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Organosilicon luminencent compositions for scintillation detectors

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Abstract. Application of organosilicon materials in the detection devices is one of the promising directions in the improvement of their characteristics. Especially efficient are these materials when used as a polymer base of the converting elements.

Described in this paper are compositions and results of the use of polymer luminescent compositions for the increase of chemical resistance and improvement of CsI and CsI (Tl) crystals' characteristics; the latter being in the form of the truncated pyramids with the cross-section as a polygonal and up to 320 mm long. They are intended for furnishing complex modular systems of calorimeters.

The authors studied the effect of the polymer structure (of the stair and branched structure), chemical nature of the luminescent admixtures and their concentration in the composition on the variation of scintillation and performance characteristics of the detectors.

It was shown that application of thin film (15±5 μm) siloxane spectrum shifting coatings to all the facets of the pyramid except for the base which serves as the output window allows not only to reliably protect the scintillator from the effect of the atmosphere moisture but also to correct efficiently its characteristics. The advantage of such coatings is a high stability of their optical and luminescent properties in time, good adhesion and chemical inertness to the scintillator material.

Application of siloxane compositions as coating for CsI gives a possibility to shift the intrinsic luminescence of the crystal towards the region of a higher transparency of the material and better sensitivity of PMT, this allowing to increase the light yield of the fast component by the factor of 1.5. In case of CsI the nonuniformity of the light yield along the pyramid can be lowered while not worsening but even increasing the mean light yield. Such coating is easily removed by a solvent and applied again to the surface not changing the size of the scintillator and the grade of surface treatment.

Keywords: scintillation detector, luminescent composition, organosilicon, radioluminescence.

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1. Introduction

Application of cesium iodide crystals for detectors in the form of truncated pyramids with a polygonlike cross-section intended for furnishing complex modular systems of calorimeters implies enhanced requirements to their scintillation and performance characteristics. The calorimeter design (ball- or barrel-shape) presumes the minimal space between separate active elements of the detector. This restricts the range of materials chosen as light-reflecting and protective elements. Traditionally, the crystals are packed in a white teflon tape and aluminized lavsan.

Provision of scintillation light transfer to the photoreceiver with minimal losses, uniformity of the light yield along the scintillator axis as well as high ratio of fast and slow components of the luminescence in fast CsI scintillators is realized basically by their surface treatment. However, the conventional methods of such treatment, including polishing of all the pyramid facets and partial matting for the increase of the light output uniformity cannot ensure stability of scintillation parameters due to insufficient chemical resistance of alkali halides (AHC). Therefore, in some cases before packing their surface is covered with organosilicon varnish [1]. Application of protective coating on CsI surface brings to a natural conclusion on the necessity to conduct all operations on changing the coefficient of light collection for separate parts of the scintillator using films that possess different optical and spectral-luminescent properties and which can be easily removed when necessary.

The purpose of the present paper is the development of investigations focused on the improvement of CsI detector characteristics by changing chemical, optical and spectral-luminescent characteristics of their surface owing to application of organosilicon spectrum-shifting coatimgs (s.s.c.).

2. Choice of a polymer base for spectrum-shifting compositions

The performance properties of organosilicon coatings depend on the nature of organic radicals. The most universal polymers are polyphenylsiloxanes which together with high thermal stability possess high radiation resistance and good moisture proof properties. The phenyl bonds in the polymer are also important for an efficient excitation energy transfer to the luminescent admixtures (l.a.) [2].

Taking into account all said above, the authors have chosen solutions of polyphenylsiloxane resins – organosilicon varnishes: KO-08, KO-85 and solutions of organosilicon block-copolymers with a stair structure (BSP-Lest) containing phenyl bonds as a polymer base for the developed s.s.c. The chosen polymers, as well as solvents for them have a nonpolar character which is distinguished by a low moisture absorption. In order to make higher optical transparency of varnishes, the authors used a method of purification. The latter includes a sorption trapping of impurities with the use of silica adsorbents, aluminium oxide and hydroxide which allow to increase light transmission of organosilicon films up to 99% in the wavelength range above 300 nm.

3. Object and methods of investigation

Blanks of CsI scintillators in the form of hexagonal truncated pyramids 220-mm in height with a side of the lower base 70 mm and those in the form of truncated tetrahedral pyramids 320 mm in height, with the lower base side 58 mm and the upper one 45 mm, were taken for the experiments. Characteristics of the pyramids are given in Table 1. Absorption spectra of crystals and compositions were measured using the spectrophotometer SF-26 in the range of 215…650 nm.

Light output of CsI crystals, the ratio of the fast and low components of their luminescence were measured by a single-photon method (the method of delayed coincidences) [3] with the scintillations in crystals excited by the annihilation γ-quanta from a radioactive ^{22}Na source. A 9822QKB photomultiplier was used as a photodetector in the stop channel. The light output of the fast UV component was determined using the same PMT but at excitation from the ^{137}Cs source. The light output and its uniformity along the scintillator length were measured for CsI(Tl) using a PMT R669 and ^{22}Na isotope.

The radioluminescence spectra of the studied crystals were measured using a monochromator MDR-23 and PMT-100 at excitation by γ-quanta from ^{241}Am. The luminescent admixtures used for making s.s.c. are given in Table 2.

4. Results and discussion

The most important characteristic of the material used as a base of s.s.c. is its transparency in the region of the luminescence spectrum of used luminophors. Introduction of luminophors and increase of their concentration worsens the transparency of the convertor. Deterioration of transparency at the increase of l.a. concentration restricts the range of their allowed concentration: $\leq 1\times10^{-4}$mole/l for l.a. of yellow-green and $\leq 1\times10^{-5}$ mole/l for l.a. of yellow-orange luminescence.

Fig. 1 shows the transmission spectrum of the film coating on the base of purified organosilicon varnish KO-08 containing as l.a. sfPDmaP 15±5 µm thick (curve 1) at the allowed concentration and RL spectra of CsI scintillators without a coating (curve 2) and with it (curve 3).

As one can see from Fig.1 s.s.c. is highly transparent, and its spectral-luminescent characteristics coincide with

Table 1. Spectral-luminescent characteristics of CsI and CsI(Tl) scintillators

Scintillator	Maximum of the lumin. spectrum, nm	Lumin. time, ns	Wavelength λ, nm	Absorption coefficient, cm^{-1}
CsI				
Main line	300	5-10	300	0.010
Additional line	>400	1000	400	0.005
CsI(Tl)				
Main line	550	900	420	0.008
Additional line	420	$(2\text{-}3)\cdot10^3$	550	0.005
			650	0.005

Table 2. Spectral-luminescent properties of luminescent admixtures [4-6]

N/N	l.a.	Wavelength in the maximum of the absorption spectrum, nm	Wavelength in the maximum of the luminescent spectrum, nm	Quantum yield, %	Luminescence time, ns
1	POPOP	364	420	0.41	1.44
2	TPB	345	450		1.6
3	TB-PVD	305	360		0.24-0.62
4	PPO	305	360	0.51	
5	Coum.1	360	410		
6	sfPDdmaP	395	495	0.55	
7	1-N-3-fSPP	395	550	0.7	
8	fSPP	412	495		
9	sfPOdmaP	400	513		
10	4-MNA	395	495		

l.a. see Table 2), i.e. meet requirements to the provision of conversion efficiency.

Shown in Fig. 2 are transmission spectra of CsI(Tl) sample: curve 1 – without a coating; curve 2 – with a coating on the base of KO-85 varnish; curve 3 – with a coating KO-85+sfPDmaP; curve 4 – with a coating KO-85+1-N-3-fSPP.

The transmission spectra of CsI crystal Ø30×4 mm are presented in Fig. 3: curve1 – without a coating; curve 2 – with a coating on the base of KO-08 varnish; curve 3 – with a coating KO-08+TB-PVD+Coum.1.

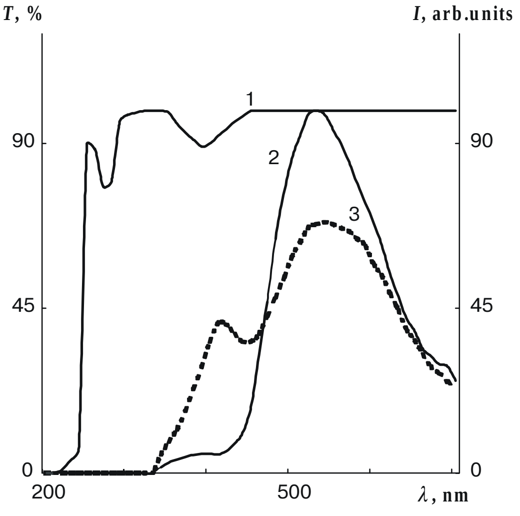

Fig. 1. Spectral-luminescent properties of s.s.c. based on the purified organosilicon varnish KO-08 containing sfPDdmaP 15±5 μm thick as l.a. at the allowed concentration: 1 – transmission spectrum of s.s.c., 2,3 – radioluminescence spectra of CsI scintillators without coating (curve 2) and with coating (curve 3).

As one can see from Figs 2 and 3, application of s.s.c. to the crystal surface makes light transmission better by 7%.

The results of the study of the effect of s.s.c. composition on scintillation characteristics of the CsI(Tl)-based detectors are presented in Table 3. The crystals were made in the form of truncated hexagonal pyramids of 320 mm height; all facets except for the big base being polished and covered with organoluminescent varnish-based s.s.c. and packed in a light reflecting paper Tyvek and aluminized lavsan.

As Table 3 shows, the application of a thin film coating without l.a. increases a bit the mean light yield of the detector, perhaps, due to the rise of the scintillator transparency. However, the distribution of this light yield becomes more nonuniform along the axis of the detector. Application of s.s.c. allows to improve the light yield C, its distribution along the scintillator axis L and to lower the nonuniformity of light collection V. This being so, the observed effect turns out to be stronger provided green luminescence l.a. are used since their relative luminescence efficiency is 4–5 times higher than that of yellow luminescence l.a. This is connected with the possibility to add a much higher (10–100 times) concentration of green luminescence l.a. to the s.s.c. material.

By varying the concentration and type of l.a., one can either increase or decrease the local light yield of different parts of the detector. When necessary, this coating can be easily removed. None – the removal or a repeat application of s.s.c.– brings the scintillator behind the size limits tolerance.

The results of the measurements of scintillation characteristics of CsI-based detectors without coating and after application of s.s.c. (thin layer 15±5 μm) to all the side facets of the truncated hexagonal pyramids except for

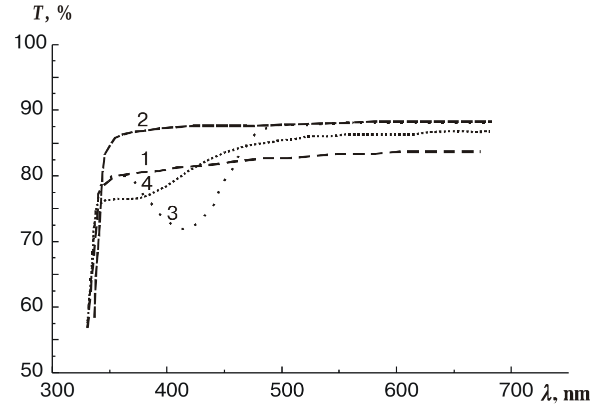

Fig. 2. Transmission spectra of CsI(Tl) crystal Ø30×4mm in size: curve 1 – without coating; 85; KO-85+fsPPD; curve 4 – with a coating KO-85+1-N-3-fSPP.

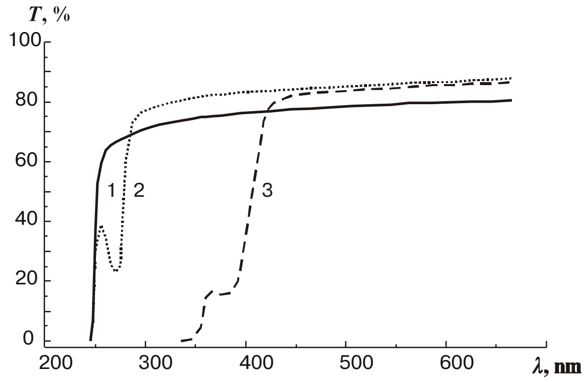

Fig. 3. Transmission spectra of CsI crystal Ø30×4mm in size: curve 1 – without coating; curve 2 – with a coating on the base of the varnish KO-08; curve 3 – with a coating KO-08+TB-PVD+Coum.1.

the big base which serve as the output windows are given in Table 4. The fluoroplast film + mailar composition were used as a light reflecting element.

Table 4 shows that the increase of F/T and light yield of the fast component of the detectors depends on the applied l.a. The best results were obtained when combination l.a. (TB-PVD+Coum1) is used. Their usage in the creation of thin film (15±5 μm) s.s.c. ensures the improvement of fast component light yield up to 80% and F/T up to 8%.

Basing on further investigations the authors found that though the application of organosilicon block-copolymers as film base provides the improvement of physical-mechanical properties of s.s.c. the compositions on their basis have low stability of the spectral-luminescent properties in the performance process. Scintillation parameters of the detectors based on CsI scintillators with s.s.c., made of the organosilicon varnish KO-08 did not practically change for two years.

Table 3. Scintillation characteristics of CsI(Tl)-based detector

Scintillator	Coating composition	Light yield, %	Nonuniformity of light collection, %
1	Without coating	34.41	6.94
1	KO-08	36.84	9.47
1	KO-08+ sfPDdmaP	4009	4.74
1	KO-08+ sfPOdmaP	39.96	4.21
1	KO-08+1-N-3-fSPP	37.82	4.12
1	KO-08+4-MNA	39.04	4.34
2	Without coating	36.64	4.98
2	KO-08+ sfPOdmaP	38.82	4.34
3	Without coating	36.94	4.89
3	KO-085	37.82	6.82
4	KO-085 +1-N-3-fSPP	37.94	3.92
	Without coating	36.81	6.1
4	KO-08+4-MNA	38.52	4,12

Table 4. Characteristics of CsI-based detectors

Pyramid, N	Surface state, coating composition	F/T	Light yield from respect surface, %	Conformity with techn.
1	Polished, without coating	0.65	1.0	–
1	Varnish KO-08	0.71	1.6	+
1	Varnish KO-08	0.72	1.7	+
	Varnish KO-08	0.73	1.8	+
1	Solution of block-copolymer of stair structure + + TB-PVD +Coum.1	0.74	1.8	+
1	Solution of BSP-Lest + + POPOP +Coum.1	0.72	1.8	+
2	Polished, without coating	0.72	1.0	–
2	Solution of BSP-Lest + + TB-PVD +Coum.1	0.78	1.7	+
2	Varnish KO-08 + + TB-PVD +Coum.1	0.77	1.8	+
3	Polished, without coating	0,8	1.0	+
3	Varnish KO-08 + + TB-PVD +Coum.1	0.85	1.5	+
4	Polished, without coating	0.68	1.0	–
4	Solution of BSP-Lest + + TB-PVD +Coum.1	0.76	1.8	+
	Varnish KO-08+ + TB-PVD +Coum.1	0.76	1.8	+

Conclusions

Thus, the application of organosilicon s.s.c. is one of the promising trends for the improvement of detector characteristics since allows to change the approach itself to the problem of leveling light collection factor. There appears a possibility to change not only its time constant and light yield of separate areas of the crystal by varying the spectral composition of the scintillator luminescence increase of the relative contribution of fast CsI scintillators but also to raise their stability due to variation of chemical properties of the surface.

Appendix

PPO – 2,5-phenyloxzolyl
TB-PVD – 2-(4-tretbutylphenyl)-5-(4-biphenyl)-oxadiazol)-1,3,4
POPOP – 1,4-di-2-(5phenyloxzolyl)
Coum 1 – dietylamino-4-methylcoumurin
1MN – morpholinonaphthalenedicarboxylic anhydride
4-MNA – 4-morpholinonaphtallenedicarboxylic anhydride
sfPDdma – 2-(4-ftuorosulfonylphenyl)-5-(4'-dimethylaminophenyl) -1,3 - oxazol
sfPOdmaP – 2-(4- ftuorosulfonylphenyl)-5-(4-)-1,3-oxazol
fsPP – 1,5-diphenyl 3-(4'- ftuorosulfonylphenyl)-2-pyrazoline
1-N-3-fsPP – 1-(1-naphtyl)-3-(4- ftuorosulfonylphenyl)-5-phenyl- 2- pyrazoline

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