Functional Materials 13, No.3 (2006)

Investigation of scintillation characteristics for CsI:Tl and NaI:Tl crystals under different surface treatment conditions

L.A.Andryushchenko, A.Yu.Boyarintsev, B.V.Grinyov, I.V.Kilimchuk, A.M.Kudin, V.A.Tarasov, Yu.T.Vyday

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

The influence of mechanical and chemical methods of CsI:Tl and NaI:Tl crystals surface treatment on their scintillation characteristics at registration of short-range ionizing radiation has been investigated. It is shown that application of ultrathin silicon dioxide powder obtained by sol-gel method and organosilicon liquids at the polishing stage provides the near-surface layer of CsI:Tl and NaI:Tl crystals with minimum light yield nonuniformity. After grinding of the crystal surface, the stability of scintillation characteristics can be achieved by the surface treatment with tetraethoxy silane and oligo-(siloxane hydride) liquid. Application of thin-film organosilicon coating on the CsI:Tl crystal surface turned to the radiation source has improved the pulse-height resolution by 3–5 % in the absolute value at registration of X-ray radiation with E = 5.9 keV.

Исследовано влияние химико-механических методов обработки поверхностей кристаллов CsI:Tl и NaI:Tl на их сцинтилляционные характеристики при регистрации малопроникающего ионизирующего излучения. Показано, что применение на этапе полировки ультрадисперсного порошка диоксида кремния, полученного золь-гель методом, и кремнийорганических жидкостей обеспечивает получение приповерхностного слоя кристаллов CsI:Tl и NaI:Tl с минимальной неоднородностью светового выхода. После шлифования поверхности кристаллов стабильность сцинтилляционных характеристик во времени может быть достигнута за счет обработки поверхностей тетраэтоксисиланом и олигогидридсилоксановой жидкостью. Нанесение тонкопленочного кремнийорганического покрытия на поверхность кристалла CsI:Tl, обращенную к радиоактивному источнику, улучшило амплитудное разрешение на 3–5 % по абсолютной величине при регистрации рентгеновского излучения с E = 5,9 кэВ.

The scintillation crystals being used in production of radiation detectors are subjected to mechanical and chemical surface treatment. A defective near-surface layer appears during mechanical treatment of the crystals. This layer is characterized by a dense network of micro-cracks. The thickness of the surface layer enriched in defects is 10 to 20 μm. An increased content of impurity ions is also observed in the near-surface layer of tens and even hundreds micrometers thickness [1]. The penetration of impurities in surface layer of CsI crystal is explained by increased concentration of vacancies in this layer and its diffusion towards the surface [2]. At relaxation processes occurring in the surface layer, the physicochemical surface state of treated single crystal changes in time [3, 4] causing instability of some scintillation parameters. The spectrometric characteristics of detectors are defined by the scintillator individual properties (structure, activator content, hygroscopicity, impurities, etc.) [5, 6]. Therefore, the crystal surfaces should be treated taking into account their peculiarities. So, CsI:Tl and NaI:Tl crystals differ substantially in the structural characteristics and hygroscopicity, thus defining distinct approaches to treatment thereof. The state of the radiation entrance surface of these scintillators influences heavily the radioluminescence at registration of the short-range radiations (alpha, X-ray and soft gamma) [2, 4]. The main goal is this work is to investigate the effect of various surface treatment methods of CsI:Tl and NaI:Tl crystals on their spectrometric characteristics at registration of short-range radiation.

The first investigations were done using CsI:Tl crystal samples of ∅25×20, mm size (Nos. 1, 2) with Tl concentration $C_{Tl} = 4\cdot10^{-2}$ mol. %. The samples Nos. 1 and 2 were examined at two energies of alpha-particles from ^{239}Pu isotope: $E_1 = 5$ MeV and $E_2 = 2$ MeV. The indicated energy values were provided by special collimators. The light yield (L) and energy resolution (R) were measured for two shaping times on the analyzer: $\tau_1 = 1$ μs and $\tau_2 = 2$ μs. A Hamamatsu R1307 photomultiplier (PMT) was used as photoreceiver. All samples were placed on PMT without optical contact.

The surfaces of CsI:Tl crystals (Nos. 1, 2) turned to the radioactive source were at first ground using a composition containing ethylene glycol and electric corundum with the abrasive grain size 20 μm, and then polished with ethylene glycol and aluminum oxide with the abrasive grain size 0.3 μm. After the measurements were made, these surfaces were subjected to the same grinding, but without the further polishing. Then the similar measurements were done again. Besides of the light yield and energy resolution, determined were the specific light yield L/E and nonproportionality of response Δ as $\Delta = (L_1/E_1 - L_2/E_2)/(L/E)_{av}$, here $(L/E)_{av}$ is the average value of the specific light yield).

The consideration of measurement and calculation results demonstrates that the deep grinding results in increasing L/E by 60 % at registration of alpha-particles with energy E_2 and by 30 % at E_1 as compared to L/E for the polished surface. The disrupted layer formation due to such treatment results in increasing of the Δ by 20 %. At the same time, the energy resolution absolute value is worsened by 1 to 3 %. At increasing shaping time, the Δ absolute value is observed to increase by 3 to 5 % for the ground surface of CsI:Tl crystals. So it is evidenced that the light yield at alpha-particle energy E_2 is increased due to the slow decay components. It is well known that slow component [7] in CsI is connected with increased concentration of vacancy [2] in surface layer.

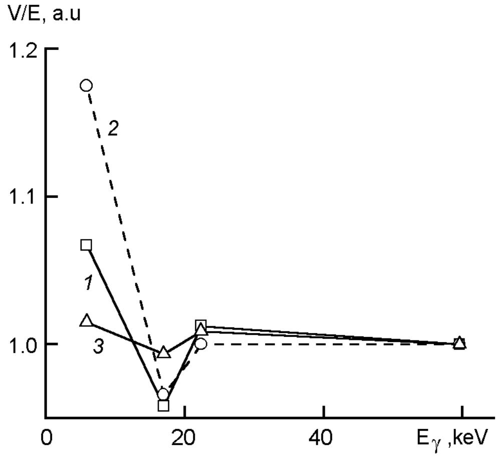

Fig. 1. Dependences of the normalized specific light yield on quantum energy for CsI:Tl crystals: *1* — without coating, *2* — thin-film organosilicon coating at the PMT side, *3* — thin-film coating at the source side.

The influence of treatment methods using thin-film organosilicon coatings of 15±5 μm thickness on the scintillating characteristics was studied on two CsI:Tl samples of ∅30×5, mm size. The Tl concentration in the first sample was $C_{Tl} = 4\cdot10^{-2}$ mol.%, in the second, $C_{Tl} = 7\cdot10^{-2}$ mol.%. The butt surfaces of the crystals were ground and polished using the method specified for the CsI:Tl crystals (Nos. 1, 2), and then thin polishing was carried out using ethyl alcohol ultrafine silicon dioxide powders with grain size no more than 0.15 μm obtained by sol-gel method. Thin-film organosilicon coatings were applied on the one of the crystal butts. During the light yield measurements, this butt was oriented either toward the source, or toward PMT. The light yield was determined under irradiation with X-ray and soft gamma-radiation sources ^{55}Fe (E = 5.9 keV), ^{241}Am (E_1 = 17 keV, E_2 = 59.6 keV), and ^{109}Cd (E = 22.4 keV). The normalized specific light yield as a function of photon energy for the sample with Tl concentration $C_{Tl} = 7\cdot10^{-2}$ mol.% at various arrangements of the surface with applied thin-film organosilicon coating relative to a source is demonstrated in Fig. 1.

The influence of the thin-film organosilicon coating on L/E is manifested itself most in the low energy range and in case of the treated surface oriented towards PMT. When this surface is oriented towards the

Table 1. Influence of thin-film organosilicon coating on the specific light yield L/E and light yield nonproportionality Δ of response for CsI:Tl crystals

Photon energy, keV	L/E without coating, a.u.		L/E with coating at PMT side, a.u.		L/E with coating at source side, a.u.	
	$C_{Tl} = 4\cdot10^{-2}$ %	$C_{Tl} = 7\cdot10^{-2}$ %	$C_{Tl} = 4\cdot10^{-2}$ %	$C_{Tl} = 7\cdot10^{-2}$ %	$C_{Tl} = 4\cdot10^{-2}$ %	$C_{Tl} = 7\cdot10^{-2}$ %
5.9	7.12	7.63	9.8	9.66	9.66	9.49
17	6.52	6.85	8.29	7.94	9.41	9.29
22.4	–	7.24	–	8.22	–	9.43
59.6	6.71	7.15	8.41	8.22	9.5	9.35
	Δ, %		Δ, %		Δ, %	
	9	11	17	19	3	2

radiation source, the light yield nonproportionality decreases substantially that is associated with the specific light yield decrease for 5.9 keV radiation. The L/E values for two above-mentioned samples at various orientations of treated surface are presented in Table. The specific light yield nonproportionality for the 5.9 keV and 17.0 keV energies is more pronounced for the sample with higher activator concentration (see Table). It is shown, that application of a thin-film organosilicon coating on the scintillator entrance window decreases the non-proportionality by 5 times and improves the pulse-height resolution absolute value by 3–5 % at registration of X-ray radiation with $E = 5.9$ keV.

The influence of NaI:Tl surface treatment method was studied using the scintillator samples of ∅20×2, mm size. The surface oriented towards the radiation was studied. The scintillators were placed in containers as standard X-ray detectors. The light yield was determined under irradiation with the same X-ray and soft gamma-radiation sources used in the above-mentioned experiment. Before measurements, some samples were polished by standard technique using a mixture of ethyl and isobutyl alcohols. Another treatment method consisting in deep grinding and polishing using ultrafine powders and organosilicon liquids was applied to the other group of samples. The new method provides a high transparency of NaI:Tl single crystal in the scintillator emission range. Well known that cleaved crystals are preferred for applications in the X-ray region below 10 keV [8]. So, several detectors were made on the basis of NaI:Tl single crystal with cleaved planes as an entrance surface for radiation.

The energy dependences of the specific light yield for the above detectors are shown in Fig. 2. As it is seen in the Figure, the character of this dependence for NaI:Tl crystals in the low radiation energy region differs substantially from the dependence for CsI:Tl crystals. The specific light yield at low energies is lower than at harder radiation. It is true for all used methods of entrance surface treatment. In other words, the nonproportionality of response has opposed sign [9] in low energy region for NaI:Tl crystals. The new treatment method using organosilicon liquids and ultrafine powders allows to increase L/E for 5.9 keV X-rays as compared to the standard polishing technique. This fact evidences that this treatment method results in a decreased thickness of layer with low scintillation efficiency [10]. Note that nevertheless the surface quality attainable for cleavage is not obtained.

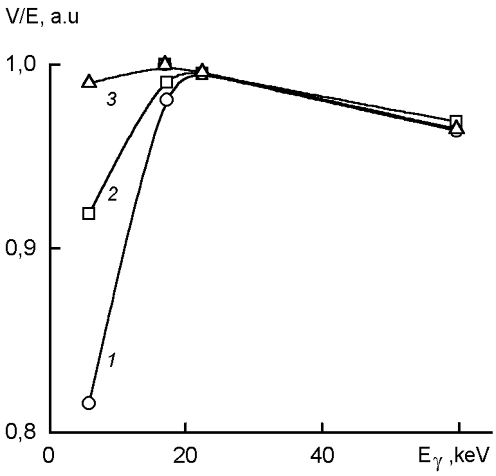

Fig. 2. Dependences of the specific light yield on photon energy for NaI:Tl crystals: *1* — standard polishing method, *2* — new treatment method, 3 — cleavage.

Thus, the radiation entrance surfaces of the NaI:Tl crystals obtained by cleavage provied the best scintillation characteristics. It should be noted that CsI:Tl crystal has not a cleavage plane. In practice it is necessary to machine and polish the crystal surfaces to provide the required shape and size. The optimum treatment method for CsI:Tl and NaI:Tl crystals, as the research results have shown, is the deep grinding and polishing using ultrafine powders obtained by the sol-gel method. An important factor is the subsequent surface treatment with compositions containing organosilicon liquids. Thin-film organosilicon coating put on the radiation entrance surface of crystal reduces the nonproportionality between the light yield and radiation energy, improves the energy resolution, and also provides the stability of the scintillation characteristics in time.

References

1. V.I.Solomonov, S.G.Mikhailov, Pulsed Cathodoluminescence and it Application for Analysis of Condensed Media, RAN, Ural Div., Ekaterinburg, (2003) [in Russian].
2. A.M.Kudin, E.P.Sysoeva, E.V.Sysoeva, et al., *Nucl. Inst. and Methods in Phys. Res.*, **A 537**, 105 (2005).
3. B.V.Grinyov, V.P.Semynozhenko, Scintillation Detectors of Ionizing Radiation for Hard Service Conditions, Osnova, Kharkov (1993) [in Russian].
4. Yu.T.Vyday, V.A.Tarasov, A.M.Kudin, et al., *Instr. & Exp. Technique*, **49**, 314 (2006).
5. A.A.Vorobyov, Mechanical and Thermal Properties of Alkali-halide Single Crystals, Vysshaya Shkola, Moscow, (1968) [in Russian].
6. L.M.Shamovsky, Crystalophosphors and Scintillators in Geology, Nedra, Moscow, (1985) [in Russian].
7. A.N.Panova, B.V.Grinyov, F.F.Lavretiev, et al., *J. Appl. Spectr.* **71**, 502 (2004).
8. Catalog of the Crismatec. Scintillation Detectors, Saint-Gobain Ceramiques Industrielles, France (1992).
9. A.M.Kudin, A.A.Ananenko, Yu.T.Vyday, et al., *VANT*, **4**, 111 (2001).
10. A.M.Kudin, B.V.Grinyov, V.Yu.Gres, et al., *Functional Materials*, **13**, 54 (2006).

Дослідження сцинтиляційних характеристик кристалів CsI:Tl і NaI:Tl при різних способах обробки поверхні

Л.А.Андрющенко, А.Ю.Бояринцев, Ю.Т.Видай, Б.В.Гриньов, І.В.Килимчук, О.М.Кудін, В.О.Тарасов

Досліджено вплив хіміко-механічних методів обробки поверхні кристалів CsI:Tl і NaI:Tl на їх сцинтиляційні характеристики при реєстрації малопроникаючого іонізуючого випромінювання. Показано, що застосування на етапі полірування ультрадисперсного порошку діоксиду кремнію, отриманого золь-гель методом, і кремнійорганічних рідин забезпечує отримання приповерхневого шару кристалів CsI:Tl і NaI:Tl з мінімальною неоднорідністю світлового виходу. Після шліфування поверхні кристалів стабільність сцинтиляційних характеристик у часі може досягатись за рахунок обробки поверхонь тетраетоксисиланом і олігогідридсилоксановою рідиною. Нанесення тонкоплівкового кремнійорганічного покриття на поверхню кристала CsI:Tl, яка обернена до радіоактивного джерела, покращило амплітудне розділення на 3–5 % за абсолютною величиною при реєстрації рентгенівського випромінювання з $E = 5{,}9$ кеВ.