Advanced scintillation materials – 2013

State of surface and scintillation response of hygroscopic crystals to excitation by X-rays and low energy

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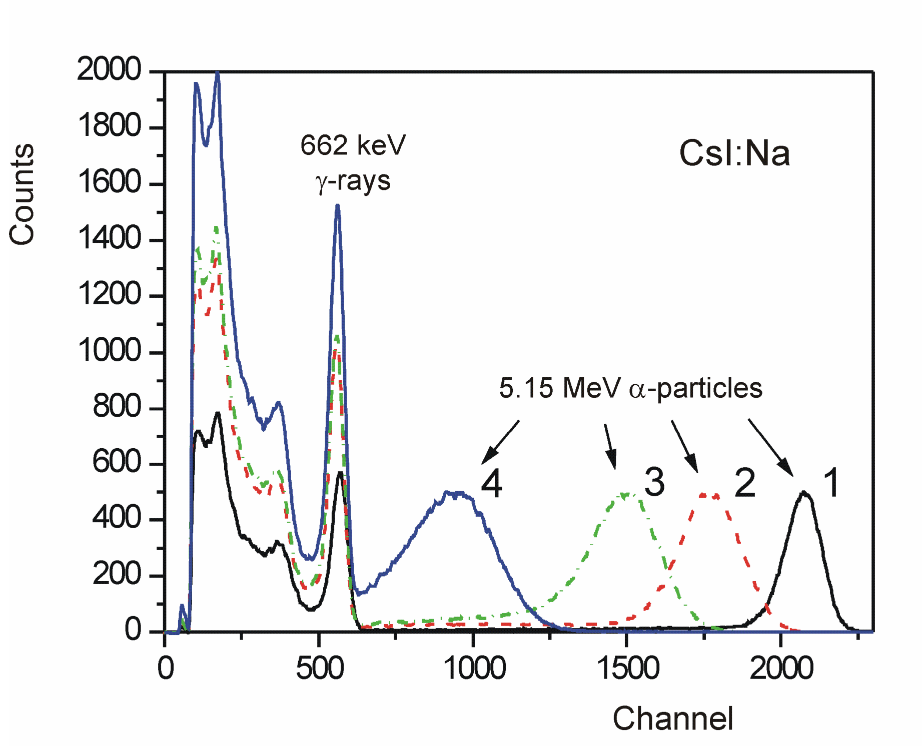
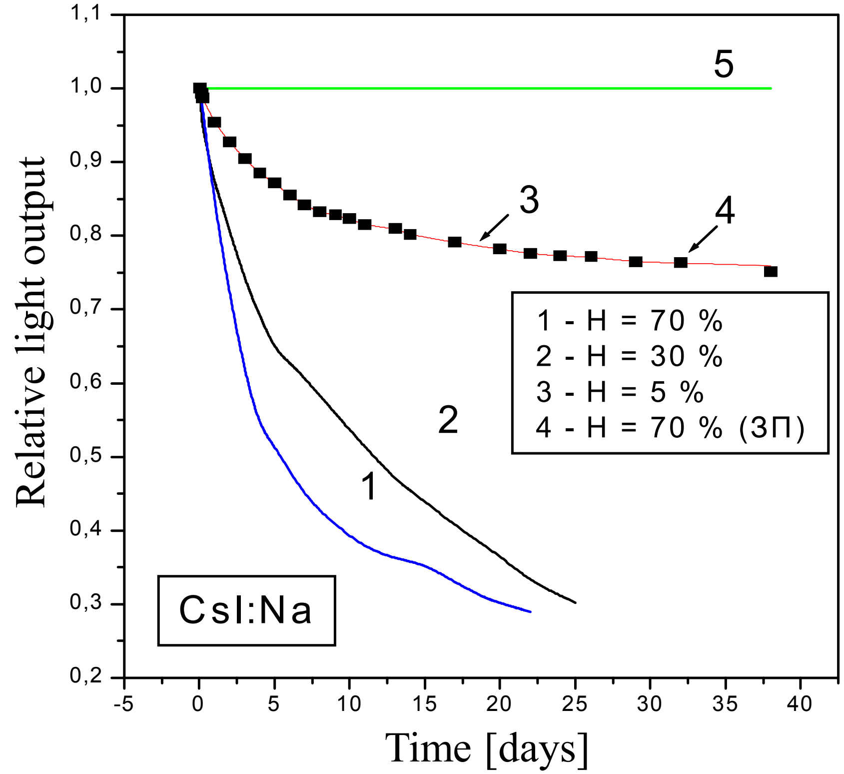
Dead Layer in CsI:Na Crystal



Pulse height spectra of CsI:Na crystal at aging: 1 – after 1 hour; 2 – 12 hours; 3 – 3 days; 4 – 6 days. ^{239}Pu source with collimator.

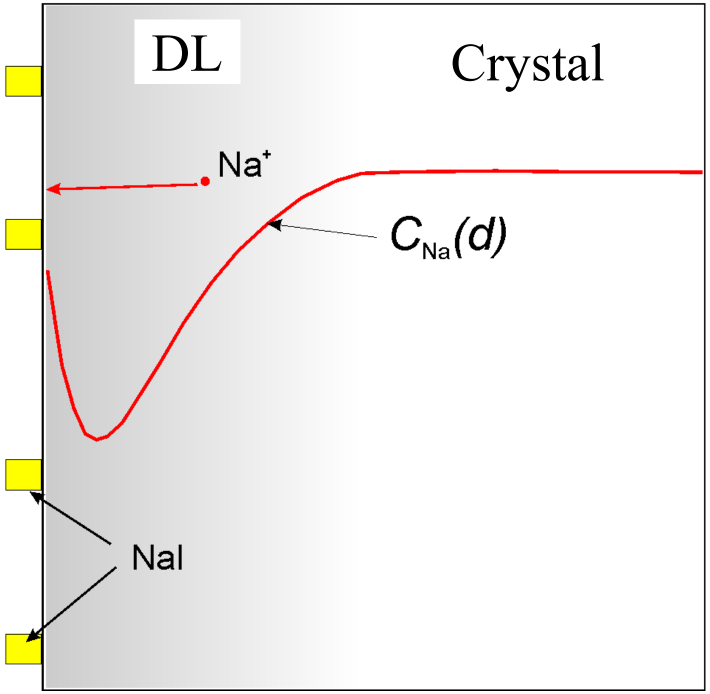


Degradation of light output of CsI:Na crystal during storage at different H. Excitation by α-particles and γ-rays.

It is well known that CsI:Na widely used for gamma-rays detection not alpha-particles

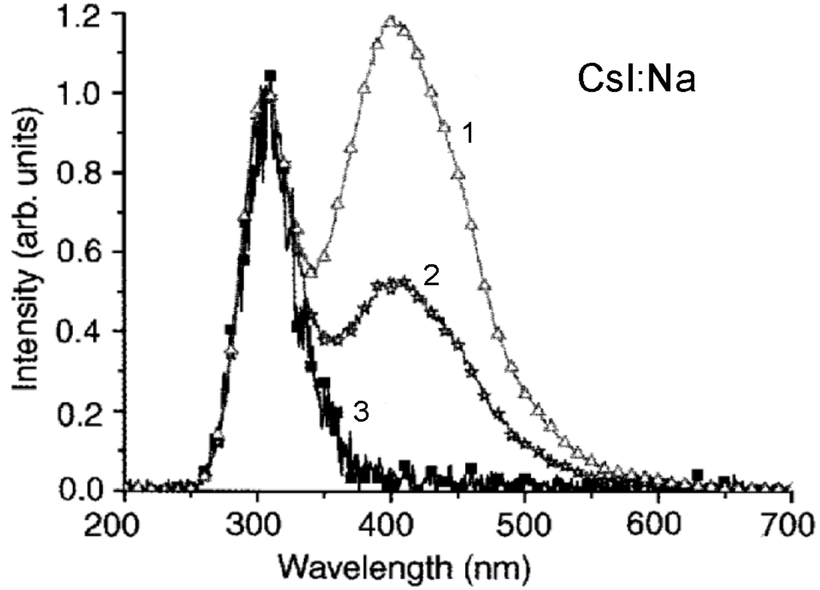
Surface Effects and Dead Layer in Scintillation Materials on a Base of CsI Crystal

Tchaikovsky-Rosenberg (1980)



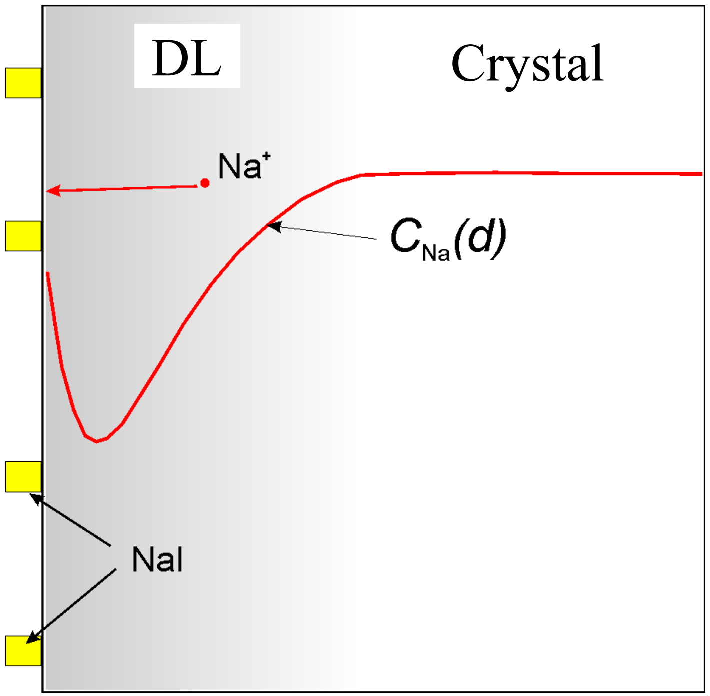
Model of dead layer in CsI:Na crystal.
It supposes Na^+ diffusion to surface.

Dinca L.E., Dorenbos P., et al.
NIMA. Vol. A 486 (2002)141.

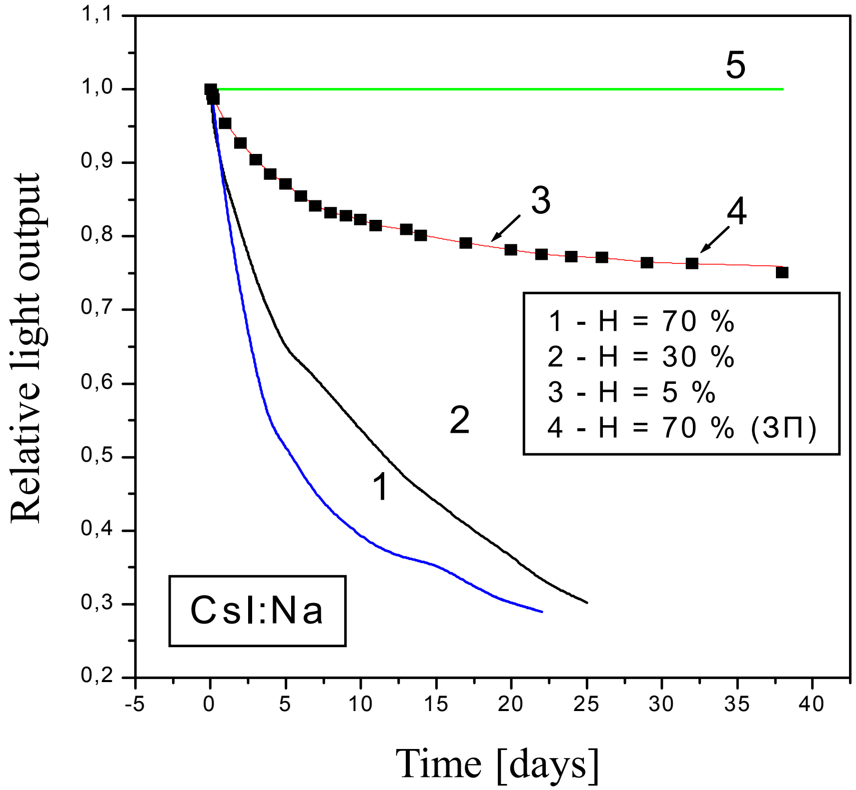


X-ray Luminescence of CsI:Na Crystal at different depth of penetration:
U_a = 60 кВ (1); U_a = 35 кВ (2) и U_a = 10 кВ (3)

Contradiction between kinetic of Dead Layer appearance and new phase formation on a surface



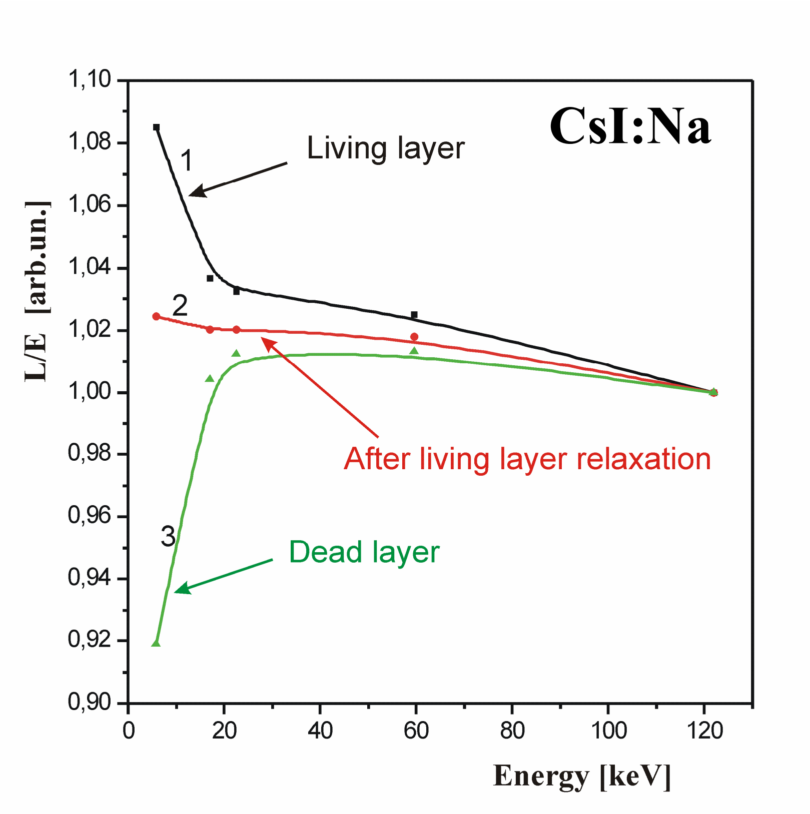
NaI nano-crystals appear after > 6 months of aging.



Peak of full alpha-particle absorption disappears after some days.

There is another process which is responsible of light output degradation

Dead layer profile.
Initially we reveal a living layer near surface not a dead one.
Living layer reveals itself as increasing of *η*.

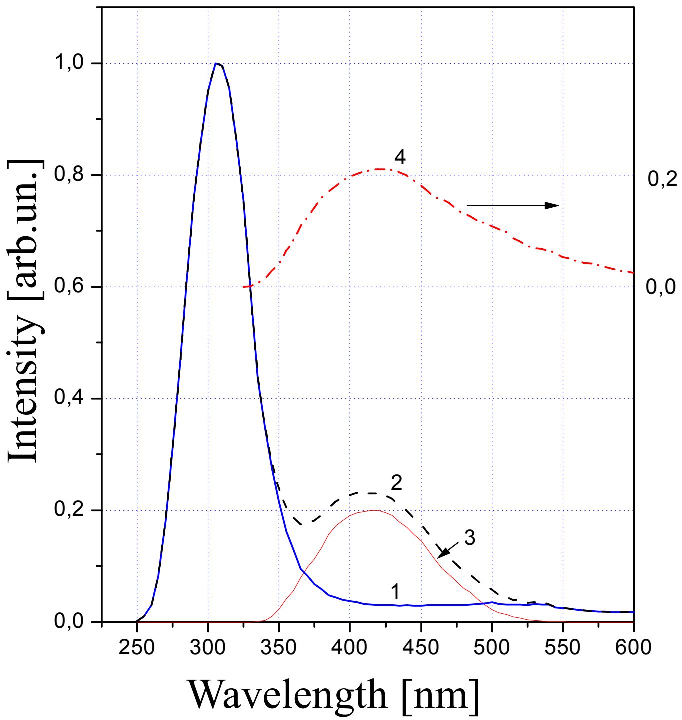


Specific light yield as a function of energy during crystal aging:
1 – one hour; 2 - 19 days; 3 – 22 days.

Difference Δη is +9…+30% depending surface treatment condition.

There is a simple explanation of L/E increasing: number of light emission centers is increased. Vacancies can play role of additional emission centers.
A.V.Gektin, et al. Role of vacancy defects in luminescence of CsI // Optics and Spectr. vol. 72, 5 (1992) 1061-1063.

P_{pl} ~ 50 … 80 g/mm^2;
P_{cd} ~ 1 … 3 g/mm^2
H ~ 6 … 8 kg/mm^2



Radio-luminescence spectra of CsI crystal after polishing

Estimation of C_{VV}

Influence		S_{RL}, %	C_D, cm^{-3}
Quenching	Volume	18	1.5×10^{17}
Deformation, ε = 15%	Volume	13	1.1×10^{17}
Irradiation, D = 3200 Gy	Volume	1,5	1.3×10^{16}
Polishing	in layer 8 μm	2,5	**~ 7×10^{17}**
CsI:Na crystal with $C_{Na} = 8.4\times10^{17}$ cm^{-3}		100	

Vacancy concentration in living layer is comparable with optimum C_{Na} in CsI:Na crystal

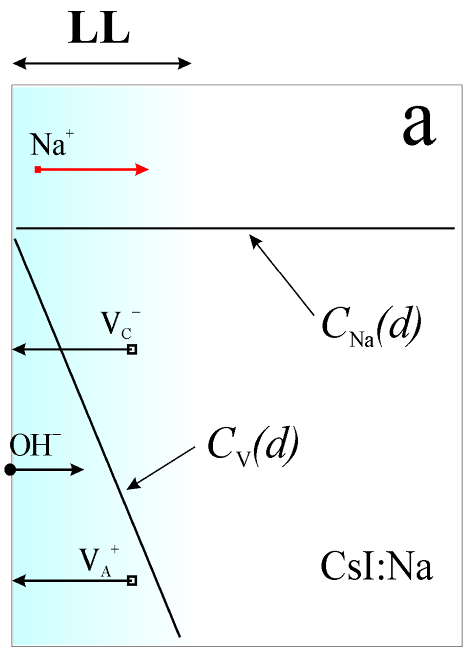
J. Opt. Technology, vol. 77 (2010) 300

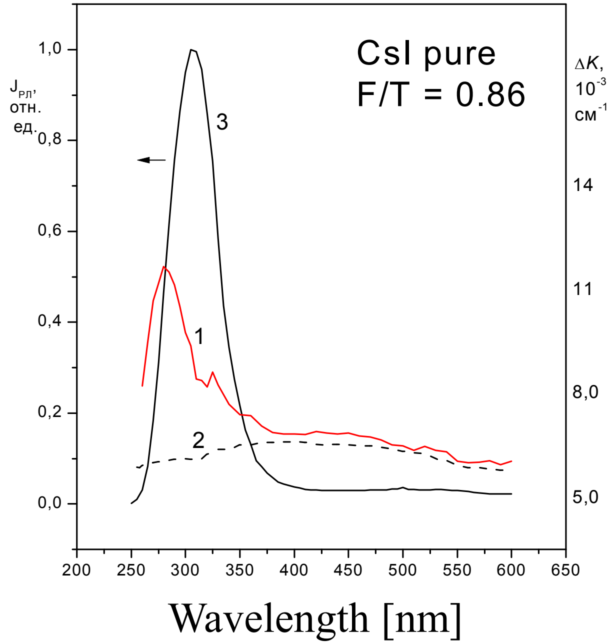
Consequences of Living Layer relaxation

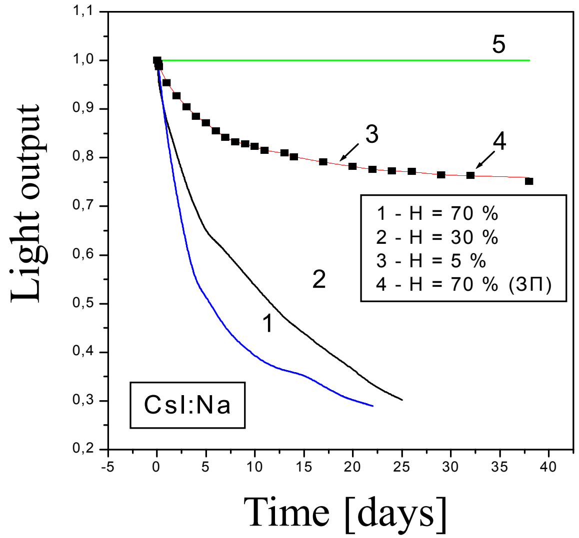
1. **Vacancy flow is directed to surface. It means that Na^+ ions will be shifted from surface to the depth of crystal. So sodium distribution should be non-homogeneous;**
2. **Vacancy flow also results in diffusion of impurity inside the crystal. Surface impurities will be engulfed by crystal volume;**
3. **Symmetry of full absorption peak of α-particles will be changed. Initial peak broadening to right side should be changed on opposite (left side).**
4. **Formation of NaI inclusions on a surface of CsI:Na crystal begins after relaxation of living layer only.**
5. **Term “dead” during first 6 months means an absence of full absorption peak. Nevertheless detection efficiency do not change.**

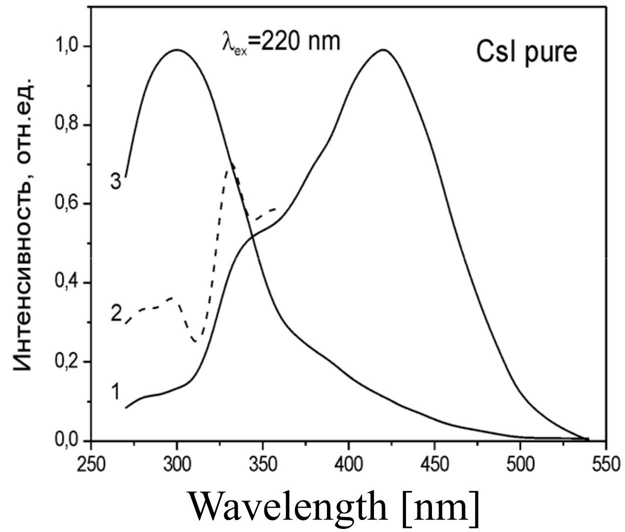
We can verify conclusion 1, 2, 3 and 5.

2. Surface impurities will be engulfed by crystal volume.



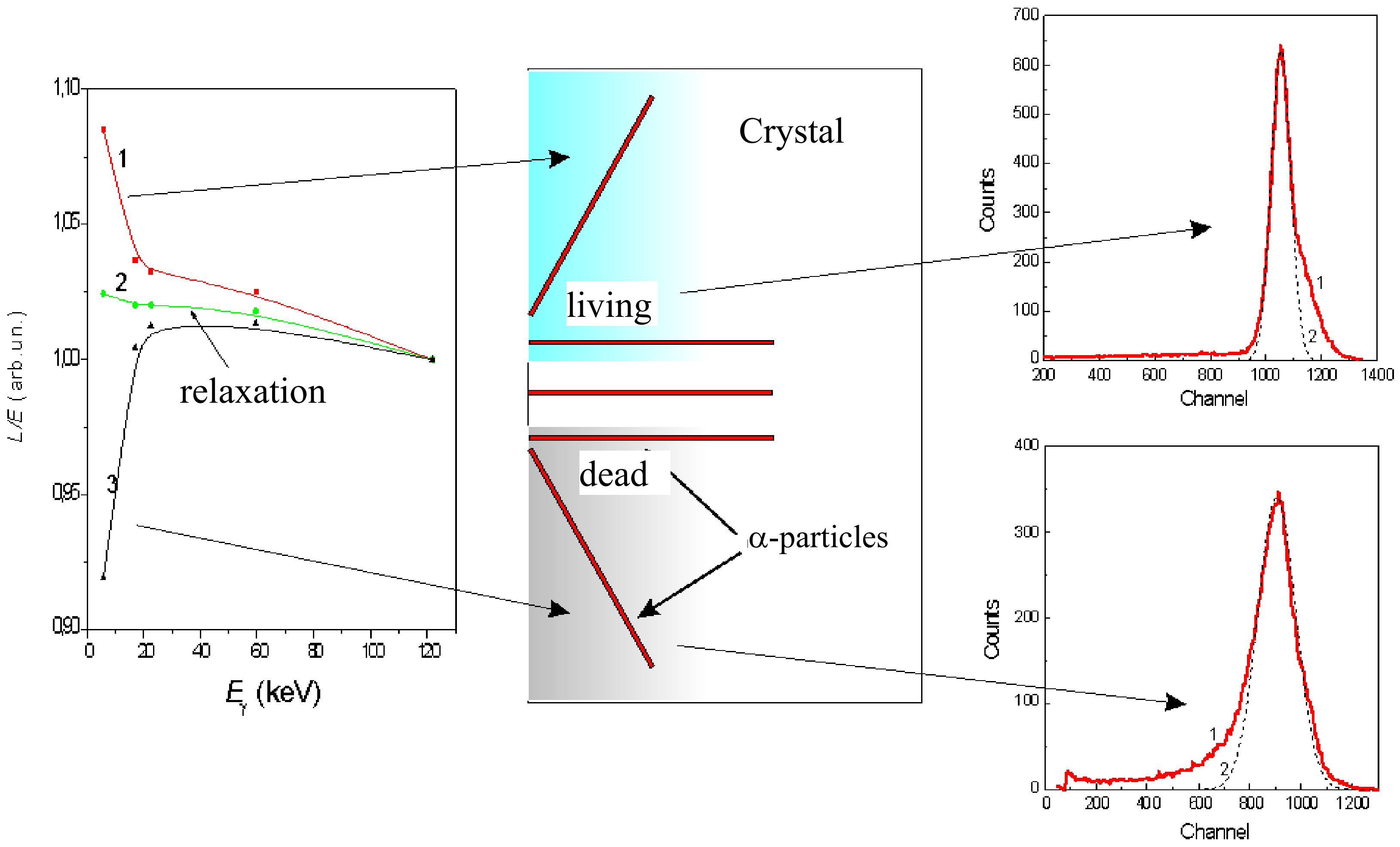




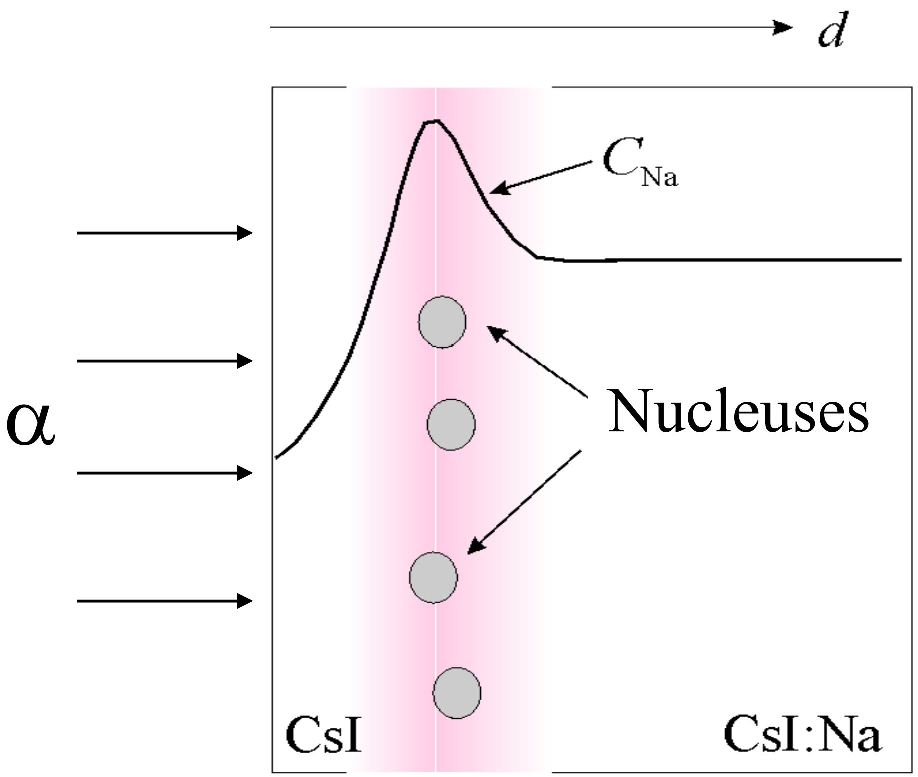


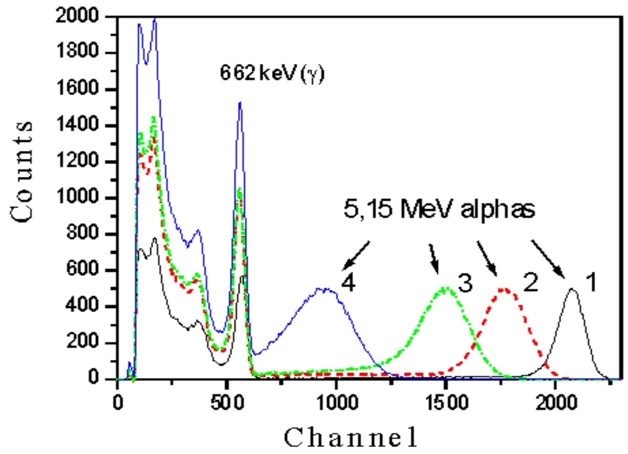
J. Opt. Technology, vol. 77 (2010) 300

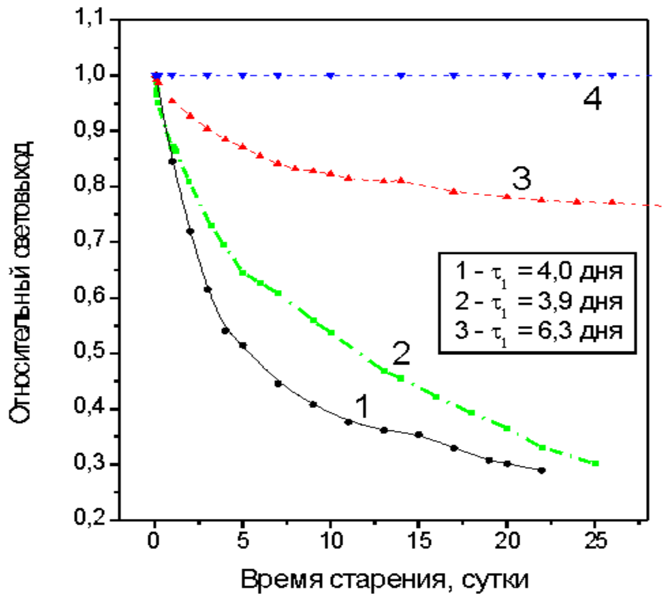
3. Full absorption peak (for α-particles) has a different symmetry during CsI:Na crystal aging.



1. Vacancy flow to surface should results in a shift of activator distribution in living layer

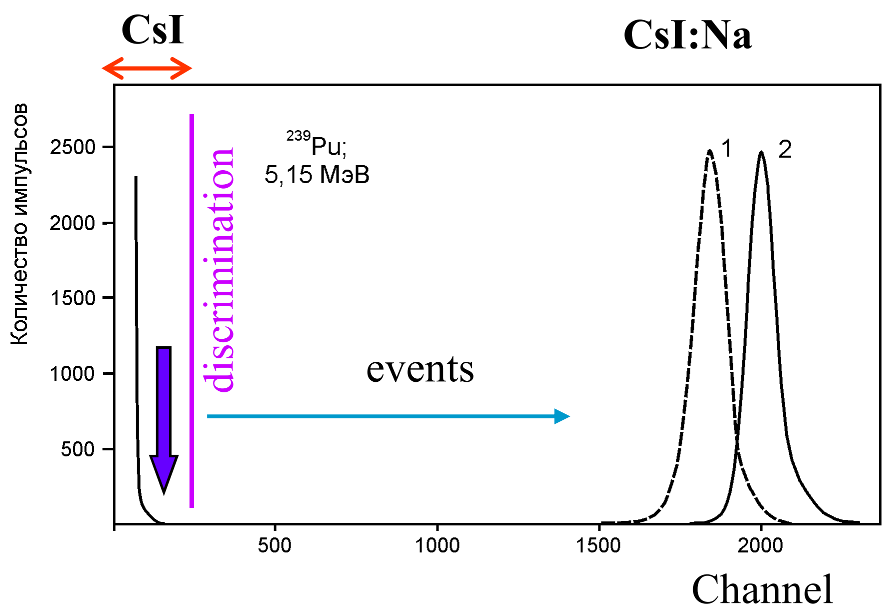






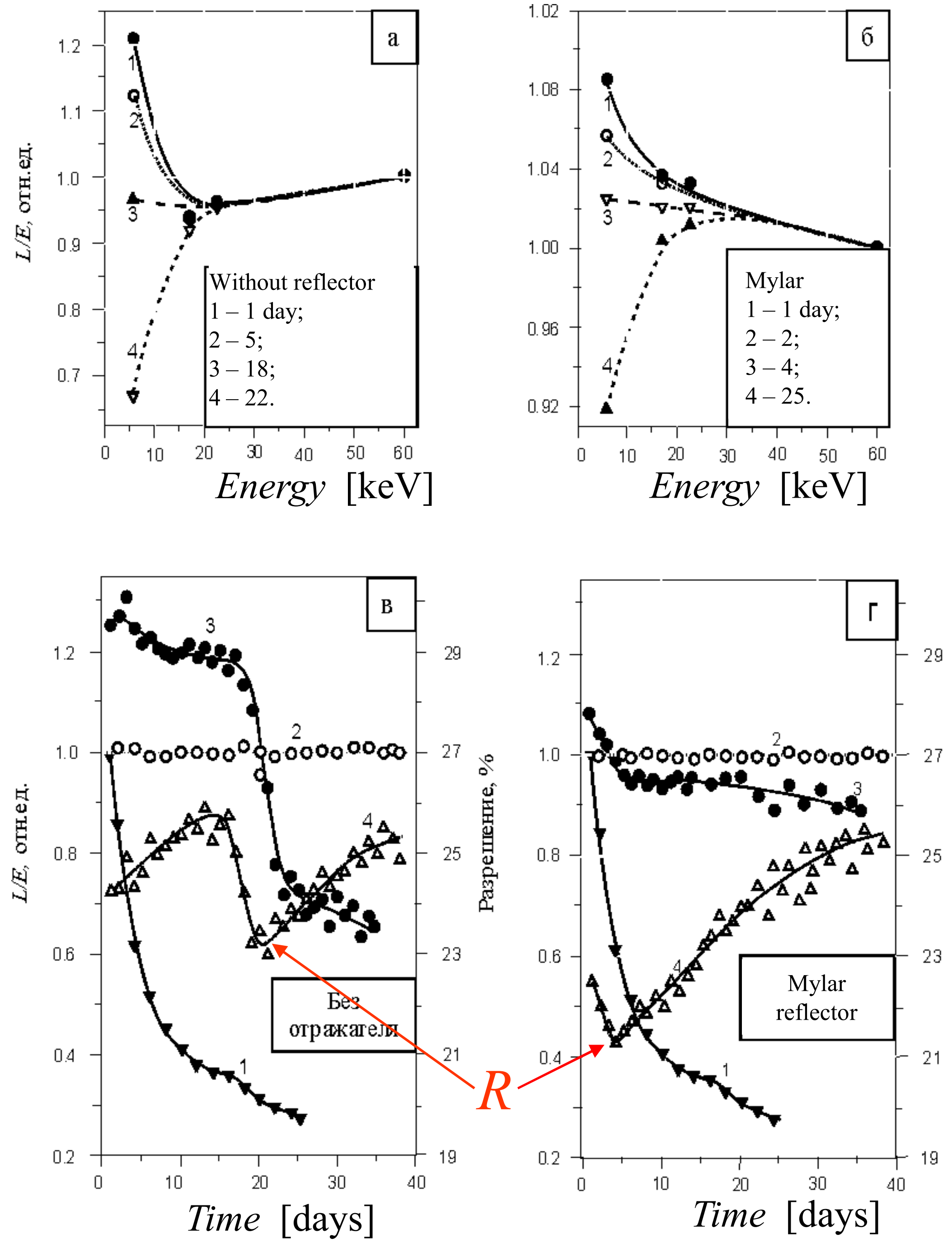
4. **So enriching of surface by Na take place after living layer relaxation only.**

5. **Term “dead” during first 6 months means an absence of full absorption peak. Nevertheless detection efficiency do not change for α-particles.**



At big threshold of discrimination detection efficiency ε for CsI pure ε = 0, for CsI:Na with DL *ε = const*.

For particle counting Dead Layer not exist!
Real Dead Layer be formed after 6 months aging.

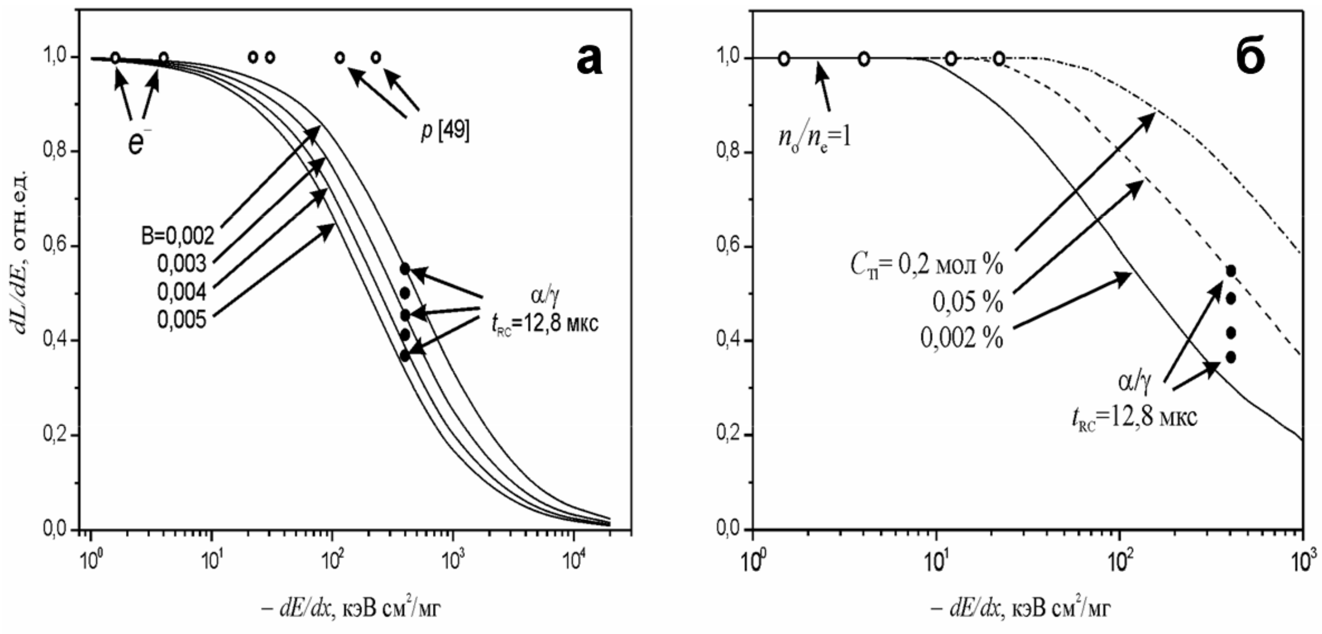


Dead Layer, Non-proportionality of Response and Energy Resolution in low energy diapason

Resolution R_{60} (at 60 keV) has a minimum value when nPR is minimal (homogeneous distribution of scintillation efficiency)

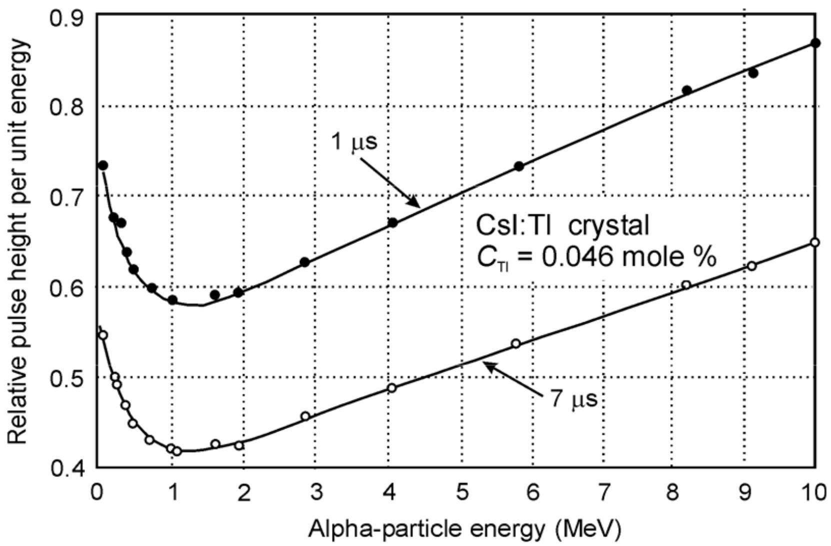
Problems Atom. Sci. Technol., vol. 4 (2001) 111

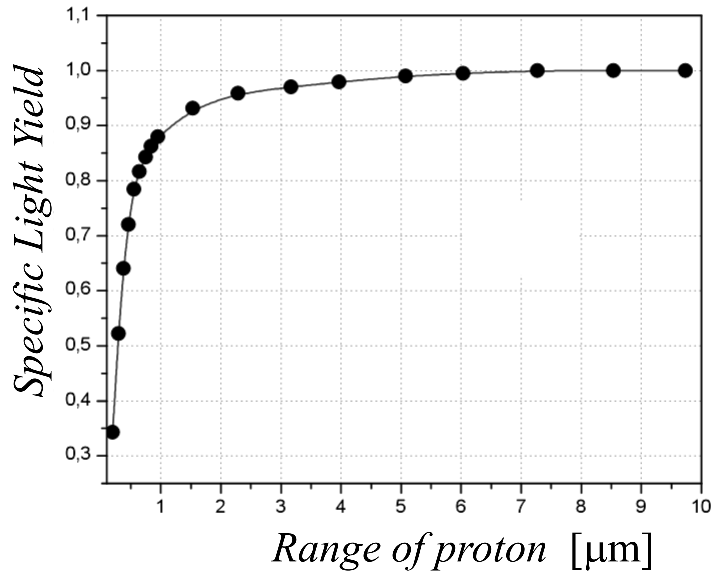
Application of Living Layer to Theory Verification



A.M.Kudin, Dr.Sci.
Thesis, 2007

Usikov, Vyday, et al. 1983

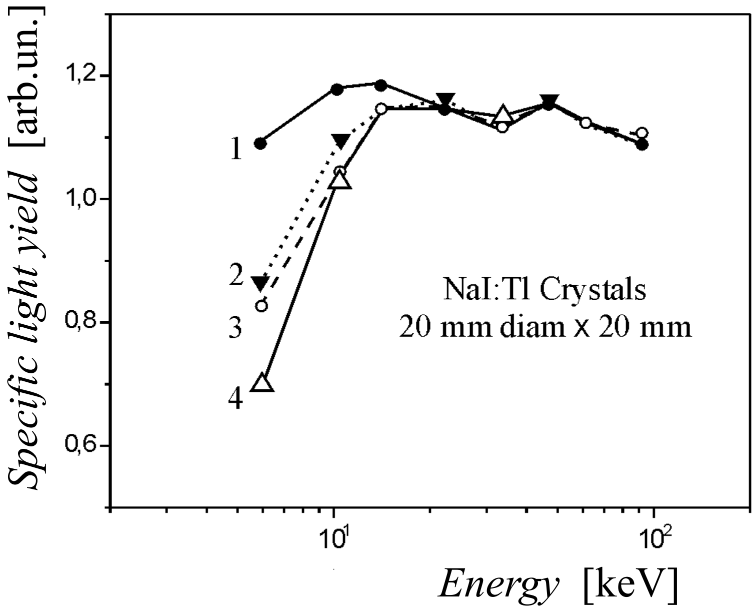




Gwin, Murray, 1963

Dead Layer in NaI:Tl Crystal

W.G.Kaizer, et al. IEEE TNS 1962



1 – cleavage plane;
2 – polished by alcohol;
3 – water polishing;
4 – grinding.

3 stages of water interaction

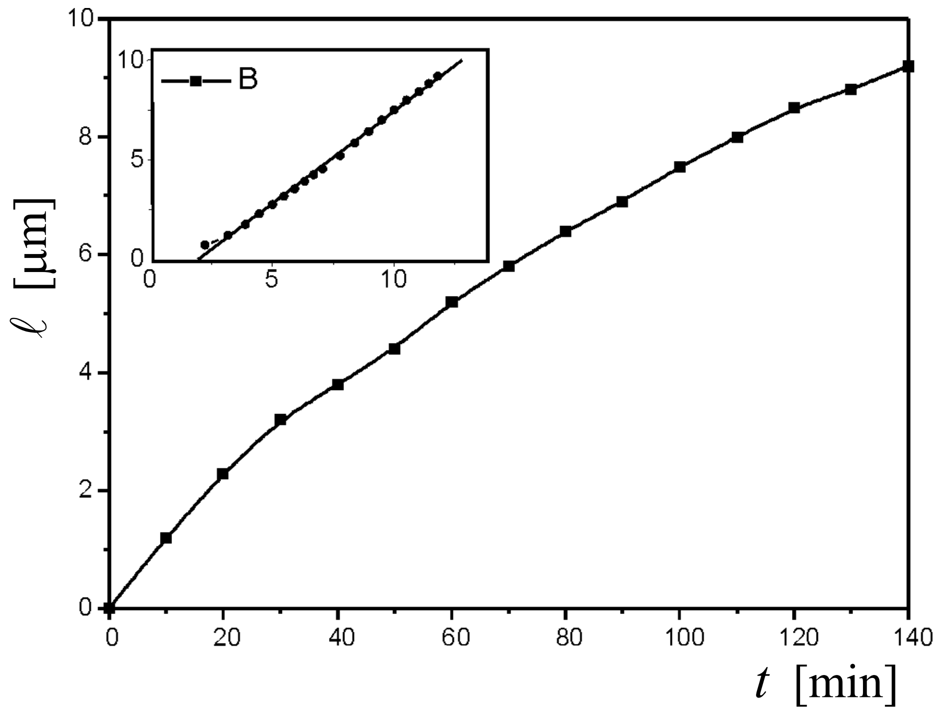
Aquation

Dehydration

Equilibrium
aquation ↔ dehydration

Aquation

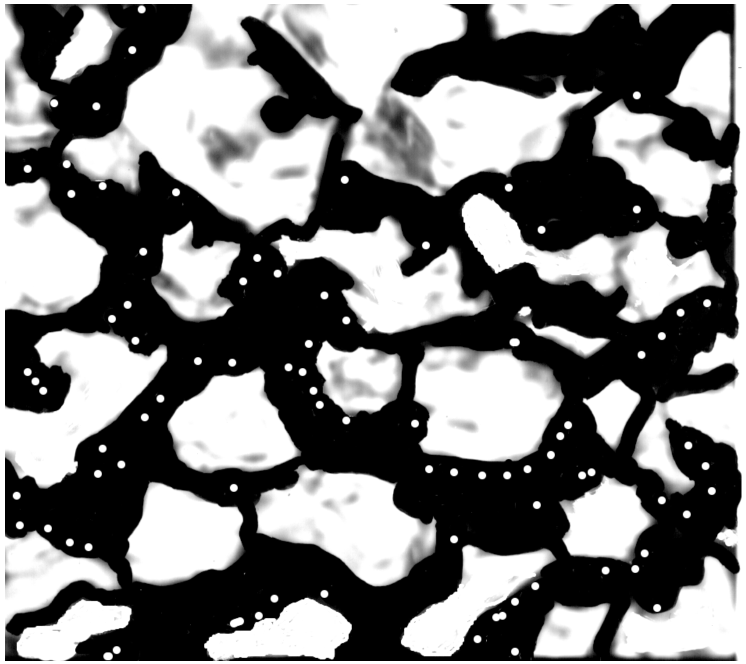
Liquid film of NaI solution is formed



Thickness ℓ of water film on crystal surface as a function of exposure time t.
In insert: dependence ℓ *vs* $\sqrt{t}$.

Dehydration

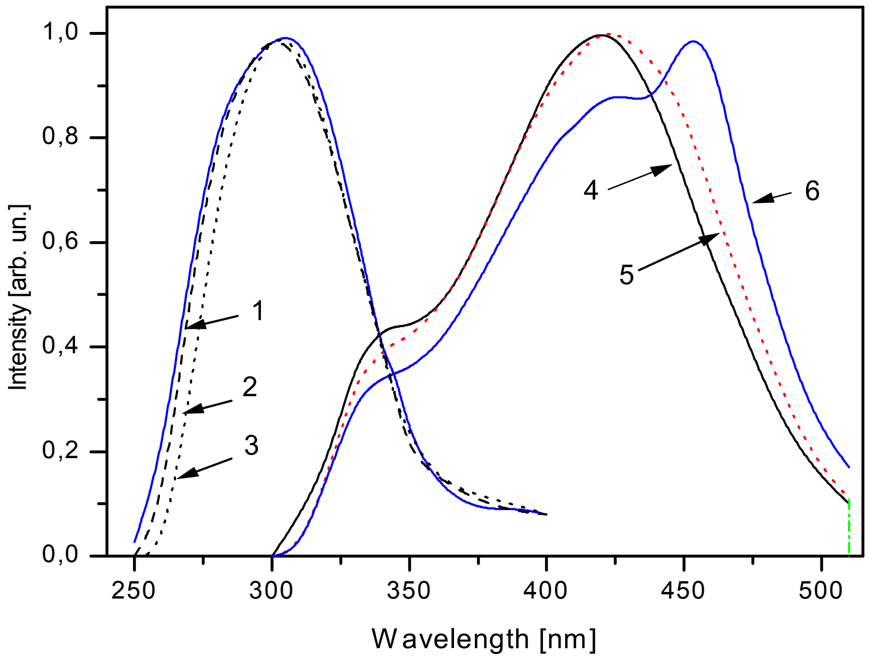
Crystal growth from saturated solution

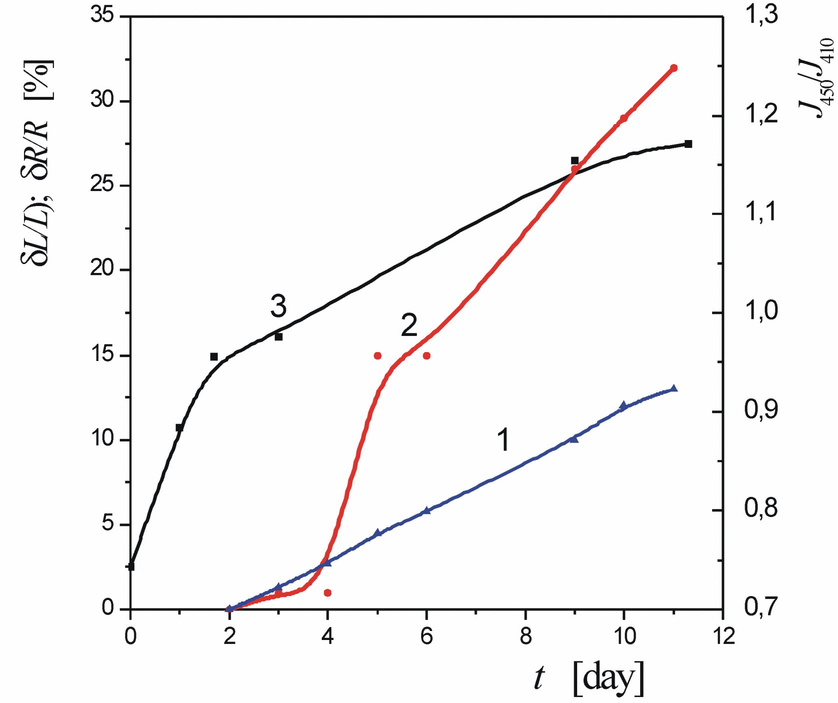


Photograph (× 390) of crystal surface during dehydration on a stage of TlI phase appearance

Func. Materials, vol. 6 (1999) 777

Equilibrium state
Aquation ⟷ dehydration





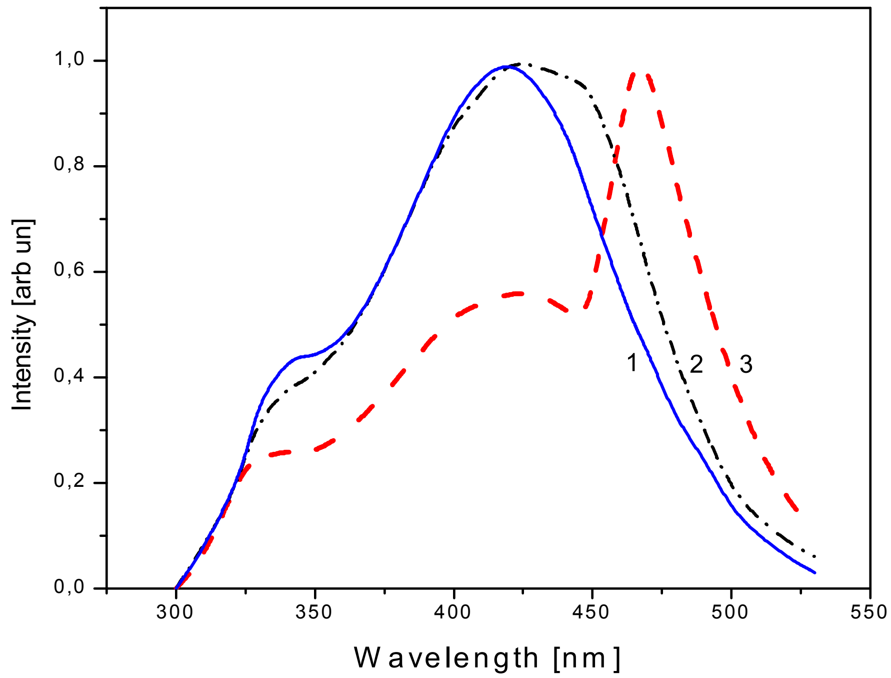
Radioluminescence spectra of NaI and NaI:Tl:
NaI: 1 – initial; 2 – 9 days; 3 – 17 days.
NaI:Tl: 4 – initial; 5 – 3 days; 6 – 34 days.

Degradation of L (1), R (2) and changing in ratio J_{450}/J_{410} (3) during NaI:Tl storage in non-hermetic housing.

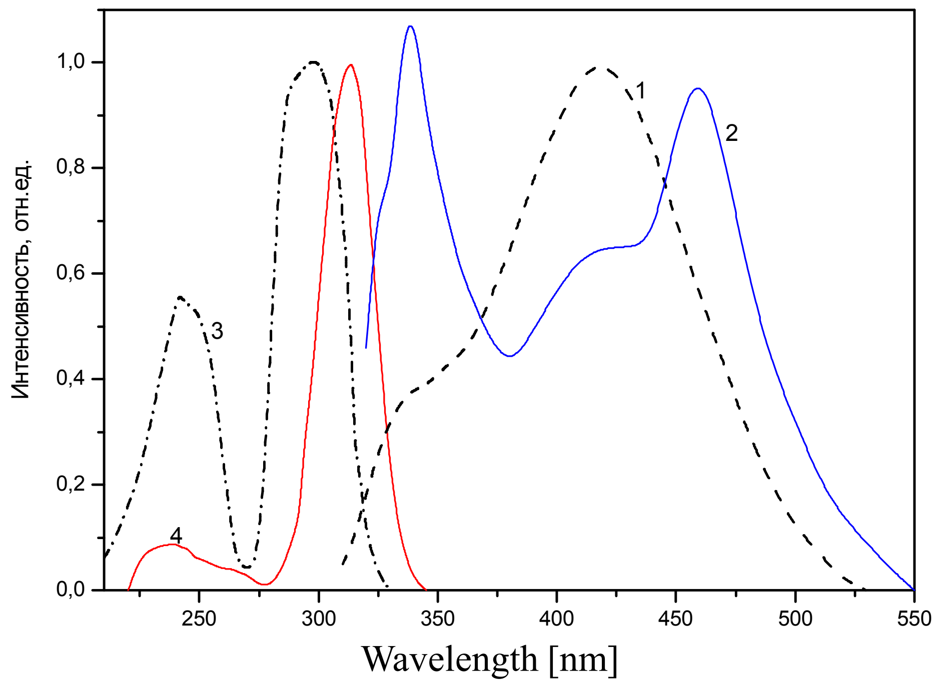
Increasing of ratio J_{450}/J_{410} is useful method for diagnostic of NaI:Tl aquation

Func. Materials, vol. 5 (1998) 495

Effect of Hydration on Luminescence of NaI:Tl



Radioluminescence of NaI:Tl:
1 – initial; 2 – 5 days; 3 – 40 days.
Thin liquid film of water on surface (3)



Photoluminescence and excitation spectra of hydrated NaI:Tl: 1- excited at 293 nm, 2 -314 nm. Excitation spectra for 420 nm emission (3) and 460 nm (4).

New luminescent band on surface well correspond to known $(Tl^{+})_n$ centers in NaI lattice which appear at high thallium concentration.

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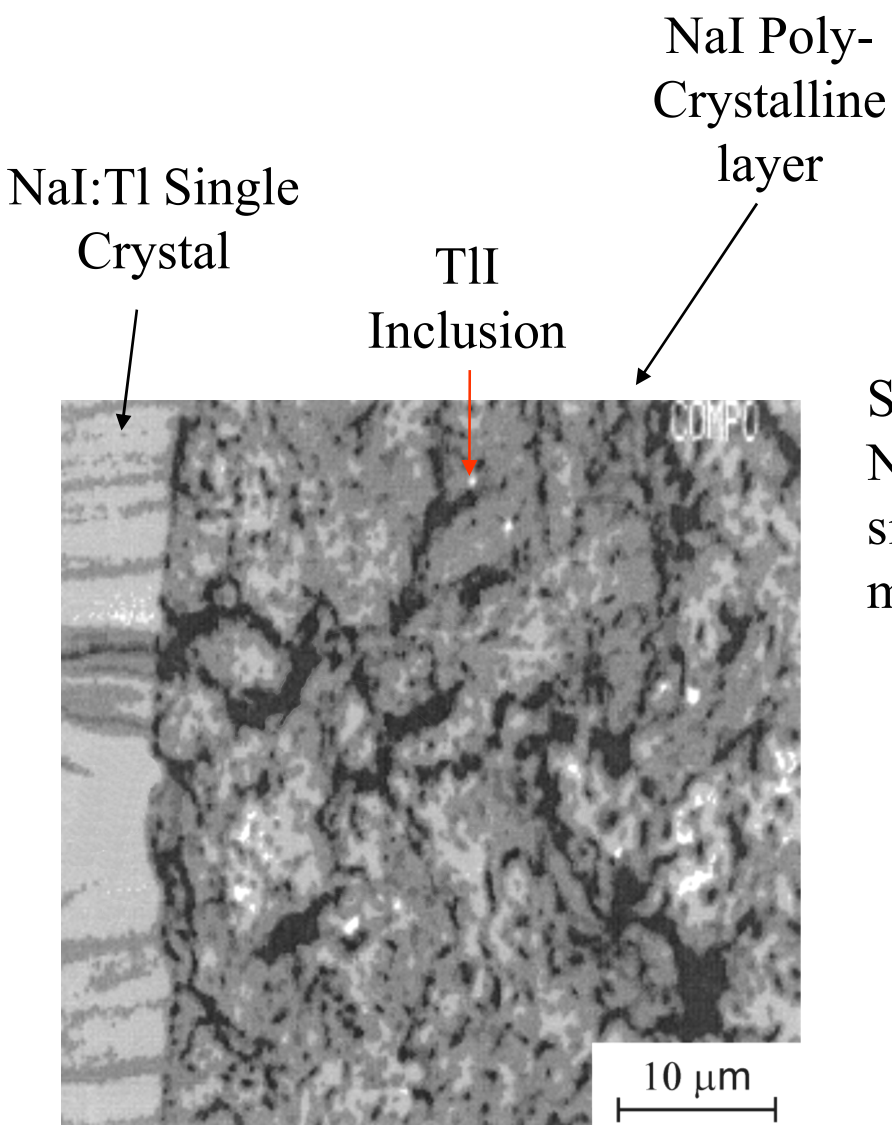


Structure of doughy crust on a surface of NaI:Tl crystal after dehydration. Left side is a single crystal. Scanning electron microscopy.

Polycrystalline layer of NaI on a entrance window of scintillator can be used as diffusion reflector.

Patent 98115845 UA, 2001

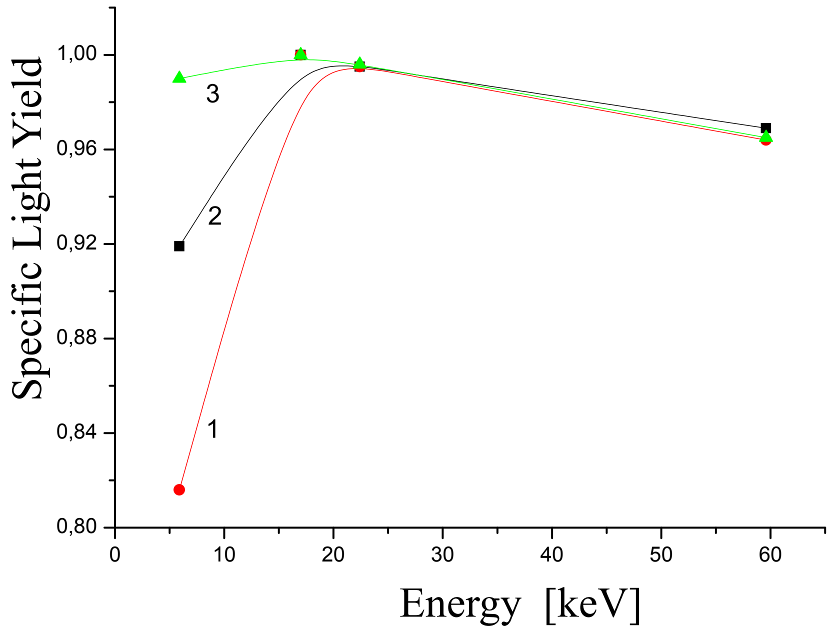
Dead Layer in NaI:Tl Crystal

Nature or DL – radiolysis of water on surface

Alexandrov, Aluker, et al. Introduction in physics and chemistry of surface. Riga, Zinatne, 1989

Light yield of NaI:Tl (mirror cleavage plane) after aquation/dehydration

Aquation [min]	Light output *L/E*		
	5,9 keV	22,4 keV	59,6 keV
0	1,025	1,032	1
5	0,948	1,029	1
15	0,827	1,026	1

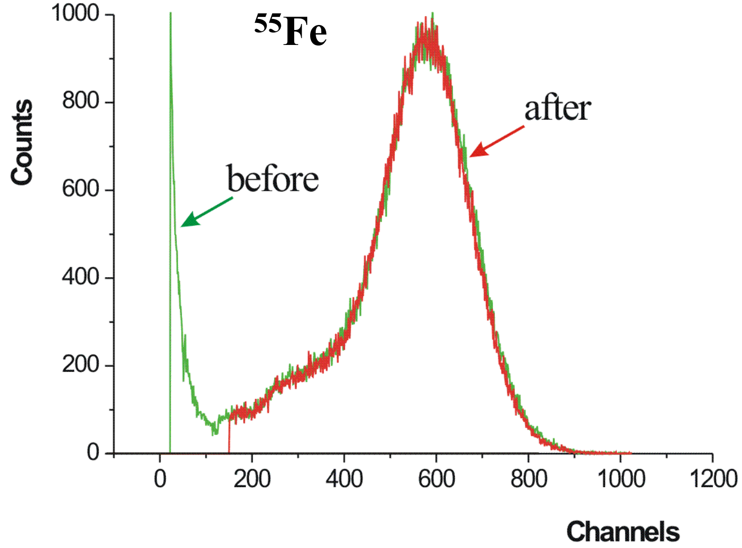


Dependence of *L/E vs E* for NaI:Tl:
1 – alcohol polishing, 2 – new method,
3 – cleavage plane.

H_2O molecule is a trap for electron. Its affinity to electron is ~ 1 eV. Recombination with hole results in dissociation of molecule.

The essence of photochemical modification of surface

Effect of microwave drying

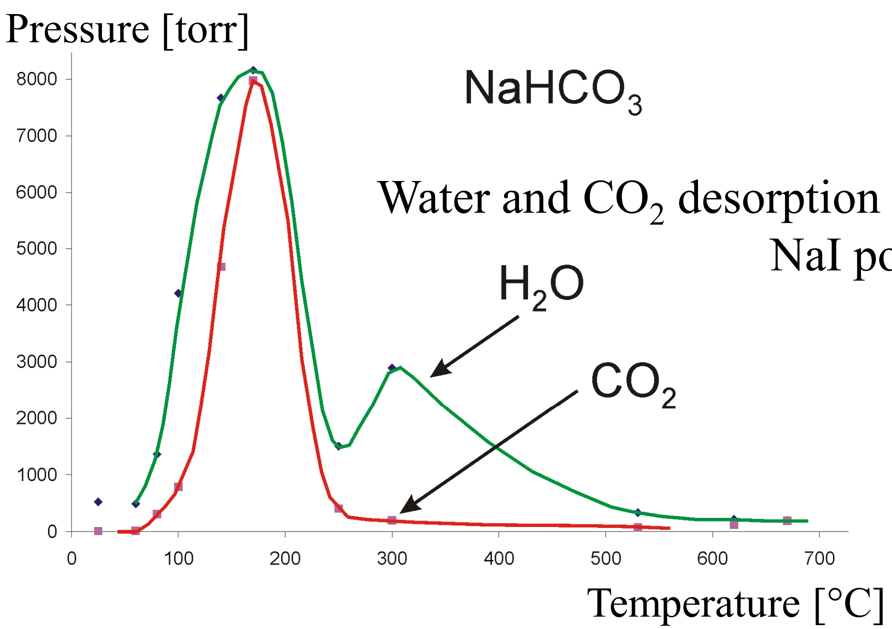


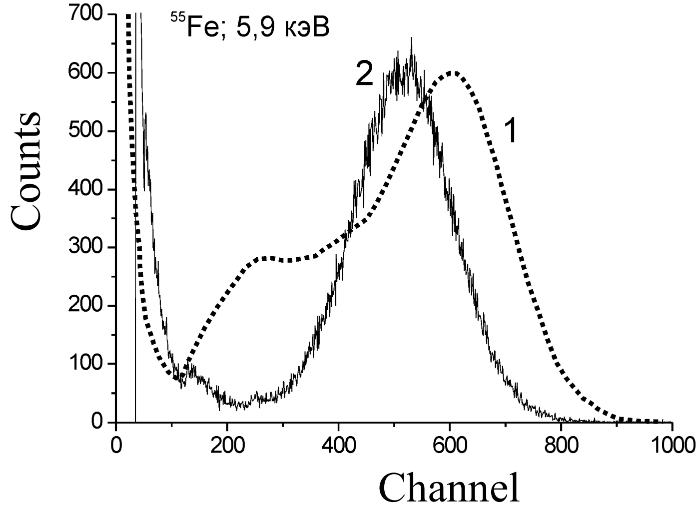
Since removing of water do not improve light yield it has been suppose that surface is contaminated by NaOH.

In this case:

$$\mathbf{NaOH + CO_2 \rightleftarrows NaHCO_3}$$

It has been shown that UV light accelerates reaction (4-6 minutes)



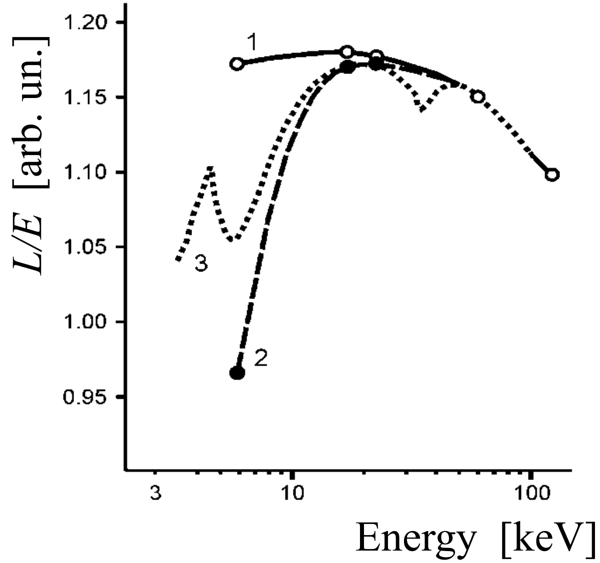


1 – before, 2 – after modification.

Phys. Surface Engineer., vol. 9 (2011) 256

Photochemical modification of surface

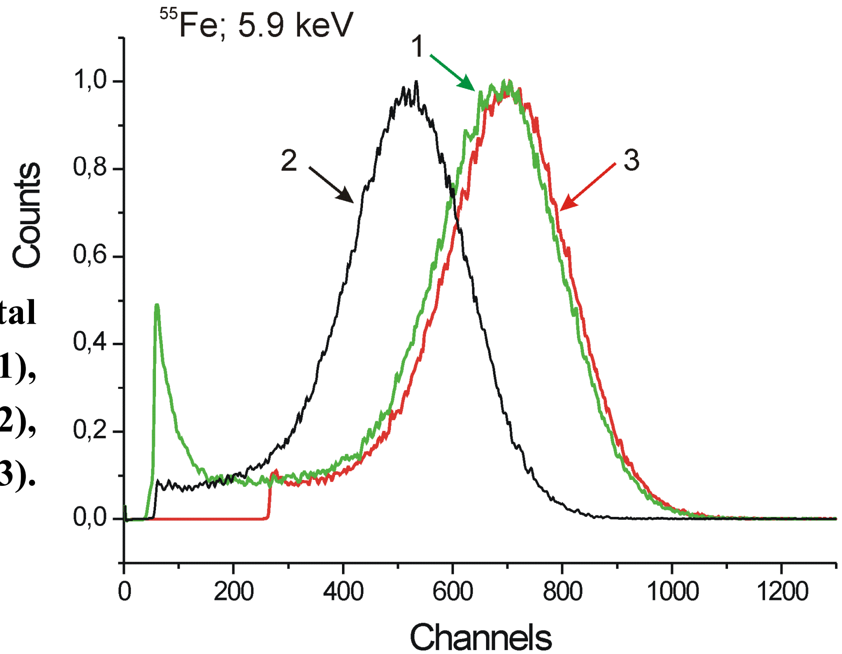
Dead layer



nPR at low energy for NaI:Tl crystal

Effect of Photo Chem. Modification on light yield and energy resolution of NaI:Tl

Measure condition	*L*, channel	*R*, %
Cleavage plane	662	**40.5**
Aquation of clev. plane	502	**50.2**
Ph.Ch.Mod., one hour	645	38.6
Ph.Ch.Mod., next day	702	**37.9**



Pulse height spectra of NaI:Tl crystal
Cleavage plane (1),
Aquation of cleavage plane (2),
after Ph. Ch. Mod. (3).

Patent 102771 UA, 2013

Application for patent, 2013