Scintillation efficiency improvement by mixed crystal use

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Motivation and outlines

- **Can we use advantages of the last years theoretical studies for some practical use?** *We mean the model of thermalisation stage responsibility for the later survival of electron excitation*

- **What is following from the general model? How to apply this knowledge to doped crystals?**

- **Can we manage the thermalization distance by :**
  - **doping (rare solutions)**
  - **move to the mixed crystals (heavy solutions)**

- **Experimental data… old data, last results, perspectives**

- **Alternative mechanisms**

Maximal scintillator light yield

Scintillator efficiency:

$$N_{ph} = \beta \, S \, Q$$

$$\beta = \frac{E_\gamma}{E_{e-h}}$$

E_γ *quantum energy*

E_{e-h} *= ~ 2.4 E_g*

S *energy transfer efficiency*

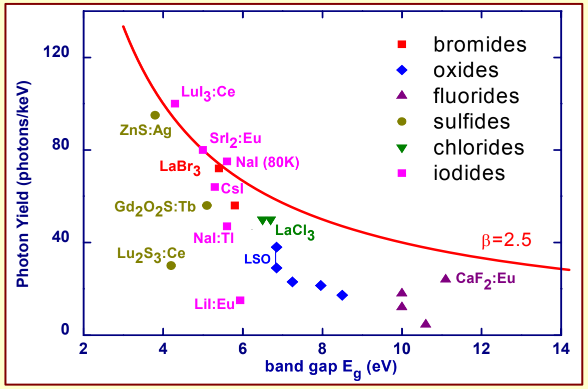
Q *luminescence center efficiency*

Q is ~ 1 for many typical activators, Ce, Eu etc

S is also ~1 for many hosts.

1-5% of uniform distributed activator minimizes the transfer length to 2-5 a (lattice parameters)

β – e-h creation efficiency is a key to the new material search and investigation



P.Dorenbos, SCINT, 2009

Primary stages of scintilltion (track formation and energy relaxation)

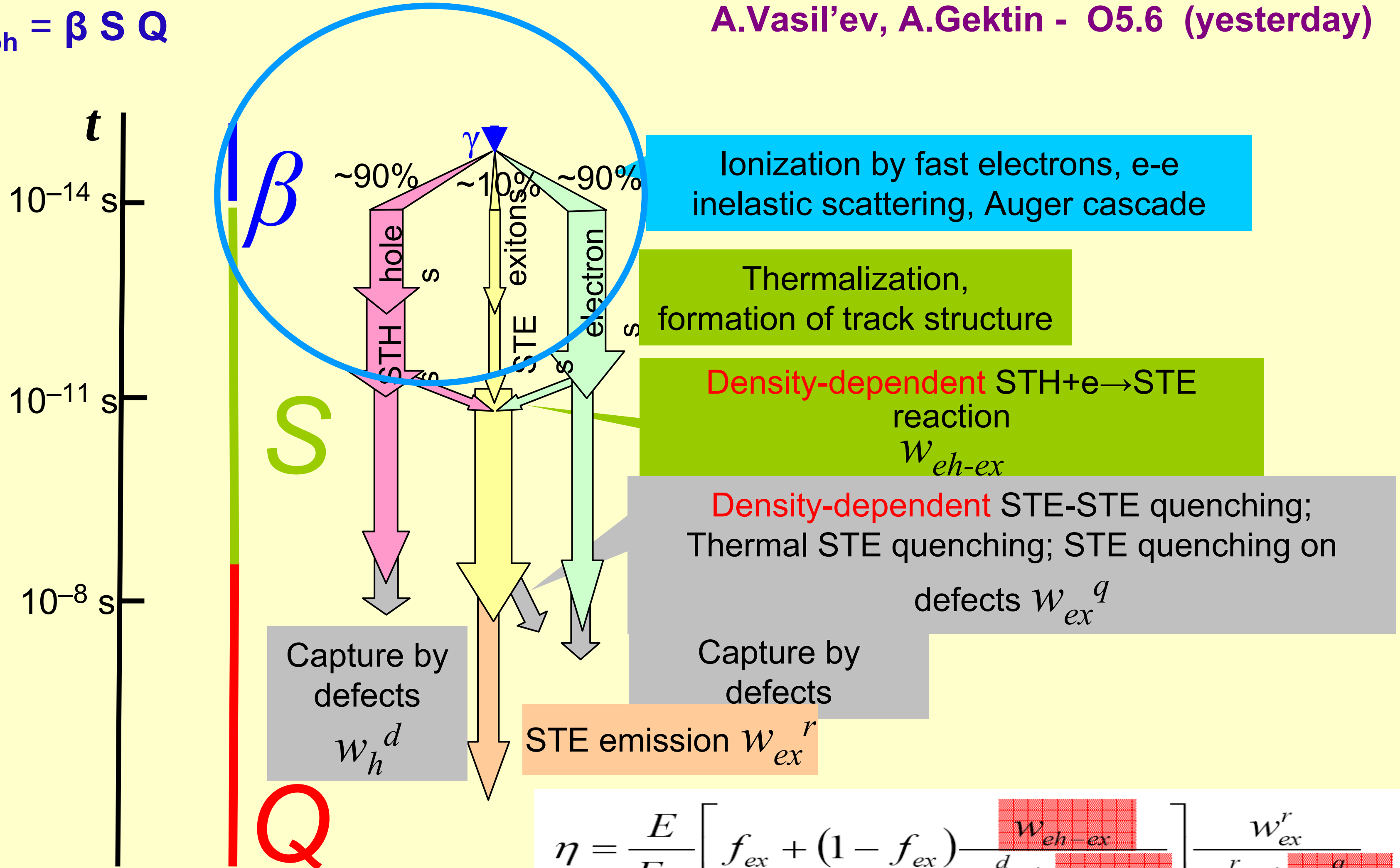
Main contributors to the track theory developments :

- R.T.Williams, …. see - SCINT – O2.9, O2.19, O6.6
- A.N.Vasil'ev… see – SCINT – O5.6, O5.9
- S.Kerisit, Z.Wang, F.Gao…
- A.Canning … see –SCINT – O7.5
- V.Nagirnyi, M.Kirm… See – SCINT - O2.2
- W.Setyawan… et al

Scintillation process; from the absorption to photon emission

$N_{ph} = \beta\ S\ Q$

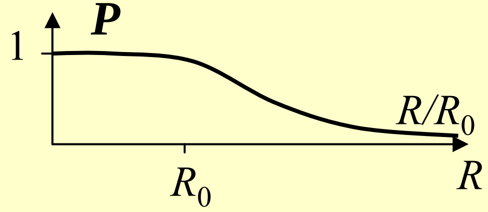
A.Vasil'ev, A.Gektin - O5.6 (yesterday)

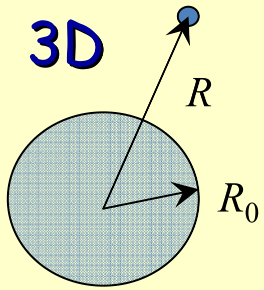


$$\eta = \frac{E}{E_{eh}}\left[f_{ex} + (1 - f_{ex})\frac{w_{eh-ex}}{w_h^d + w_{eh-ex}}\right]\frac{w_{ex}^r}{w_{ex}^r + w_{ex}^q}$$

3D diffusion-controlled recombination

Recombination probability





Black sphere $P = \begin{cases} 1, & r_{eh} < R_0 \\ R_0/r_{eh}, & r_{eh} > R_0 \end{cases}$

Coulomb $P = 1 - \exp(-R_{Ons}/r_{eh})$

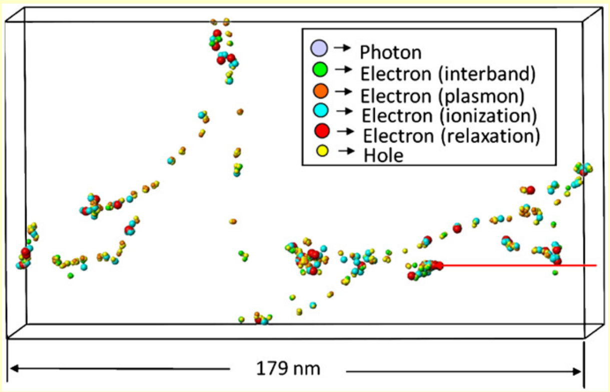
$$\frac{e^2}{\varepsilon R_{Ons}} = k_B T$$

ε=5.7 T=300K R_{Ons}=10 nm

T=77K R_{Ons}=38 nm

T=10K R_{Ons}=300 nm ???

For thermalized excitations $R_{Ons}/r_{eh} \ll 1$
– exciton yield after thermalization should be low

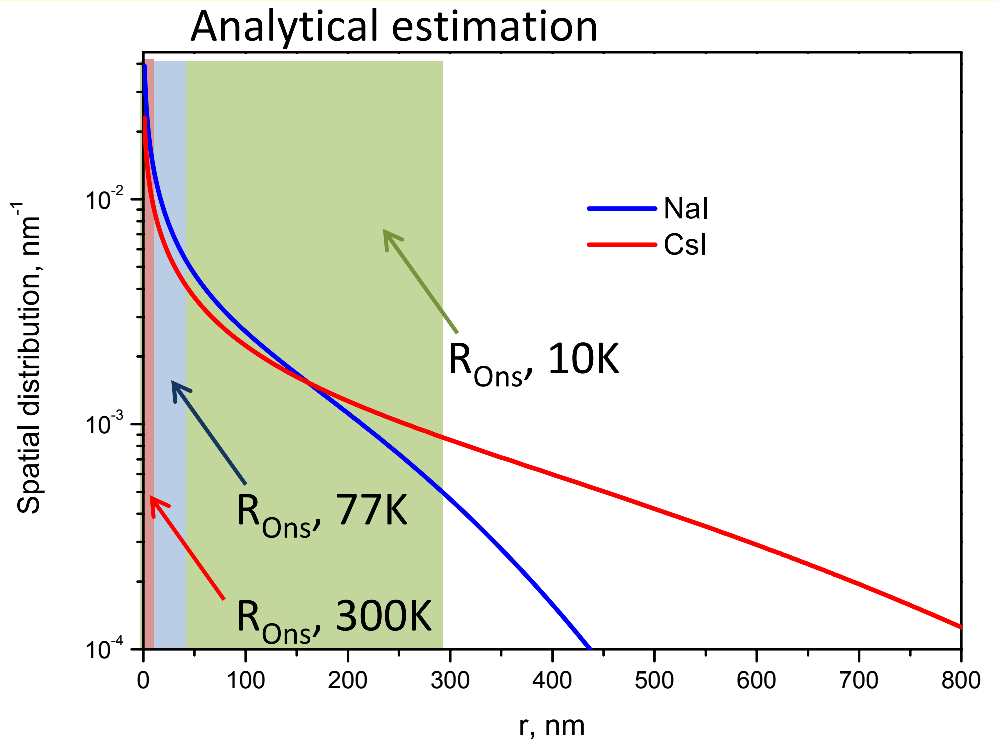


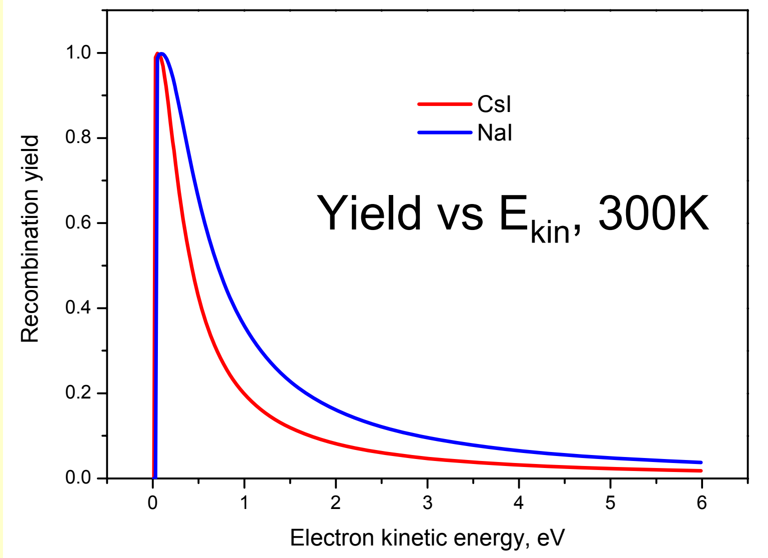
Simulated spatial distribution of e–h pairs for a 10 keV photon event in CsI,
where electrons and holes are distinguished by size and color, as indicated in legend.
NWEGRIM code.

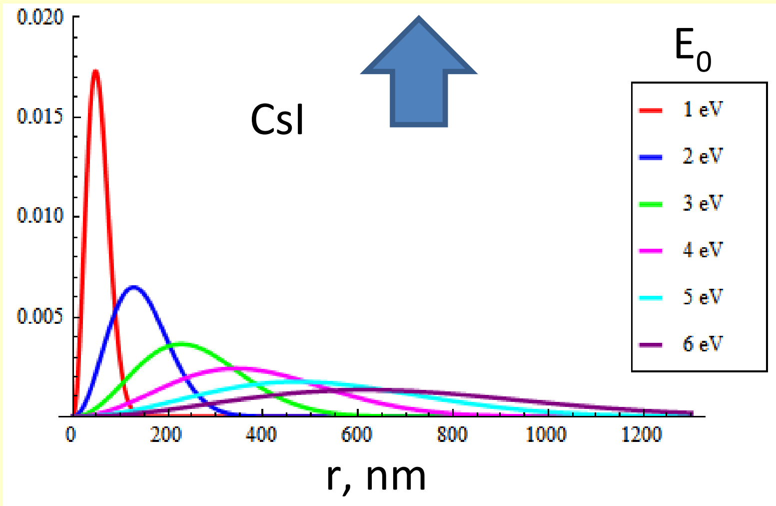
F. Gao et al., Nucl. Instr. and Meth. A (2010)

Spatial distribution of thermalized electrons (binary crystals)

See Vasil'ev, O5.6

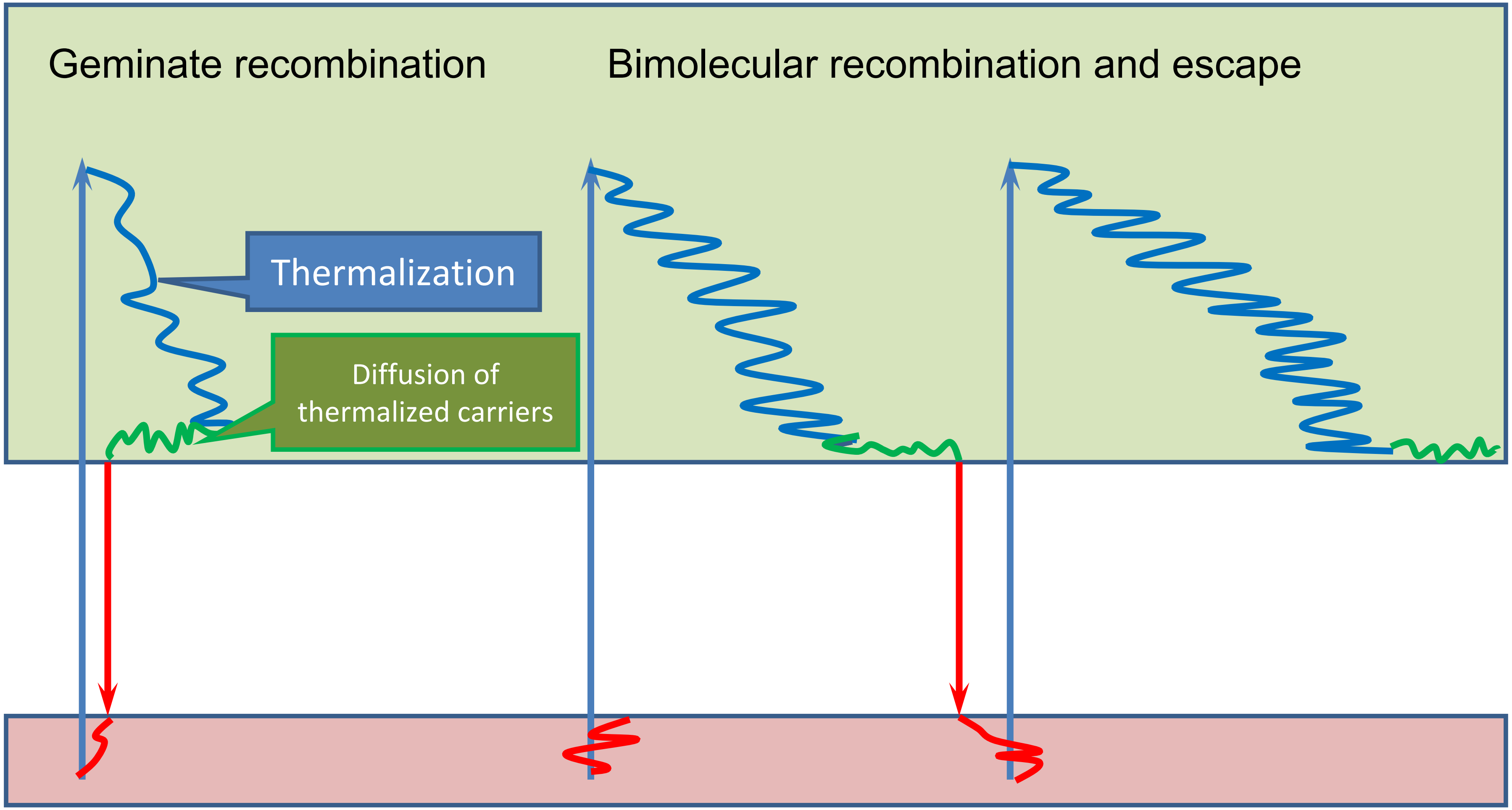




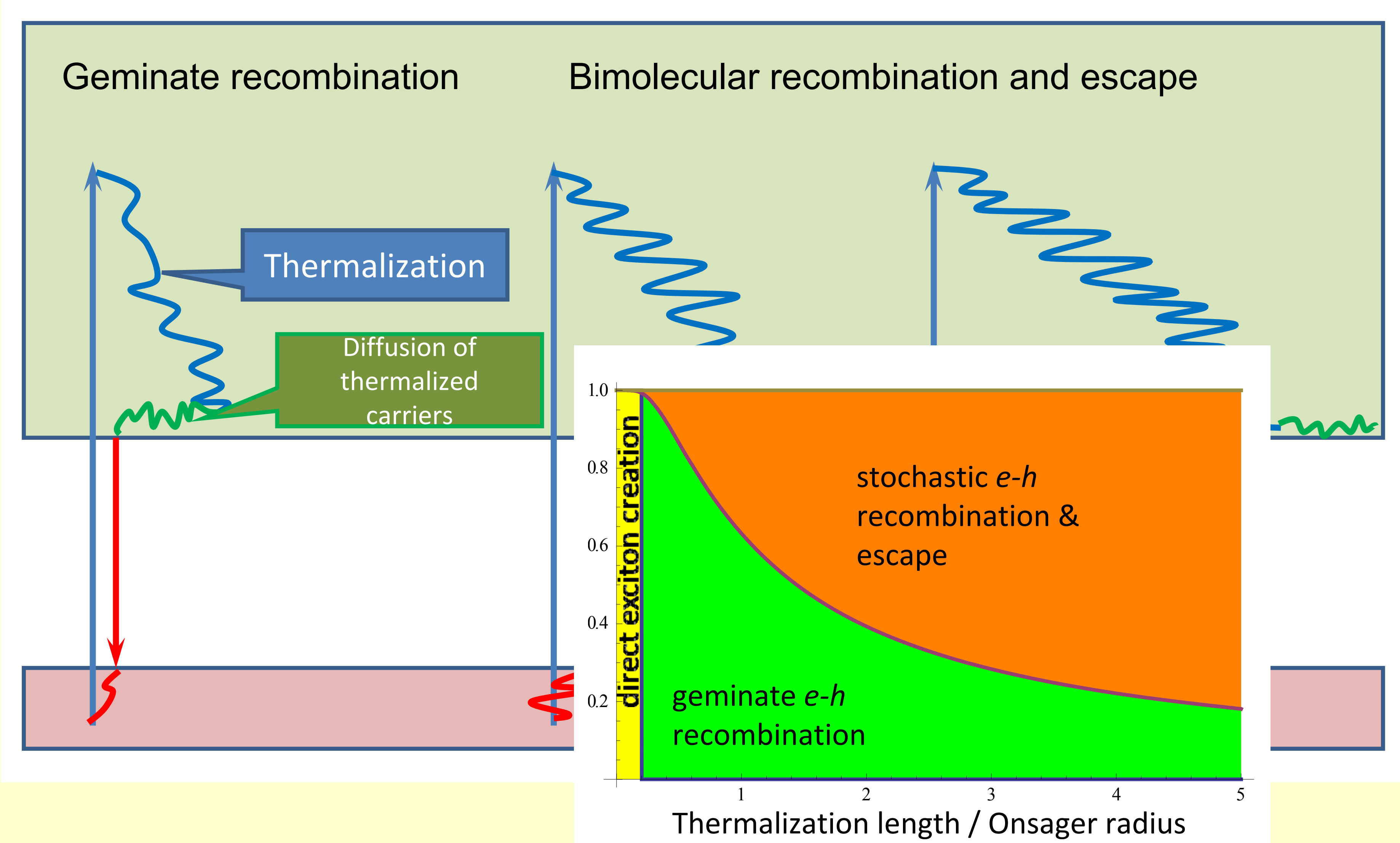


	R_{Ons}, 300K	Yield, 300K	Yield, 77K
CsI	9.87 nm	0.24	0.44
NaI	9.05 nm	0.34	0.58

Electron-hole separation and recombination



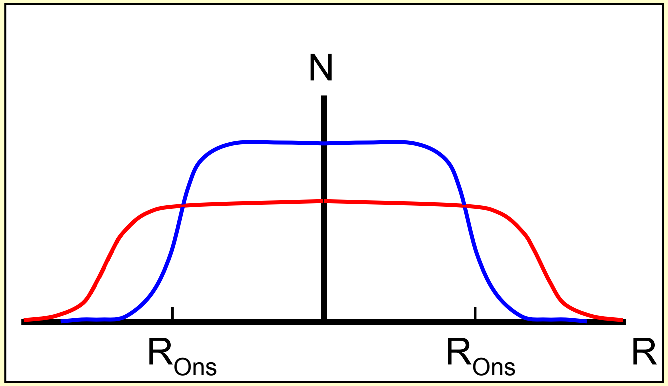
Electron-hole separation and recombination



How we can manage thermalization length?

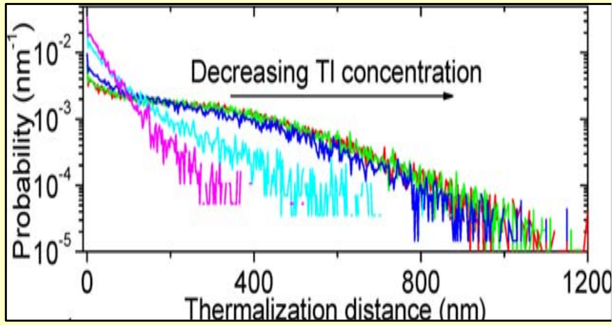
What we have to do to improve the yield?

The goal is to concentrate e-h pairs at the distance less then Onsager radius, to minimize the volume of stochastic recombination and escape losses.



Two ways for e-h separation management

- Doped/activated crystals (rare solutions)
- Mixed crystals (hard solutions)



Z. Wang, Y. Xie, B. D. Cannon… 2011

See also S.Gridin…O5.9

Coupled processes of thermalization and spatial diffusion

Mean square of the thermalization distance $$< r^2 >_{E_{e0}\to E_e^{kin}} = 6 \int_{E_e^{kin}}^{E_{e0}} \frac{D^R(E')}{S(E')} dE'$$

Spatial distribution function $$f(r, l_e(E_{e0})) = \frac{3\sqrt{6}\, r^2}{\sqrt{\pi}\, l_e^3(E_{e0})} \exp\left(-\frac{3r^2}{2 l_e^2(E_{e0})} \right)$$

where thermalization length is $$l_e(E_{e0}) = \sqrt{< r^2 >_{E_{e0}\to k_B T}}$$

Thermalization length for one LO phonon branch

$$l_{e,LO}^2(E_{e0}) = \frac{8}{3} a_B^2 \left(\frac{\tilde{\varepsilon}}{m_e^* / m_0} \right)^2 \tanh\left(\frac{\hbar\Omega_{LO}}{2k_B T} \right) \int_{\hbar\Omega_{LO}}^{E_{e0}} \left(\frac{E'}{\hbar\Omega_{LO}} \right)^2 \frac{1}{\ln(4E'/\hbar\Omega_{LO})} \frac{dE'}{\hbar\Omega_{LO}}$$

$$= \frac{1}{24} a_B^2 \left(\frac{\tilde{\varepsilon}}{m_e^* / m_0} \right)^2 \tanh\left(\frac{\hbar\Omega_{LO}}{2k_B T} \right) \mathrm{Ei}\left(3 \ln\left(\frac{4E_{e0}}{\hbar\Omega_{LO}} \right) \right),$$

We have to choose/engineer materials with

- higher effective masses in the whole relaxation region $E_{kin} < E_g$

- higher LO phonon energies

Possible mechanisms of reduction of electron-hole separation in solid solutions

❑ Modification of hot stage of relaxation

- Modification of phonon spectrum (additional phonon branches)
- Modification of electron spectrum – increasing of elastic scattering (Bragg scattering in case of regular crystal)

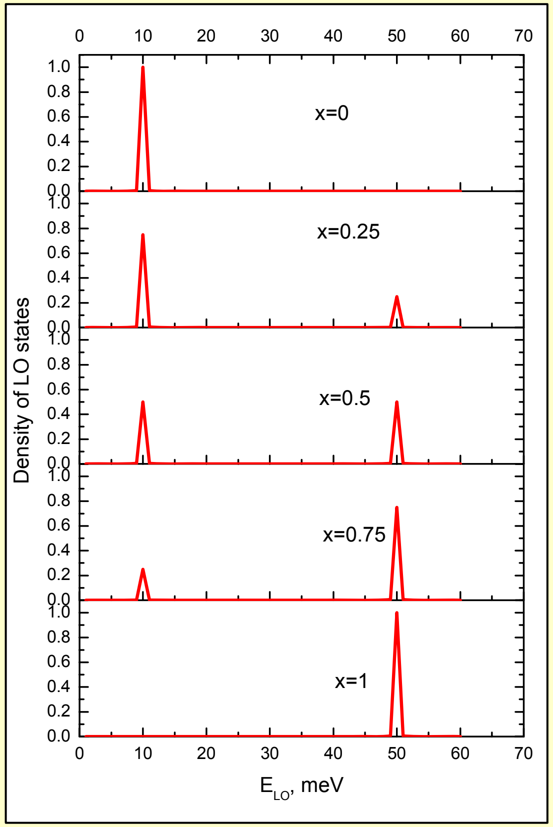
❑ Modification of diffusion of thermalized carriers

- Non-uniformity of solution (in particular, clusterization) and scattering
- Anderson localization of carriers in disordered systems

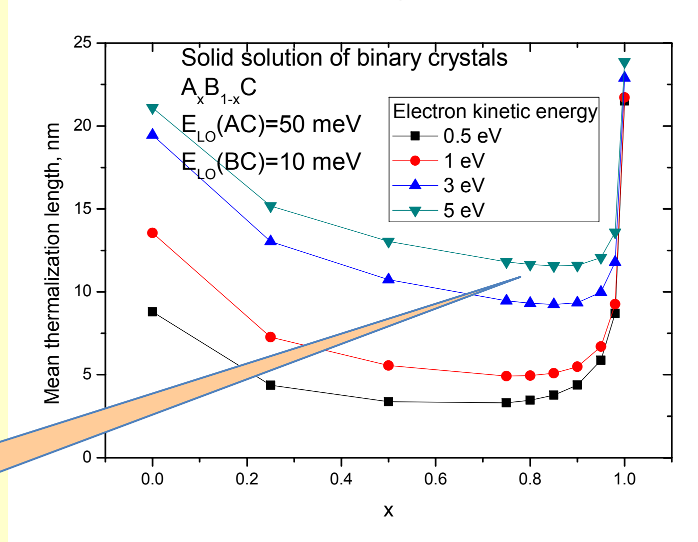
Modification of phonon spectrum (additional phonon branches)

Mixed – $A_xB_{1-x}C$ crystal model

Density of LO states

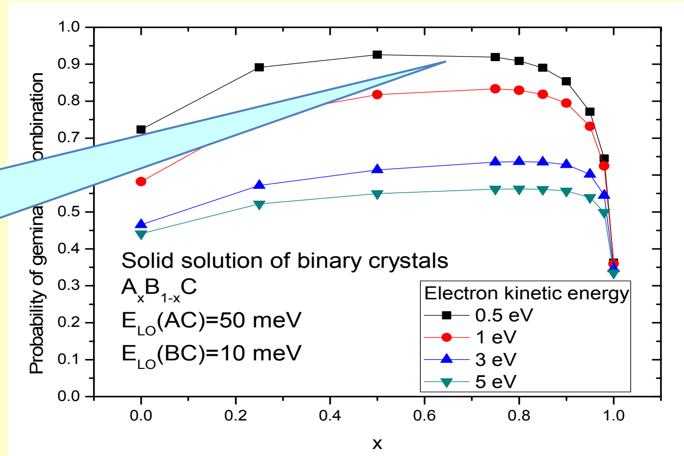


Mean thermalization length vs X concentration



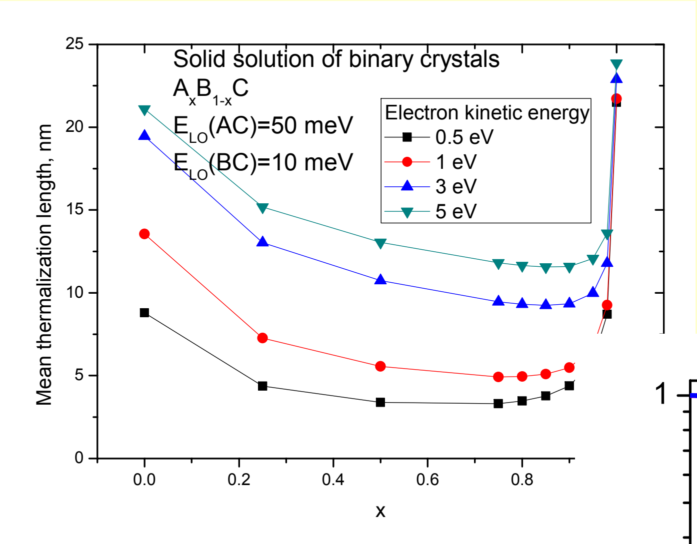
Thermalization length decrease

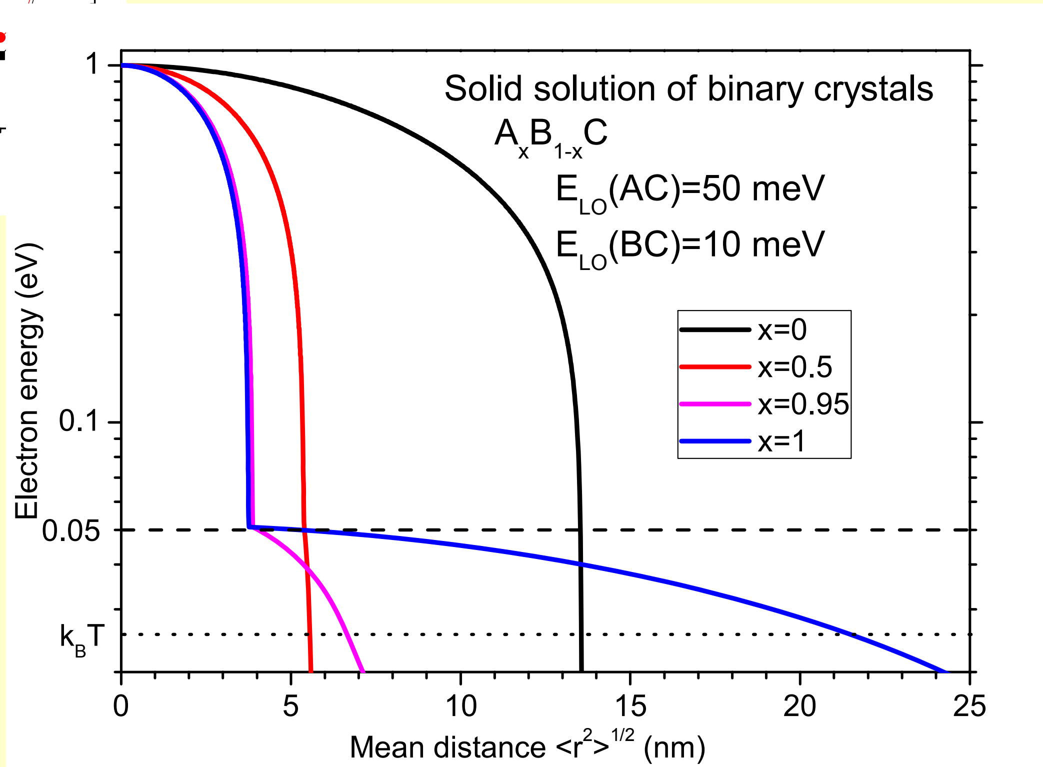
Probability of geminate recombination



Recombination probability increase

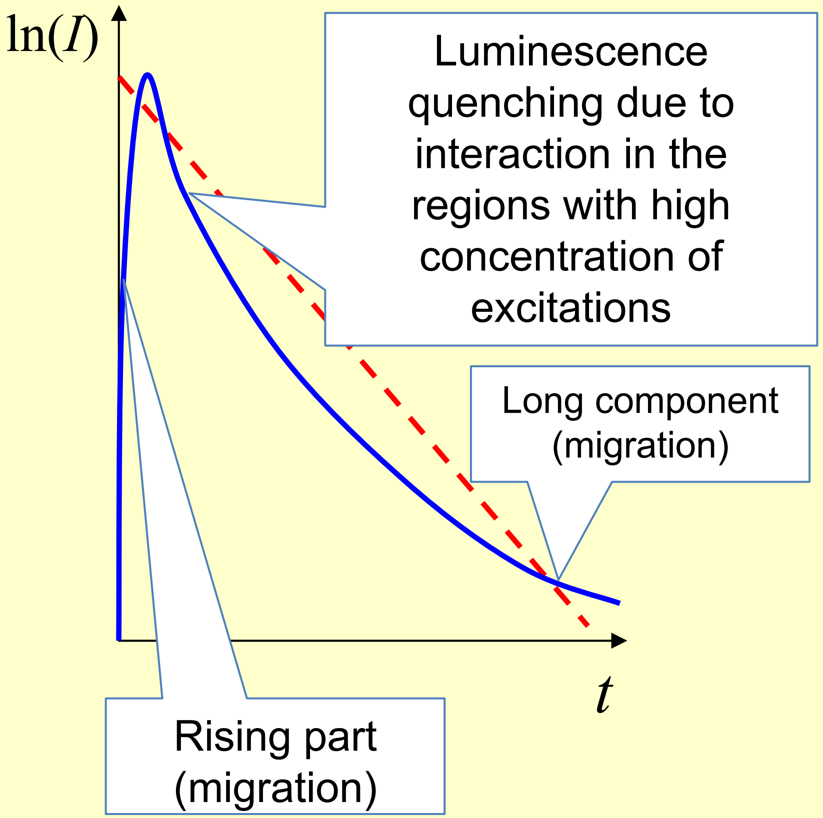
Modification of electron spectrum – increasing of elastic scattering (Bragg scattering in case of regular crystal)



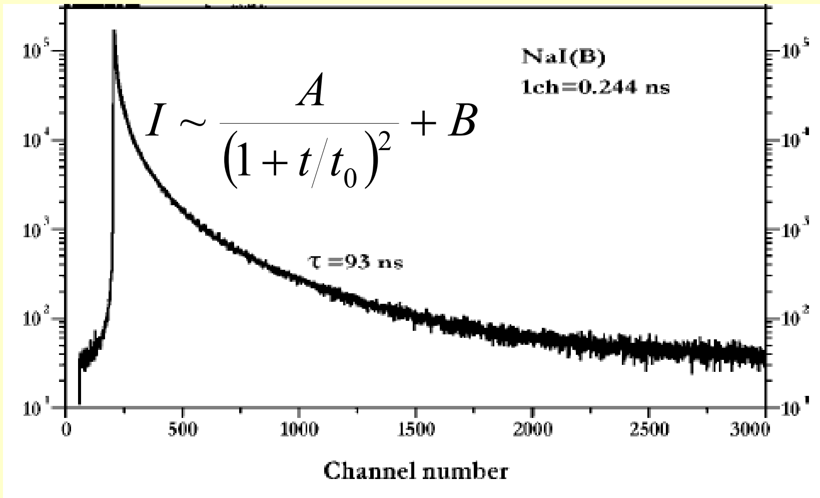


Modification of kinetics in scintillators

Scintillator kinetics



Essentially non-exponential decay kinetics for pure NaI



M. Moszyński, et al. Study of Pure NaI at RT and LNT, *IEEE TNS 2003*

From the theory to experiment

- The database… Old and new experimental data
- The yield and decay kinetics analysis…
- Selection of proper experimental conditions *(the same growth and components, activator content structure etc)*
- No “masked phenomena”

Mixed halides. CsI-CsBr

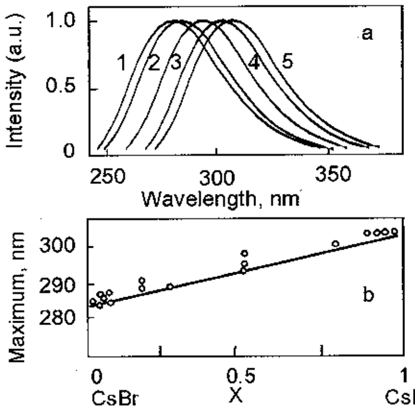


Fig.1. a) Radioluminescence spectra of mixed CsI_x-$CsBr_{1-x}$ crystals: (a) x=0.01(1), x = 0.08 (2), x = 0.45 (3), x=0.8 (4), x = 1 (5). (b) Maximum position of UV emission band on the content of mixed components.

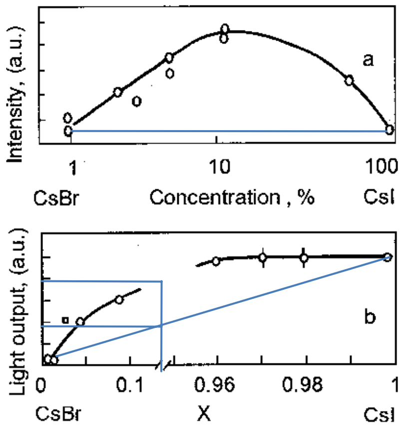


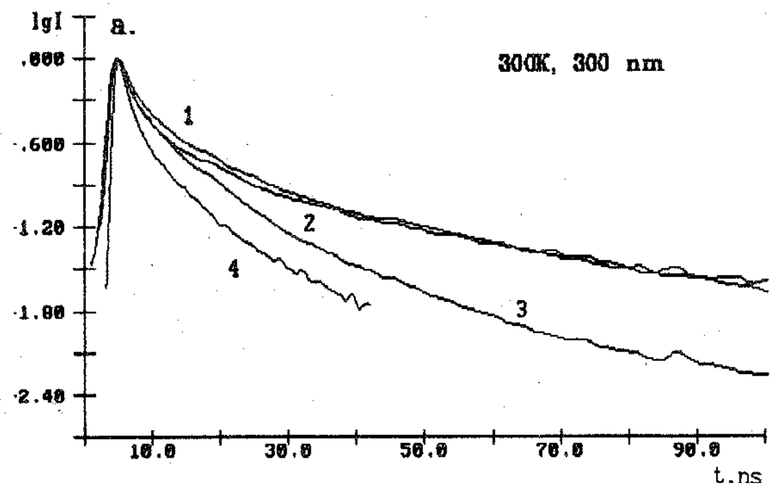
Fig.2. Concentration dependence of intensity (a) and light output (b) of CsI-CsBr crystals.

A. Gektin, N. Shiran, V. Shlyahturov and A. Belsky, Proceedings of SCINT'95, Delft, **1995**

First note – 1987

(Kubota… Gektin, Shiran)

Fast CsI scintillator…

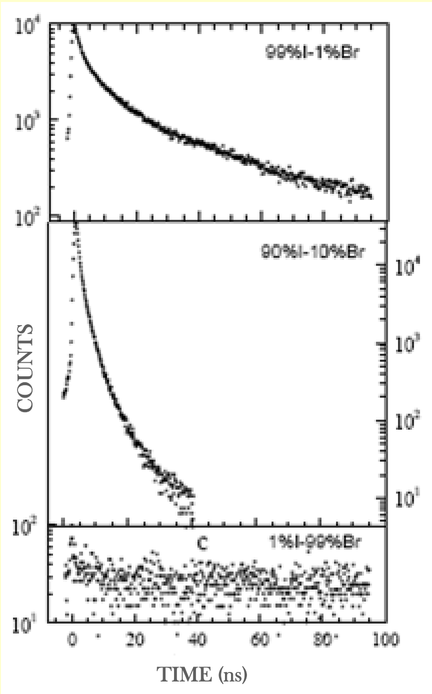


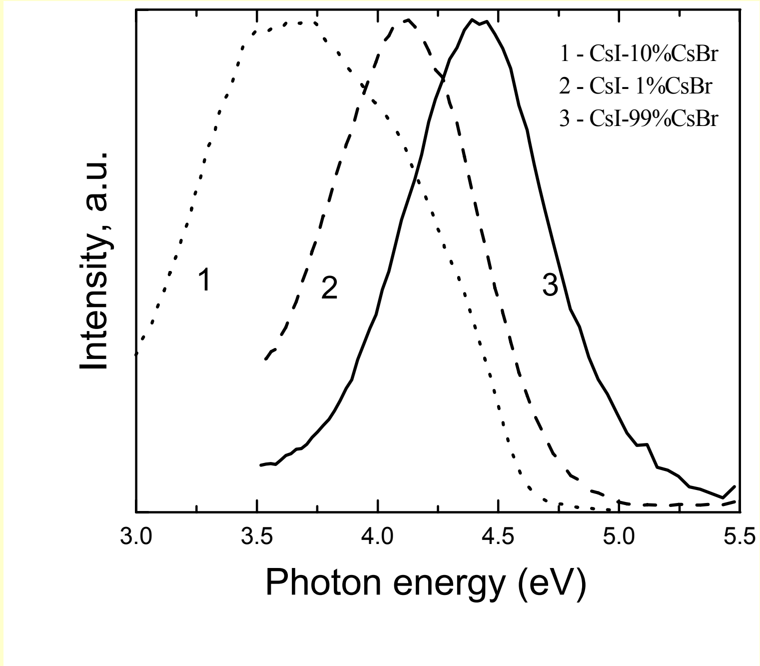
UV-luminescence decay kinetics in doped CsI crystals. 1 – CsI; 2 – CsI-RbI; 3 – CsI-CsCl; 4 – CsI-CsBr.

A.N. Belsky, A.V.Gektin, V.V.Mikhailin et al., Preprint ISC-91-3, Kharkov, **1991**

Mixed halides. CsI-CsBr

X-ray emission spectra and decay kinetics of $CsI_{1-x}Br_x$ solid solutions





A.N. Belsky, A.V. Gektin et al.,

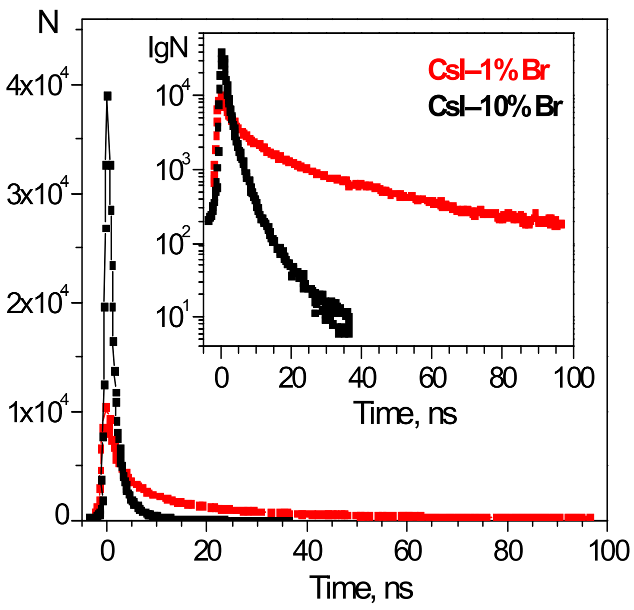
Proceedings of SCINT'95, Delft, 1995

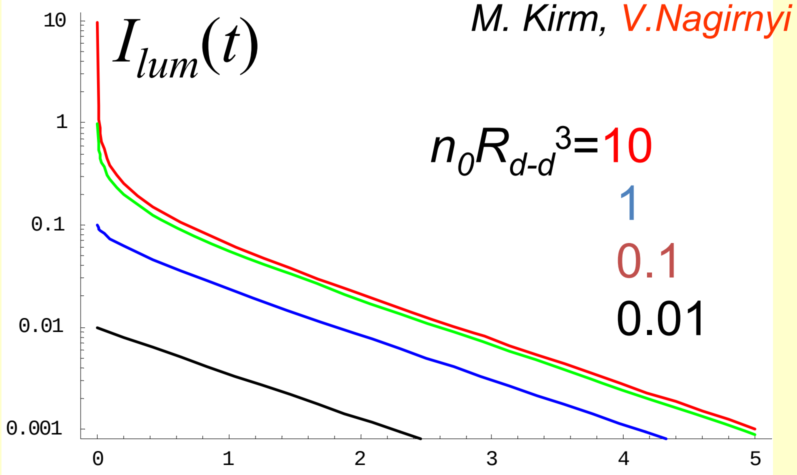
1988

Interaction of excitations in the regions with high excitation concentration

(2005)

CsI-CsBr (data reconstruction)





t/τ_r

Dipole-dipole transfer:

$$I_{lum}(t, n_0(\mathbf{r})) = \frac{n_0(\mathbf{r})}{\tau_r} \frac{\exp(-t/\tau_r)}{1 + \frac{2\pi^2}{3} n_0(\mathbf{r}) R_{d-d}^3 \operatorname{erf}\left(\sqrt{t/\tau_r}\right)}$$

* Pulse intensity increase with simultaneous decay time shortening

$R_{d\text{-}d}$=2.1 nm for $CdWO_4$

M. Kirm et al, PRB 79, 233103 (2009)

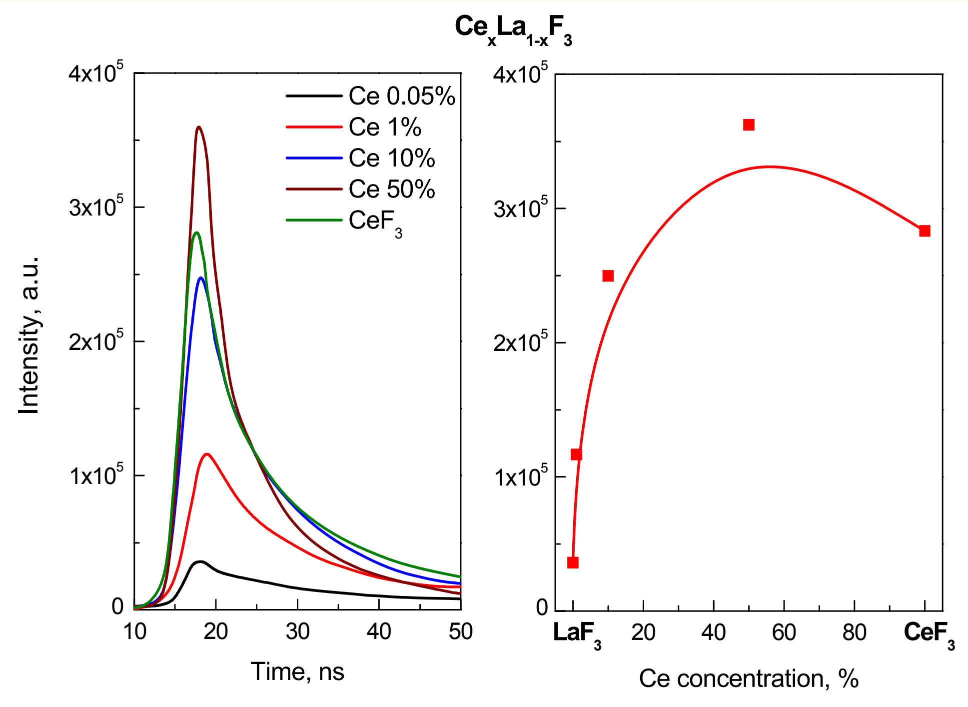
- Similar behavior for CsI:CsCl

$R_{d\text{-}d}$=2.9 nm for CsI

- Problem is the limited solubility

R.T.Williams et al, PSS(b) 248, 426 (2011)

Mixed fluorides: $Ce_xLa_{1-x}F_3$



A.N. Belsky, A.V. Gektin et al., Proceedings of SCINT'95, Delft, 1995

Pulse shape and decay kinetics of $Ce_xLa_{1-x}F_3$

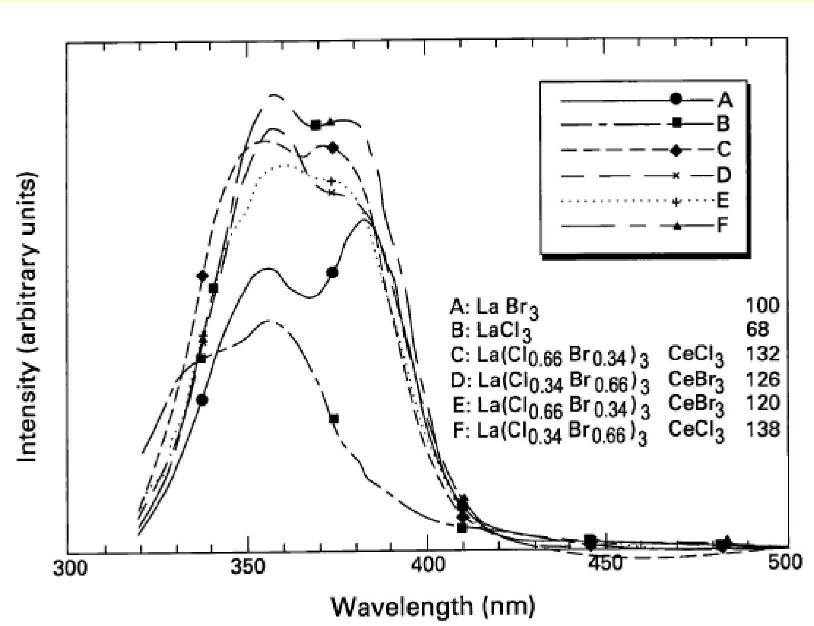
X-ray excitation (10 keV).
Left – original linear scale data; right – intensity vs cation mixture rate.

Mixed halides 20 years late

(54) SCINTILLATOR COMPOSITIONS, AND RELATED PROCESSES AND ARTICLES OF MANUFACTURE

Srivastava et al. (45) Date of Patent: Aug. 1, 2006

GE Research

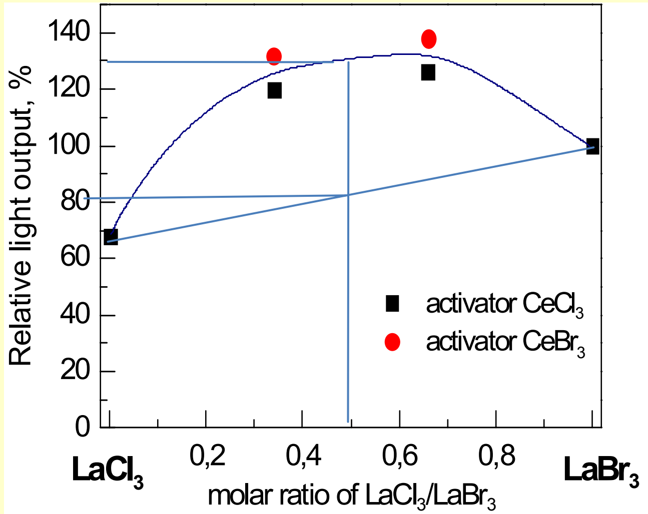


Emission spectra under UV excitation

TABLE 1

SAMPLE	COMPOSITION	ACTIVATOR	LIGHT OUTPUT*
A**	$LaBr_3$	—	100
B**	$LaCl_3$	—	68
C	$La(Cl_{0.66}Br_{0.34})_3$	$CeCl_3$	132
D	$La(Cl_{0.34}Br_{0.66})_3$	$CeBr_3$	126
E	$La(Cl_{0.66}Br_{0.34})_3$	$CeBr_3$	120
F	$La(Cl_{0.34}Br_{0.66})_3$	$CeCl_3$	138

*Relative percent for samples B–F, as compared to sample A.
**Comparative samples.



Sulphides: $Ca_{1-x}Sr_xS$

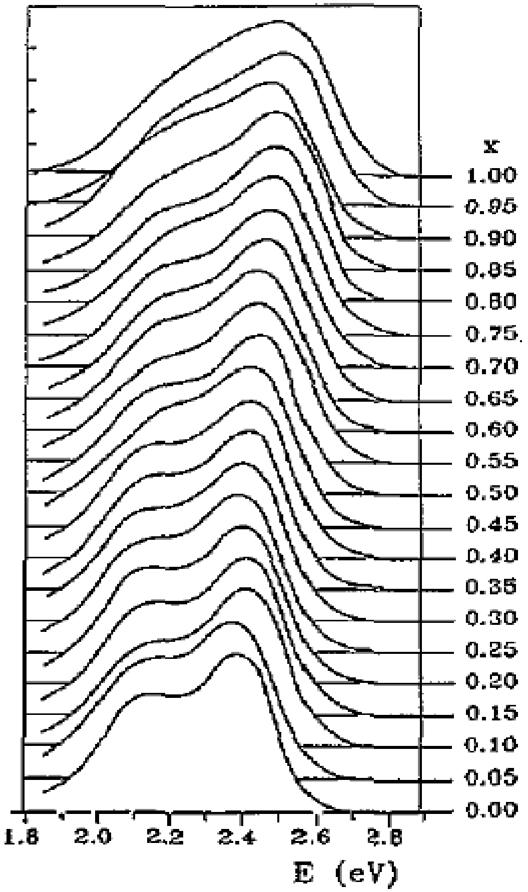
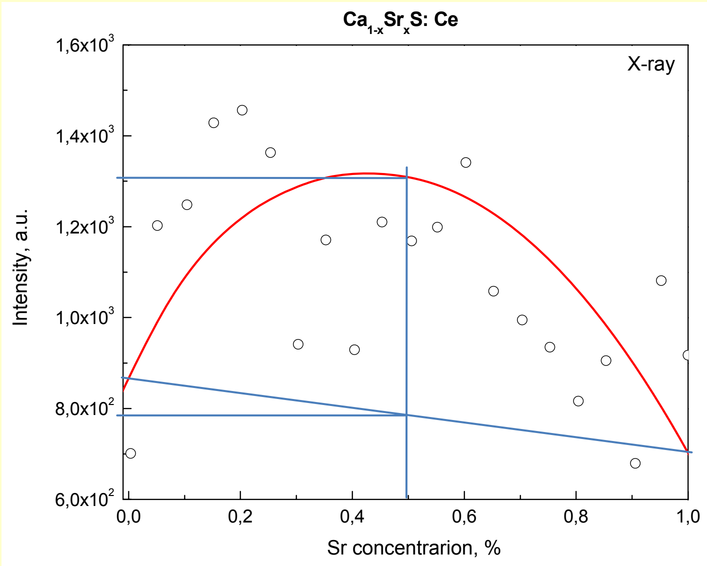


Figure 2. Luminescence spectra of Ce^{3+} in the concentration range of solid solutions $Ca_{1-x}Sr_xS$ (x-ray tube excitation; $T = 300$ K.

[A. Belsky et al., J. Phys.: Condensed Matter 5 (1993) 9417-9422]

Ce^{3+} luminescence spectra for the solid solution (mixed crystals) of $Ca_{1-x}Sr_xS$ at X-ray excitation (30 kW, 10 mA)

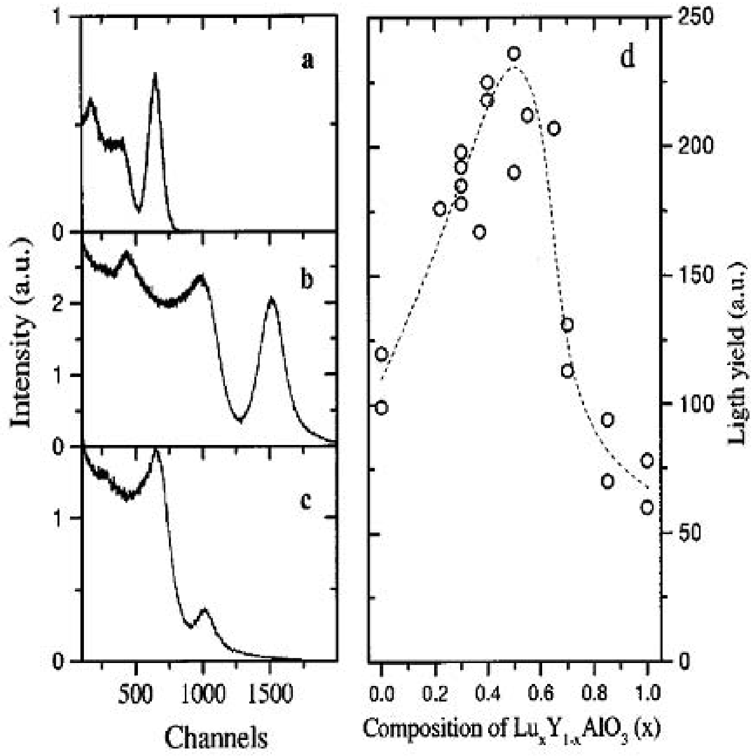


Oxides: LuYAP

(2000-2001)

Amplitude distribution of scintillation pulses under Cs X-ray excitation:

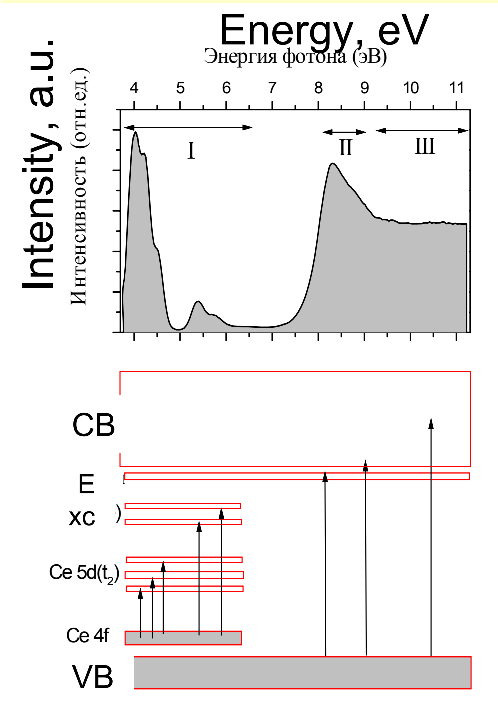
(a) LuAP:Ce,
(b) (b) LuYAP(70%Lu):Ce,
(c) YAP:Ce.
(d) Light yield measured in Ce-doped Lu Y AlO crystals of various composition.

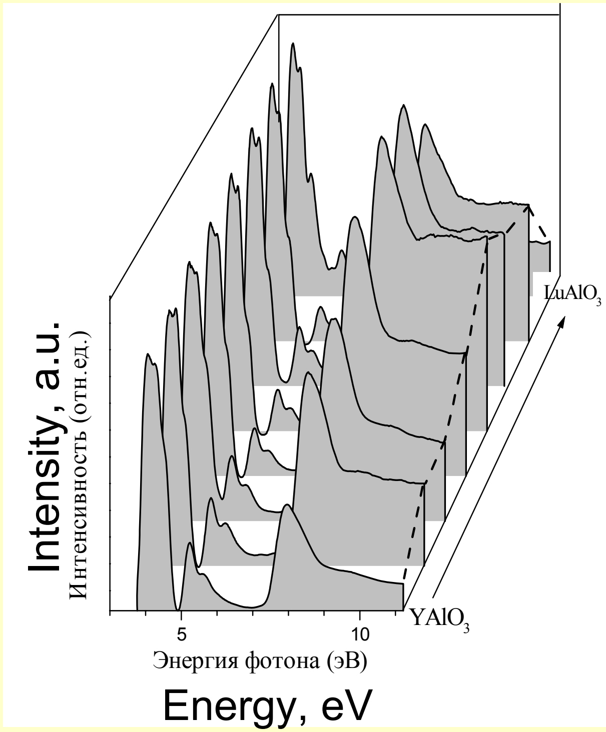


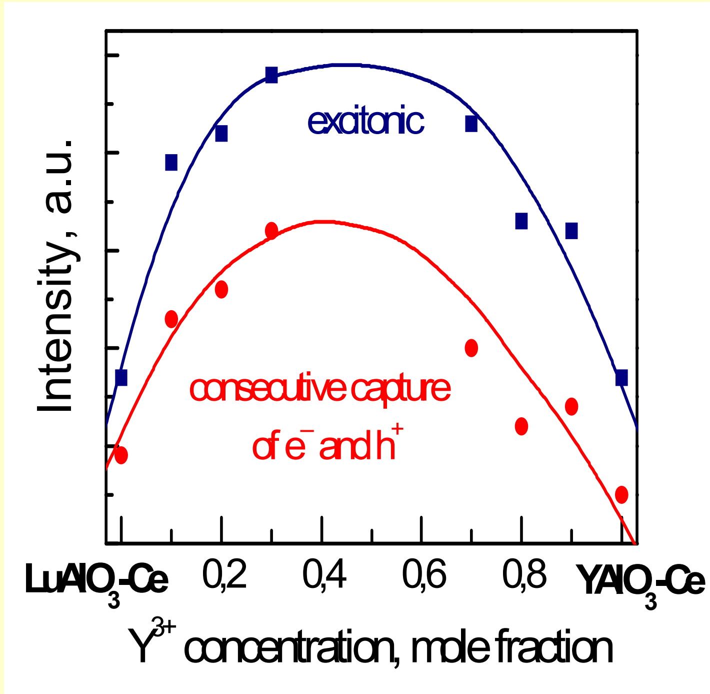
A.N. Belsky E. Auffray, P. Lecoq, C. Dujardin, N. Garnier, H. Canibano, C. Pedrini, and A. G. Petrosyan. IEEE Trans. Nucl. Sci. 48 (2001) 1095

$Lu_{0.5}Y_{0.5}AlO_3$-Ce

Excitation and luminescence spectra of $(Lu,Y)AlO_3$-Ce





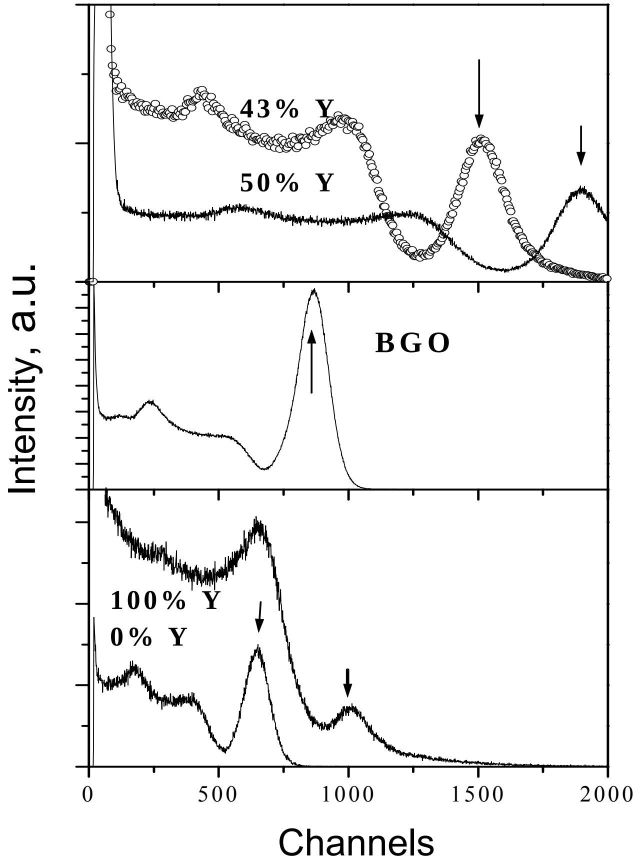


Excitation of $Lu_{0,5}Y_{0,5}AlO_3$-Ce

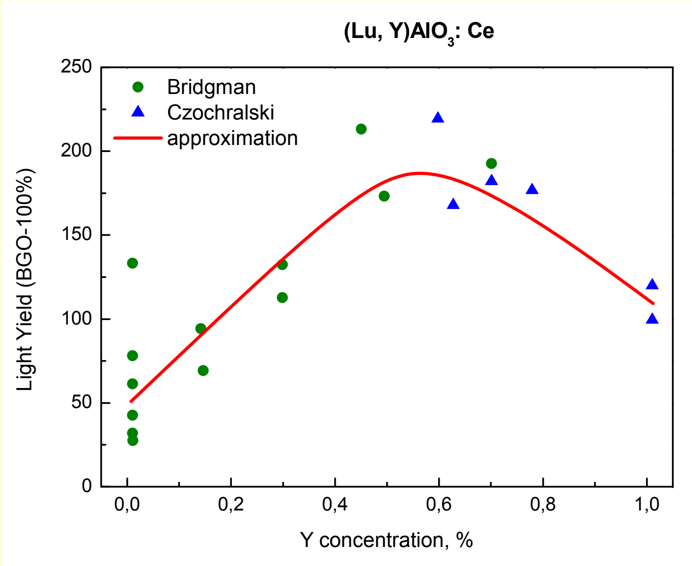
Luminescence of $Lu_{0,5}Y_{0,5}AlO_3$-Ce

[A.N. Belsky, W. Blanc, C. Dujardin et al., Proceedings of SCINT'99, Moscow, 1999]

Scintillation in (Lu,Y)AlO_3-Ce



[A.N. Belsky, W. Blanc, C. Dujardin et al., Proceedings of SCINT'99, Moscow, 1999]

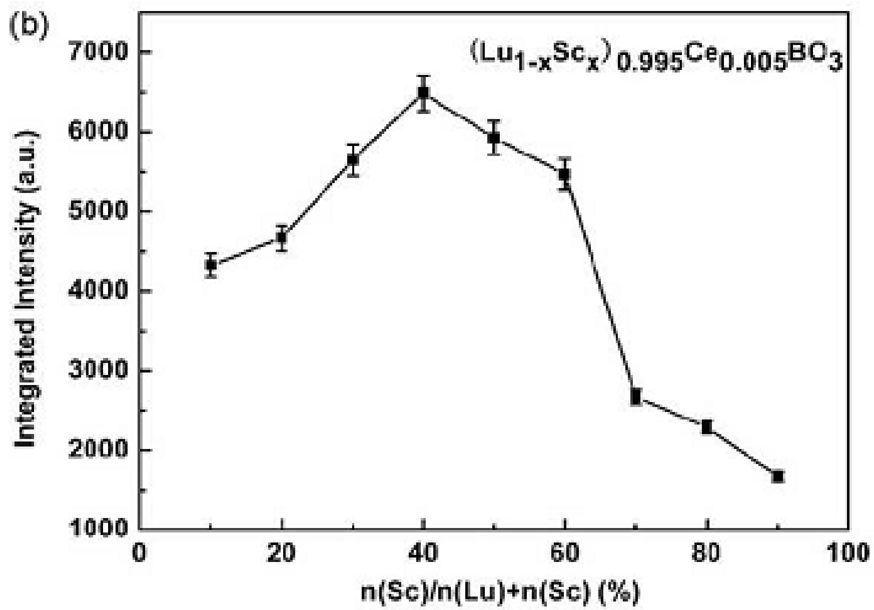


Light output of solid solution of (Lu,Y)AlO3-Ce depending on Y cocentration. Bridgemen growth from the same raw material (A.Petrosian) (set one - ▼, set 2 - ▲, set 3 - ●)

Gamma excitation amplitude spectra of (Lu,Y)AlO_3-Ce.

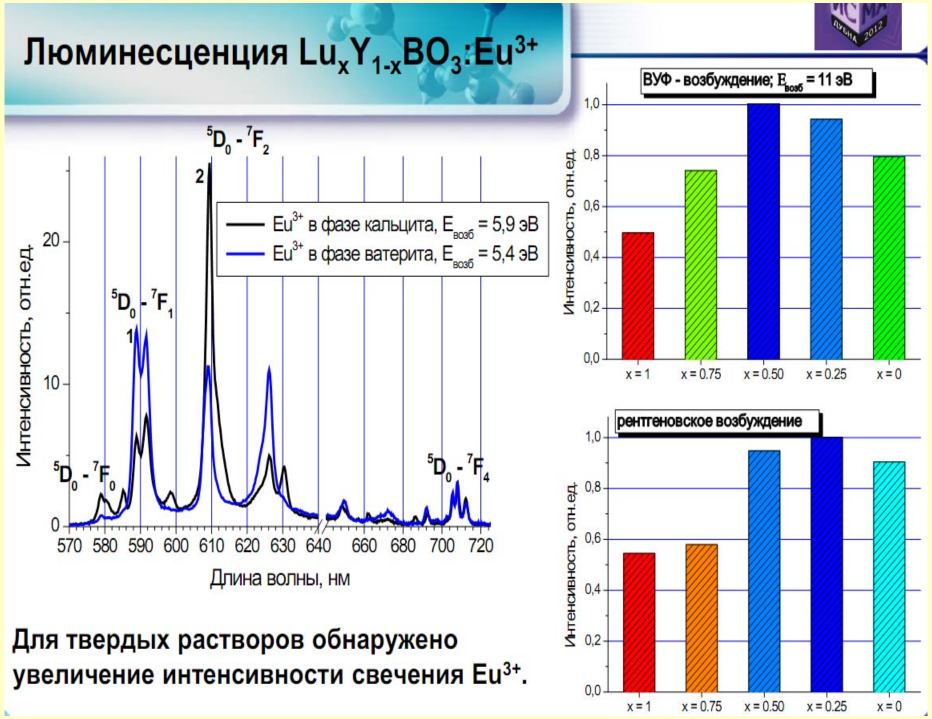
(*Single photon counting)*

Mixed Borates – (Lu-Sc)BO_3:Ce



Y. Wu et al. / Journ Alloys Comp *509 (2011) 366–371*

Mixed oxides - borates - $Lu_{0.75}Y_{0.25}BO_3$:Eu



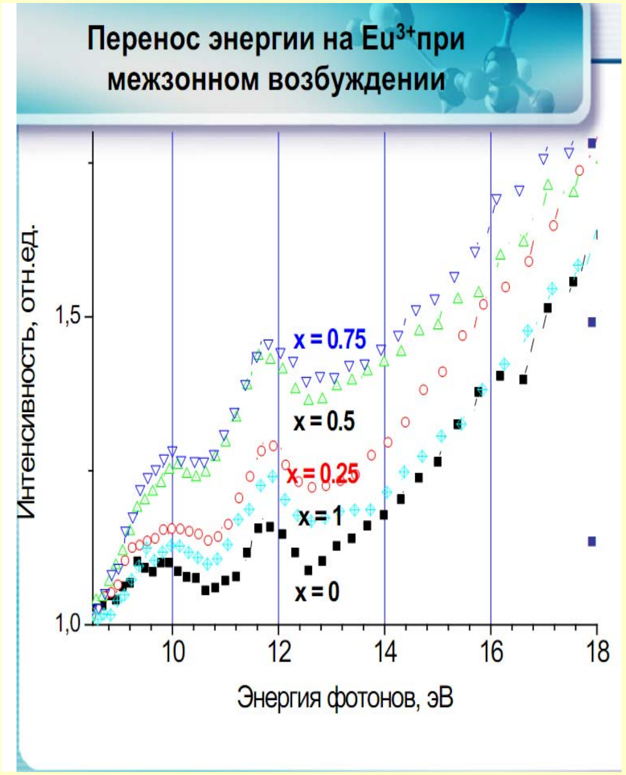
Luminescence spectra of

$Lu_{0.75}Y_{0.25}BO_3:Eu^{3+}$

E_{ex} = 5.4 eV (1) and
E_{ex} = 5.9 eV (2).

[D. Spassky, ISMART 2012, Dubna, 2012]

Mixed oxides - borates - $Lu_{0.75}Y_{0.25}BO_3$:Eu



Excitation spectra of

$Lu_xY_{1-x}BO_3:Eu^{3+}$

with
x = 0 (curve 1),
x = 0.25 (2),
x = 0.5 (3),
x = 0.75 (4)
x = 1 (5),

λ_{em} = 590 nm, T = 300 K.

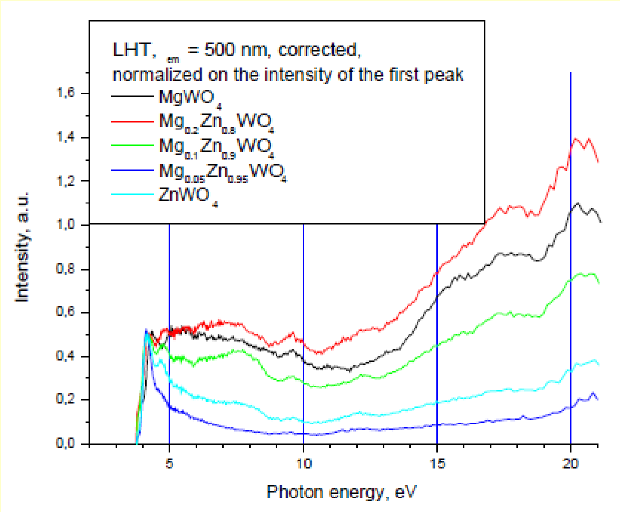
[D. Spassky, ISMART 2012, Dubna, 2012]

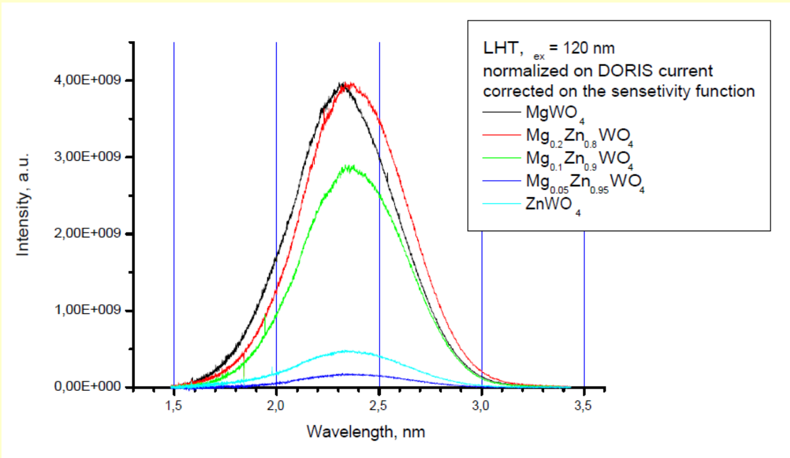
Oxides (intrinsic luminescence) - $Zn_xMg_{1-x}WO_4$

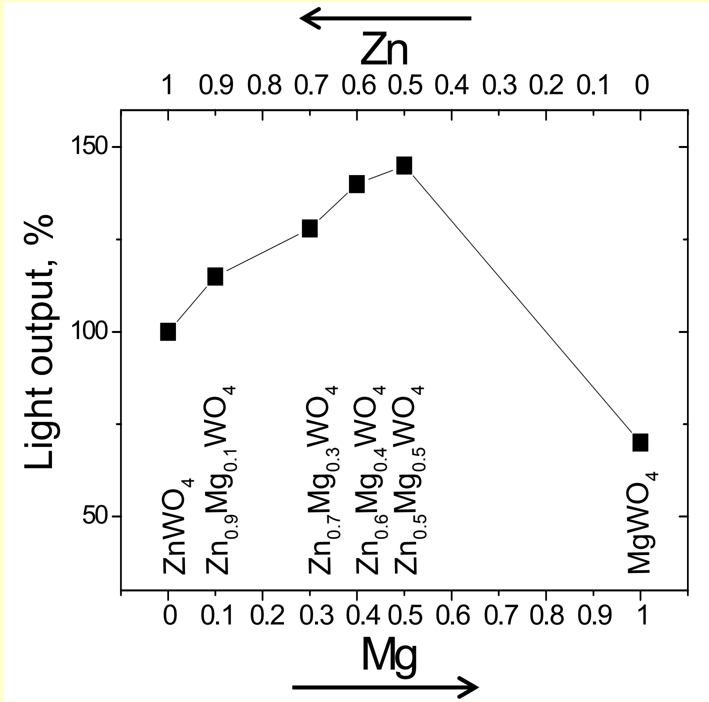
Excitation and luminescence spectra

2013

D.Spassky – O2.18

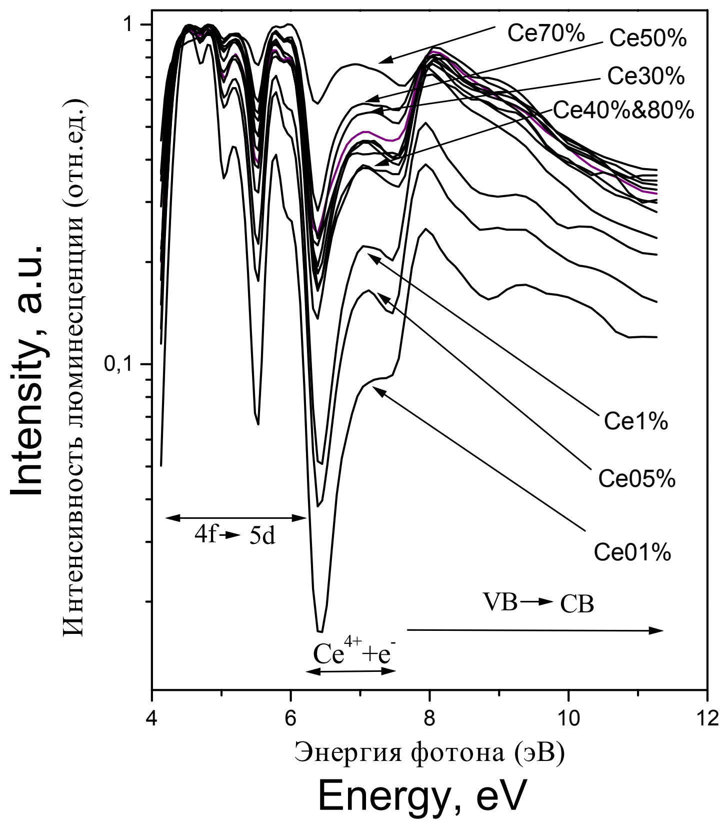




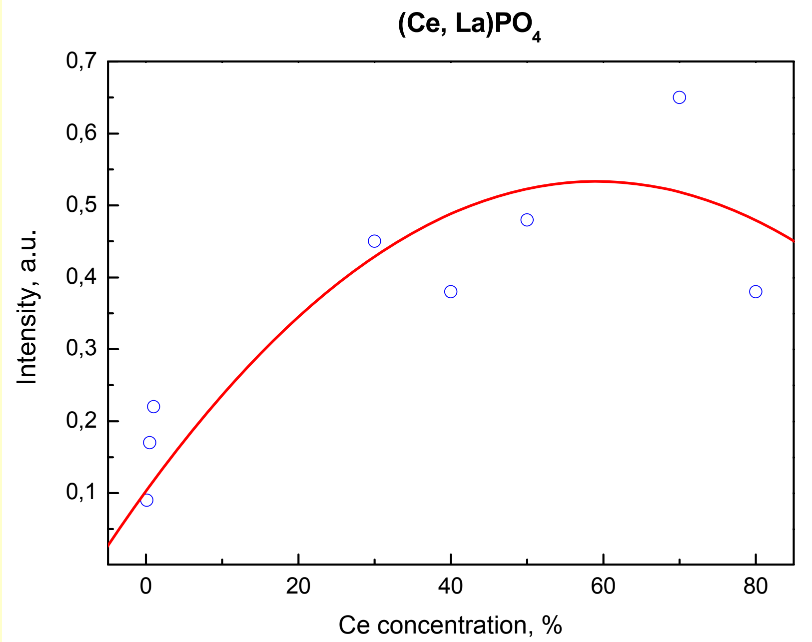


I.Tupitsina, D.Spassky, 2013
Private communication

Mixed oxides, $(Ce,La)PO_4$

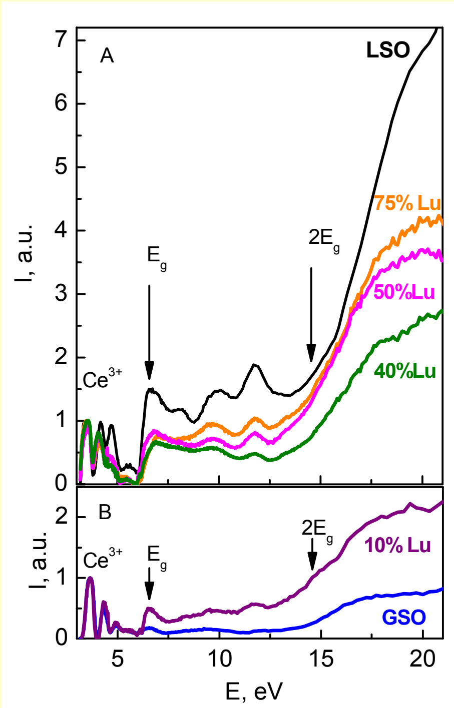


[A.N. Belsky, 2000]

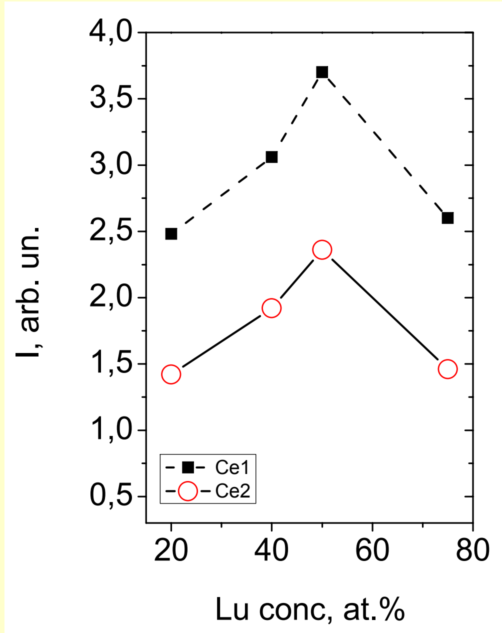


Excitation spectra of solid solution $(Ce,La)PO_4$ at Ce absorption area and its intensity vs Ce concentration

Mixed oxides, silicates - LGSO:Ce



Excitation spectra of 400 nm luminescence at T=300K.

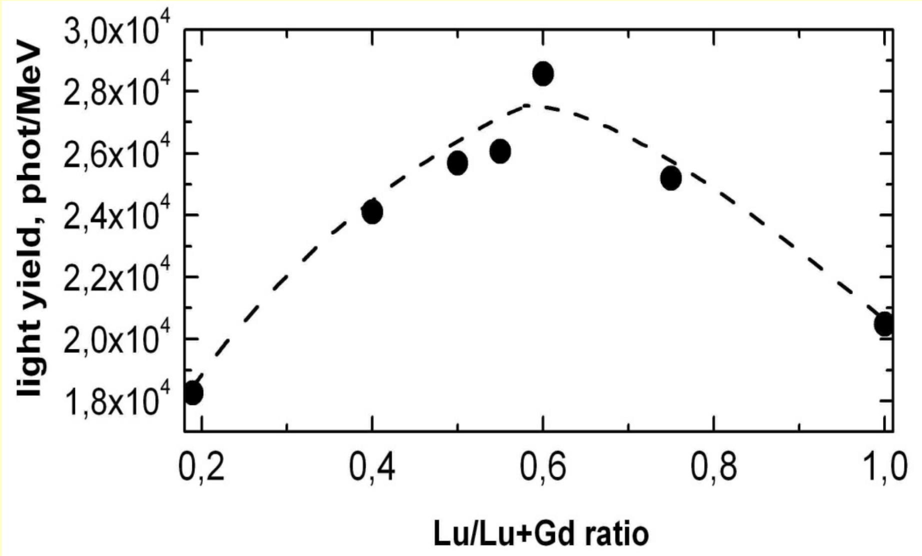


Ratio of intensities I(30 eV)/I(7 eV) of Ce1 (400 nm) and Ce2 (530 nm) excitation.

<u>Important!</u> The best efficiency of carrier multiplication and transfer to luminescence centers corresponds to 50:50 Gd:Lu rate

See details - O.Sidletskiy – O2.5

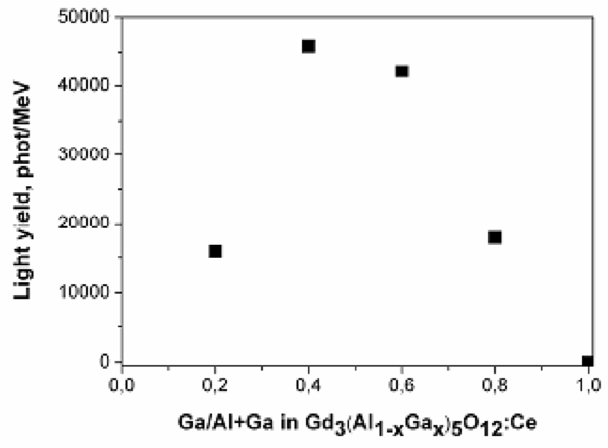
Mixed oxides, silicates - LGSO:Ce



Light yield in LGSO:Ce crystals with monoclinic C2/c structure vs. host composition

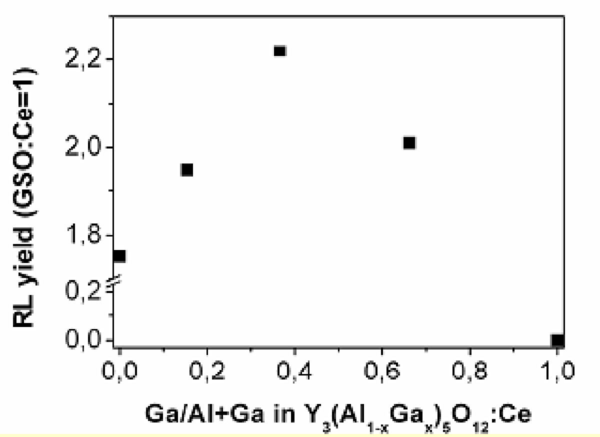
1. O. Sidletskiy, V. Bondar, B. Grinyov, et al. *J. Cryst Growth*, 312 (2010) 601
2. O.Sidletskiy, A. Belsky, A. Gektin, et al. *Crys Growth & Des*, (2012), 12, 441

Oxides, garnets – GAGG and YAGG



$Gd_3(Al_xGa_{1-x})_5O_{12}$:Ce
(GAGG)

Kei Kamada, et al / Cryst. Growth Des. 11 (2011), 4484–4490.

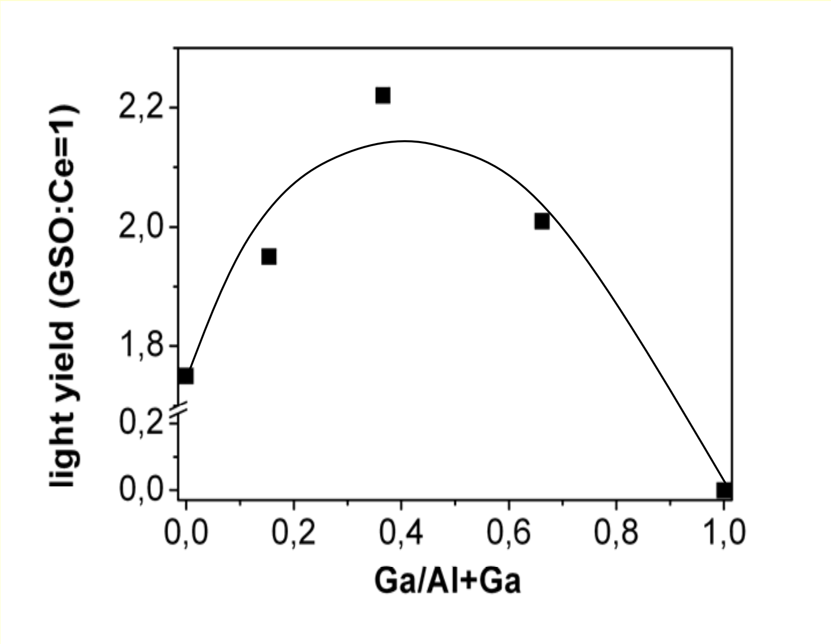


$Y_3(Al_xGa_{1-x})_5O_{12}$:Ce
(YAGG)

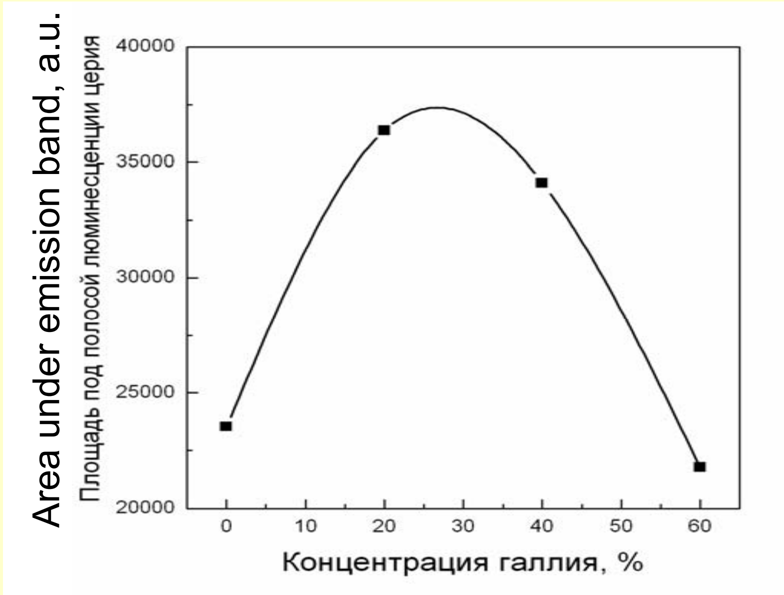
O. Sidletskiy, V. Kononets, K. Lebbou, S. Neicheva, O. Voloshina, V. Bondar, V. Baumer, K. Belikov, A. Gektin, B. Grinyov, M.-F. Joubert, Mater. Res. Bull. Materials Research Bulletin 47 (2012) 3249–3252

Mixed oxides, garnets - YAGG:Ce

Scintillation yield and radioluminescence intensity dependence for mixed YAGG



[1] O.Sidletskiy, V. Kononets, K. Lebbou, S.Neicheva, O.Voloshina, V.Bondar, V.Baumer, K.Belikov, A. Gektin, M– F. Joubert., Materials Research Bulletin, Vol. 47, No. 11. (2012), pp.3249-3252

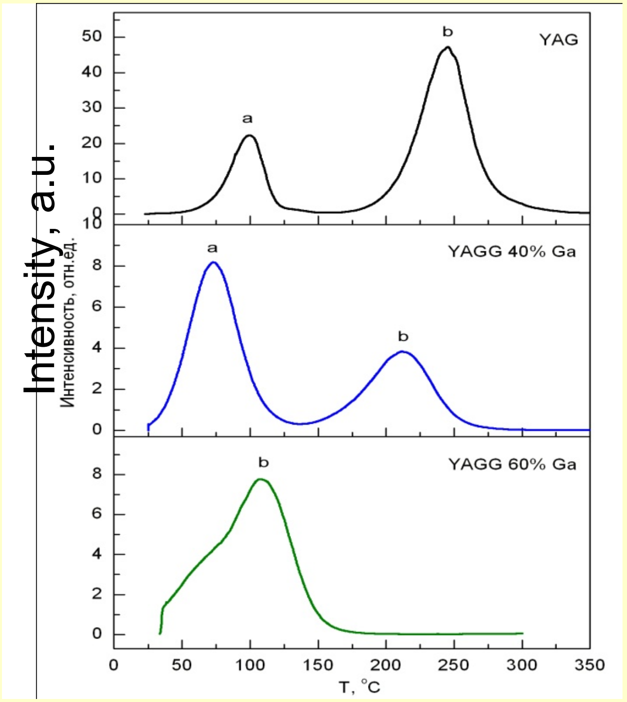


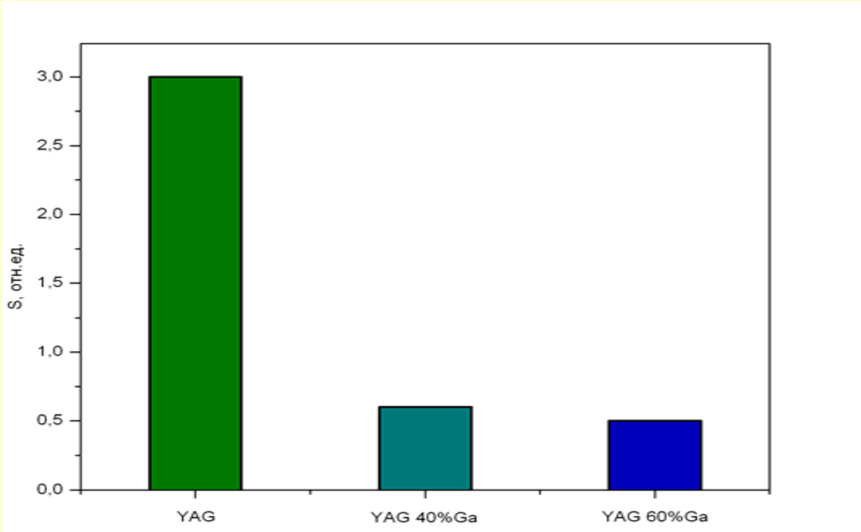
Integral radioluminescence yield vs Ca concentration

Mixed oxides - YAGG:Ce

Energy storage in mixed YAGG:Ce scintillators

TSL (Thermo luminescence) for YAGG:Ce





TSL efficiency for YAG:Ce and YAGG:Ce with different Ga concentration

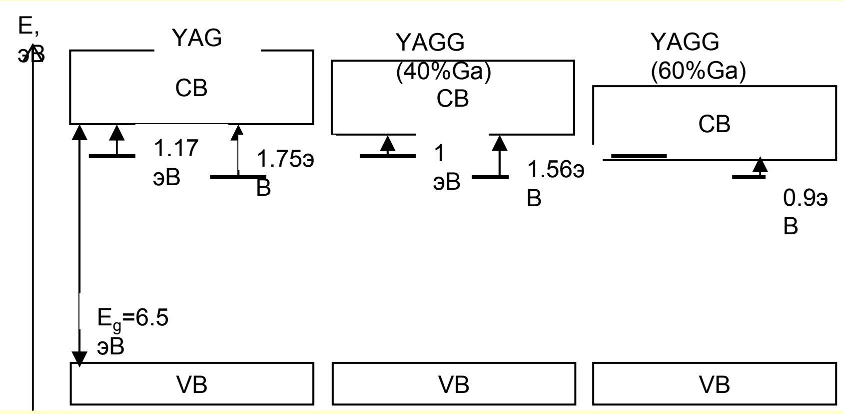
	a		b	
	T_{max}, °C	E_a, eV	T_{max}, °C	E_a, eV
YAG: Ce	**102**	**1.17**	**250**	**1.75**
YAGG (40%Ga):Ce	**80**	**1.02**	**217**	**1.56**
YAGG (60%Ga):Ce	**-**	**-**	**119**	**0.9**

Traps parameters

Ga doping allows to decrease the energy storage in YAGG comparing to YAG:Ce crystals

e-h separation and/or conduction band modification?

Band structure change with Ga doping.



Ga doping (shift to mixed crystals)

* Decrease the CB bottom level

- Decrease of shallow traps influence

- ….

M.Nikl …

*** There are some alternative mechanisms that influence to light yield with similar or even higher rate**

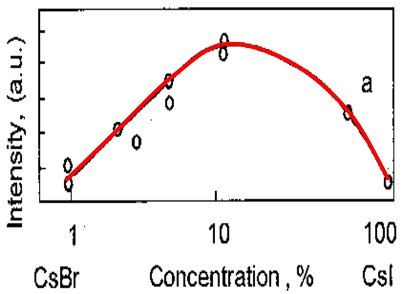
**** Crystal performance, initial purity and activator concentration are crucial for the experimental study of phenomena**

***** Decay time measurement could be more efficient for the model verification than yield test**

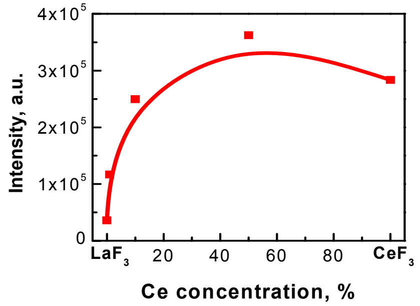
****** We need in more detailed theoretical estimations for doped and mixed crystals**

CONCLUSIONS

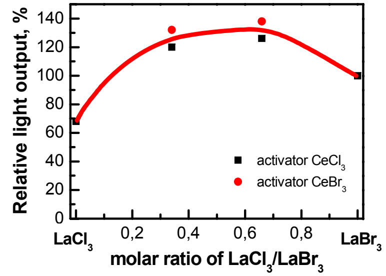
CsI-CsBr



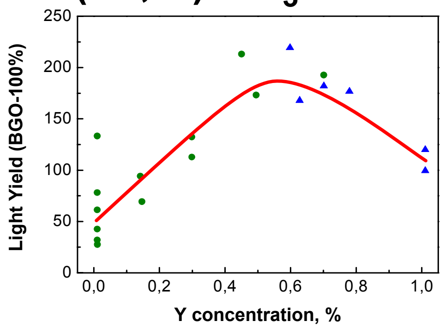
$Ce_xLa_{1-x}F_3$



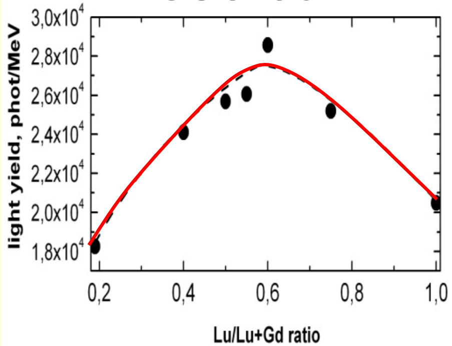
$LaCl_3$-$LaBr_3$



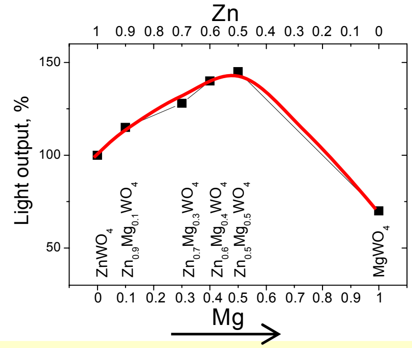
(Lu, Y)AlO_3: Ce



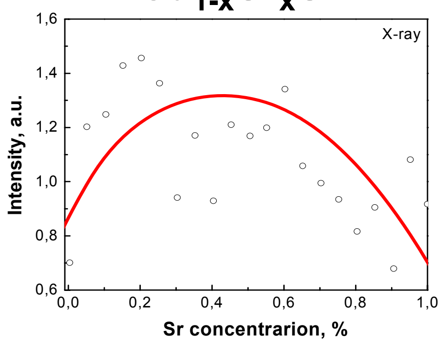
LGSO:Ce



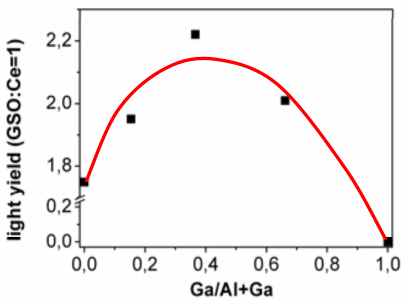
$Zn_xMg_{1-x}WO_4$



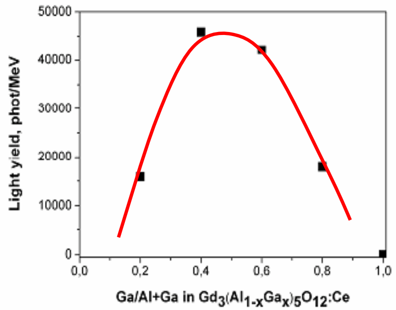
$Ca_{1-x}Sr_xS$



YAGG:Ce



$Gd_2(Al_xGa_{1-x})_5O_{12}$:Ce



Thank you for your attentions!