Surface hydration and dehydration processes in NaI(Tl) crystals

A.S.Gershun, *V.Yu.Gres', S.I.Vasetsky, A.M.Kudin,*
P.V.Mateychenko, V.F.Tkachenko

Alkali Halide Crystal Department, Science and Technology Association
"Institute for Single Crystals", National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001 Kharkiv, Ukraine

It is shown that the interaction of NaI(Tl) crystal surface consists of three processes:hydration, quasi-equilibrium state and dehydration. Dehydrated surface is a textured polycrystal layer contented crystals of the main NaI phase, formation of the second TlI phase and some amount of NaOH impurity. The heat treating in CO_2 atmosphere allows to decrease the NaOH content in the surface layer and use it as an effective diffusion light layer.

Показано, что взаимодействие поверхности кристаллов NaI(Tl) с влагой можно описать тремя процессами: гидратации, квазиравновесного состояния и дегидратации. Дегидратированная поверхность представляет собой текстурированный поликристаллический слой, содержащий кристаллы основной фазы NaI, образования второй фазы TlI и незначительное количество примеси NaOH. В результате прогрева в атмосфере CO_2 можно понизить содержание NaOH в приповерхностном слое и использовать его в качестве эффективного диффузного светоотражателя.

Scintillators based on alkali iodides, CsI(Na) and in particular NaI(Tl), are hygroscopic. The crystal surface interaction with moisture results in deterioration of their characteristics and even in failure of scintillators [1]. As far as is known to us, only one cause of the light yield deterioration was considered in literature for NaI(Tl) and CsI(Na) crystals, namely, the formation of so-called "dead layer" near the surface being in contact with atmospheric moisture [2–4]. The detector production process includes always a surface contact with water or with humid air, thus, the formation of a deteriorated near-surface layer is inevitable. Methods allowing to avoid that layer formation and even to recover it are known [1, 5], but the formation mechanisms considered before are contradictory [2, 6, 7]. Other possible processes resulting in deterioration of scintillation characteristics were not studied.

The purpose of this work is to study the hydration and dehydration processes of NaI(Tl) crystal surface aiming at development of an initial model of their run and elucidation of attendant effects.

It is reasonable to subdivide the interaction process of the hygroscopic crystal surface with moisture into three stages: hydration, i.e., formation and time-depended development of a crystal surface layer dissolved by water; quasi-equilibrium state, when the water adsorption and evaporation are balanced; and dehydration, when the water evaporation results in precipitation of the solute or its crystallohydrate from the solution.

Crystals containing different thallium concentrations, C (0.05 and 0.1 mass.%) as well as undoped NaI crystals were used in experiments. The hydration process was studied under atmospheric pressure at 15 °C and 80 % of relative humidity, fresh-made
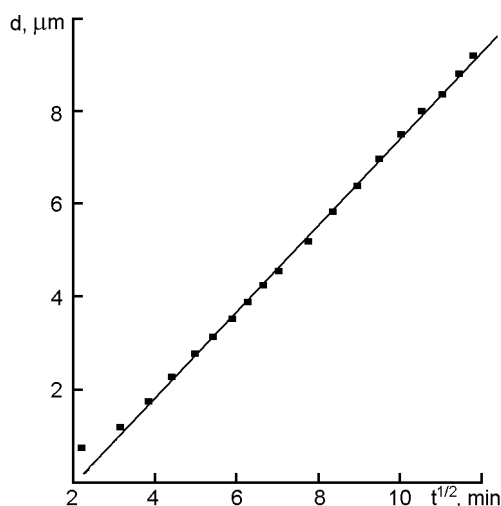
Fig. 1. Film growth kinetics on the NaI(Tl) crystal surface during its hydration

Fig. 2. NaI(Tl) crystal surface in the course of its dehydration at the second phase formation stage (x390).

cleavages were used. The water film thickness, d, was monitored by X-ray analysis method using a DRON type two-crystal diffractometer in Cu K_β and Mo K_α emissions. The dehydration process was observed in a "dry room" using a MIM-7 optical microscope, the duration of preceding hydration did not exceed a half hour. The composition of phases formed was examined by X-ray phase analysis (XPA) and scanning electron microscopy combined with X-ray microanalysis using a JSM-820 electron microscope provided with a Link AN 101853 energy dispersion microanalysis system. The surface phase composition was studied additionally by thermogravimetry using a MOM derivatograph.

The quasi-equilibrium state of the "NaI(Tl) + H_2O" system was modelled using standard $\varnothing30 \times 40$ mm and $\varnothing30 \times 5$ mm NaI(Tl) detectors in containers with drilled 1 mm diameter hole which was closed by scotch after 1 h of exposure. The light yield , L, and energy resolution, R, of detectors were measured using [137]Cs (662 keV) radionuclide source. The radioluminescence (RL) of $\varnothing30 \times 5$ mm detectors was measured using a MDR-23 monochromator and PMT-100 under excitation by gamma radiation from a [241]Am source (60 keV, 1.8 curie). The spectra were corrected under account for the PMT spectral sensitivity and the monochromator dispersion.

Hydration process. Water adsorbed on the NaI(Tl) crystal surface dissolves the latter resulting in formation of a film with thickness increasing in time. The kinetics of the film thickness time-d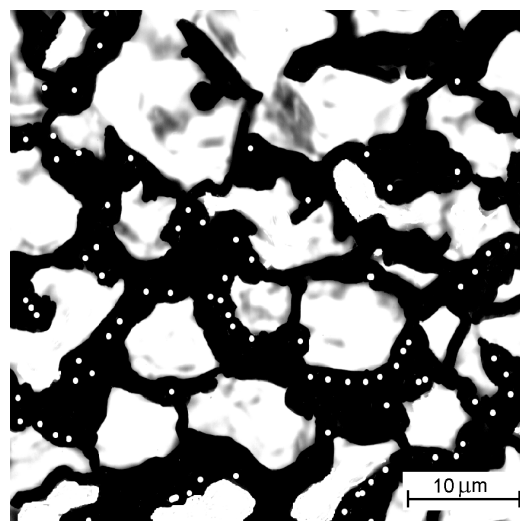epended variation is presented in Fig. 1. The hydration process is seen to consist of two stages: a fast one having a duration of about 15 min and a slower one lasting from several hours to several days, depending on the hydration time. The drop of the film growth rate can be due to that at the second stage it is controlled likely by the diffusion of the main substance in the solution from the crystal surface to the solution-air interface and thus is not defined by the crystal hygroscopicity but by properties of the solution formed on its surface.

It is obvious that the film growth will stop in a closed volume after a certain time. In quasi-equilibrium conditions when the water adsorption and evaporation are balanced, the main substance content in the film becomes equalized through its thickness and a saturated aqueous NaI solution is formed (1787 g/l [8]). The concentration of TlI dissolved together with the main substance is easy to calculate. So, for the crystal containing $C = 0.1$ % Tl by mass, the thallium iodide concentration in the solution is 2.89 g/l, thus exceeding considerably its solubility limit in water (0.06 g/l [9]) but being lower that the TlI solubility in the saturated NaI solution which can be estimated from data given in [10]. Therefore, a TlI phase formation in the solution is hardly possible (the second phase precipitation occurs at the dehydration stage when the solution becomes supersaturated, see below). A prolonged (several hours or days) storage of crystals in quasi-equilibrium conditions results in a degradation of their spectrometric characteristics. This is believed to be due to TlI phase
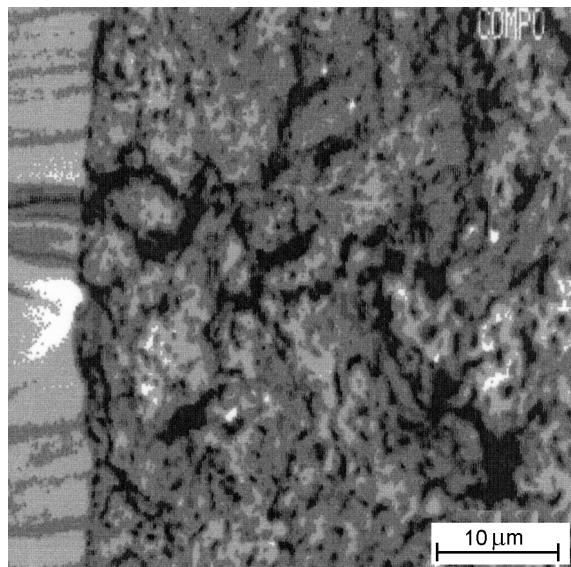
Fig. 3. Dehydrated surface image obtained using scanning electron microscopy in the reflected electron mode.

formation in the solution [1]. It has been in [7] that L and R values for detectors with hydrated surface were not degraded at once but after a certain time interval. As the spectrometric characteristics become worsened, the RL spectrum is changed considerably. Against the background of continuously dropping emission intensity in the 415 nm band (luminescence of Tl^+ centers), the 460 nm one appears and increases in its intensity; this band is due to luminescence of complex $(Tl^+)_n$ centers [7]. For the formation of complex activator centers, the appearance of areas with enriched activator content on the crystal surface is necessary. Such areas must belong just to the crystal surface, since there is no activator lu-

minescence in the liquid phase. The Tl^+ ions aggregation on the crystal-solution interface can be due to fluctuations of the "crystallization front". In the quasi-equilibrium conditions, the dissolution and crystallization processes do not stop. Those are reversible with respect to the main substance while for the activator, the distribution coefficient is much less than 1, so after some time, a "concentration shock wave" is formed before the front. As a result, areas enriched in the activator can arise at the surface. The alternation of areas enriched in and depleted of thallium is like to be a cellular structure that is often observed when a crystal is grown in non-equilibrium conditions [11].

Dehydration process. The water evaporation results in the solution supersaturation and the crystallization of solutes. It is known [3] that at room temperature $NaI \cdot 2H_2O$ crystallohydrate precipitates from NaI aqueous solution. In our case, where the crystallization on the single-crystal NaI substrate is possible, it is reasonable to expect the growth of NaI crystals on the interface. The growth conditions are non-uniform over the surface and are hindered at intercellular boundaries (areas enriched in Tl^+) due to the mechanism referred to as "step growth poisoning". The process of NaI islands generation and growth was observed in the dry room using optical microscope. The activator is not included essentially into growing crystals and is displaced off to the cell boundaries due to crystallization concentrating process [12]. As the critical supersaturation becomes attained, the second phase is observed to precipitate. The picture of the crystal surface taken at the stage of the sec-
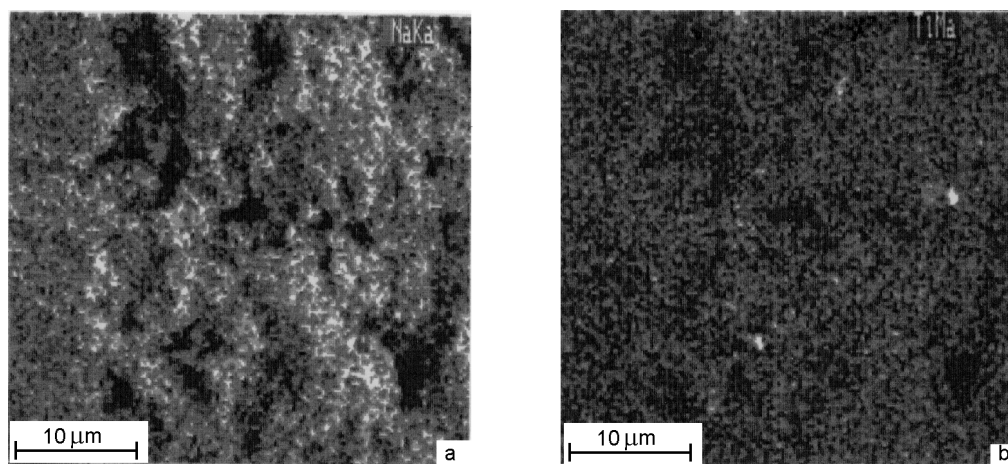

Fig. 4. Dehydrated surface images obtained using scanning electron microscopy in the X-ray mode for main substance grain (a) and impurity inclusion (b).
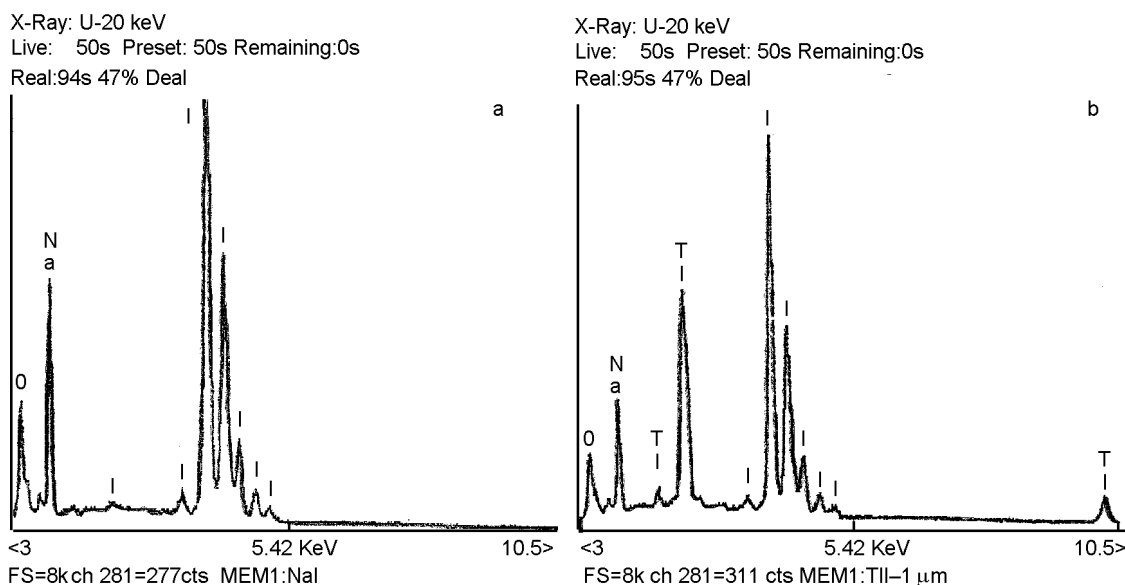
Fig. 5. Spectra of characteristic X-rays obtained using scanning electron microscopy for main substance grain (a) and impurity inclusion (b).

ond phase formation (Fig. 2) shows clearly chains of released particles of about 1 μm size in gaps between the growing islands attaining the size of 3 to 7 μm. The particle colour (yellow) corresponds to that of TlI.

At the end of the dehydration process, a loose semi-transparent white crust is formed at the crystal surface. Figs. 3 and 4 present photos of the dehydrated surface taken using scanning electron microscopy in the reflected electron mode (Fig. 3) and X-ray one (Fig. 4). A fine-crystalline structure of the surface is seen as well as bright white grains of about 1 μm in size having a higher atomic number than the matrix. Fig. 5 shows the spectra of characteristic X-rays of those inclusions (a) and of larger grains (b). The comparison of the spectra (Fig. 5a, b) with photos of Fig. 4 (a, b) allows to ascribe unambiguously the inclusions to TlI phase and the matrix, to NaI.

The loose crust formed at the dehydrated surface has a density of about 1.8 g/cm^3 being about a half of that of NaI crystal. The dehydrated surface structure and phase composition were studied using XPA. The crust has been found to be a textured poly-crystalline layer of NaI containing a small amount of NaI·2H$_2$O crystallohydrate (less than 1 % by mass). The XPA data have been confirmed by the crust heating up to 300 °C followed by the exposure for 2 h under thermogravimetric method. The observed mass loss is 1 to 2 %, thus evidencing that the crystallohydrate is absent prac-

tically (otherwise, the mass loss would be of 20 %). Besides, NaOH and NaIO$_3$ impurities have been detected in the crust in trace amounts.

According to [13], the semi-transparent polycrystalline layer bound firmly to the NaI(Tl) crystal surface can be used as an efficient reflector. A substantial advantage of such a reflector consists in that its thickness depends on the surface hydration extent; in our experiments, it was from 3 to 15 μm. Note that, unlike crystals with hydrated surface, scintillators provided by such reflector do not contain complex activator centers. A conclusion of importance can be drawn therefrom, namely, that it is complex activator centers and not the TlI phase that are responsible for L and R degradation. For a crystal subjected preliminarily to a short-time hydration, the disappearance of $(Tl^+)_n$ centers following the second phase formation results in L and R recovery.

Data presented in Fig. 6, curve 1, show that the reflector produced in this manner exhibits a drawback consisting in a low light yield in UV region. This can be caused by OH$^-$ ions with their broad absorption band having a maximum in 250 nm region [14] that overlaps in part the NaI(Tl) emission spectrum. The crystal heat treatment in CO$_2$ atmosphere allows easily to convert the hydroxide to carbonate, thus recovering completely the crystal RL spectrum (Fig. 6, curve 2) and improving the detector light yield [15]. Data on the light yield and energy resolution for ∅30x5 mm detectors

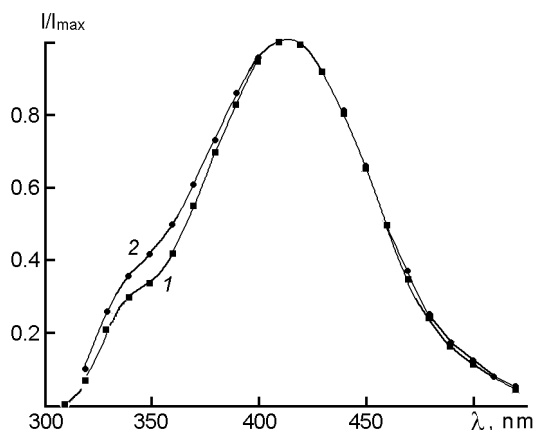Fig. 6. Radioluminescence spectra for detectors produced using the usual technology (1) and in CO_2 atmosphere (2).

Table.

Detector No.	Atmosphere	R, %	L, rel. units
1	air	7.5	3.5,
2	air	7.8	3.5
3	CO_2	6.9	3,7
4	CO_2	7.1	3.8

produced according to [13] and [15] are presented in the Table below.

Crystals with so dehydrated surface exhibit the scintillation characteristics comparable to those of standard detectors while crystals treated in CO_2, the improved ones. This allows to use the surface layer as a light reflecting one in detectors for soft radiation.

References

1. B.V.Grinyov, V.P.Seminozhenko, Scintillation Detectors of Ionizing Radiation for Hard Service Conditions, Osnova, Kharkiv (1993) [in Russian].
2. V.V.Averkiev, V.K.Lyapidevsky, V.A.Prorvich et al., *Prib. i Tekhn. Eksper.*, No. 3, 152 (1982).
3. V.T.Sotnikov, N.G.Starzhinsky, *Ukr. Fiz. Zh.*, **29**, 235 (1984).
4. L.P.Smolskaya, S.P.Panova, S.G.Kuznetsova, *Zh. Prikl. Spektr.*, **56**, 259 (1992).
5. Yu.T.Vyday, L.B.Zagariy, Yu.A.Tsyrlin, *Prib. i Tekhn. Eksper.*, No. 2, 74 (1990).
6. Yu.T.Vyday, L.B.Zagariy, G.V.Ptitsyn, in: Production and Study of Optical and Scintillation Materials, ISC Publ., Kharkiv, No. 12, 127 (1984) [in Russian].
7. S.I.Vasetsky, A.S.Gershun, V.Yu.Gres' et al., *Functional Materials*, **5**, 495 (1998).
8. I.T.Goronovsky, Yu.P.Nazarenko, Brief Reference Book on Chemistry, Naukova Dumka, Kiev (1974) [in Russian].
9. T.I.Darvoid, E.G.Morozov et al., Main Thallium Compounds, Luminophor Ltd. Publ., Stavropol' (1997) [in Russian].
10. F.Ya.Kulba, E.V.Mironov, *Zh. Neorg. Khim.*, No. 2, 2734 (1957).
11. I.I.Kisil', N.I.Kraynyukov, D.L.Stroilova, in: Single Crystals and Engineering, ISC Publ., Kharkov, No. 2, 25 (1970) [in Russian].
12. A.B.Blank, Analysis of Pure Substances Using Crystallization Preconcentration, Khimia, Moscow (1986) [in Russian].
13. B.G.Zemskov, Yu.V.Permyakov, USSR Pat. No. 1457605.
14. A.V.Egranov, E.A.Radzhabov, Spectroscopy of Oxygen and Hydrogen Centers in Alkali Halide Crystals, Nauka, Novosibirsk (1992) [in Russian].
15. A.S.Gershun, V.Yu.Gres', B.G.Zaslavsky et al., Ukrainian Pat. No. 98115845.

Процеси гідратації та дегідратації поверхні кристалів NaI(Tl)

О.С.Гершун, В.Ю.Гресь, С.І.Васецький, О.М.Кудін, П.В.Матейченко, В.Ф.Ткаченко

Показано, що взаємодія поверхні кристалів NaI(Tl) з вологою може бути описана трьома процесами: гідратації, квазірівноважного стану та дегідратації. Дегідратована поверхня є текстурований полікристалічний шар, який вміщує кристали основної фази NaI, скупчення другої фази TlI та невелику кількість домішки NaOH. У результаті прогріву у атмосфері CO_2 можна знизити вміст NaOH у приповерхневому шарі та використати його як ефективний дифузний світловідбивач.