ISSN 1027-5495. Functional Materials, 23, No.1 (2016), p. 40-44.
doi:http://dx.doi.org/10.15407/fm23.01.040

Radiation-hard plastic scintillators with 3-hydroxyflavone derivatives

Yu.A.Gurkalenko, P.N.Zhmurin, V.N.Lebedev, V.N.Pereymak, O.V.Svidlo

Institute for Scintillation Materials, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Nauky Ave., 61001 Kharkiv, Ukraine

Received October 10, 2015

New compositions of radiation-hard plastic scintillators (PS) with content of 3-hydroxyflavone (3HF) derivatives are proposed. It is shown, that the new PS based on polystyrene with these dopants have both the higher radiation hardness and the higher light output, than PS with original 3HF.
Keywords: plastic scintillators, radiation-hard, 3-hydroxyflavone polystyrene.

Предложены новые составы радиационно-стойких пластмассовых сцинтилляторов (ПС) с содержанием производных 3-гидроксифлавона (3HF). Показано, что новые ПС на основе полистирола с указанными добавками имеют не только более высокую радиационную стойкость, но и более высокий световой выход, чем ПС с исходным 3HF.

Радіаційно стійкі пластмасові сцинтилятори з похідними 3-гідроксіфлавону. *Ю.А.Гуркаленко, П.М.Жмурін, В.М.Лебедєв, В.М.Переймак.*

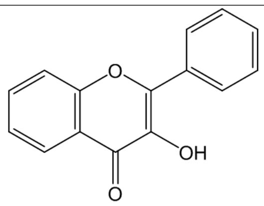
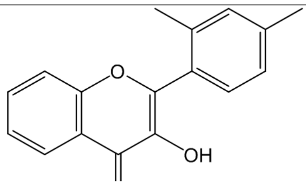
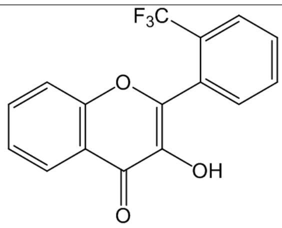
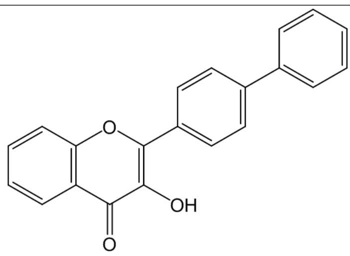
Запропоновано нові склади радіаційно-стійких пластмасових сцинтиляторів (ПС) з вмістом похідних 3-гідроксифлавону (3HF). Показано, що нові ПС на основі полістиролу із зазначеними домішками мають не тільки більш високу радіаційну стійкість, але і більш високий світловий вихід, ніж ПС з первісним 3HF.

1. Introduction

Plastic scintillators (PS) are widely used for manufacturing of detecting devices in high-energy physics experiments. The particle physics development is provided both by studied particles energy increase, and by accelerated particles beam luminosity increase. At the present time energy of 15.4 TeV ($15.4 \cdot 10^{12}$ eV) releases as a results of collision of two protons on colliding beams of the Large Hadron Collider LHC (CERN, Switzerland) at the integral luminosity of $1.7 \cdot 10^{34}$ $cm^{-2}s^{-1}$ [1]. At these conditions the total radiation effect on the closest to the beam axis PS can reach of 10 Mrad for 10 years of detector operation [2]. After planned upgrade in 2016–2018 years the LHC beam protons energy will double, and the luminosity will increase on the order [3]. Accordingly, the total dose of irradiation on the mounted particle detectors will increase on the order too.

However, widely used detecting devices, mounted on the beams of the collider LHC, commercial PS do not meet new requirements of the radiation hardness. The doses of the light output of half-reducing ($D_{1/2}$) of commercial PS SCSN-81T, BC-408 and UPS923A are in limits of 1–2 Mrad, and of radiation-hard UPS-98RH — 5.1 Mrad [4].

The main cause of the light output reducing under irradiation influence is formation of different radiolysis products, which effectively absorb the light in wavelength range from 300 to 400 nm, i.e. in the field of emission of the majority of luminescent dopants (LD), used for activation of a poly-

Compound code (dopant)	Structural formula	Compound name H D B H
1214		3-Hydroxy-2-phenyl-4H- chromen -4- one (3-hydroxyflavone or 3HF)
1227		2-(2,4-Dimethylphenyl)-3- hydroxy - 4H- chromen -4- one
1229		3- Hydroxy -2-(2-(trifluoromethyl) phenyl)-4H- chromen -4- one
1231		2-([1,1'-Biphenyl]-4-yl)-3- hydroxy - 4H- chromen -4- one

mer base of PS [5]. Therefore, one of the ways of the PS radiation hardness increasing is applying LD, the emission spectrum of which must be in more long-wave range, out of the absorption band of the radiolysis products. The most effective way of implementing this idea is use of phosphors with the large Stokes shift. One of such phosphors is 3-hydroxyflavone (3HF), which was used for obtaining the radiation-hard PS in the work [6]. PS with binary composition (activator and polymer base) have shown better radiation hardness relatively to PS with ternary composition (activator, shifter, polymer base). I.e. 3HF is better to use as an activator to remove the influence of radiolysis products in the transmission of radiation to a spectrum shifting dopant. However, 3HF is not an effective activator, because of its absorption band maximum is at wavelength of 360 nm and just partially overlaps with the emission band of polystyrene matrix with the maximum at 280 nm. This fact and the little quantum yield of 3HF (about 40 %) lead to reducing the quantum yield of the PS with 3HF relatively to the PS with conventional ternary composition.

In the present work investigations of binary and ternary scintillation systems on polystyrene base with different derivatives of 3HF were performed with the purpose to increase the light yield and the radiation hardness of obtained compounds.

2. Experimental

Modification of 3HF molecules was performed in the following way. All 3HF derivatives were synthesized by the Algar-

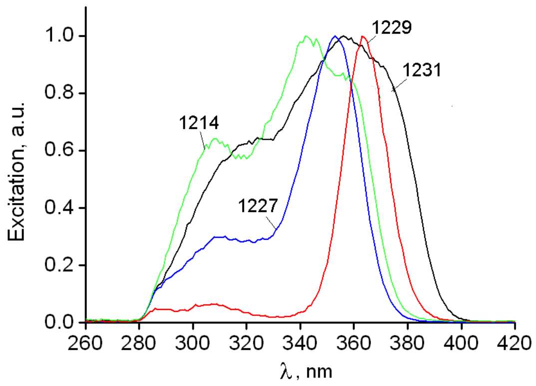


Fig. 1. Excitation spectra of luminescence band 530 nm of 3HF molecules and its derivatives in toluene with concentration of 10^{-5} mol/liter.

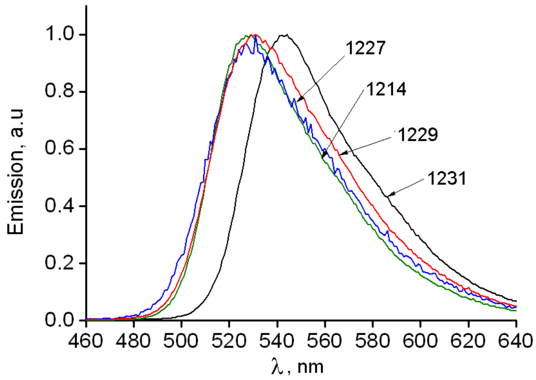


Fig. 2. Luminescence spectra of 3HF (1214) and its derivatives (1227, 1229, 1231).

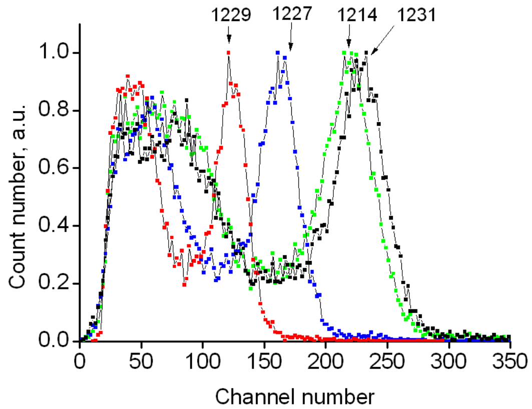


Fig. 3. Pulse height distributions of Bi-207 source, measured with PS, contained 3HF or its derivatives.

Flynn-Oyamada reaction by oxidation of *o*-hydroxyphenylstyrylketones to flavones with hydrogen peroxide through produced dihydroflavanols [7]. For this, equimolar amounts of *o*-hydroxyacetophenone and different benzaldehyde derivatives were dissolved in ethanol and while mixing aqueous sodium hydroxide solution was added. Obtained chalcone was subjected to oxidation with 30 % hydrogen peroxide for several hours, then neutralized with diluted mineral acid, filtered, washed with water and dried. Obtained derivatives of 3-hydroxyflavone was purified by recrystallization from methylene chloride and hexane.

Table 1 shows the compounds that have been used by us as fluorescent dopants in manufacture of the PS, as well as abbreviations (codes) of these substances.

For production of the PS with different compositions, fluorescent dopants were placed in glass vials and dissolved in styrene at 80°C, purged with argon for 15 min and polymerized by thermal radical polymerization at temperature of 150°C for 5 days. From obtained bar the samples were cut with the shape of cylinders of 16 mm diameter and of 10 mm height, and then polished to optical purity. Compositions of manufactured PS are shown in Table 1.

To measure the light output, the PS samples were mounted on a photomultiplier through immersion fluid and excited by monoenergetic conversion electrons of a radiation source Bi-207. The light output was determined by position of the peak maximum of electrons with energy of 975 keV. To measure the time characteristics of the PS it was used an electron source Sr-90. Time characteristics were determined by the delayed coincidence method with a two-channel system of two PMT Hamamatsu 9800 with Start and Stop channels. As a start pulse the Cerenkov radiation signal from a pure polymethylmethacrylate sample was used.

To determine radiation hardness, the PS samples were placed in air medium into radiation field of a Co-60 source with the dose rate of 50 rad/min and were irradiated with dose of 3.3 Mrad. Measurements of the light output of the samples were performed right away after the irradiation.

3. Results and discussion

Molecules of 3HF have the unique luminescent property — presence of the large Stocks shift due to transfer of a proton in excited state. The absorption band maximum of 3HF is located in region of 350 nm, at the same time the luminescence band has the maximum at 530 nm. By attaching different substituents to the 3HF molecule,

Table 2. Compositions of the PS and their light output before (*L0*) and after irradiation with dose of 3.3 Mrad (*L*), and the ratio of the light outputs of irradiated to unirradiated PS (*L*/*L0*)

PS sample number	Polysterene PS compound	Light yield before irradiation, (*L0*)	Light yield after irradiation with dose 3.3 Mrad (*L*)	*L*/*L0*, %
1	2 %	1214 (3HF)	64	49
2	2 %	1227	47	29
3	2 %	1229	40	29
4	2 %	1231	68	55
5	2 % *p*-TP + 0.05 1214	56	38	68
6	2 % *p*-TP + 0.05 % 1227	56	27	48
7	2 % *p*-TP + 0.05 % 1229	56	39	69
8	2 % *p*-TP + 0.05 % 1231	85	63	74
UPS923A	Standard 2 % *p*-TP + 0.05 % POPOP	100	47	47

one can modify its spectrum luminescent properties.

As already mentioned, 3HF derivatives can be used in composition of PS or as an activator, and for this the main excitation band must coincide with polystyrene luminescence band (280 nm), or as an shifter, in this case their excitation band must coincide with the luminescence band maximum of the activator. Traditionally, molecules of paraterphenyl (*p*-TP) with the maximum emission of 360 nm is used as activators of the PS. Fig. 1 shows excitation spectra of obtained 3HF derivatives. Measurements were carried out in toluene solution at a concentration of 10^{-5} mol/liter and at observation wavelength of 530 nm, corresponding to the luminescent band of the studied compounds. As can be seen from Fig. 1, by modifying the 3HF molecules one can change the width of the excitation band of the narrow peak (compound 1229) to a significant broadening of its (compound 1231). The maxima of the luminescence bands do not vary more than 20 nm.

The excitation spectra show that molecules of compound 1231 have the widest excitation band, which is the best suited for use as activator in the PS composition, based on polystyrene.

Fig. 2 shows the luminescence spectra (1214) of 3HF and its derivatives 1227, 1229, 1231. It can be seen that the luminescence band of 3HF (compound 1214) when is modified, does not change significantly, only 1231 derivative has the band maximum which not significantly, on 10 nm, shifted to the red range of luminescence.

In Fig. 3 the pulse height distributions of Bi-207 source are shown, which measured with the PS, contained 3HF or its derivatives (Table 1, PS 1–4). Fig. 3 and Table 1 show that the PS with various 3HF derivatives exhibit significantly different light output.

As can be seen from Fig. 3, the highest light output is inherent in the PS with activator 1231 (Table 2 PS 4), i.e. ~ 10 % larger than that of the PS with unmodified 3HF. This result is somewhat predictable, since 1231 derivative has the widest excitation spectrum (Fig. 1).

Measured temporal luminescent spectra of the PS with 3HF (1214) and its derivatives (1227, 1229, 1231) activators show, that all scintillation compositions have practically similar rise times of intensity of a scintillation flash from level of 0.1 to level of 0.9, equal to 0.9 ns, that is usual for the PS on the basis of polystyrene [8]. As a result of the exponential fit of the kinetic curves obtained we can see that decay time of scintillation flash of all PS is also close to 5.6, 4.8, 5.8 and 4.9 ns for the PS activators 1214, 1217.1219 and 1231, respectively. From these measurements, it can be concluded that the modification of 3HF molecules does not lead to a noticeable change in the kinetic parameters.

In Table 2 compositions of the studied PS and their light output before (*L0*) and after irradiation with dose of 3.3 Mrad (*L*) are shown. Also the ratio of the light outputs after to before irradiation (*L*/*L0*) is shown, which characterizes the PS light output change as a result of radiation influence with dose of 3.3 Mrad. The light output was measured immediately after required radiation dose was collected.

From the Table 2 data, it is seen that the new scintillators with binary compositions exhibit the better radiation hardness compared to the PS with ternary compositions and the standard plastic scintillator UPS923A. Therefore, PS No. 4, containing 2 % of 3HF derivative (1231) has the higher values of the light output and the radiation hardness, than the PS with 3HF and its other derivatives.

4. Conclusions

Thus, as a result of conducted investigations it was shown that:

— use of 3HF derivatives allows to increase the parameters of PS;

— for improvement of the PS properties it is better to use molecules of 3HF derivatives as activator, than as shifter;

— use of 2-([1,1′-biphenyl]-4-yl)-3-hydroxy-4H-chromen-4-one molecules as activator allows to obtain the PS with the highest light output and radiation hardness.

References

1. Design Study of Large Hadron Collider, CERN 91-03.
2. The Level-1 Trigger Technical Design Report, CERN/LHCC 2000-038, CMS TDR 6.1, 15, 40 (2000).
3. O.Bruning, R.Cappi, R.Garoby et al., R. LHC Project Report 626. LHC Luminosity and Energy Upgrade: A Feasibility Study (2002).
4. V.G.Senchyshin, V.N.Lebedev, A.F.Adadurov et al., *Functional Materials*, **20**, 80 (2003).
5. A.D.Bross, A.Pla-Dalmau, in: Proc. of ACS Symp. Ser., 578-590 FERMILAB-PUB-90-224 (1991), p.475.
6. A.D.Bross, A.Pla-Dalmau, *Nucl. Ins. Meth. Phys. Res.*, **A327**, 337 (1993).
7. B.S.Jayashree, N.F.Anjum, Y.Nayak et al., *Pharmacologyonline*, **3**, 586 (2008).
8. J.B.Birks, The Theory and Practice of Scintillation Counting, Pergamon Press, London (1964).