE) are expected to get the dose D up to 10 Mrad at the rate about 0.1 krad/hr. Furthermore, there are plans of gradual increase of the LHC luminosity by the order of magnitude in future. The CMS upgrade project [1] describes the new detector version which would be able to operate at the increased-luminosity LHC conditions. The maximum dose accumulated in the CMS HE "critical" zones upon the LHC ultimate shutdown is estimated in Ref. [1] as 30 Mrad. This sets very hard requirements on the radiation tolerance of the detector (in particular, on the HE scintillators and light guides). Therefore, a development of materials for radiation detectors with high radiation resistance becomes an important problem.

A luminescent material is regarded as radiation-resistant up to the dose of radiation $D = D_F$, for which its luminescence characteristic changes on a half of it initial value (i.e. for value that is true for $D = 0$) [2] (see p. 205). On the first step of the above mentioned problem solution (i.e. the problem of the development of a luminescent radiation-resistant material) it is necessary to find a radiation resistance material for the basis component of such a composition (or according to Birks terminology (see book [2], p. 55) we have to use not basis component but "main constituent or solvent"). Our previous paper [3] gave the answer on this question. We have investigated the light transmittance T as a function of an integrated radiation dose D for commercially available silicone dielectric gels. It was namely SKTN-med (20 Pa), SKTN-med (100 Pa), Sylgard-184, Sylgard-186, Silgard-527, and SUREL-SL-1 [4, 5, 6]. The samples were irradiated by the electrons from accelerator in the National Science Centre "Kharkov Institute of Physics and Technology". The study was performed up to integrated radiation doses equal to 90.6 Mrad. It was shown that the T-values, practically, did not change with increase in the radiation dose D. For the light of wavelengths longer than 400 nm the reduction of the T-values did not exceed measurement error (namely 5%) up to D=90.6 Mrad. Some insignificant increase in light transmittance T for some gels (SKTN-med (20 Pa), SKTN-med (100 Pa), Silgard-527, and SUREL-SL-1) was obtained. It can be caused by the effect of a partial solid-state recrystallization that appears as the result of the action of ionizing radiation. It is known [7] that the improve-

*Corresponding author E-mail address: galunov@isma.kharkov.ua

ment of structure perfection can lead to reduction of a dispersion of light photons and therefore to increase in a transparency of a material. It should be also note that the dielectric gels can be used in the wide range of working temperatures, they do not chemically react with the materials used in a scintillation technique, they are non-hygroscopic, and they possess high transparency in the range of a luminescence of a lot of scintillation materials [3, 4, 5, 6].

In some instances a luminescent material can be used as a light guide that shifts the light of scintillator in a longer-wavelength region and collects this light on a photodetector. The approaches to develop a light-shifter light guide and an organic scintillator are different.

The concentration of luminescent centres C_1 in scintillator has to be high. Really, the ionizing radiation loses it energy mainly in the base material. The probability of energy transfer from excited molecules of a scintillator base material to luminescent molecules is equal to

$$W(r) = P_0(R_0/r)^{2m}, \quad (1)$$

where P_0 is a probability of electronic excitation (or molecular exciton for crystals) to decay without transfer, R_0 is a representative radius of the excitation (exciton) capture, r is the distance of the transfer. E.g. for dipole-dipole excitation energy transfer $m = 3$, for dipole-quadrupole energy transfer $m = 4$, etc. For Forster – Galanin excitation energy transfer mechanism (which is correct e.g. for scintillation plastics) R_0 is called the Forster radius. The electronic energy excitation transfer would be effective when $r < R_0$. It means that the values of C_1 have to be high.

Other specifications are applicable for radiative transfer of light that travels through a light guide of length l. Due to light collection and reabsorption the intensity of the light decreases from its primary value I_0 to a value I. If a concentration C_2 of luminescent molecules in such a light guide is not too high then the change in I-value can be describe by the Bouguer-Lambert-Beer law

$$I = I_0 exp(-k_\lambda l), \quad (2)$$

where $k_\lambda = \chi_l C_2$ and χ_l is a factor that characterizes the effect of the light of the wave-length λ on a luminescent molecule. So, if a scintillator emits the light of a wave-length λ_1, luminescent molecules of a light guide absorb this light and then emit the light photons of a wave-length λ_2 in such a case to obtain a light guide with low light loss the following relations have to be satisfied

$$\lambda_2 > \lambda_1; C_2 \ll C_1\,. \quad (3)$$

It means that the concentration C_2 of luminescent molecules in a light guide, which can be used as a shifter, has to be low. To develop the composite scintillators (see e.g. Ref. [8, 9]) the single crystal luminescent grains (C_1 is 100%) have to be introduced in a gel. In contrast to papers [8, 9] this paper is devoted to study the other limiting case namely "dyeing" of a gel-composition when the concentration of luminescent molecules C_2 has to be low. It should be note that such a gel-composition has to have extremely low scintillation light yield to not corrupt the scintillation signal. According to (1) this requirement can be realized just if condition (3) is satisfied, namely a concentration C_2 of luminescent molecules in a such a dyeing gel-composition has to be low.

Herein after let us call such the dyeing gel-composition as the "shifter".

2. EXPERIMENTAL DETAILS

2.1. Shifters preparation

In this work we use the silicone dielectric gel Sylgard-527 as the base material for shifters [3, 5, 6]. As the luminescent molecules, which have to shift the scintillation light to a longer-wavelength region, we used POPOP(1, 4-bis-(2 (5-phenyloxazole))-benzene), PB (1, 4-diphenyl-1, 3-butadiene), or TP (*p*-terphenyl).

The molecules of such a light shifter were introduced in dielectric gel according to the following technique. Firstly, we dissolve a sample of luminescent shifter molecules in toluene. After that the necessary amount of the toluene solution is introduced in the first component of a gel. The excess solvent (toluene) is removed. Then the second component of the dielectric gel is added. The gel composition is carefully mixed, and after that it is introduced into a forming container, in which it left up to complete polymerization of the gel composition. As the result, the shifter is obtained and can be taken from the forming container.

2.2. Irradiation of the samples

As in our previous work [3] the samples were irradiated by the electron accelerator of the National Science Centre "Kharkov Institute of Physics and Technology" by the electrons with the energy about 9.2 MeV at the room temperature. During irradiation the radiation dose rate was practically uniform and was equal to 0.23±0.01 Mrad/h. Inhomogeneity of irradiation of the samples did not exceed 5%. The samples were, consistently (by one sample of each type), exposed to radiation until they accumulated the necessary integrated radiation dose. To control radiation doses with an accuracy of ±10% HARWELL Red 4034 plastic dosimeters were used. Details one can find in [3].

2.3. Measurements of scintillation light yield

The set of gamma sources allowed us to calibrate the energy scale of the measuring setup. We used a single crystal of stilbene as the reference for shifters. Comparison of scintillation signals excited by photons of gamma-radiation from radionuclide source

^{137}Cs (662 keV) was made for reference scintillator and other samples. We run the measurements using conversion electrons from ^{137}Cs (622 keV) and alpha-particles from ^{239}Pu (5.15 MeV). It allows us to obtain the relative scintillation light yield for shifters.

2.4. Measurements of luminescence spectra

The luminescent spectra were measured by spectrofluorimeter Varian Cary Eclipse using stable flux of an exciting light. Nevertheless for different wavelength λ the intensities of the exciting light can differ. Therefore the direct comparison of an efficiency of the process of light transformation in shifter for different range of a spectrum is not correct. Such a comparison can be done only for the cases of same excitation spectra. To characterise the general influence of radiation on a luminescence spectrum (Fig.1) we calculated the total number of accounts in the range of the spectrum between wavelength λ_S ("start" point of the spectrum) and λ_F ("final" point the spectrum).

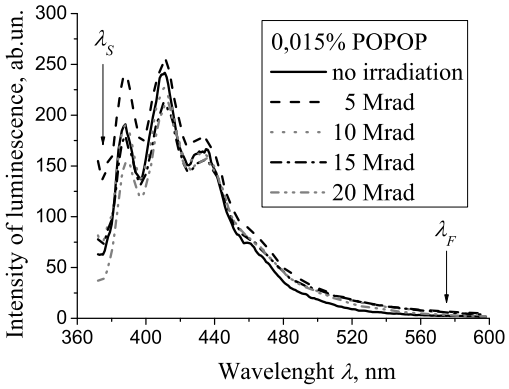

Fig.1. *Luminescence spectra of POPOP (0.015%) in Sylgard-527 for different accumulated doses of radiation D*

So, we obtained the following value

$$S = \sum_{\lambda_S}^{\lambda_F} N(\lambda), \tag{4}$$

where $N(\lambda)$ is the number of counts in a luminescence spectrum obtained for wavelength λ. The values of λ_S and λ_F were not changed for a series of the measurements for samples with of the same luminescent molecules, i.e. when the excitation spectra were the same. The S-value characters an efficiency of the process of light transformation in shifter.

Let S_R denote the relative value of S (4). We use the following definition of the S_R-value. If an $S(D)$ is the S-value obtained for a given dose of irradiation D, and $S(0)$ is the S-value obtained for dose of irradiation D=0 then:

$$S_R \equiv S(D)/S(0)\,. \tag{5}$$

Just the S_R-value directly characterizes the radiation resistance of a material. For $S_R \geq 0.5$ the material is still radiation resistant (see book [2], p. 205).

2.5. Measurements of transmittance

The measurements of light transmittance T in the range from 300 to 700 nm were performed by Shimadzu-2450 spectrophotometer with the integrating sphere. The comparison channel remained blank and the light flux in it was calibrated to be the same as the light flux falling on a sample in measuring channel. The inaccuracy of the calibration was limited by 0.5%. The value of light transmittance T was calculated as follows:

$$T = (I/I_0) \cdot 100\%, \tag{6}$$

where I_0 is the light flux in comparison channel, I is the light flux, which has passed through a sample in measuring channel. Actually, the T-value (6) is a relative light transmittance, where $T = 100\%$ it is light transmittance of air.

3. RESULTS AND DISCUSSION

The luminescent spectra and the light transmittance T were measured according to techniques those were described in the subsections 2.4 and 2.5 respectively. For all the samples the light yield does not exceed a few percent of the light yield of a stilbene single crystal.

3.1. POPOP in Sylgard-527

The luminescence of the shifters was excited by light of wavelength λ_{Ex}=360 nm. Fig.1 shows the luminescence spectra of POPOP in Sylgard-527 for concentration of POPOP C_{POPOP}=0.015%. It also demonstrates the choice of λ_S=375 nm and λ_F=575 nm for the case of POPOP. The S-values increase with concentration of C_{POPOP} up to 0.01%. For C_{POPOP}=0.015% the S-value reduces. In should be note that for C_{POPOP}=0.015% a weak tendency to form a crystallization phase of POPOP inside the gel composition is observed (see Fig.1).

The luminescence spectra practically do not change after irradiation for the samples those contain POPOP. Only the intensities of their lines slightly change. For D=5 Mrad (dash line) the intensity increases, and for the higher dozes they have a very weak tendency (within the experimental error) to decrease with D.

Fig.2 shows S_R be plotted against the dose of irradiation D. Fig.2 demonstrates that for doses up to 20 Mrad the samples contain POPOP are enough proof against the action of radiation.

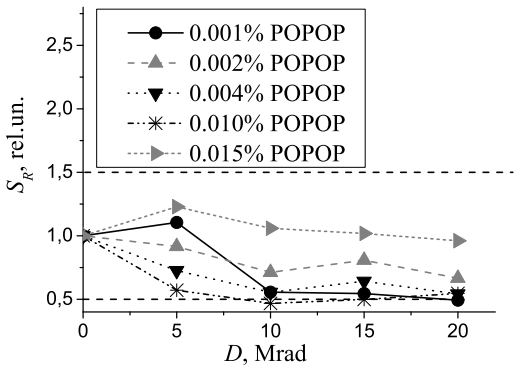

Fig.2. *S_R (5) against D for different concentration of POPOP in Sylgard-527*

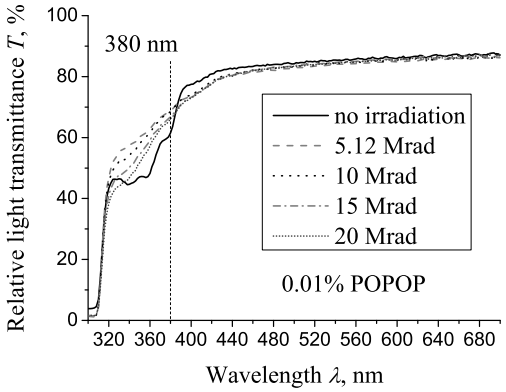

Fig.3. *Relative light transmittance T of the sample contains 0.01% POPOP in Sylgard-527 as a function of wavelength λ for different D*

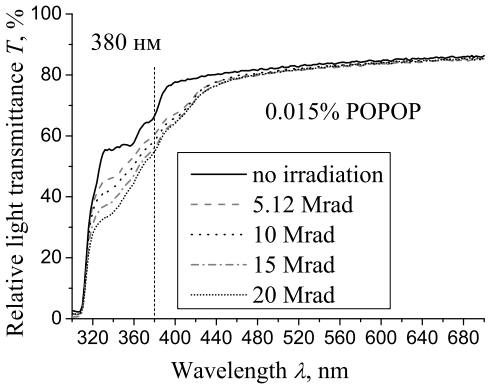

Fig.4. *Relative light transmittance T of the sample contains 0.015% POPOP in Sylgard-527 as a function of wavelength λ for different D*

Figs.3 and 4 shows the change in the relative light transmittance T with λ for C_{POPOP} equal to 0.01% and 0.015% respectively. In the region of the luminescence ($\lambda > 380$ nm) T-value practically does not change with dose D. It means that the probability of a colour centre formation is very low. It is typical situation for all the samples. For $\lambda < 380$ nm one can see that the T-values increase with the dose of radiation D. Transmittance T increases with absorption decrease. It means that the concentration of POPOP molecules which are not damaged by radiation decreases with the dose increase. It should be note that the change of T-value does not exceed 15%. For low concentrations of POPOP (not exceeds 0.01%) the dependence that Fig.3 demonstrates is typical.

3.2. PB in Sylgard-527

The luminescence of the shifters contains PB was excited by light of wavelength λ_{Ex}=360 nm. With increase of PB concentration the S-value (4) has the same tendency to grow like in the case of the gel-compositions contain POPOP. Fig.5 shows the change in the relative intensity of luminescence S_R with integrated radiation dose D. For the gel compositions containing PB the values of λ_S and λ_F were taken equal to 375 nm and 575 nm, respectively.

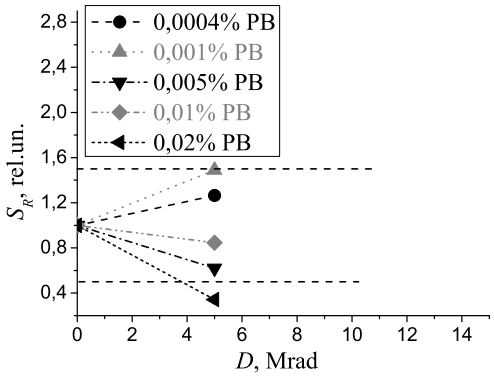

Fig.5. *S_R (5) against D for different concentration of PB in Sylgard-527*

Fig.5 demonstrates that for doses up to 5 Mrad the samples containing PB (barring the sample with 0.02% PB) are enough proof against the action of radiation For PB concentration 0.02% a weak tendency to form a crystallization phase of PB was observed.

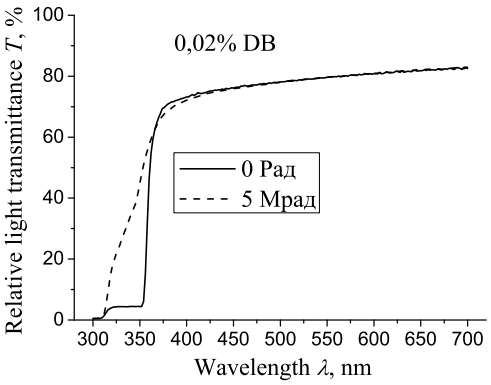

Fig.6. *Relative light transmittance T of the sample contains 0.02% PB in Sylgard-527 as a function of wavelength λ*

The measurements of the relative light transmittance T has shown the following. In the region of the luminescence ($\lambda > 360$ nm) T-value practically does not change with dose. It means that the probability of a colour centre formation is very low. In the ab-

sorption band of PB molecules ($\lambda < 360$ nm) one can see that the T-values increase after irradiation. It means that the concentration of PB molecules those are not damaged by radiation decreases after irradiation. Unlike the case of POPOP the change of T-value is high (see Fig.6). The highest difference in T-values before and after irradiation was for the sample with highest concentration of PB (0.02%). Fig.6. demonstrates that this difference, which appears in the absorption band. It is about 50%. Such the difference decreases with concentration of PB. For 0.0004% PB in gel-composition (which is minimal concentration of in our study) this difference does not exceed 20%. Nevertheless such the value obtained for D=5 Mrad exceeds the analogous values those were obtained for D=20 Mrad with the samples contain POPOP.

3.3. TP in Sylgard-527

The luminescence of the shifters contain TP was excited by light of wavelength λ_{Ex}=280 nm. Fig.7 shows the luminescence spectra of shifters contain 0.01% TP. It also demonstrates the choice of λ_S=300 nm and λ_F=500 nm, which were used to calculate the S-values (4). The S-value obtained for different shifters grows with increase of TP concentration C_{TP} up to 0.01%. For C_{TP}-values higher than 0.01% a tendency to form a crystallization phase of TP inside the gel composition is observed and the luminescence falls.

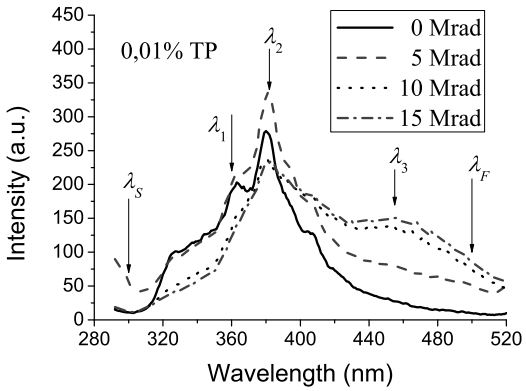

Fig.7. *Luminescence spectra of TP (0.01%) in Sylgard-527 for different accumulated doses of radiation D*

Fig.7 demonstrates the luminescence spectra of TP (0.01%) in Sylgard-527 for different accumulated doses of radiation D. For D=0 (solid line) one can see the main peaks those are characteristic for TP, namely the luminescence in the regions of λ_1=360...365 nm and λ_2=380...390 nm. For doze of D=5 Mrad (dash line) the luminescence spectra practically do not change after irradiation. Only the intensity for $\lambda > \lambda_2$ slightly grows after irradiation. For dozes 10 and 15 Mrad the luminescence in the regions of λ_1 and λ_2 decreases with D-value increase. This is accompanied by the growth of the luminescence intensity in the region of λ_3=450...460 nm (see Fig.7). For all the D-values the total effect of irradiation results in some increase of the luminescence intensity, and therefore the S-value has the tendency to grow with integrated radiation dose D.

Fig.8 shows the change in the relative intensity of luminescence S_R with integrated radiation dose D for the gel compositions with TP. Fig.8 also demonstrates that for doses up to 15 Mrad the samples containing TP are enough proof against the action of radiation. On can see some increase of S_R with D.

The measurements of the relative light transmittance T (Fig.9) gave the following results. In the region of the luminescence ($\lambda > 360$ nm) the T-value practically does not change with dose D. It means that the probability of a colour centre formation is extremely low for TP in gel-composition as well. In the absorption band ($\lambda < 360$ nm) the T-value decreases, i.e. the absorption increases with growth of the dose of radiation. The change of T-value in the region of absorption band for the gel-compositions with C_{TP} up to 0.01% does not exceed 15% ... 18%.

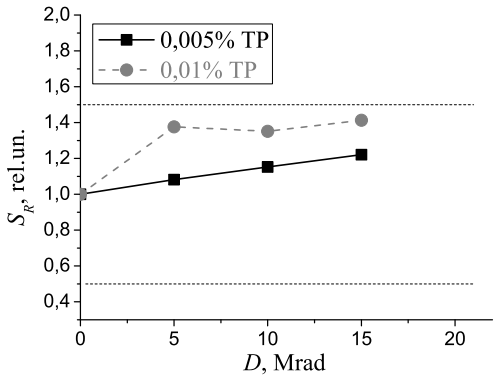

Fig.8. *S_R (5) against D for concentrations 0.005% and 0.01% of TP in Sylgard-527*

The comparison of the data those were obtained from the measurements of luminescence and light transmission may result in the following explanation. The luminescence of TP in Sylgard-527 is caused by many factors. The result of their coaction largely depends on the change of the chemical composition of a sample that originates from action of ionizing radiation.

For low doze of irradiation (D=5 Mrad) the concentration of TP molecules, which are not damage by radiation, may decrease extremely slowly in comparison with a decrease of the concentration of impurity molecules. They have to be such a type of impurity molecules those quench the TP luminescence. It accompany by weak generation of some other luminescent centres with luminescence in the range of λ_3=450...460 nm (see Fig.7).

The action of the larger D-valued (10 and 15 Mrad) on TP molecules can result in appreciable production the other luminescent centres with luminescence in the range of λ_3.

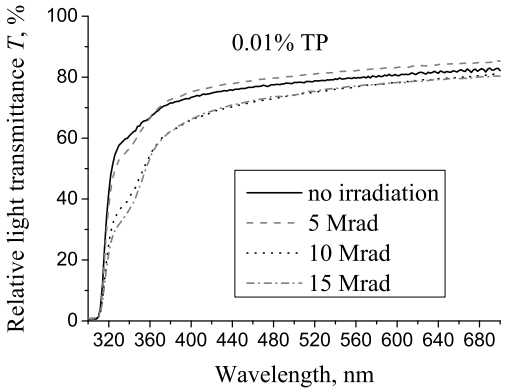

Fig. 9. *Relative light transmittance T of the sample contains 0.01% TP in Sylgard-527 as a function of wavelength λ for different D*

This type of centres has to have a very effective luminescence because the luck of the luminescence of TP molecules has to be compensated by their luminescence. Such the explanation is in a good agreement with the results obtained for S_R values, namely S_R slightly growth with D (see Fig. 8). Nevertheless this interesting result has to be investigated more carefully.

4. CONCLUSIONS

1. Many factors influence on the resulting mechanism of the luminescence process in a shifter and on it properties. The result of such the influence is not same for different compositions.

2. The examples of POPOP and TP in Sylgard-527 have shown that it is possible to obtain the as radiation resistant materials for shifters by dyeing the gel-composition.

3. Introduction of PB in Sylgard-527 demonstrates that such a problem is not trivial and could not be solved for each combination of the materials.

4. With increase of the concentration of luminescent molecules in gel-composition the S-value (4) has the tendency to grow.

5. For high concentration of luminescent molecules when the tendency to form their crystallization phase inside the gel composition takes place the S-value (4) decreases.

6. Molecules of POPOP and TP absorb the violet light. It will be interesting to develop the gel-compositions those absorb the light in blue region. We will discuss this problem in our future works.

ACKNOWLEDGEMENTS

This work was supported by the State Fund for Fundamental Research of Ukraine (project No. F58/06, "The effect of large radiation doses on scintillation and optical properties of novel types of organic detectors").

References

1. CMS Collaboration, Technical proposal for the upgrade of the CMS detector through 2020, CERN-LHCC-2011-006, CMS-UG-TP-1, LHCC-P-004, CERN, Geneva, 2011.

2. J.B. Birks. *The theory and practice of scintillation counting*, Oxford, London: "Pergamon Press Ltd". 1967, 662 p. (p. 55, 205).

3. A.Yu. Boyarintsev, N.Z. Galunov, N.L. Karavaeva, A.V. Krech, I.V. Lazarev, L.G. Levchuk, T.A. Nepokupnaya, V.D. Panikarskaya, V.F. Popov, P.V. Sorokin, O.A. Tarasenko. Study of radiation-resistant gel bases for composite detectors // *Functional Materials*. 2013, v. 20, N6, p. 471–476.

4. M. Schatz. *Silikonovy Kaucuk (in Czech)*. SNTL-Nakladatelstvi Technicke Literatury, Praha 1975.

5. Information about Dow Corning brand Silicone Encapsulates. http://bdml.stanford.edu/... .../twiki/pub/Rise/PDMSProceSS/... .../PDMSdatasheet.pdf.

6. OSTEK Materials. Dow Corning 527 silicone dielectric gel. http://www.ostec-materials.ru/... .../materials/dow-corning-527silikonovyy-dielektricheskiy-gel.php.

7. N.Z. Galunov, V.P. Seminozhenko, A.M. Stepanenko. Electronic processes and radioluminescence for crystalline systems with different structure perfection // *Molecular Crystals and Liquid Crystals*, 2001, v. 361, N1, p. 287–292.

8. N.Z. Galunov, B.V. Grinyov, N.L. Karavaeva J.K. Kim, Y.K. Kim, O.A. Tarasenko, E.V. Martynenko. Development of new composite scintillation materials based on organic crystalline grains // *IEEE Transactions on Nuclear Sciences*. 2009, v. 56, N3, p. 904-910.

9. S.K. Lee, J.B. Son, K.H. Jo, B.H. Kang, G.D. Kim, H. Seo, S.H. Park, N.Z. Galunov, Y.K. Kim. Development of large-area composite stilbene scintillator for fast neutron detection // *Journal of Nuclear Science and Technology*. 2014, v. 51, N1, p. 37-47.

СВЕТОВОДЫ НА ОСНОВЕ ДИЭЛЕКТРИЧЕСКИХ ГЕЛЬ-КОМПОЗИЦИЙ

Н. З. Галунов, Н. Л. Караваева, С. У. Хабусева, А. В. Креч, Л. Г. Левчук, В. Ф. Попов, А. Д. Самохин, П. В. Сорокин

Спектросмещающие световоды, которые позволяют смещать сигнал со сцинтиллятора в более длинноволновую область и передавать его фотоприемнику, были разработаны на основе радиационно-стойкой гель-композиции Sylgard-527. В качестве люминесцентных молекул в нее вводились молекулы POPOP (1,4-бис-(2-(5-фенилоксазолил))-бензола), PB (1,4-дифенил-1,3-бутадиен), либо TP (p-терфенила). Анализируется: количество отсчетов в диапазоне спектра люминесценции S, относительное значение этой величины S_R, значение коэффициента пропускания до и после облучения. Наилучшие результаты получены для POPOP и TP.

СВІТЛОВОДИ НА ОСНОВІ ДІЕЛЕКТРИЧНИХ ГЕЛЬ-КОМПОЗИЦІЙ

М. З. Галунов, Н. Л. Караваєва, С. У. Хабусєва, А. В. Креч, Л. Г. Левчук, В. П. Попов, А. Д. Самохін, П. В. Сорокін

Спектрозміщуючи світловоди, які дозволяють зміщувати сигнал сцинтилятору в більш довгохвильову область і передавати його до фотоприймача були розробленні на основі радіаційно-стійкої гель композиції Sylgard-527. В якості люмінесцентних молекул в неї вводились молекули POPOP (1,4-бис-(2-(5-фенилоксазолил))-бензол) PB (1,4-дифеніл-1,3-бутадієну), або TP (-терфенила). Проаналізовано: кількість відліків у діапазоні спектра люмінесценції S, відносне значення цієї величини S_R, значення коефіцієнта пропускання до и після опромінення. Найкращі результати отримані для POPOP и TP.