Nuclear Instruments and Methods in Physics Research A 486 (2002) 40–47

NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH
Section A

www.elsevier.com/locate/nima

Functional possibilities of organosilicon coatings on the surface of CsI-based scintillators

L.A. Andryustchenko[a], A.M. Kudin[a,*], V.I. Goriletsky[a], B.G. Zaslavsky[a], D.I. Zosim[a], T.A. Charkina[a], L.N. Trefilova[a], D. Renker[b], S. Ritt[b], D.A. Mzavia[b]

[a] *Institute for Single Crystals, NAS of Ukraine, 60 Lenin Avenue, 61001 Kharkov, Ukraine*
[b] PIBETA *Collaboration, Paul Scherrer Institute, CH 5232 Villigen, Switzerland*

Abstract

It has been shown that a thin film (15 ± 5 μm) based on organosilicon coating applied to all surface of CsI and CsI(Tl) scintillators excluding the output window, can combine the following functions: (1) covering from atmospheric effects; (2) scintillation light convertor of luminescence towards the region of higher spectral sensitivity of the photoreceiver and (3) ancillary surface for performance of operations on changing the light collection coefficient without the risk to exceed limited size tolerations. Wavelength-shifting coating effect on radiation hardness of pure CsI is discussed. After irradiation a new absorption bands appear in the range 250–300 nm mainly. So, contrary to the 310 nm emission, the energy losses for converted light remain the same. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cesium iodide scintillator; Spectrum shifting coating; Yield uniformity; Energy resolution

---

1. Introduction

CsI and CsI(Tl) crystals are widely used in high-energy physics. For instance, in the experiment PIBETA [1] the ball-like calorimeter (2 m in diameter) consists of 240 “pure” CsI-based detectors in the form of hexagonal and pentagonal truncated pyramids 220 mm in height. The BaBar [2] calorimeter includes 5760 CsI(Tl) detectors in the barrel-shaped cross-section and 820 ones in the caps. The total number of detectors in the calorimeter BELLE [3] is 8816. The signal is registered with the help of PMT with a quartz window of the type R9822Q for CsI and silicon PIN photodiode (Hamamatsu S2744–08) for CsI(Tl). In both cases the scintillation spectrum is not in full conformity with the spectral sensitivity of the receivers.

Scintillation characteristics of the detecting modules depend on the quality of the grown crystals and are defined to a high extent by the state of the scintillator surface, material of the reflector and elements of optical coupling [4]. Uniformity of light output along the axis of long scintillators is achieved at the final stage of their manufacturing by an additional surface treatment [5]. The so-called “tuning” of crystals at the final stage very often does not give a required result from the first attempts. Repeated polishing and matting of the extremely plastic CsI material very often results in falling outside the tolerable size limits. Let us note that rigid requirements of the

---

*Corresponding author. Tel.: +380-572-307-994; fax: +380-572-321-082.

E-mail address: kudin@isc.kharkov.com (A.M. Kudin).

PII: S0168-9002(02)00672-1

size are defined by physical sense of the experiments.

Surfaces of water-soluble scintillators, especially matted ones, degrade with time under the effect of atmospheric moisture. In some cases crystal surfaces are coated with protective organosilicon varnish prior to packing [6].

All the above-mentioned considerations have substantiated the study of properties of thin film coatings (TFC) on the basis of organosilicon polymers aiming to examine possibilities of combining functional purposes: (1) protection of scintillators from atmospheric effects and (2) shifting of luminescence towards the region of higher spectral sensitivity of the photoreceiver and (3) ancillary surface for performance of operations on changing the light collection coefficient.

2. Choice of the polymer base

The choice of TFC base is based on the results [7–9] according to which these polymers most fully meet the requirements of: (1) chemical inertness; (2) high adhesion to the scintillator material; (3) hydrofugacity; (4) stability of characteristics under rigid operation conditions. Solutions of high-molecular organosilicon polymers applied to the surface of articles after solvent evaporation leave a film on it. After a corresponding drying, this film acquires hardness, thermal and cold resistance as well as all the mentioned properties. Besides, this film levels the natural roughness of the surface, increases the degree of the surface mirror quality which allows making higher transparency of the converting units [9]. In some cases the integral luminescence of spectrum shifting luminescent dopants (SLDs) added to the organosilicon base becomes higher.

In particular, organosilicon varnishes on the basis of polymethylphenylsiloxane resines KO-08 and MF-193 were chosen as a TFC base. These varnishes were additionally purified by the sorption method for achieving a transparency of 98% at a layer thickness of 1 cm in a wavelength range of $\lambda > 300$ nm for the first type and $\lambda > 400$ nm for the second one. Solutions of block-copolymers (Lest) of the stair structure which form the most strong and hard films on the crystal surface were used in this work apart from the ones mentioned above.

3. Object of the study

3.1. CsI crystals

The experiments were carried out with the detectors cut of single crystalline boules ~500 mm in diameter and up to 200 mm in height. The crystals were grown by a modified Kyropulos method [10] with additional purification of the raw material and melt. The authors used modules in the form of hexagonal truncated pyramids 220 mm in height of the type HEX A (the diagonal of the big base being 150 mm and that of the small one being 70 mm) and HEX C (diagonals 120 and 60 mm) which did not correspond to the size tolerance in the experiment Pibeta [1]. Investigations were carried out both at the Institute for Single Crystals, Ukraine and Paul Scherrer Institute, Switzerland.

The radioluminescence (RL) spectrum of CsI crystals covers the region 250–320 nm with the maximum near 310 nm (Fig. 1). The maximum of spectral sensitivity of the PMT used lies in the region of 380 nm. At conversion of the UV luminescence into the blue region one has to take into account that the typical decay time of the fast

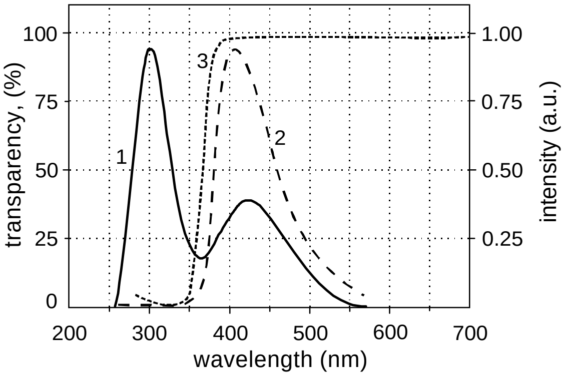

Fig. 1. Radioluminescence spectra of CsI sample ∅ 30 × 5 mm before (1) and after (2) coating with the composition "KO-08 + TB-PVD + Coum.1". (3) Transmission spectrum of the film itself.

component is about 10 ns [11]. One more peculiarity of CsI crystals is the fact that the absorption coefficient at 300 nm (usually 0.015–0.025 cm^{-1}) significantly differs from that at 400 nm ($\sim 0.005\,\mathrm{cm}^{-1}$) [12].

Apart from conventional parameters (light yield and energy resolution) a ratio F/T is often used for the evaluation of CsI quality. This ratio is defined as the output for the first 100 ns to the total output for 1000 ns.

3.2. CsI(Tl) crystals

The experiments were carried out with the detectors cut out of single crystalline boules $\sim$450 mm in diameter and up to 350 mm in height. The crystals were grown by a modified Kyropulos method with replenishment by the melted raw material. The melt was additionally purified from the oxygen-containing impurities in the feeder of the platinum crucible [13]. Modules in the form of tetrahedral truncated pyramids 327 mm in height having typical size of the upper base 58 mm and that of the lower one 45 mm did not correspond to the size tolerance in the experiment BaBar [2].

Light output and its uniformity along the scintillator axis were determined for CsI(Tl) detectors wrapping in one layer of the reflector Tyvec [5]. The measurements were made using a collimated source ^{22}Na and PMT R669 ($\lambda \sim 600$ nm) with a 20 mm step.

The luminescence spectrum of CsI(Tl) consists of two main bands. The first band is nonelementary and includes a number of overlapped bands in the region 400–440 nm. Those are caused by both intercentre transitions in Tl^+ ions and luminescence of localized excitons near lattice defects of the impurity and structural character. The second band (more intense) lies at 560 nm and is caused by the luminescence of excitons localized near Tl^+ [14]. Light output of the pair "CsI(Tl) + PD" is determined by the output of luminescence at 560 nm [15,16]. The ratio of the mentioned bands depends on concentration of the thallium; relative output of the inefficient luminescence at 400–440 nm is rather high at relatively small content of thallium (see Figs. 3 and 4). The inefficient luminescence at 400–440 nm is expedient to be converted into a longer wavelength region.

The absorption spectra of crystals and compositions were registered on the spectrophotometer SF-26 in the range 215–650 nm. Radio- and photoluminescence spectra were measured on the device SDL-23 at excitation by the gamma-line of the isotope ^{241}Am (60 keV, 6.66×10^{10} Bk).

3.3. Choice of luminescent dopants

The main criterion of choosing SLD when developing spectrum-shifting coatings was the coincidence of the absorption spectrum of SLD with the luminescence spectrum of the scintillator or with that part of it which is expedient to be converted into the region of maximum sensitivity of the photoreceiver. The fact of a possible shifting of the absorption and SLD luminescence spectra at their addition to the polymer base was also taken into consideration. For fast CsI scintillators SLD with short luminescence time of the class of oxazole, diazole and cumarine were taken for CsI(Tl)–SLD of the green and yellow luminescence of the class of pyrazoline, naphthoylenebenzimidazole, diazole, containing different substitutors, in particular, fluorine-containing ones.

Ten types of SLD were used in this work. Their main properties are presented in Table 1 according to Refs. [7,9] and the introduced abbreviations are interpreted in the appendix. From Table 1 one can see that for CsI crystals with the luminescence maximum at 310 nm it is expedient to use mixed compositions of luminophors, for example N3 and 5. For the conversion of the blue band of luminescence towards the longer wavelengths SLD of the green and yellow luminescence are suitable. The relative efficiency of the green luminophors turns out to be 4–5 times higher. This is connected with a possibility to add a higher concentration (10–100 times) of green SLD to TFC.

4. Results and discussion

4.1. CsI crystals

Fig. 1 shows the RL spectrum of CsI sample ∅ 30×5 mm before and after coating with the composition "KO-08 + TB-PVD + Coum.1". Both edge surfaces of the samples were coated with the film $15 \pm 5\,\mu$m thick. Curve 3 represents a transmission spectrum of the film itself. As one can see from the figure practically all the intrinsic luminescence of the crystal in the band 310 nm is absorbed by the film and converted into the region of 400 nm.

The analogous effect on a pyramid 220 mm high, all surfaces of which were coated with the film except that of the output window, will be observed in the indirect light only. Three factors increase the indirect light yield after conversion: (1) better coordination with the photocathode sensitivity; (2) higher transparency of CsI crystals in the range 400 nm; (3) lower refraction coefficient. The analysis of this effect shows that the factor of a better transparency of the crystal is of great importance [12]. Measurement results of the light output and F/T ratio of the pyramids are represented in Table 2. It is obvious that if L is higher by 60–80%, the F/T ratio will also increase by 5–9%.

Table 1
Main properties of the wavelength-shifting luminescent dopants

SLD	Position of absorption (λ_1), nm	Luminescence band (λ_2), nm	Quantum efficiency (η), %	Decay time (τ), ns
POPOP	312	406	0.41	1.44
TPB	345	450		1.6
TB-PVD	305	360		0.24–0.62
PPO	305	360	0.51	
Coum 1	370	410		
SfPDdmaP	395	495		
1-N-3-fSPP	412	550	0.55	
fSPP	400	495	0.7	
sfPOdma	400	513		
4-MNA	395	495	0.6	

In accordance with the results obtained we can draw an important conclusion, that light yield uniformity of modules will be improved. If it is true, an enhancement of the energy resolution is expected. Investigations carried out at Paul Scherrer Institute [17] confirm our conclusion. Fig. 2 shows the results of measurement of the PIBETA calorimeter resolution using a 44-detector "subset" directly illuminated by 70 MeV positrons, and compares them with data before lacquer surface treatment; energy resolution is clearly improved.

Protective spectrum-shifting coatings increase the radiation hardness of the detectors on the basis of CsI pure crystals since the irradiation generates unstable defects mainly absorbing in the range 250–300 nm [18]. It is known that the induced absorption is localized near the crystal surface [19] since repeated polishing allows to regenerate the transparency and light output of irradiated

Table 2
Light output and F/T of CsI modules before and after application of TFC

Type of detector	Type of TFC	Light output	F/T
	Without coating	1.0	0.65
HEX C	KO-08 + PPO + POPOP	1.6	0.71
Flaw by F/T ($F/T < 0.7$)	KO-08 + TB-PVD + POPOP	1.7	0.72
	KO-08 + TB-PVD + Coum 1	1.8	0.73
	Lest + TB-PVD + Coum 1	1.8	0.74
	Lest + TB-PVD + POPOP	1.8	0.72
HEX C	Without coating	1.0	0.72
Flaw by size	KO-08 + TB-PVD + Coum 1	1.8	0.77
	Lest + TB-PVD + Coum 1	1.7	0.78
HEX A	Without coating	1.0	0.80
Flaw by size	KO-08 + TB-PVD + Coum 1	1.5	0.85
HEX A	Without coating	1.0	0.68
Flaw by F/T	KO-08 + TB-PVD + TPB	1.8	0.76
	Lest + TB-PVD + TPB	1.8	0.76

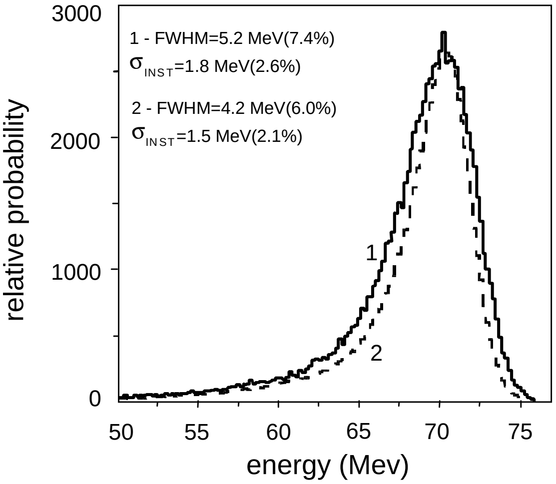

Fig. 2. Energy response of a 44-detector pure CsI array to 70 Mev/c e^+, before (1) the wavelength-shifting lacquer treatment and after (2) treatment.

crystals. Protective coatings inhibit radiation defect formation near the crystal surface, and a spectrum shifting to the range of 400 nm, where transparency changes are insignificant, allows minimizing light losses. The crystals coated with the composition "KO-08 + TB-PVD + Coum.1" withstood the irradiation with a dose of 100 krad (^{60}Co) without visible changes of the light output and F/T ratio.

4.2. CsI(Tl) crystals

The RL spectrum of CsI(Tl) ∅ 30 × 5 mm before and after coating by the composition KO-08 with sfPOdma added is shown in Fig. 3. The transmission spectrum of the film itself (15 ± 5 μm in thickness) is also presented in the same figure. As one can see from this figure the long wavelength absorption band of TFC coincides with the short wavelength one of the crystal radiation. As a result, the converter absorbs a significant part of the luminescence at 400 nm which is reradiated at 500 nm. The analogous effect will be enhanced on a module 327 mm in length due to worse conditions of light collection and a bigger number of reflections from the surfaces. The RL spectrum of the sample with a higher concentration of the dopant is presented in Fig. 4. It is seen that in this case the contribution of the inefficient luminescence at 400 nm to the total output is smaller. Nevertheless, after application of TFC in the form of MF-195 with 1-N-3-fsPP added, the band at 400 nm disappears almost completely. Instead of it an additional luminescence at 540 nm appears. Thus, TFC with SLD successfully play the role of a spectrum shifter.

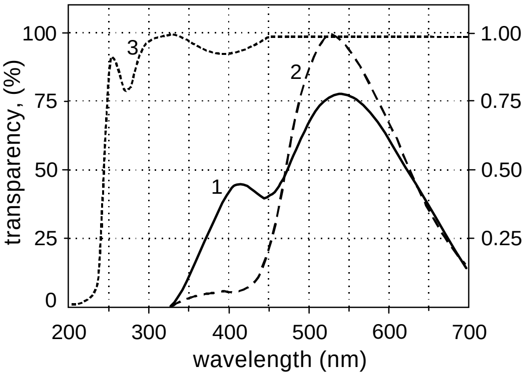

Fig. 3. Radioluminescence spectra of CsI(Tl) sample ∅ 30 × 5 mm before (1) and after (2) coating with the composition "KO-08 + sfPOdma". (3) transmission spectrum of the film itself. The content of Tl is 0.04 mass%.

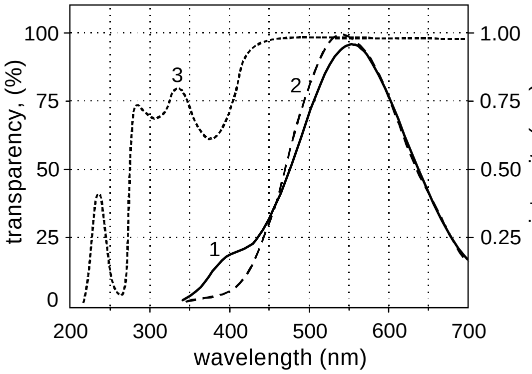

Fig. 4. Radioluminescence spectra of CsI(Tl) sample ∅ 30 × 5 mm before (1) and after (2) coating with the composition "MF-193 + 1-N-3-fsPP". (3) Transmission spectrum of the film itself. The content of Tl is 0.2 mass%.

Characteristics of the detection modules before and after application of TFC are shown in Table 3. As it follows from the table, even the use of a

Table 3
Characteristics of the detection modules

Numbers of detector	Composition of the coating	Light yield, % (>25)	Nonuniformity, % (<5)
1	Without coating	34.41	6.04
	KO-08	36.84	9.47
	KO-08 + sfPDdmaP	40.09	4.74
	KO-08 + sfPOdmaP	39.96	4.21
	KO-08 + 1-N-3-fSPP	37.82	4.12
	KO-08 + 4-MNA	39.04	4.34
2	Without coating	36.64	4.98
	MF-193	37.41	6.42
	MF-193 + sfPOdma	38.24	4.12
	KO-08 + sfPOdma	38.82	4.34
3	Without coating	36.94	4.89
	KO-08	37.82	6.82
	ÊÎ-08 + 1-N-3-fSPP	37.24	3.92
	ÌÔ-193 + 1-N-3-fSPP	37.88	3.42
4	Without coating	36.81	6.21
	MF-193	37.82	8.44
	MF-193 + 4-MNA	38.64	4.34
	KO-08 + 4-MNA	38.22	4.12

protective coating without SLD results in some increase of the mean light yield of the pyramid and a small rise of nonuniformity. A similar result is obtained at a high-quality polishing of the surfaces, i.e. at achieving maximum mirror quality.

The main result following from this table consists of the fact that application of the spectrum-shifting TFC allows not only to increase the mean light yield but also to lower its nonuniformity along the axis of the pyramid. Our experience shows that very often only the use of this technique is sufficient for achieving rather applicable nonuniformity, not exceeding 5%. Explanation of this result follows from the data of Figs. 3 and 4: the converter increases more efficiently the measured light output of those parts of the crystal where thallium concentration is lower (the relative output of the "blue" luminescence band is higher).

It should be noted that leveling of light output of long scintillators using the traditional method of polishing certain parts of the surface and matting of others is finally confined not to the change of the local output but to the variation of illumination of the detector output window. In its idea this method of leveling can be realized only for the case when the photoreceiver size is smaller than that of the output window. Should the size of PMT be bigger than that of the window the leveling can be performed only by the lowest output. The specific feature of the proposed technique consists of light output leveling by its maximum but not medium and, moreover, minimum value.

Application of this technique does not reject but complements and simplifies the standard methods described in Ref. [4]. When necessary a part of the pyramid surface can be matted or blackened. Such combined "tuning" of the detectors allows to achieve easily very high values of light output uniformity, not exceeding 1%, without a risk to violate size tolerance limits. As an example, Fig. 5 shows the light output behavior along the axis of a pyramid the surfaces of which were subjected to a combined treatment. The achieved value of nonuniformity is 0.61%. Initially, for this pyramid $L = 37.73\%$ at $u = 9.6\%$; after TFC application 39.45% and 4.2%, respectively; after matting of the film surface in the places of light output deviations towards lower values 39.21% and 0.61%, respectively. The experiments carried out showed that films based on the chosen polymers

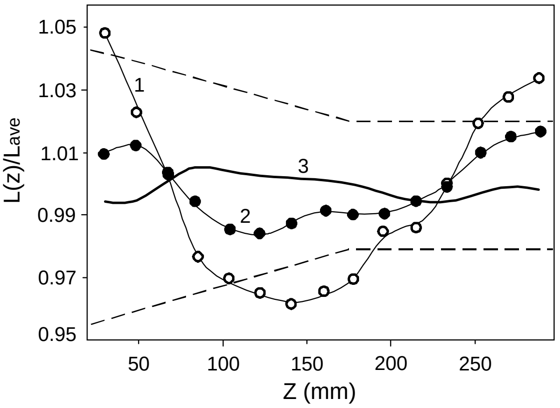

Fig. 5. Distribution of L along the z-axis of the detector CsI(Tl) in the form of pyramid. (1) All surfaces are polished; (2) all surfaces polished are coated with the composition "ÊÎ-08 + sfPOdma"; (3) the same treatment as in curve 2 and after coating the sides of pyramid are partially matted. According to Ref. [1] the requirements of $L(z)$ deviation from an average value is underlined with a dotted line.

can be easily removed or replaced by new ones, when necessary, with no harm for the scintillator surface. These results give evidence of the fact that TFC can play the role of an ancillary surface in operations on the change of light collection coefficient.

5. Stability of TFC in time

Aging of TFC. Scintillation modules with TFC were stored for 2 years under room conditions being wrapped in a black cloth. The repeated tests showed that the parameters of the detectors with TFC based on the lacquer KO-08 and MF-193 practically did not change. The films on the basis of Lest of the stair structure initially had the most attractive appearance (better mirror quality of the coated surface, high degree of antireflection, the highest hardness) and demonstrated characteristics not worse but in some cases even better than those mentioned in Table 3. Unfortunately, after 6 months the light output and nonunifomity of the detectors with such coating turned to be on the level of the values typical for the detectors without TFC. That means that these coatings preserved only a protective function.

6. Conclusion

Summing up the results of this work one can draw a conclusion that organosilicon coatings applied to the surface of scintillators successfully satisfy three functional purposes: (1) protective covering from atmospheric effects; (2) scintillation light converter of luminescence towards the region of higher spectral sensitivity of the photoreceiver and higher crystal transparency; (3) ancillary surface for performance of operations on changing the light collection coefficient. The coatings may be used as radioprotectors for pure CsI crystals. Light output of finished products was greatly increased for pure CsI crystals and insignificantly increased for CsI(Tl) after TFC application. Main results of investigations carried out should be a significant decreasing of light output nonuniformity and energy resolution enhancement for both CsI and CsI(Tl) crystals.

KO-08 should be considered to be a universal base for the spectrum-shifting TFC.

Appendix

The following abbreviations were used in the present paper:

PPO: 2,5-phenyloxzolyl;
TB-PVD: 2-(4-tertbutylphenyl)-5-(4-biphenyl)-oxadiazol)-1,3,4;
POPOP: 1,4-di-2-(5-phenyloxzolyl);
Coum 1: diethylamino-4-methylcoumarin;
1MN: morpholinonaphthalenedicarboxylic anhydride;
4-MNA: 4-morpholinonaphthalenedicarboxylic anhydride;
sfPDdma: 2-(4-fluorosulfonylphenyl)-5-(4′-dimethylaminophenyl)-1,3-oxazol;
sfPOdma: 2-(4-fluorosulfonylphenyl)-5-(4-)-1,3-oxazol;
fsPP: 1,5-diphenyl-3-(4′-fluorosulfonylphenyl)-2-pyrazoline;
1-N-3-fsPP: 1-(1-naphthyl)-3-(4-fluorosulfonylphenyl)-5-phenyl-2-pyrazoline.

References

[1] E. Frlez, et al., Nucl. Instr. and Meth. A 440 (2000) 57.

[2] BaBar Collaboration, Technical Design Report, SLAC-R-95-457, 1995.

[3] Belle Collaboration, Technical Design Report, KEK Report 95-1, 1995.

[4] B.V. Grinyov, V.P. Seminozhenko, Scintillation Detectors of Ionizing Radiations for Hard Operating Conditions, Osnova Publisher, Khakov, 1993 [in Russian].

[5] P.M. Vavra, The tuning of CsI(Tl) crystals: methods and results, Conference Record of 1998 IEEE Nuclear Science Symposium, Vol. 1, 1998, p. 525.

[6] V.M. Aulchenko, et al., Nucl. Instr. and Meth. A 336 (1993) 53.

[7] L.A. Andryhchenko, B.V. Grinev, Instrum. Exp. Tech. 41 (1998) 447.

[8] B.V. Grinyov, et al., Scintillator and phospor materials, Materials Research Society Proceedings Symposium, San Francisco, CA, 1994, Vol. 346, p. 187.

[9] G.I. Britvich, et al., Prib. Tekn. Eksp. 1 (1993) 109.

[10] V.I. Goryletsky, et al., J. Cryst. Growth 128 (1993) 1059.

[11] S. Kubota, et al., Nucl. Instr. and Meth. A 268 (1988) 275.

[12] L.A. Andryustchenko, et al., Prib. Tekn. Eksp. 4 (1997) 19.

[13] B.G. Zaslavsky, et al., J. Cryst. Growth 198–199 (1999) 856.

[14] V. Nagirnyi, et al., J. Phys: Condens. Matter 7 (1995) 3637.

[15] P. Schotanus, R. Kamermans, P. Dorenbos, IEEE Trans. Nucl. Sci. NS-37 (1990) 177.

[16] K.V. Shakhova, L.V. Kovalyova, T.B. Grinyova, Funct. Mater. 5 (1998) 36.

[17] E. Frlez, et al., Pibeta calorimeter response calibration, PSI, Annual Report , Annex 1, 1997, p.12.

[18] A.V. Gektin, N.V. Shiran, Proceedings of the International Conference on Inorganic Scintillators and their Applications, SCINT'97, Shanghai, September 22–25, 1997, p.115.

[19] D.G. Hitlin, G. Eigen, Proceedings of the International Conference on Heavy Scintillators for Scientific and Industial Applications, Crystal 2000, Chamonix, France, 1992, p.467.