

Characteristics changes of unsealed NaI(Tl) detector under atmospheric moisture effect

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The light yield and energy resolution impairment of NaI(Tl) crystals being stored unsealed is associated with changes in the scintillation efficiency, η , and the light collection coefficient, τ . It is just the depletion of the crystal in activator that is responsible for the η deterioration in the near-surface "dead" scintillator layer while changes in τ are due to the surface enrichment in thallium, no matter what is the detector size. A simple test is proposed to detect the initial stages of the crystal moistening influenced on the NaI(Tl) crystal properties.

Ухудшение светового выхода и энергетического разрешения кристаллов NaI(Tl) при негерметичном хранении связано с изменением сцинтилляционной эффективности η и коэффициента светособирания τ . За ухудшение η в приповерхностном мертвом слое сцинтиллятора ответственен эффект обеднения кристалла активатором, а за изменение τ , независимо от размеров детектора, — эффект обогащения поверхности таллием. Предложен простой тест обнаружения начальных стадий влияния влаги на свойства кристаллов NaI(Tl).

Hygroscopic NaI(Tl) crystals are widely used in science and engineering as effective scintillators but only closed in hermetically sealed containers. A break of the container sealing is well known to result in the impairment of the detector light output (L) and energy resolution (R).

The light output of a detector is the scintillation efficiency of the scintillator material (η) multiplied by the light collection coefficient (τ), thus, an impairment in L may be due to decrease in either η , or τ . According to [2–5], it is just η that decreases in the course of atmospheric moisture interaction with the crystal; this is associated with decomposition of activator emission centers [3] due to oxygen-bearing impurities penetration into the crystal [2], or else with the activator content decrease in the "dead" layer [5]. This explanation is obviously valid for

detectors of soft radiation [3, 4]. The repeated sealing of "spoiled" detectors allows to restore their initial characteristics [1].

In [6], in contrast to [2, 3], it is just deterioration of τ that is believed to cause an impairment in L . The presence of a water film on the crystal surface has been shown to result in the transparency decrease in the activator emission range, i.e. an impairment of the light collection coefficient.

In all cited works, spectrometric characteristics were noted to be degraded but no data are given on the dynamics of L and R variations. To explain effects accompanying the moistening process of NaI(Tl) crystals, their luminescence and scintillation characteristics prior to and after interaction with atmospheric moisture were studied in this work. To that end, a 0.5 mm diameter hole was drilled in the container wall of each 30×40 mm detector used in experiments;

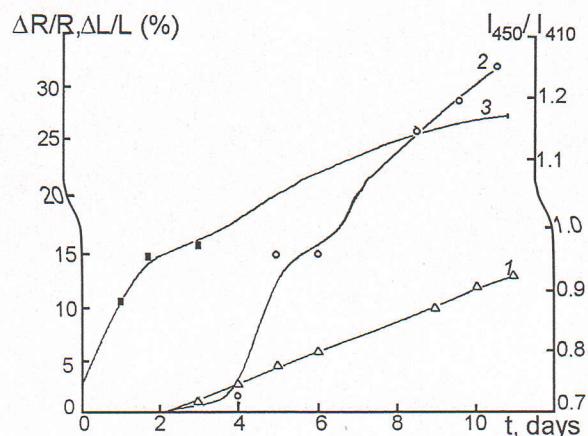


Fig.1. Time dependences of light yield, $\Delta L/L$ (1), energy resolution, ΔRR (2) and intensity ratio of RL bands, I_{450}/I_{410} (3) during the unsealed storage of detectors.

the hole was sealed then and there using Scotch tape. Variations in L and R under excitation by ^{137}Cs were monitored regularly until spectrometric characteristics were deteriorated at all. In parallel, radioluminescence (RL) variations were studied using similarly prepared NaI and NaI(Tl) detectors of 30×5 mm size with quartz windows, using an ^{241}Am γ -source (60 KeV, 1.8 Curie) being used for excitation. Thallium content in activated crystals was uniform and amounted about $4 \cdot 10^{-2}$ % (mass). The Tl^+ ion concentration changes were judged from variations in the intensity of thermostimulated luminescence (TSL) peak of Tl^0 centers under excitation by ^{241}Am (the 60 KeV γ -radiation is weakened twice at a depth about 0.3 mm).

As expected, spectrometric characteristics of unsealed detectors was deteriorated steadily. The visual examination of detectors allowed to reveal in time so-called "moistening spots" [1] on their side and back surfaces; the spots are visible as dimly yellowish green colored surface areas of 1–10 mm size. Any changes were not observed on the output surface optically contacting with glass. Changes in L and especially in R arise long before the surface ones become visible by the unaided eye. It is seen from data presented in Fig.1 that changes in R are more substantial and cannot be ascribed only to L impairment (see e.g. [7]). An obvious reason for such a shape of curves can consist in the observed surface nonuniformity (nonuniformity in τ). The color changes seem to be associated with formation of TlI [1] and TlOH [6] on

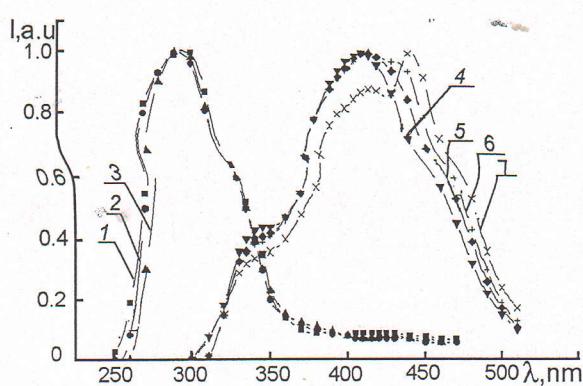


Fig.2. RL spectra variations for NaI (1–3) and NaI(Tl) (4–7) in the course of the detector moistening, unsealed storage time: 1 — 0 days, 2 — 9, 3 — 17, 4 — 0, 5 — 3, 6 — 9, 7 — 34.

the surface; both compounds are opaque in the range of the scintillator emission and not luminescent at room temperature.

Study of radioluminescence of undoped NaI crystals has shown that the intrinsic (310 nm) luminescence yield drops steadily during the unsealed storage while the spectrum shape becomes distorted. It is seen from comparison of curves 2 and 3 in Fig.2 that the greatest changes take place in the 250 nm region. These spectral changes are associated with the transparency impairment and seem to be due to the presence of NaOH impurity on the surface. It is just the above-mentioned region where the absorption of OH^- ion occurs [8]. Note that the decrease of the intrinsic NaI luminescence is not accompanied by appearance of any new emission.

A substantial new fact revealed in this work consists in that the deterioration of scintillation characteristics of NaI(Tl) is accompanied by a change in the emitted light spectral composition. Two bands are observed in the initial crystal RL, namely, 330 and 415 nm (Fig.2, curve 4) corresponding to the well-known luminescence of Tl^+ ion. In the course of time, a new band with a maximum about 450 nm and half-width of 0.19 eV (Fig.2, curve 7) becomes clearly visible on the background of the general yield drop. The absence of the latter band in spectra of undoped crystals allows to ascribe it to the activator. A similar band is observed for crystals with elevated activator content [7]; in that case, it is ascribed to the emission of complex activator centers (Tl^+)_n formed in some crystal volume portions enriched in activator. The study of the excitation spectra has shown that the

additional luminescence is excited in activator absorption bands, mainly in the 314 nm region (the absorption band of $(Tl^+)_n$ centers). Local activator supersaturations are necessary for the complex centers formation. The question is where those supersaturations arise, on the interface only or in the near-surface layer, too.

The external appearance of "spoiled" surface is easy to restore by polishing of the crystal using the alcohol mixture [6]. Such a treatment, however, does not allow to attain the initial L and R values in all cases and is unsuitable as a rule to restore the initial RL spectrum. For example, the spectrum of the re-polished NaI(Tl) crystal (Fig.2) corresponds to the curve 5 but not to the 4 one. This means that a fraction of formed complex centers is positioned within the crystal volume. The crystal RL coincided with the initial one only when a 0.4 mm thick surface layer was eliminated.

The change extent of RL spectra for crystals containing the complex centers is characterized usually by the intensity ratio on 450 and 410 nm wavelengths [7]. The change of that ratio with time is presented in Fig.1, curve 3. The increase of I_{450}/I_{410} , i.e. the intensity redistribution in favour of complex centers, is seen to be in correlation with the change in scintillation properties of NaI(Tl), namely, the curve 3 is symbate to the 2 one (presenting variations of R), thus, both changes can be concluded to have the same reason.

Thermostimulated luminescence studies of polished NaI(Tl) crystals having the "dead layer" have confirmed in principle the results of [5]. The intensity of peaks associated with the main emission centers, Tl^0 (103 K) and Tl^{++} (236 K [9]), is reduced 11 and 3 times, respectively, in the depth of about 0.3 mm. As compared to the above, the intensity increase of 135 K and 175 K peaks associated anyhow with the oxygen presence in the lattice [5, 9] amounts no more than 20 %. The oxygen-bearing impurities seem to penetrate the crystal only on a small depth about 10 μ [1].

Thus, the presence of water film on the NaI(Tl) crystal surface results in a considerable depletion of the crystal in activator, therewith, Tl^+ ions diffuse to the surface from a macroscale (about 0.4 mm or even more deep) layer. This process is accompanied by the surface enrichment in thallium. In spite of both processes are interrelated, it is reasonable to consider them separately. The first process results in a decrease of η

and in a characteristics impairment of soft radiation detectors. Let its influence on volume scintillators be considered. If the dead layer depth is assumed to be 0.5 mm, then, the fraction of the crystal volume responsible for the low light yield amounts 12 % for 25×25 mm size detectors, 5.5 % for 51×51 mm and 3 % for 100×100 mm ones. That is, the dead layer causes an asymmetrical photopeak broadening and the R deterioration depends on the detector size. For large detectors, this effect is of little importance. The second effect allows to explain known facts more completely. Thallium iodide forms, due to its low water solubility, accumulations on the interface which are transformed into a new phase in the course of time. The luminescence of $(Tl^+)_n$ centers is the spectral manifestation of those accumulations. The reabsorption of the activator emission by those centers results in the light loss at the reflection on boundaries, similarly to the case of "volume" complex centers [9]. The TII phase formation causes a partial loss of the crystal transparency and, what is of particular significance, sharp nonuniformities of the light collection coefficient. Since the change of the luminescence spectrum occurs long before detectable R and L impairment and the more before observable surface changes, it can be used as a simple means for the early diagnostics of the detector moistening.

To conclude, the impairment in spectrometric characteristics of NaI(Tl) detectors under unsealed storage is associated with changes of both the material scintillation efficiency and of the light collecting coefficient. The η decrease occurs only in the near-surface crystal layer and is due mainly to its depletion in the activator. The η decrease effect is of substantial significance for detectors of alpha radiation and X-rays. The τ deterioration is associated with changes in absorption and reflection characteristics of the crystal surface and is of importance for detectors of any shape and size. It is caused by the crystal surface enrichment in activator resulting in the formation of complex $(Tl^+)_n$ activator centers and release of TII phase. The observed additional emission in 450 nm range is due to the complex activator centers and reflects the surface enrichment by the latter. The appearance of that emission can be used as a test for the early stages of the crystal moistening which cannot be detected visually.

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**Зміни характеристик негерметичного детектора
NaI(Tl) під впливом атмосферної вологи**

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Погіршення світлового виходу й енергетичного розрішення кристалів NaI(Tl) при негерметичному зберіганні пов'язане зі змінами сцинтиляційної ефективності η і коефіцієнту світлозбирання τ . Погіршення η у поверховому мертвому шарі сцинтилятора спричиняється ефектом збідення кристалу активатором, а зміни τ , незалежно від розміру детектора — ефектом збагачення поверхні талієм. Запропоновано простий тест для виявлення початкових стадій вплива вологості на властивості кристалу NaI(Tl).