ISMA

Luminescence fundamental limits for alkali halide scintillators

A. Gektin[1], N.Shiran, A.Belsky[2], A. Vasil'ev[3]

[1] Institute for Scintillation Materials, 60 Lenin Ave., 61001, Kharkov, Ukraine

[2] Laboratoire de Physico-Chimie des Materiaux Luminescents, UMR 5620 CNRS, Universite Claude Bernard Lyon 1, 69622 Villeurbanne Cedex, France

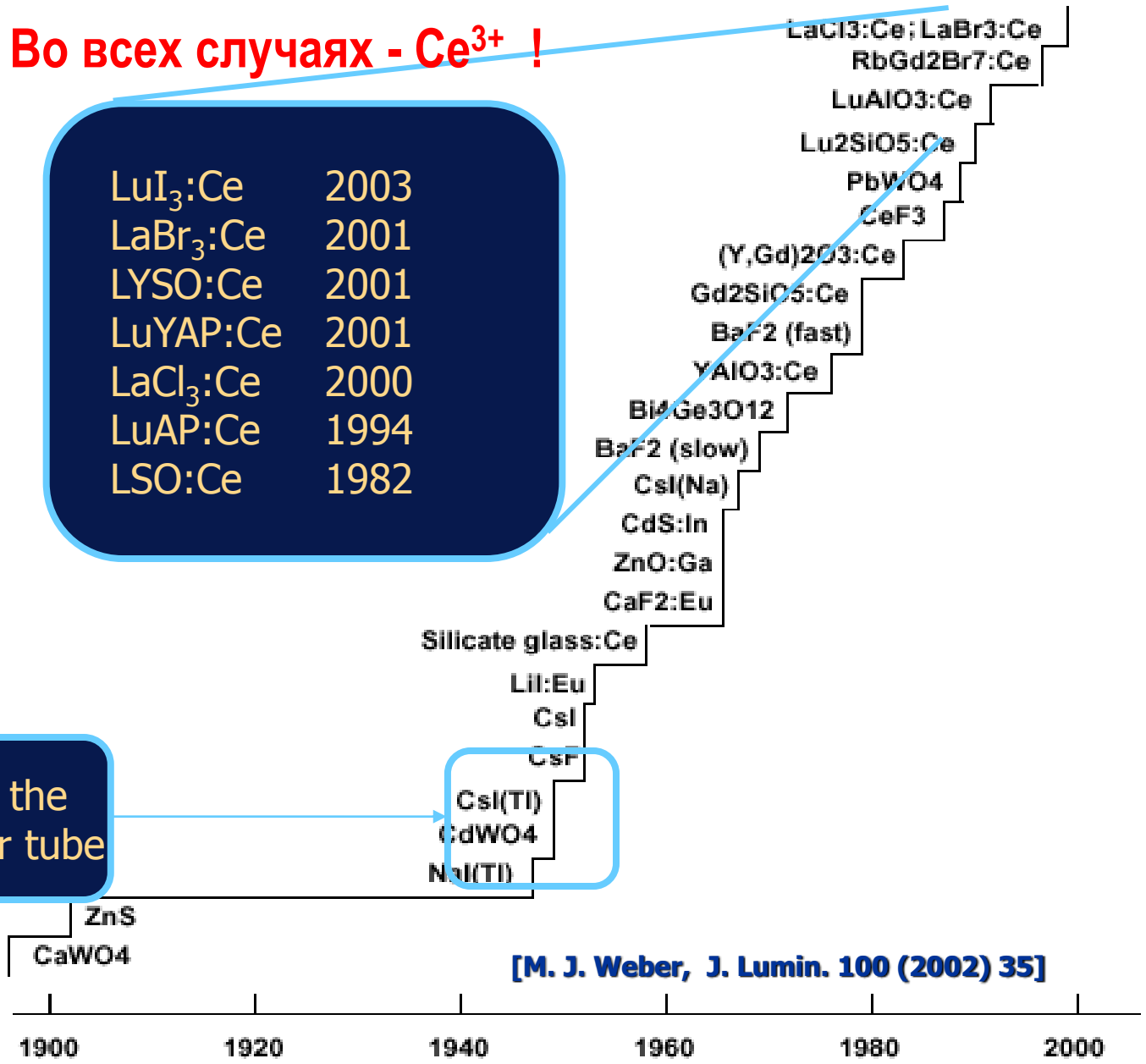
[3] Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University, 119991, Moscow, Russia

История поиска и открытий

Во всех случаях - Ce^{3+} !

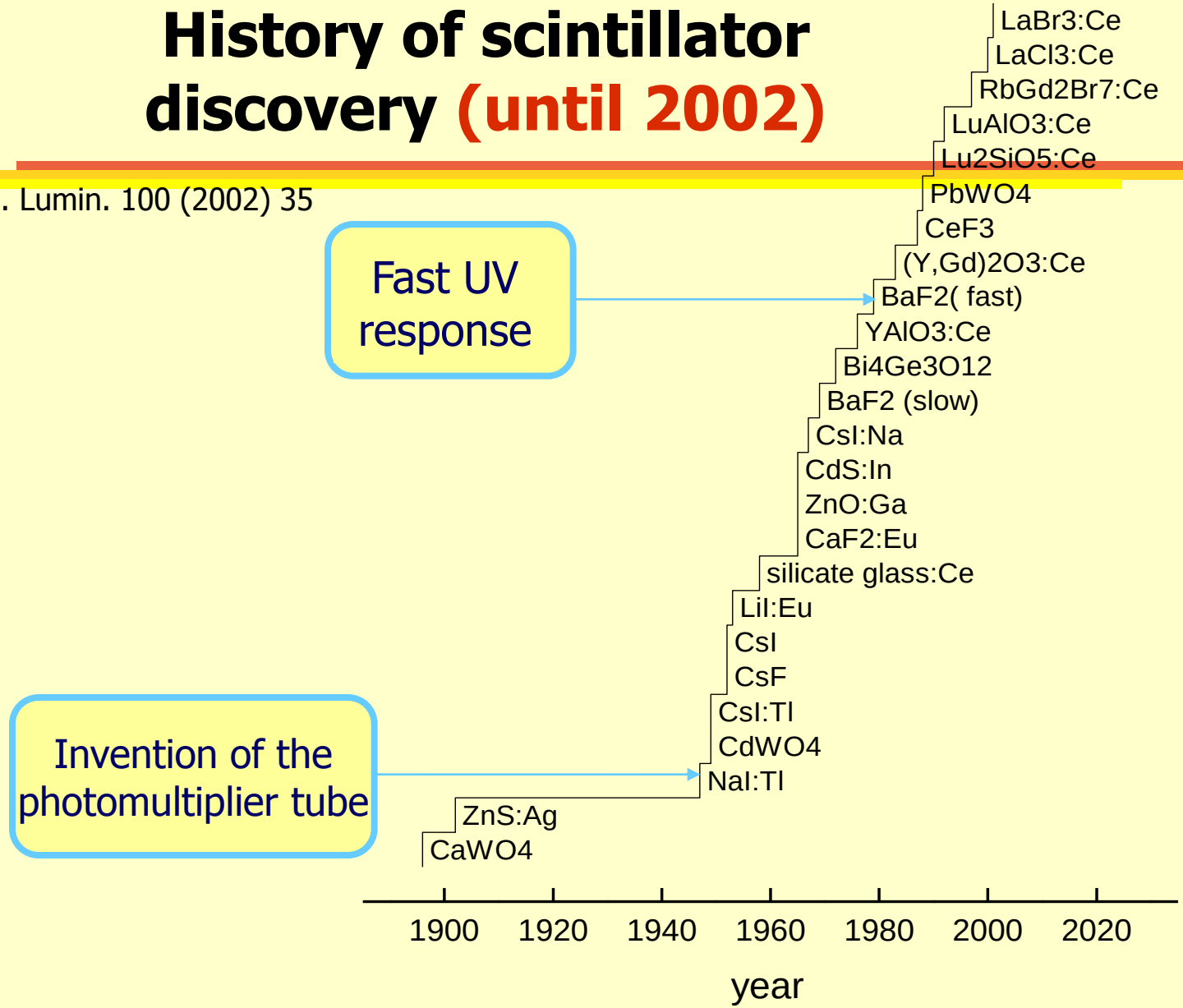
LuI_3:Ce	2003
$LaBr_3$:Ce	2001
LYSO:Ce	2001
LuYAP:Ce	2001
$LaCl_3$:Ce	2000
LuAP:Ce	1994
LSO:Ce	1982

Invention of the photomultiplier tube



History of scintillator discovery (until 2002)

M. J. Weber J. Lumin. 100 (2002) 35



History of scintillators

Recent Developments in the Inorganic- Scintillator Field

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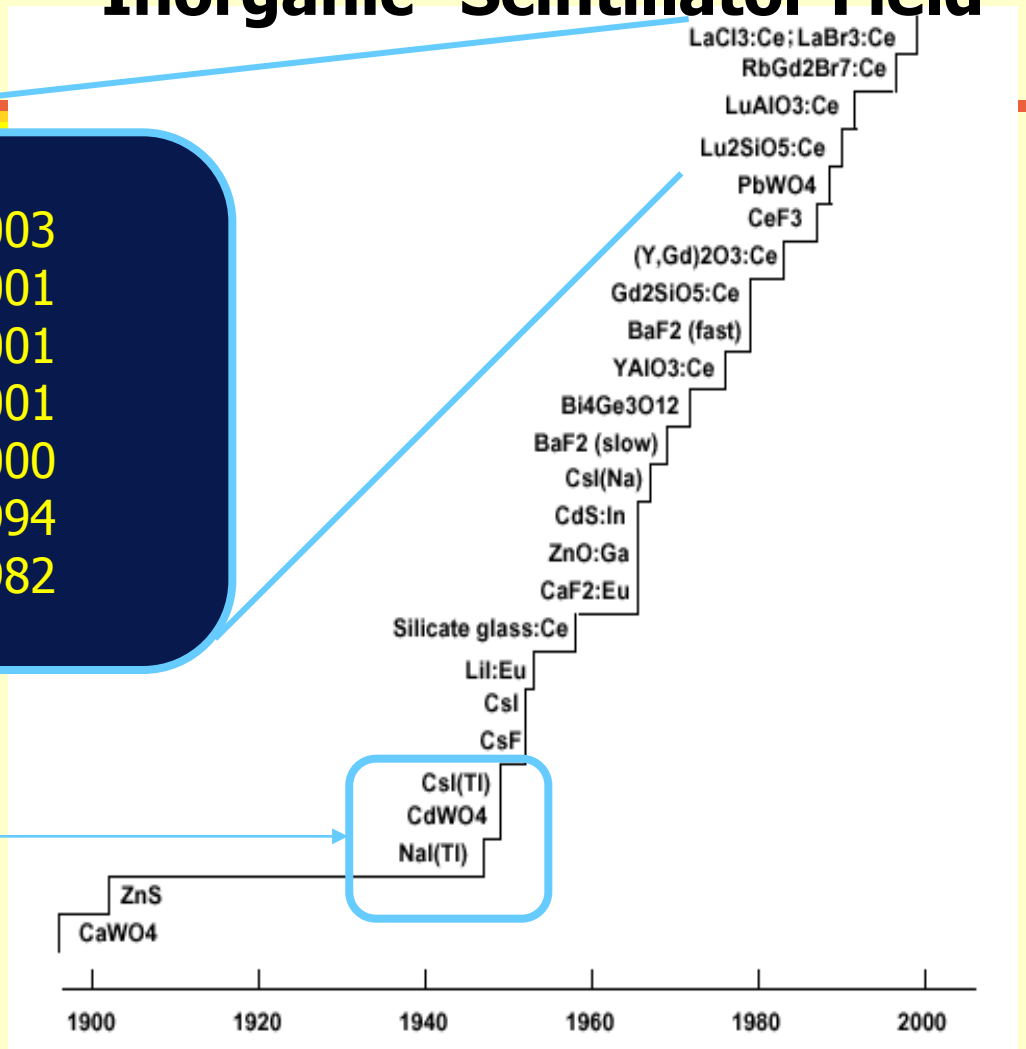
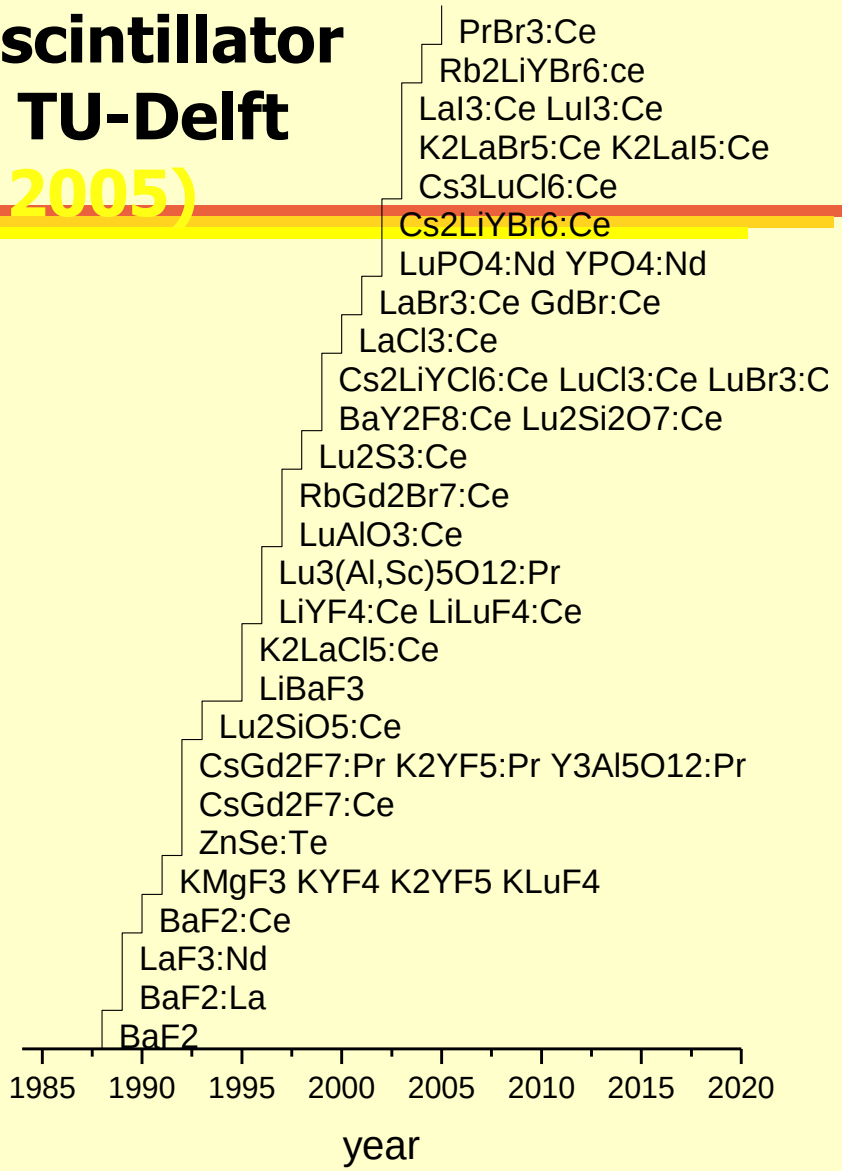


M. J. Weber, J. Lumin. 100 (2002) 35

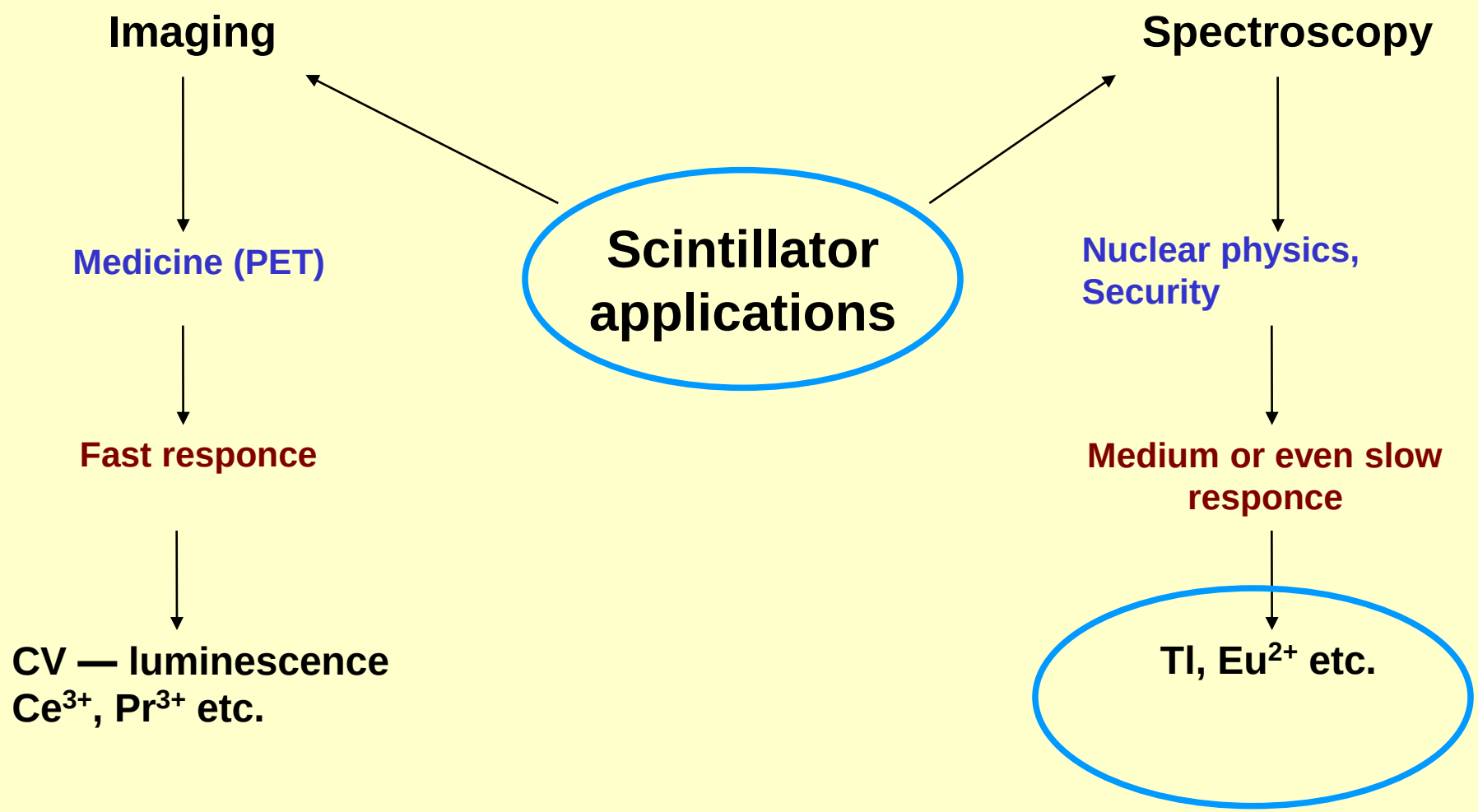
History of scintillator research TU-Delft (until 2005)

Main trend:

Towards increasingly smaller band gap materials with exclusively Ce^{3+} activation



Logics and motivation



Is it possible to improve scintillation efficiency of conventional scintillators?

Optimal scintillator

Effective = efficient + available + cheap

efficient ~ 100.000 ph/MeV, 3% resolution (662 kev)

available ~ size 400 mm

cheap ~ 3 $/cc

History (2008-2009) and start point:

Two ways to obtain (develop) new efficient scintillator:

A - search of new compounds (Successfully done!)

- (-) Deep scientific search !?
- (-) Ability to grow large crystal ?
- (-) Crystal cost ?

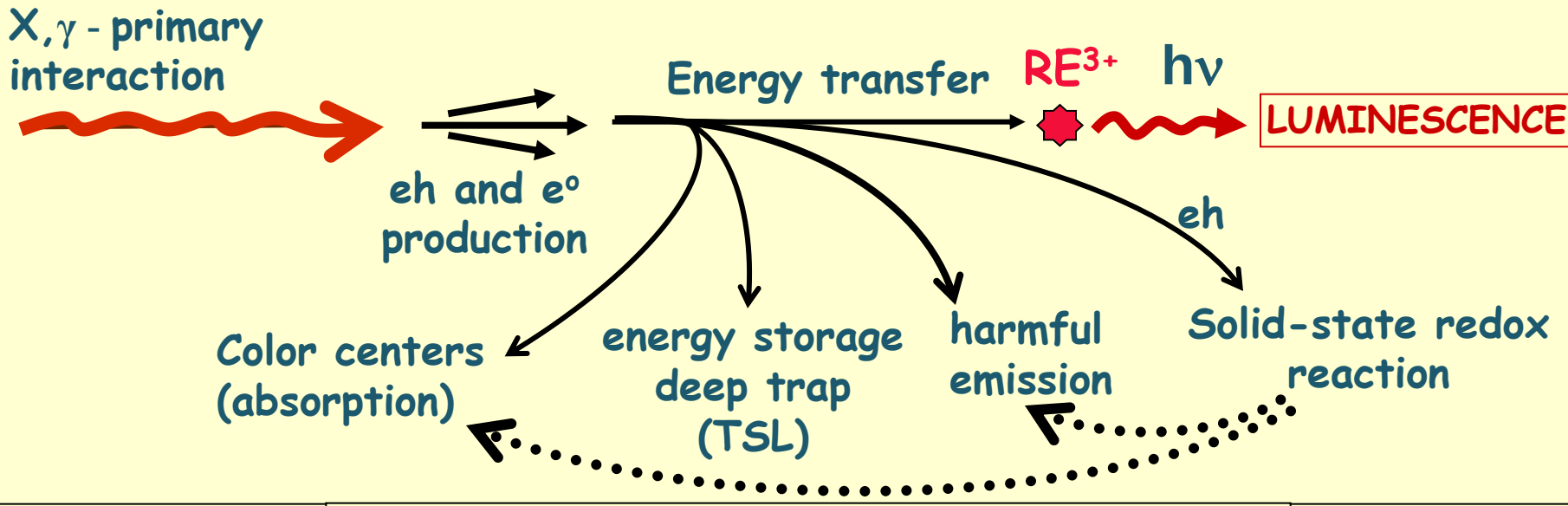
B - modification of conventional scintillators

- (-) Need in modification idea ?!
- (+) Existed technologies of industrial growth!

What was done last years?

- ✓ Maximal yield for alkali halides is far from the fundamental limit . *Some limits could be described*
- ✓ Why alkali-earth (AE) halides are more efficient? *The yield is close to fundamental limit*
- ✓ Can we obtain (grow) scintillators with the large size and high industrial efficiency? *Why not? What are the problems?*
- ✓ Natural “bottle neck” (self absorption) and *overpass ways*

СХЕМА ПРЕВРАЩЕНИЯ ЭНЕРГИИ В ШИРОКОЗОННОМ ДИЭЛЕКТРИКЕ



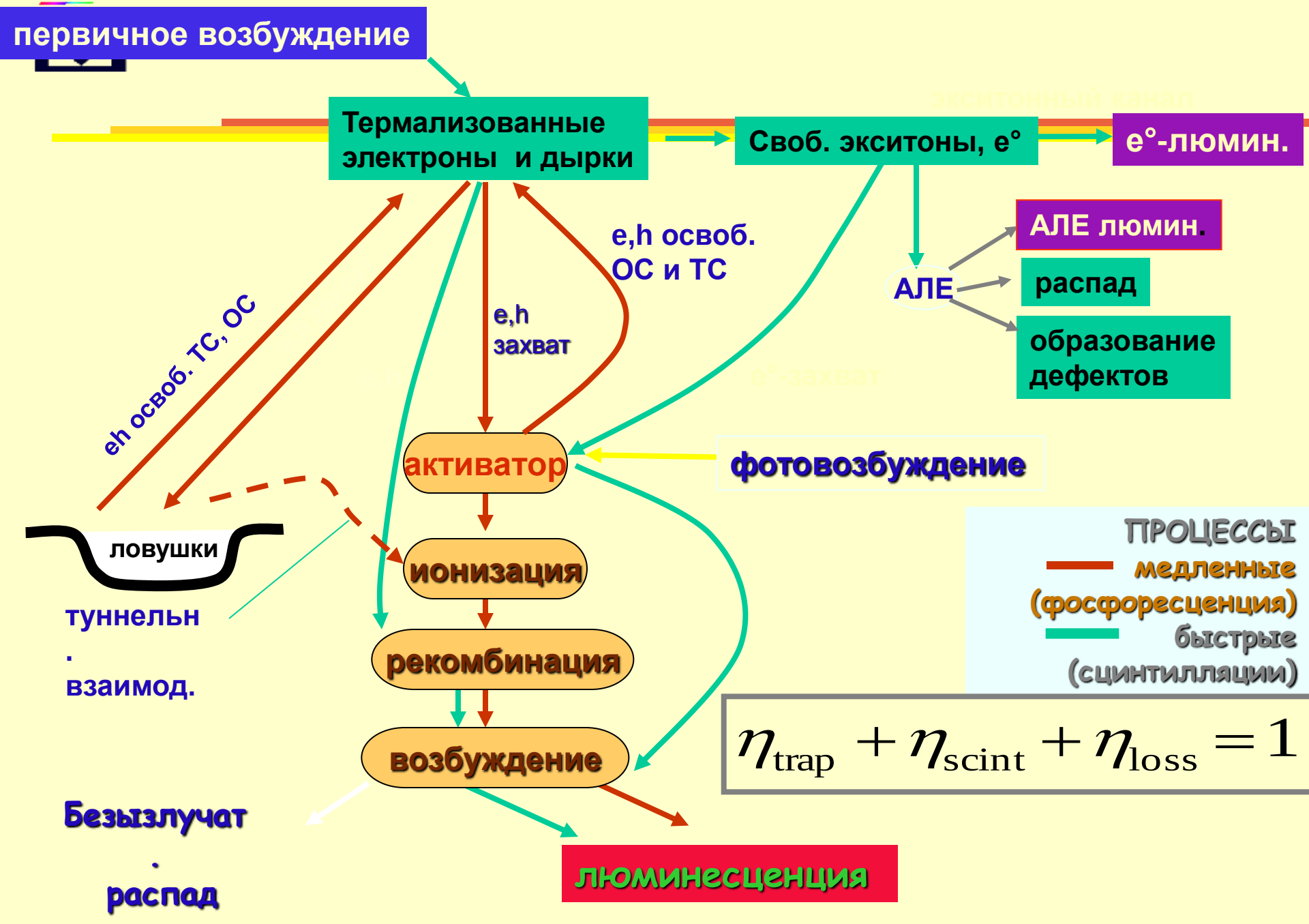
$$\eta_{trap} + \eta_{scint} + \eta_{loss} = 1$$

η_{trap} — **захват носителей заряда ловушками**

η_{scint} — **излучательная рекомбинация**

η_{loss} — **безызлучательная рекомбинация**

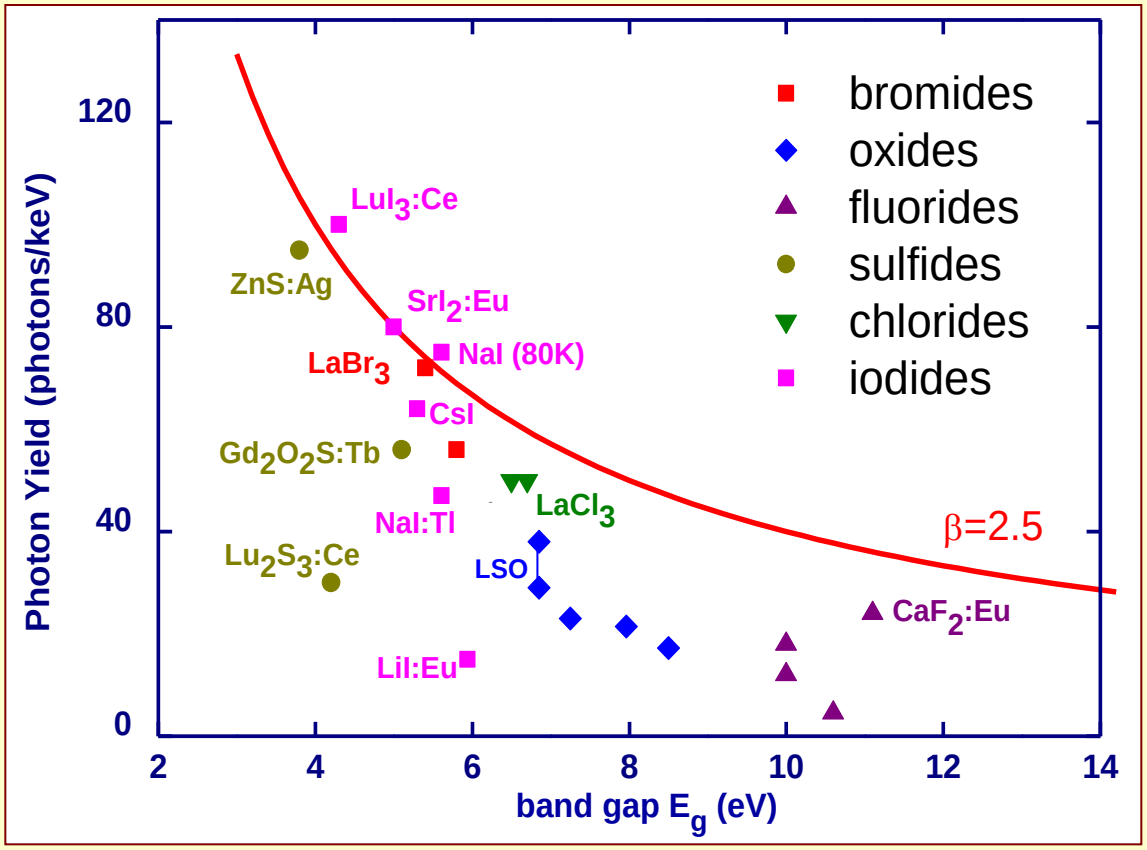
СХЕМА ПРЕВРАЩЕНИЯ ЭНЕРГИИ В ШИРОКОЗОННОМ ДИЭЛЕКТРИКЕ



Most efficient new scintillators (2007→2012)

Crystal	ρ g/cm^3	Lum λ, nm	LY ph/Mev	R, % ^{137}Cs	Decay τ, ns	Hygro-scopy	References
CaI_2 :Eu	3.96	467	110.000	5,2	1.000	strong	Cherepy, Moses, Derenzo, Bizarri, Bourret et al. 2007 - 2012
SrI_2 :Eu	4.55	435	115.000	2.6	1.500	strong	
Ba_2CsI_5 :Eu	4.9	435	102.000	2.55	383;1.500	medium	
$SrCsI_3$:Eu	4,25	458	73.000	3.9	2.200	medium	Zhuravleva et al. 2012
BaBrI :Eu	5.2	413	97.000	3,4	500	low	Bizarri et al. 2011
NaI : Tl	3.67	415	44.000	5.6	230	strong	
CsI : Tl	4.53	560	56,000	6.0	980	no	
CsI : Na		420	46,000	6.4	600	low	

Fundamental limits to the yield

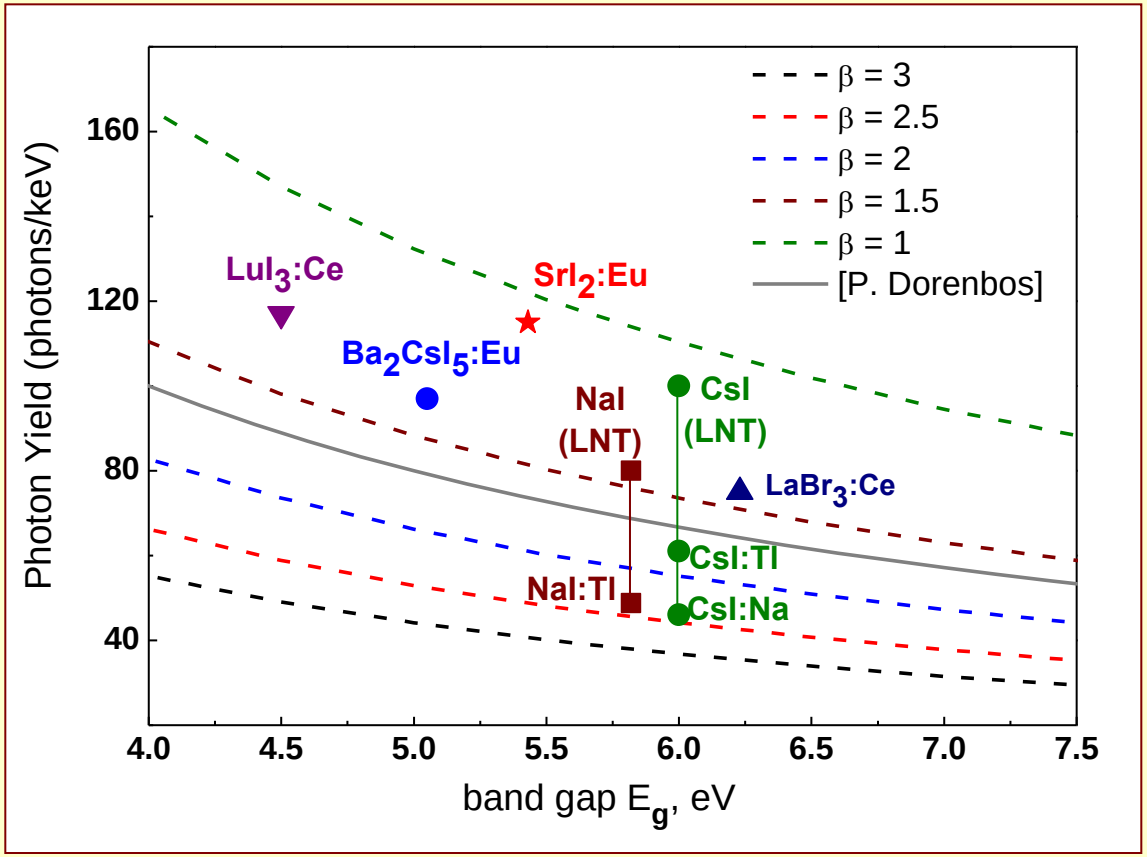


$$N_{eh} = \frac{E_\gamma}{\beta E_{gap}}$$

$$\frac{N_{ph}}{E_\gamma} \leq \frac{1}{\beta E_g}$$

P.Dorenbos, 2009

Fundamental or maximal yield?



Recent Developments in the Inorganic-Scintillator Field

Scintillation Light Yield Gamma-ray detection

$$N_{photon} = \frac{E_\gamma}{E_{e\text{-}h}} \; S \; Q$$

Eγ gamma-ray energy

Ee-h = ~ 2.5 Egap

S transport/transfer efficiency to LC

Q quantum efficiency of LC

Models

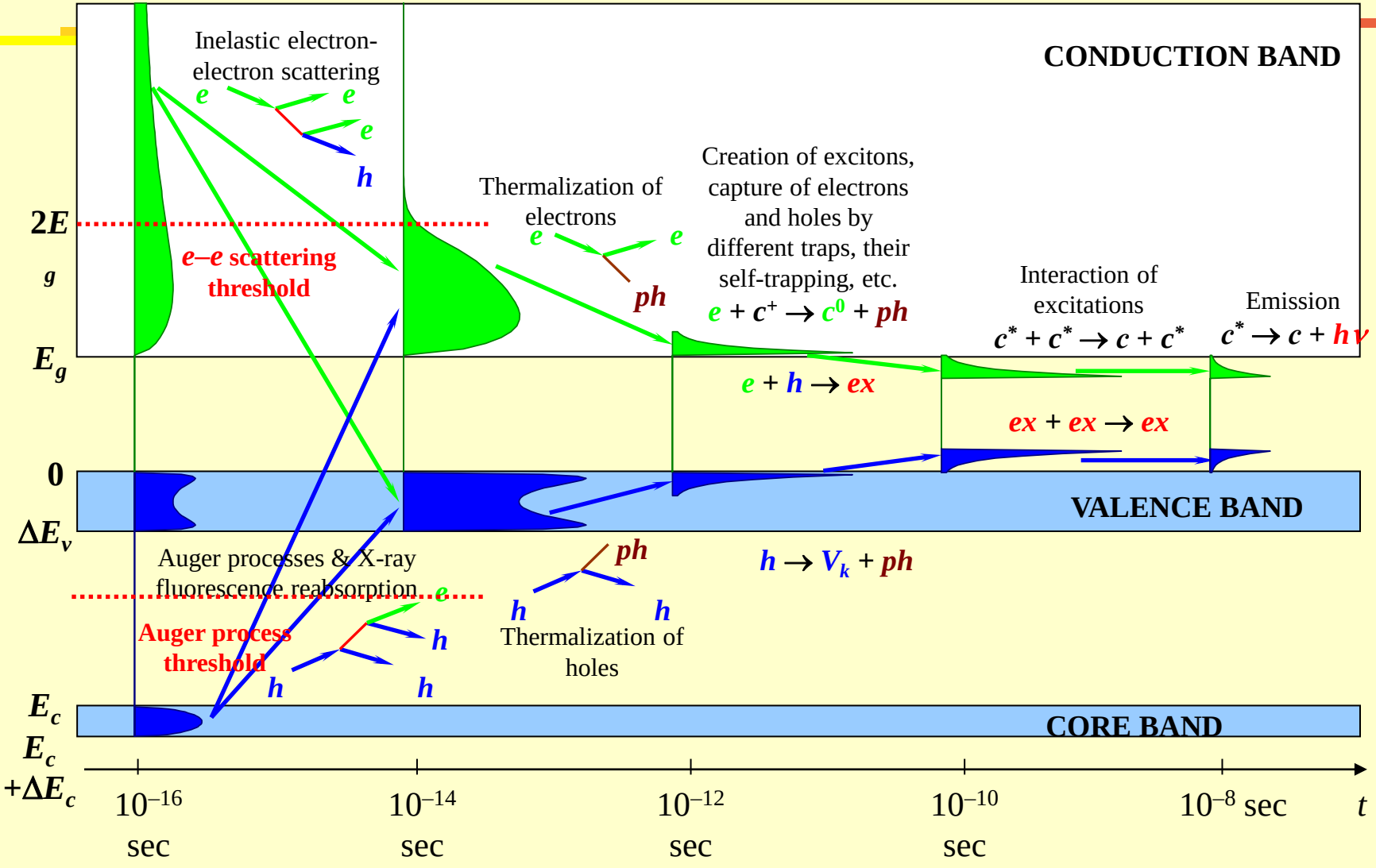
Traditional approach

$$LY \approx 10^6 SQ / \beta E_g = \eta 10^6 / E_g;\ \eta = SQ/\beta;\ \eta = 0{,}5$$

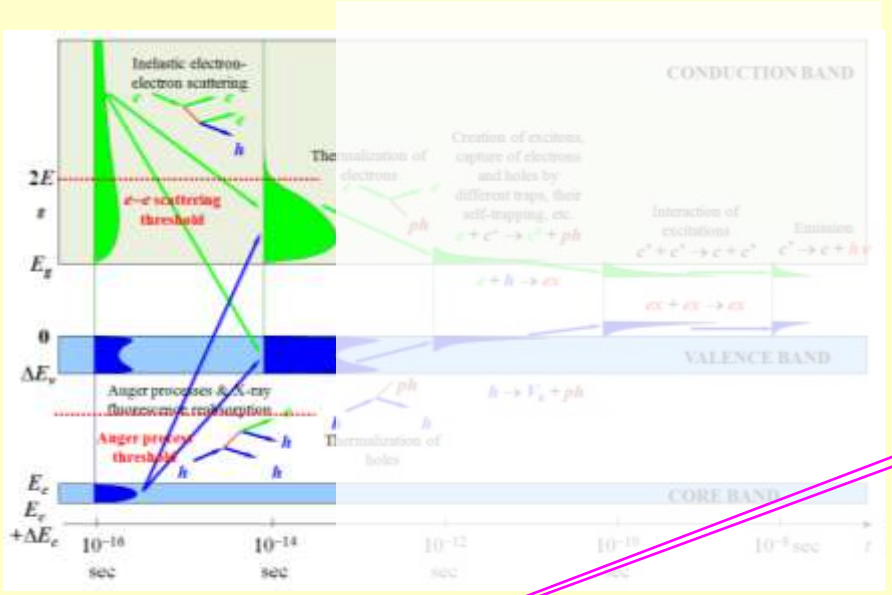
The first assumption does not work properly

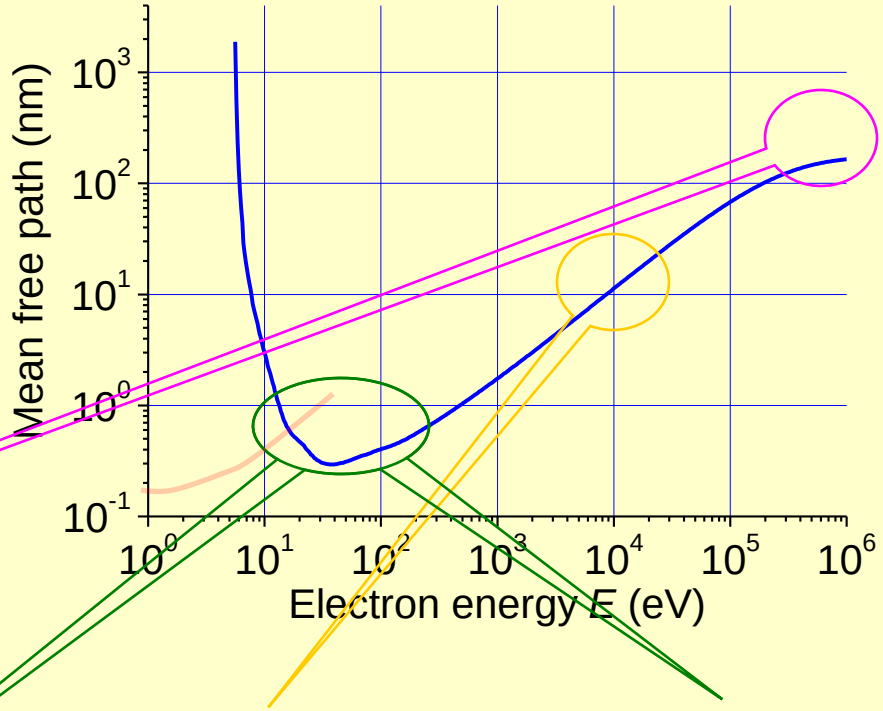
The second assumption has to based on the track structure analysis

Scheme of electronic excitations relaxation in crystals with “simple” energy structure

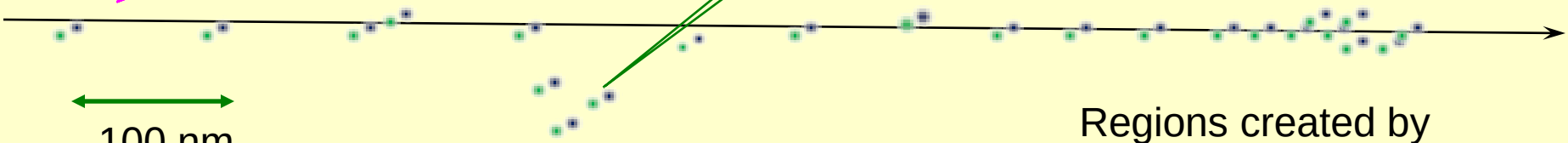


Spatial track structure for e-e scattering stage
(prior to thermalization)





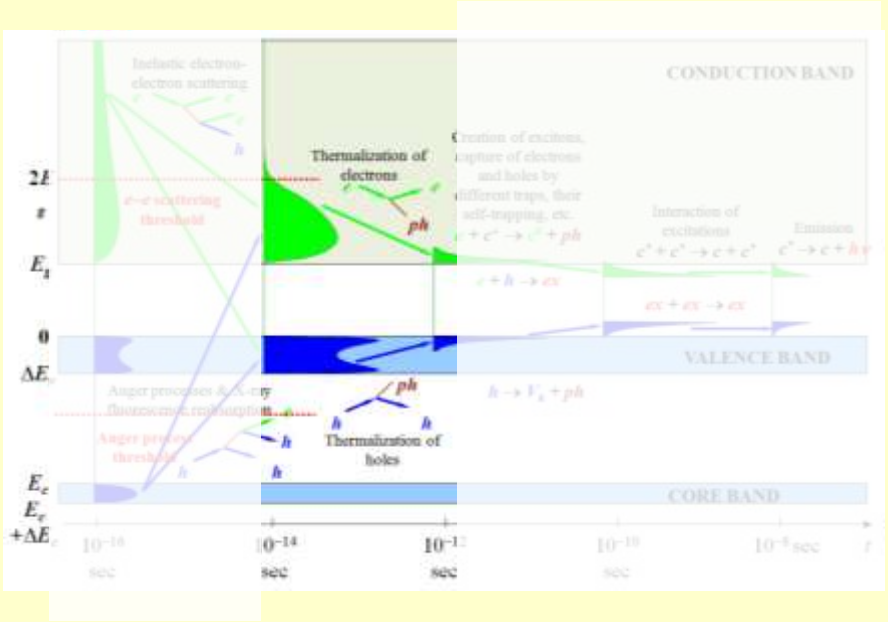
‘Real’ track structure

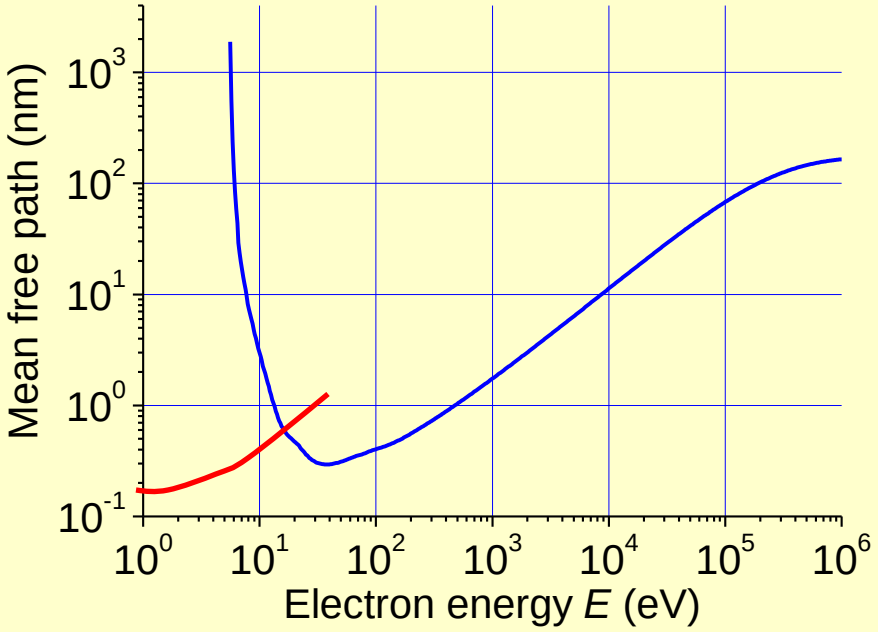


100 nm

Regions created by different virtual photons are overlapped

Spatial track structure for phonon scattering stage (after thermalization) for small thermalization radius



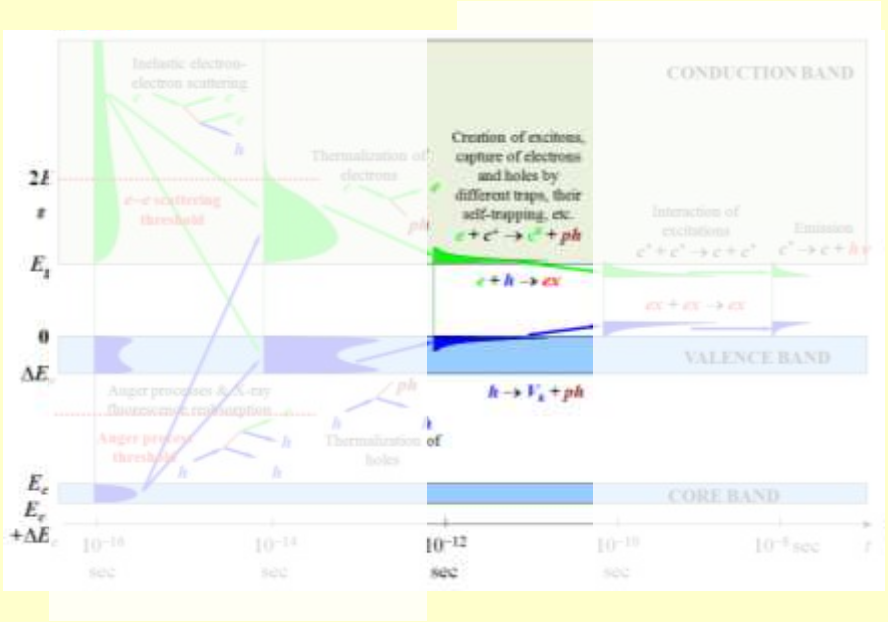


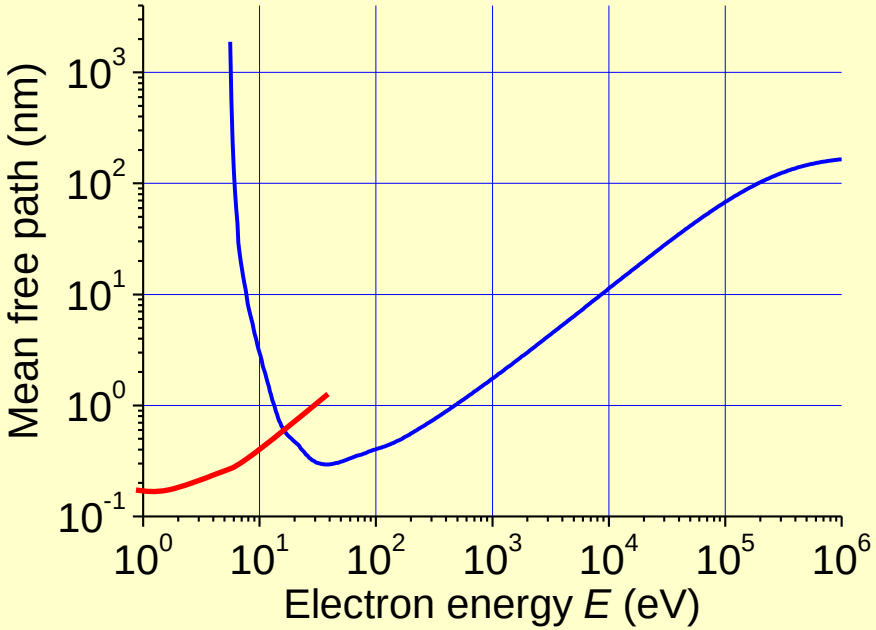
‘Real’ track structure

100 nm

Regions created by different virtual photons are overlapped

Spatial track structure for e-h Onsager recombination stage for small thermalization radius



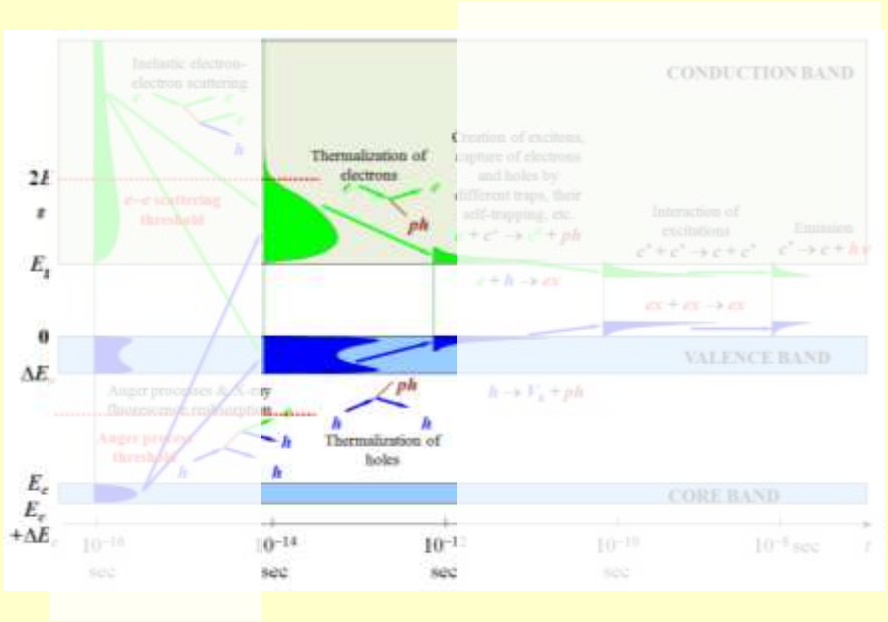


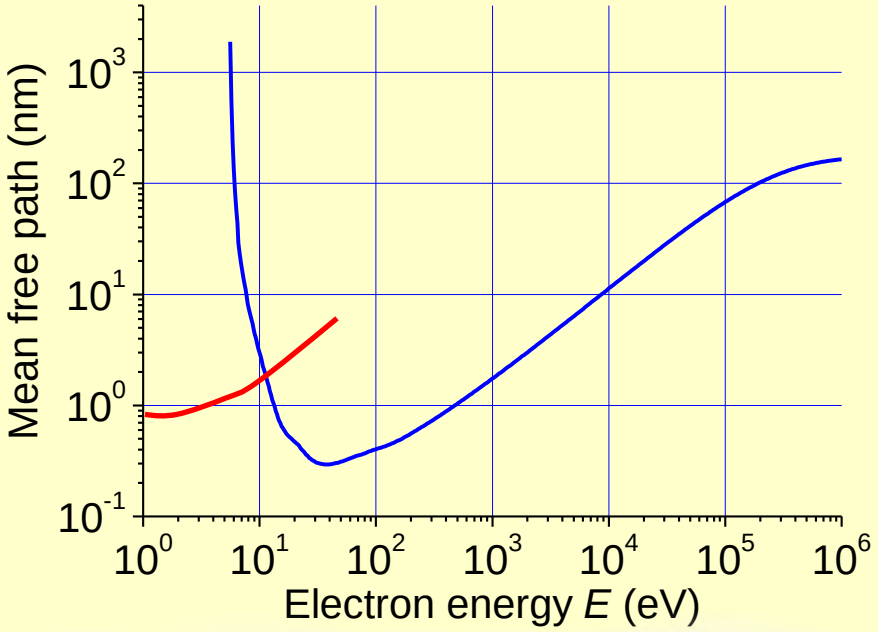
'Real' track structure

Onsager radius10 nm

Regions created by different virtual photons are overlapped

Spatial track structure for phonon scattering stage (after thermalization) for large thermalization radius





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100 nm

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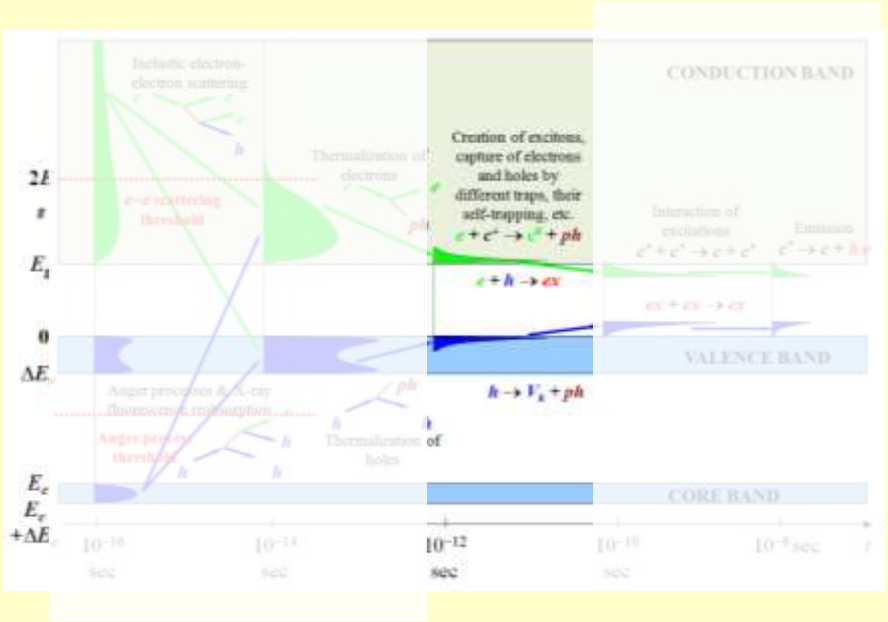
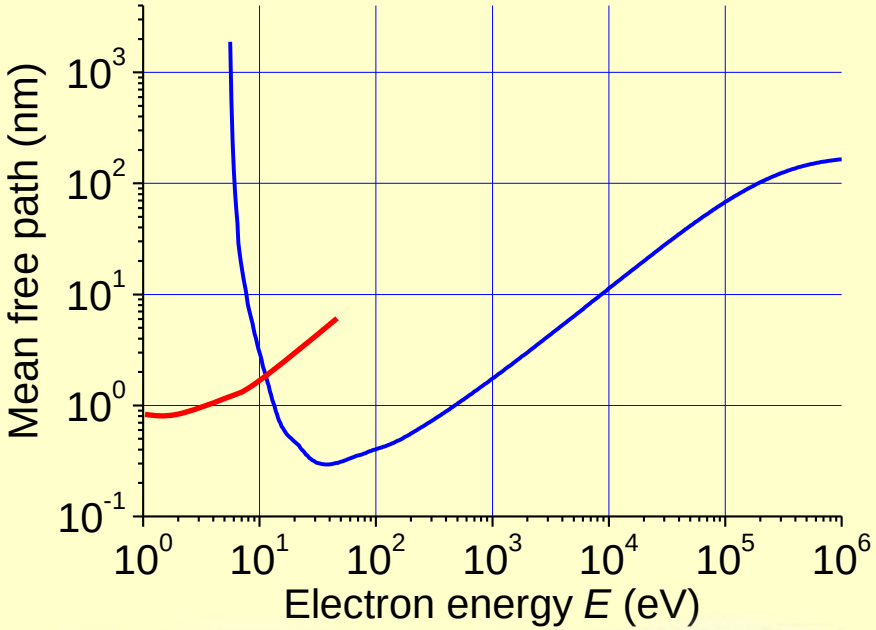




‘Real’ track structure

- Onsager radius10 nm

Spatial distribution of electrons, holes and excitons due to mobility in e-e passive energy domain

Two types of carrier mobilities: thermalization length (mobility of hot electrons and holes) and mobility of thermalized excitations (electrons, holes & excitons).

High-energy part of ionization track – individual electron-hole pairs and small non-overlapping clusters of excitations. Negative role of mobility: the higher thermalization length (in comparison with Onsager radius), the lower the recombination yield.

Low-energy part of ionization track – overlapping clusters of excitations. Mean distance between interacting excitations increases with increase of the mobility of excitons. Positive role of mobility: the higher the mobility, the lower the quenching of excitation due to high EE density.

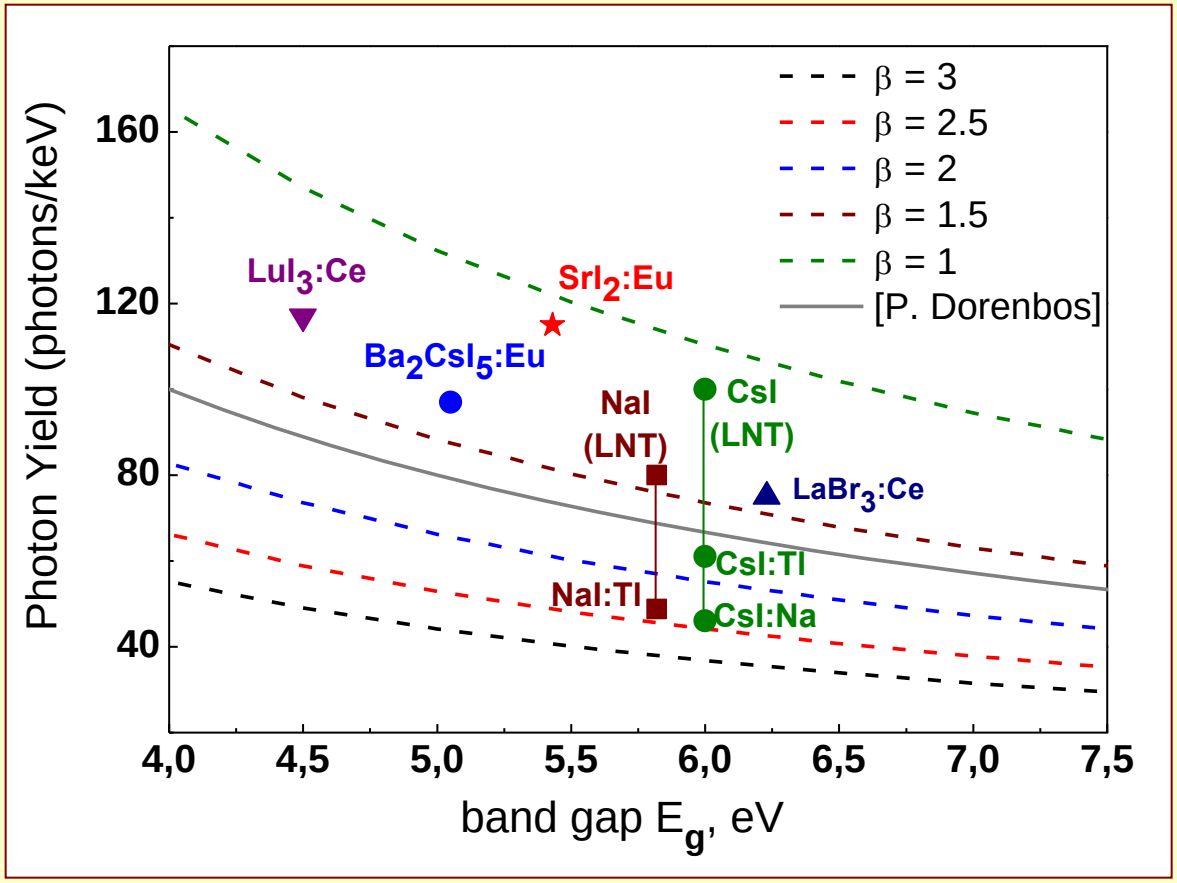
"Ideal" scintillator: Low hot mobility (high yield of excitons) and high thermalized mobility (low interaction).

Binary alkali halides:

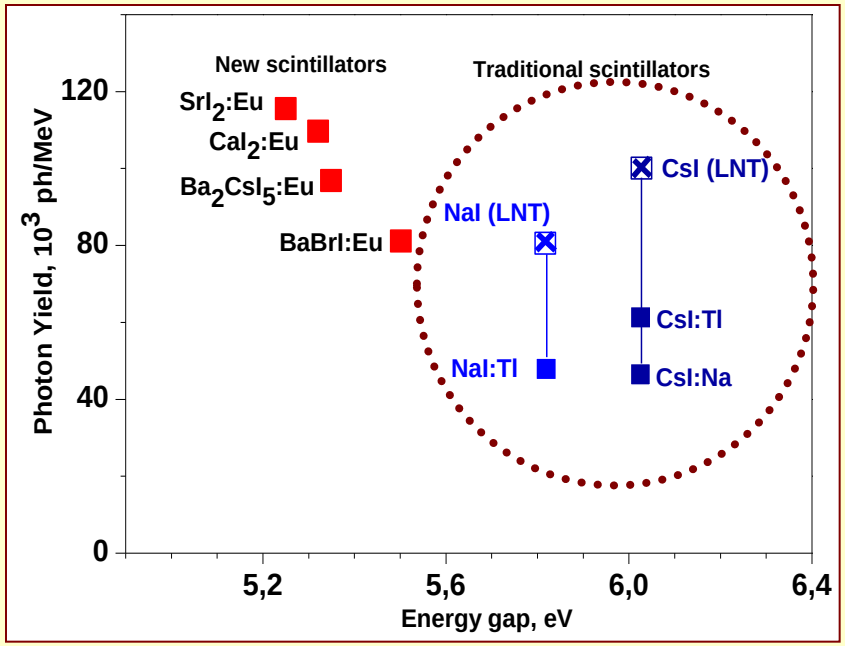
Can the yield achieve theoretical limit?

Can we improve conventional alkali halide scintillators?

Fundamental or maximal yield?



Fundamental limits to Light Yield of NaI and CsI based scintillators (LY vs. E_g)



Experimental data are far from theoretic limit for NaI and CsI based crystals

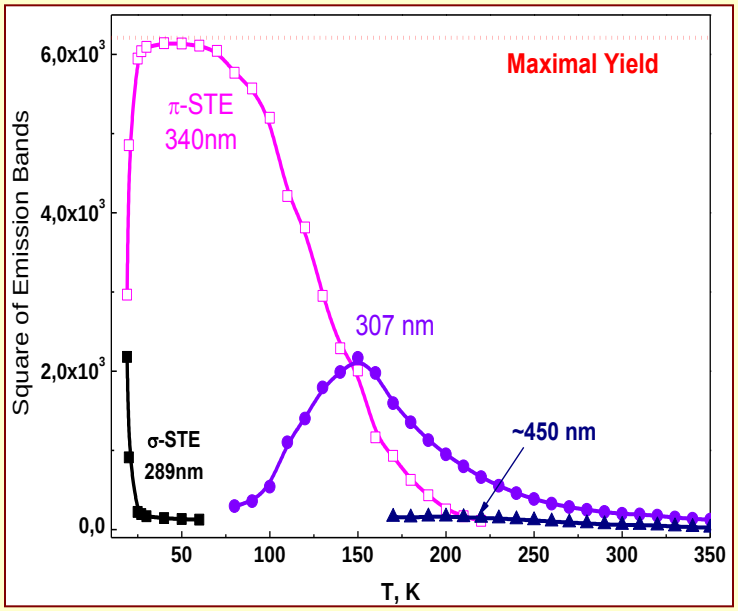
Crystal	E_g, eV	LY, ph/Mev theor.	LY, ph/Mev expim.
NaI (77K)	5.8	*86.000*	**80.000**
NaI:Tl (RT)			45.000
CsI (77K)	6.1	*82.000*	**~100.000**
CsI:Tl (RT)			56.000
CsI:Na (RT)			46.000

✓Pure NaI and CsI possess extremely high photon yield at LNT

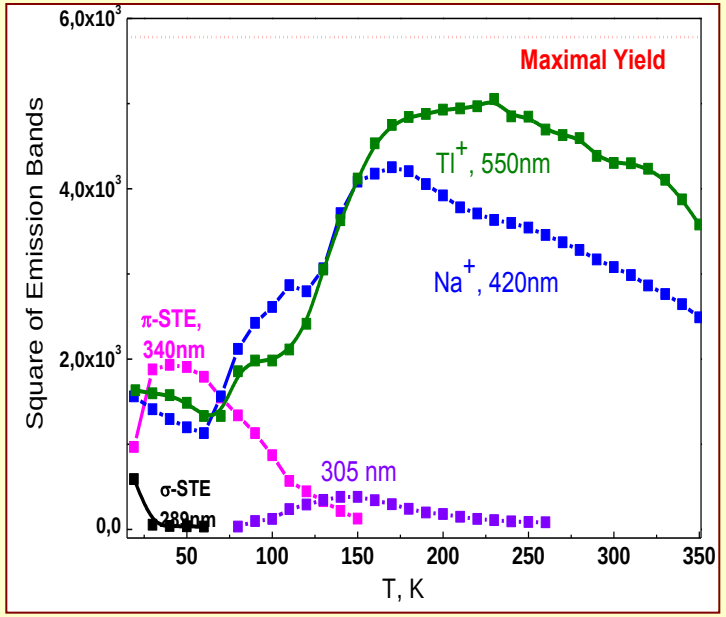
[V.Sciver,1958; Persyk,1980; Moszynski et al, 2010]

Exciton based luminescence

Pure CsI emission



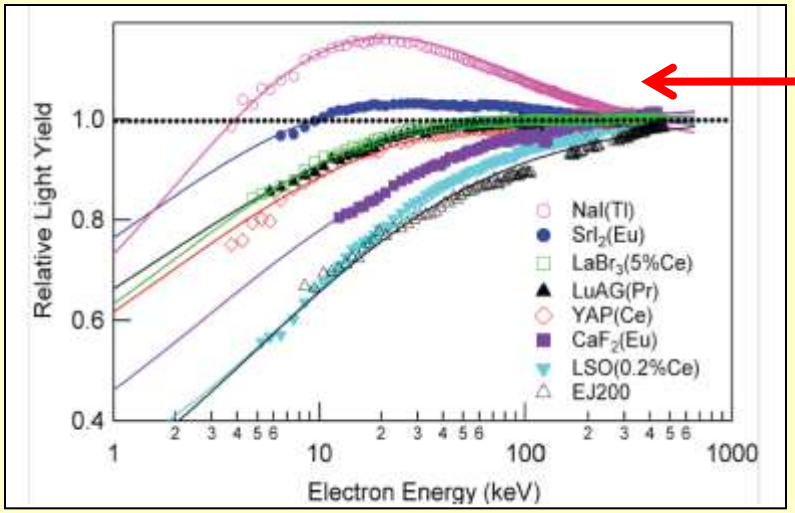
CsI:Na and CsI:Tl emission



Resume :

* It is possible to separate different types of emission
* STE and defect trapped exciton emissions are dominated
* Self trapping creates the best conditions for maximal yield
* Other relaxation mechanisms lead to an extra efficiency losses

Non-proportionality analysis for alkali halides



Electron response of some scintillators
[S. A. Payne, W. W. Moses et al., *IEEE TNS, 2011*]

The high-energy decrease of the scintillator efficiency shows that significant fraction of individual electron-hole pairs are thermalized at distances larger than Onsager radius

$$p = 1 - \exp\left(-R_{Ons}/r_{eh}\right)$$

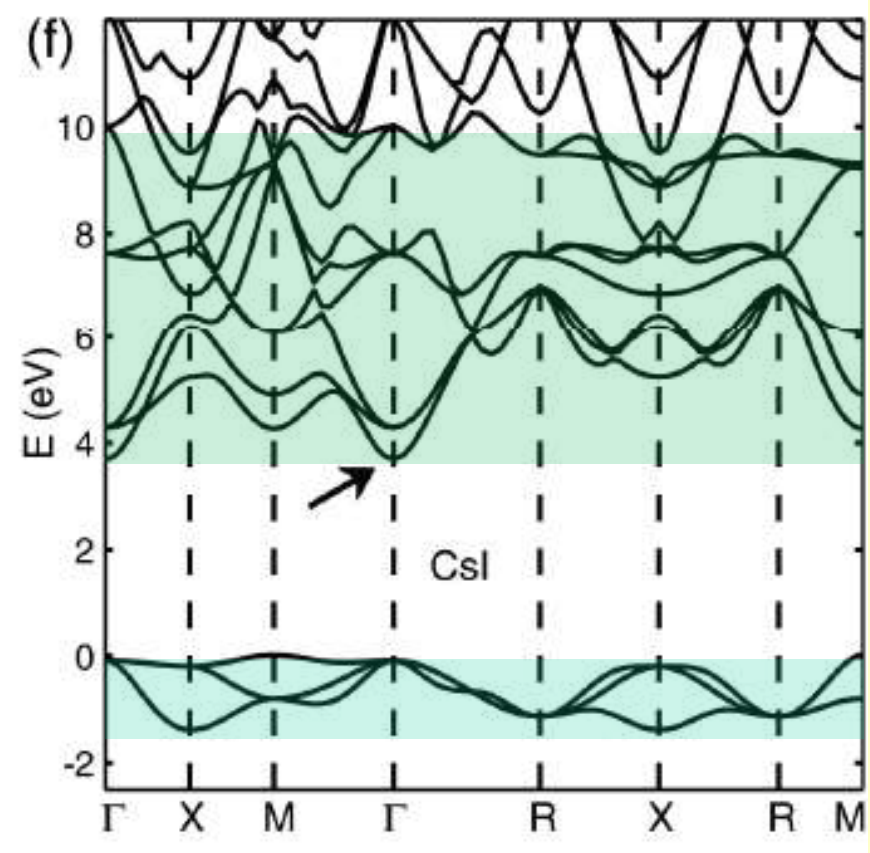
$$\frac{e^2}{\varepsilon R_{Ons}} = k_B T$$

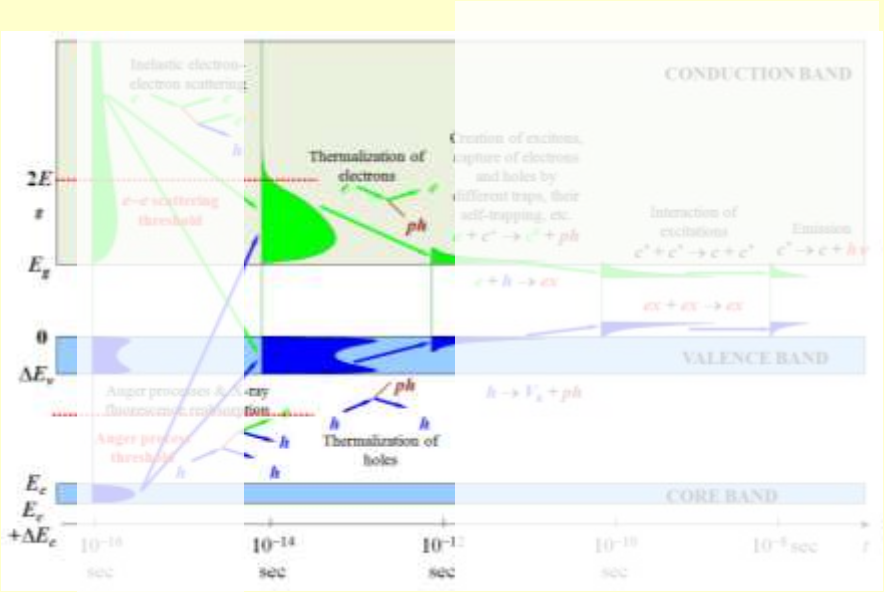
1) We can increase Onsager radius – by decreasing the temperature. Pure CsI and NaI have yield ~ 100,000 ph/MeV at 77K ! ($R_{ons,77K}=4R_{Ons,300K}$)

2) We can decrease thermalization distances - by choosing of complex halides.

What is the physics of the thermalization distances decrease in this case?

Starting states for thermalization ($E_{kin}<E_g$)





Band structure calculations

from W. Setyawan et al. , *IEEE TNS*, 2009

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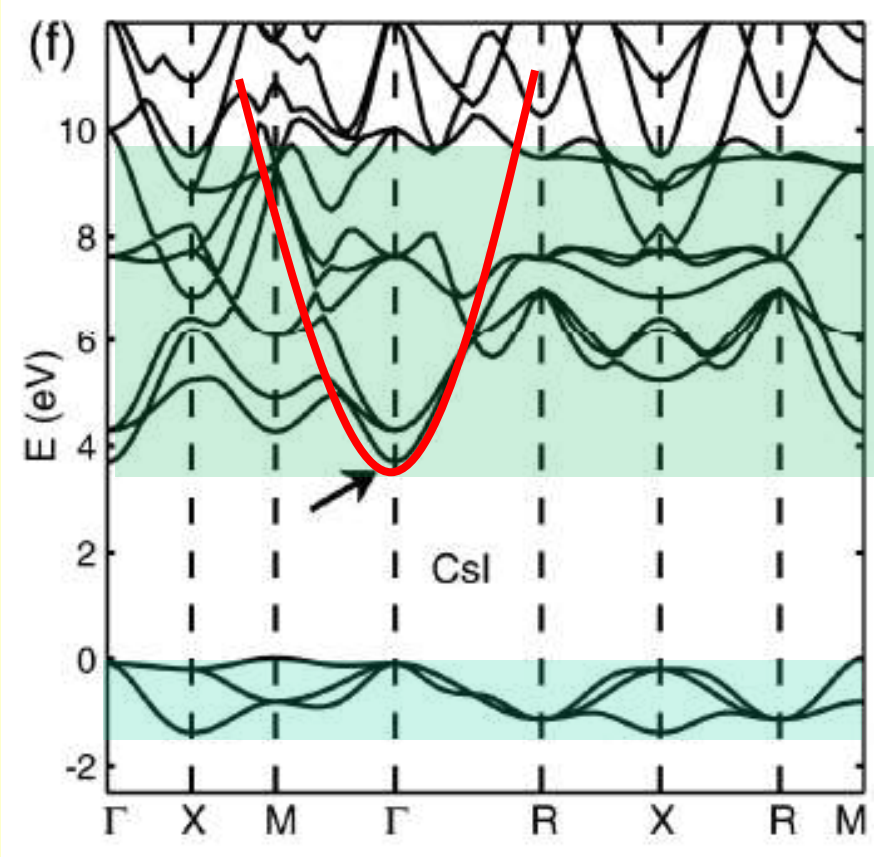


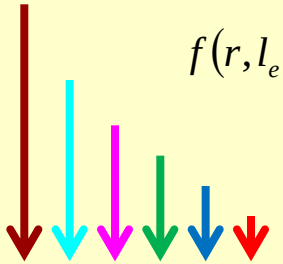
Band structure calculations

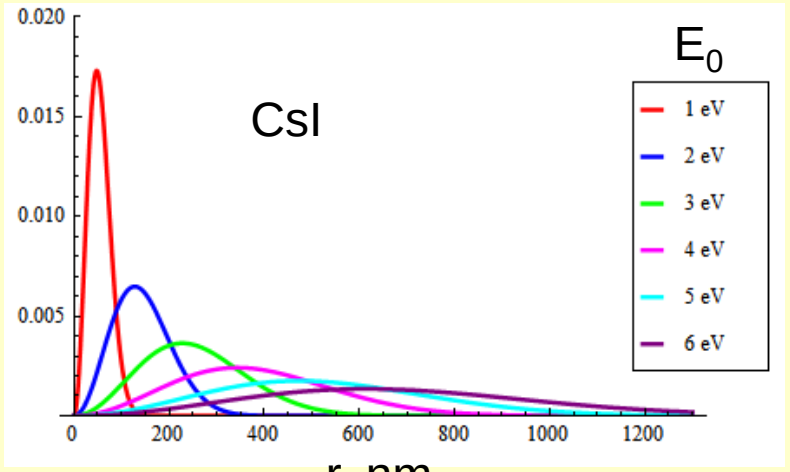
from W. Setyawan, R. M. Gaume et al. *IEEE TNS*, 2009

Thermalization for parabolic band and one LO phonon starting from energy E_0

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

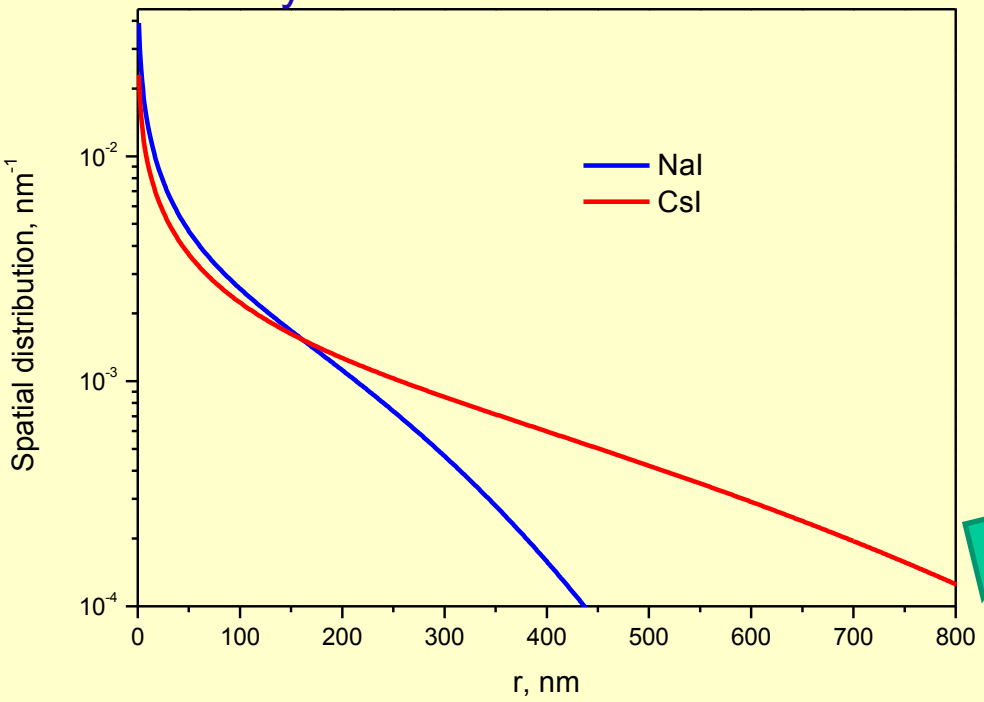
$$f\left(r, l_e(E_{e0})\right) = \frac{3\sqrt{6}\, r^2}{\sqrt{\pi}\, l_e^3(E_{e0})} \exp\left(-\frac{3r^2}{2 l_e^2(E_{e0})} \right)$$

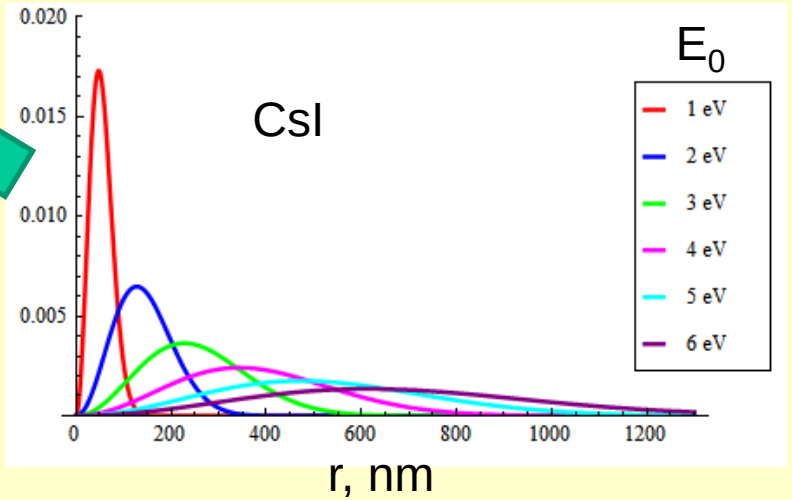




Spatial distribution of thermalized electrons

Analytical estimation





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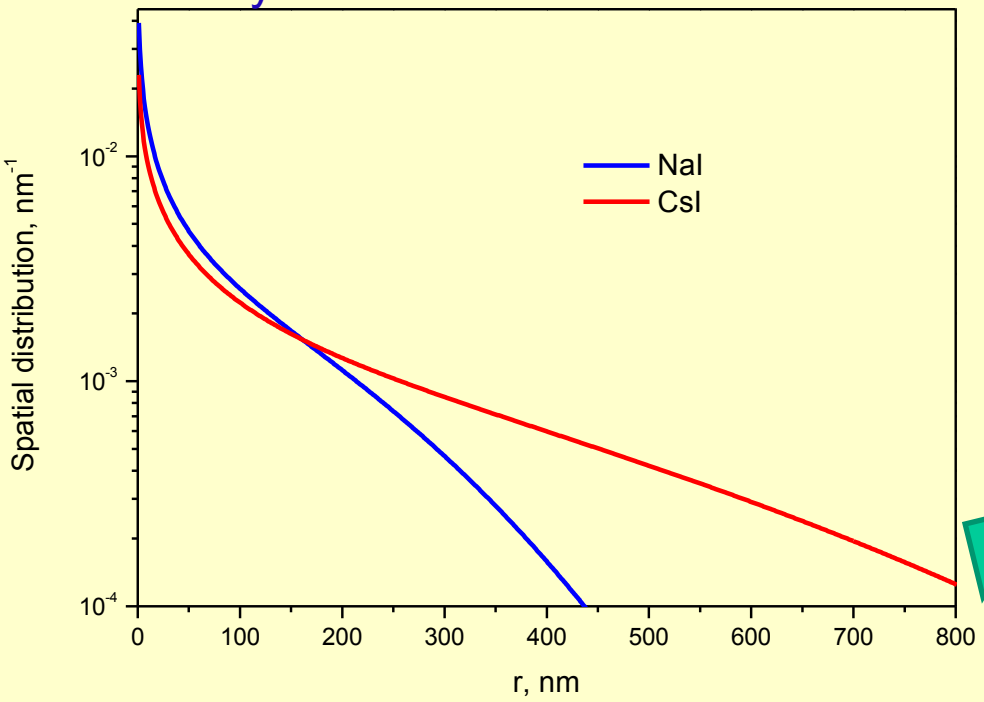
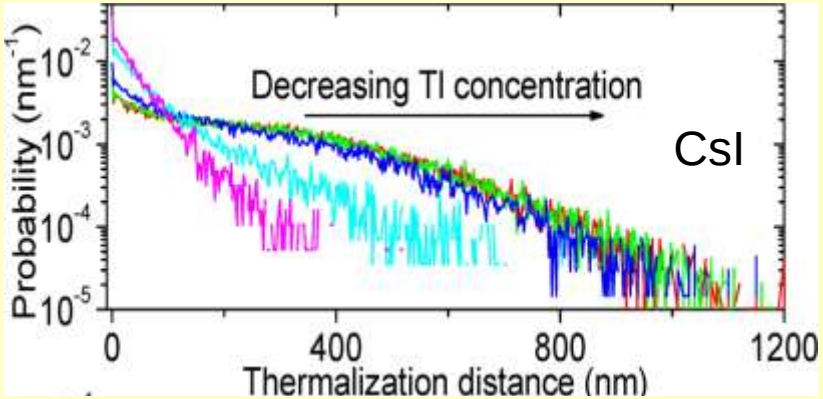
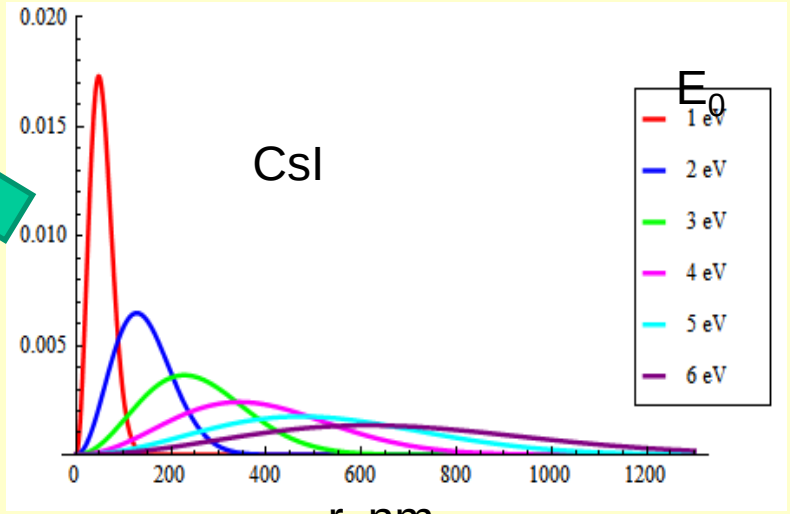


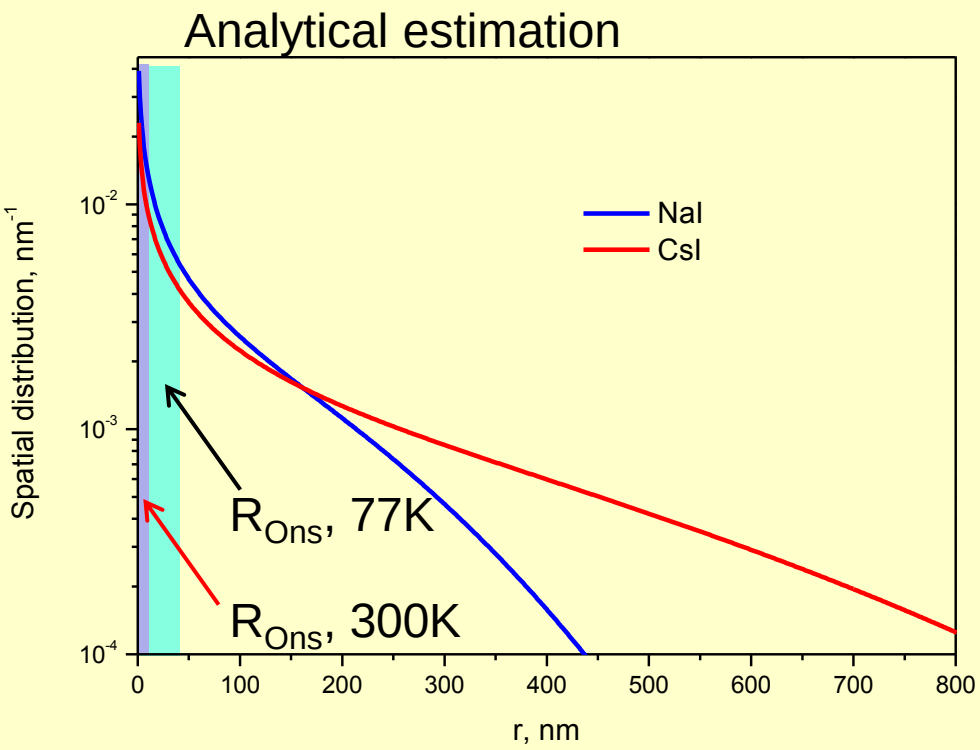


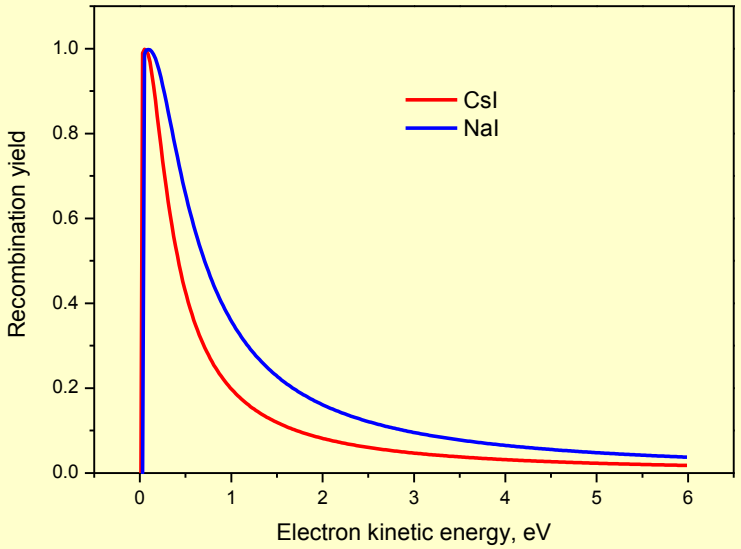
Computer simulation of electron thermalization in CsI and CsI(Tl),

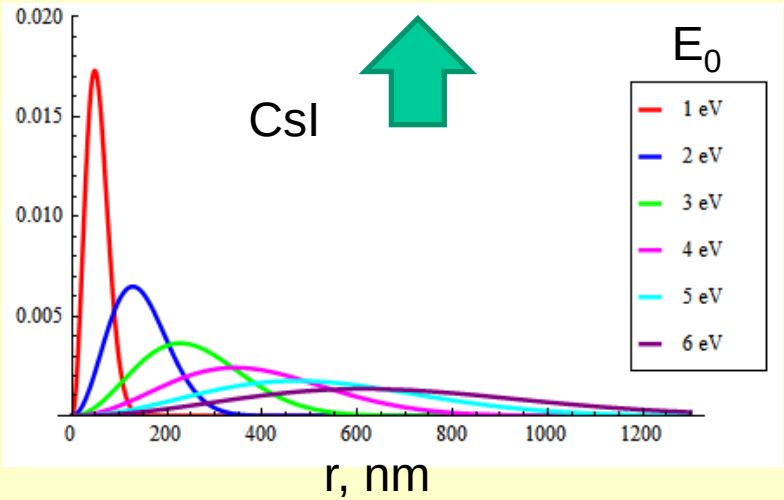
Z. Wang, Y. Xie, B. D. Cannon et al. 2011



Spatial distribution of thermalized electrons







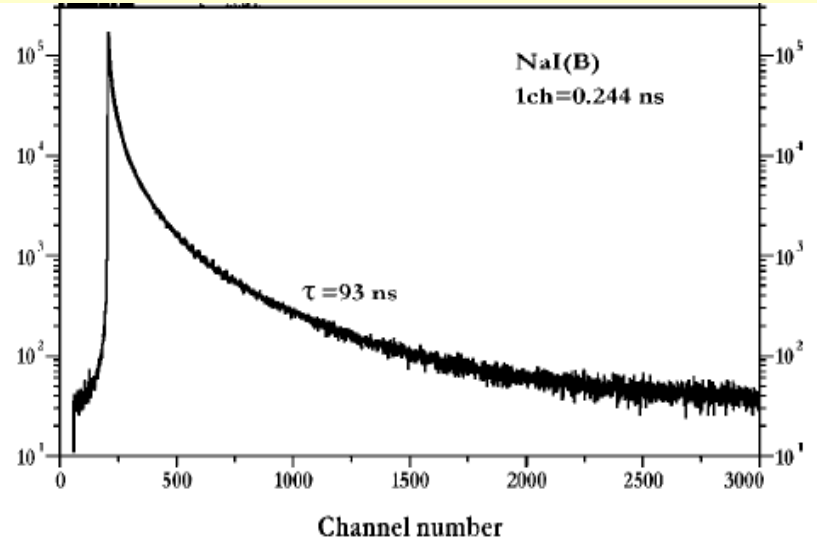
	R_{Ons}, 300K	Yield, 300K	Yield, 77K
CsI	9.87 nm	0.24	0.44
NaI	9.05 nm	0.34	0.58

Bimolecular recombination in alkali halides

Genetic recombination yield << 1 for NaI & CsI

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

Essentially non-exponential decay kinetics for pure NaI



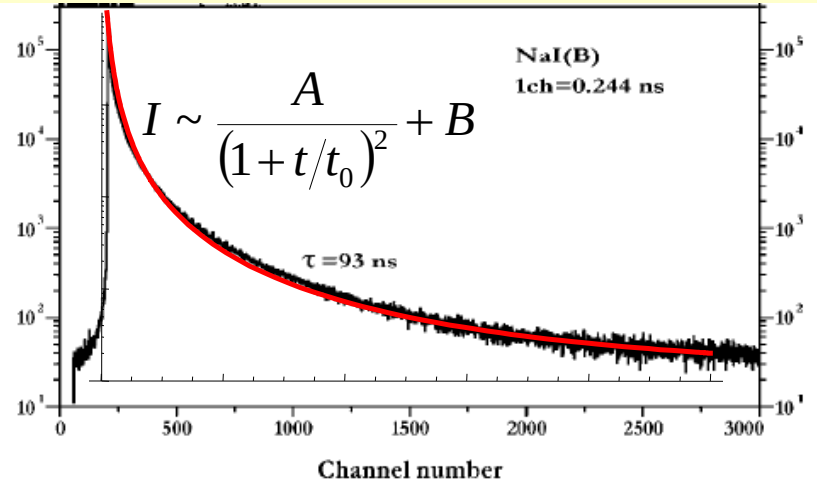
M. Moszyński, et al. Study of Pure NaI at Room and Liquid Nitrogen Temperatures, *IEEE TNS 2003*

Bimolecular recombination in alkali halides

Genetic recombination yield << 1 for NaI & CsI

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

Essentially non-exponential decay kinetics for pure NaI



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

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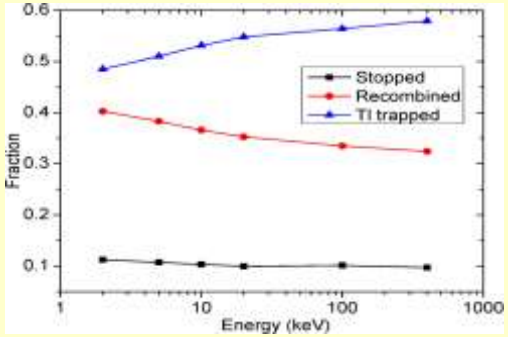
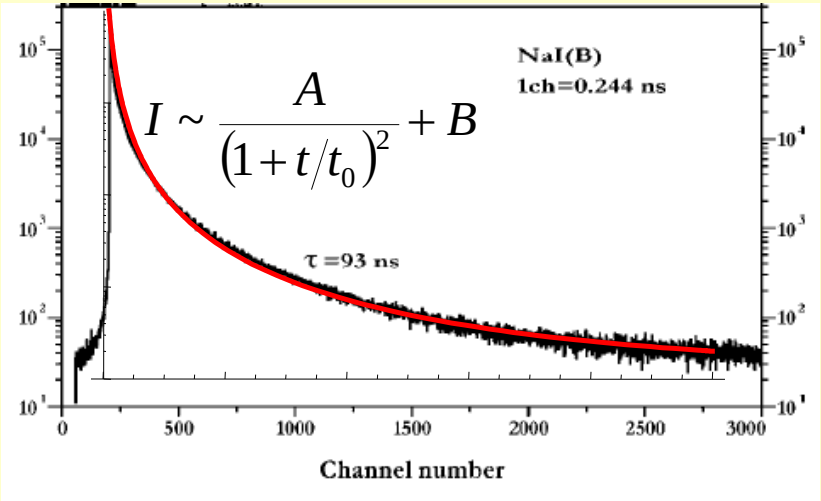


Changes in the fractions of stopped, recombined, and Tl-trapped electrons as a function of incident energy for CsI:Tl [S. Kerisit, K. M. Rosso, B. D. Cannon et al. 2009]



Essentially non-exponential decay kinetics for pure NaI

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

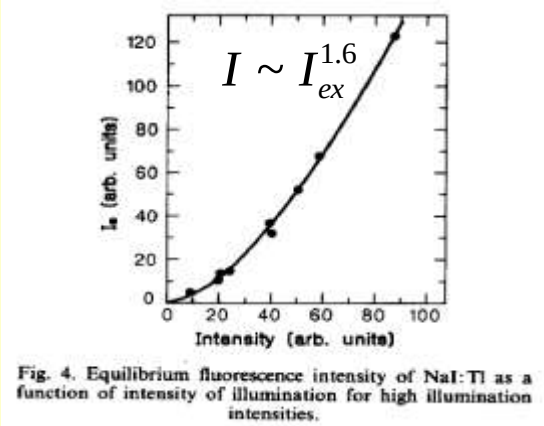


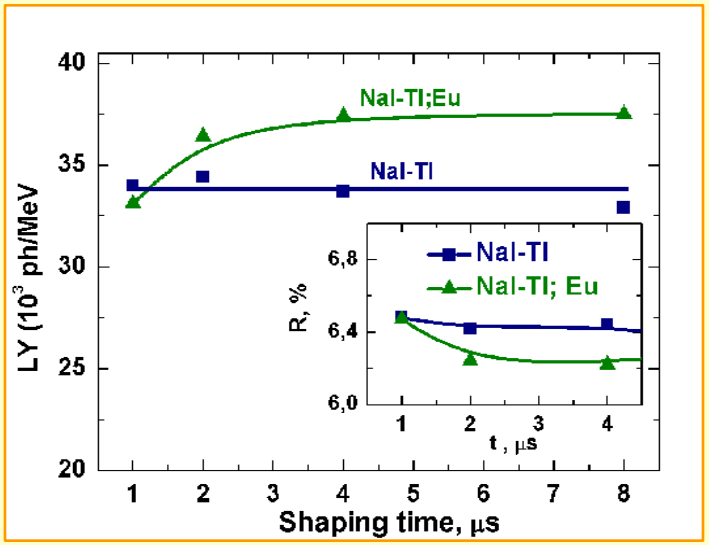
Fig. 4. Equilibrium fluorescence intensity of NaI:Tl as a function of intensity of illumination for high illumination intensities.

Non-linear VUV excitation of NaI:Tl [E.Loewinger et al. 1988]

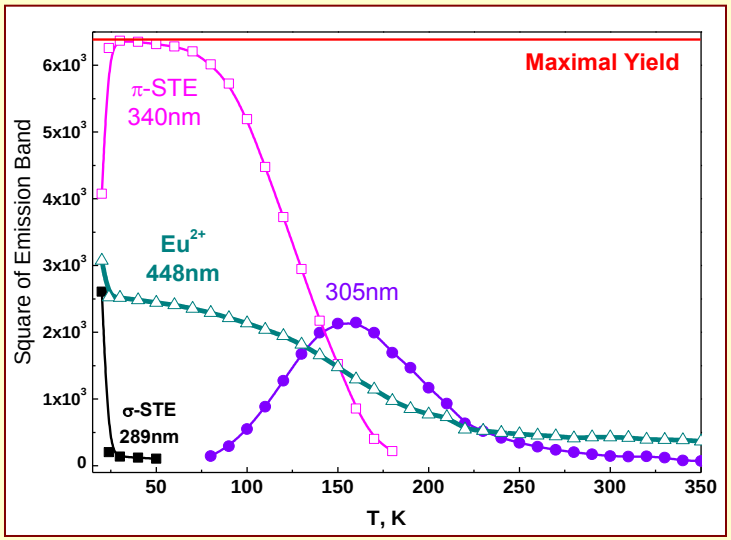
NaI & CsI (both pure and doped) show significant non-linear bimolecular recombination

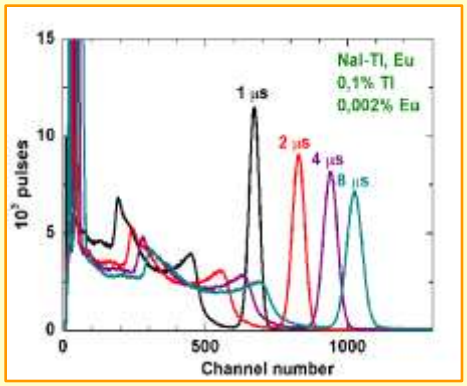
Can we use co-doping to collect more excitations?

NaI :Tl,Eu



CsI:Eu emission vs temperature





Eu,Tl – co-doping of NaI increases light yield comparing to conventional NaI:Tl

Scintillation efficiency improvement

"Synergy" of Eu and Tl co-doping in NaI crystals

Crystal	Tl, m%	Eu, m%	Lum, nm	Decay, ns	LY, %	R, %
NaI-Tl	$1 \cdot 10^{-1}$		415	230	100	6.4
NaI-Tl, Eu	$1 \cdot 10^{-1}$	$1 \cdot 10^{-3}$	445	230 (26%) 1000 (74%)	110	6.2
NaI-Eu		$1 \cdot 10^{-1}$	445	1000	60	9.5

- Introduce of hundred times lower Eu-concentration (10^{-3}%) than Tl (0.1%) leads to Tl emission suppression and higher light output.
- Thus, Eu co-doping allows to get better scintillation performance of NaI:Tl.
- It costs some losses at decay and claim for larger integration time.

Binary alkali halides -
the yield could not reach fundamental limit !

✓The maximal CsI or NaI scintillation yield corresponds to STE relaxation at LNT

✓Temperature rise leads to the STE luminescence quenching and DTE emission that lower due to transfer and stabilization losses. Eu^{2+} co-doping allows slightly increase the NaI(Tl) yield only

✓Thermalization length is much higher than Onsager radius in alkali halides – therefore geminate recombination yield is much less then unity.

✓We can decrease thermalization distances – by choosing of complex halides

What materials are characterized by lower thermalization length? Why Alkali Earth Halides?

How thermalization length depend on material parameters?

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

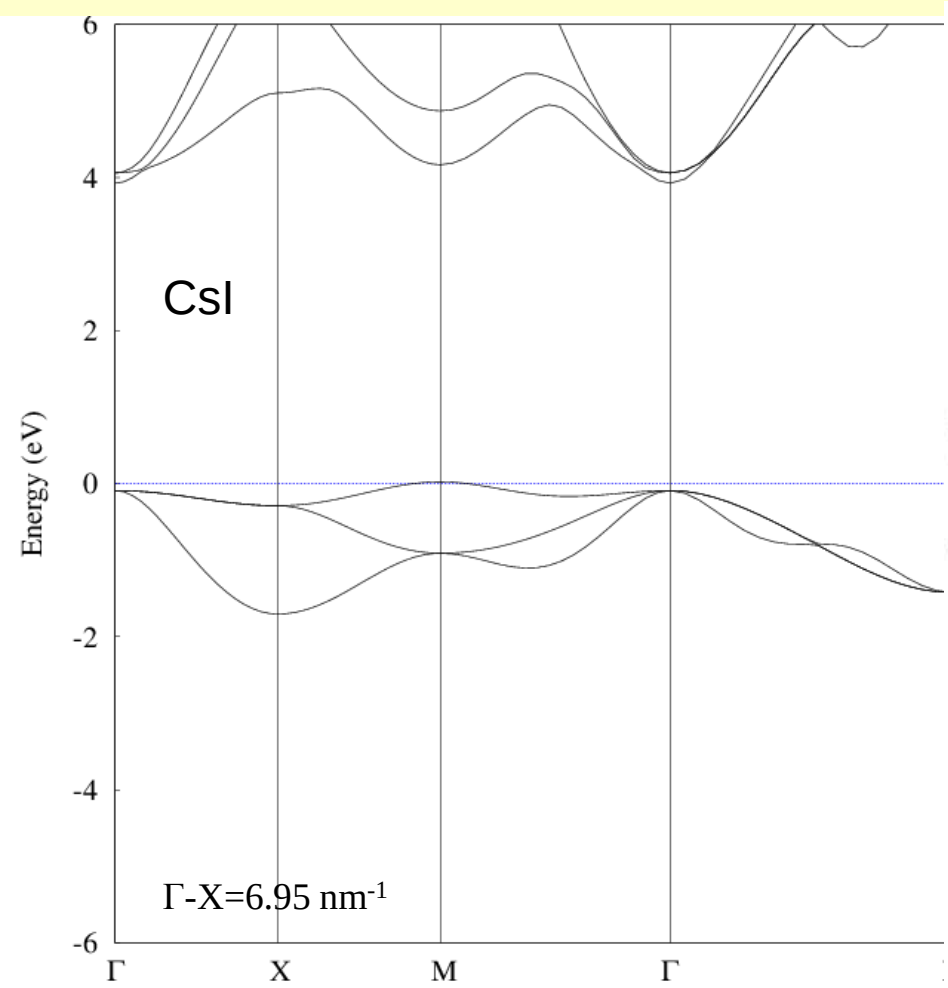
We should choose materials with

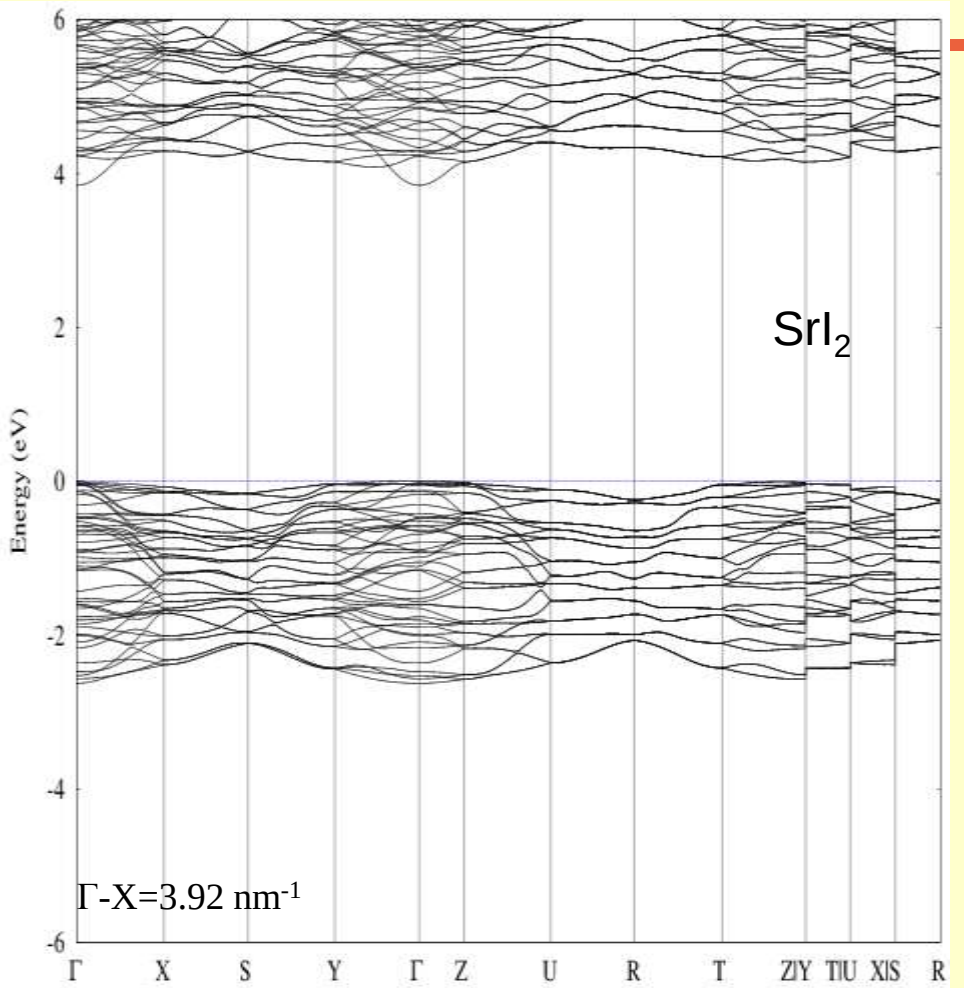
- **higher effective masses** in the whole relaxation region $E_{kin} < E_g$ and
- higher LO phonon energies (see Vasil'ev, Kirkin, SORMA West 2012, 12C-2):

Why AE halides? - Lower thermalization length in complex halides result in higher yield of geminate recombination!

Complex halides with many atoms in elementary cell (e.g. SrI_2 with 24 atoms in elementary cell)

Comparison of CsI and SrI_2 electronic structures





[1] W. Setyawan and S. Curtarolo, Comp. Mat. Sci. 49, 299 (2010).
[2] S. Curtarolo, W. Setyawan, S. Wang, J. Xue, K. Yang et al. Comp. Mat. Sci. 58, 227 (2012).
[3] W. Setyawan, R. M. Gaumé, S. Lam, R. S. Feigelson, and S. Curtarolo, ACS Comb. Sci. 13(4), 382 (2011).

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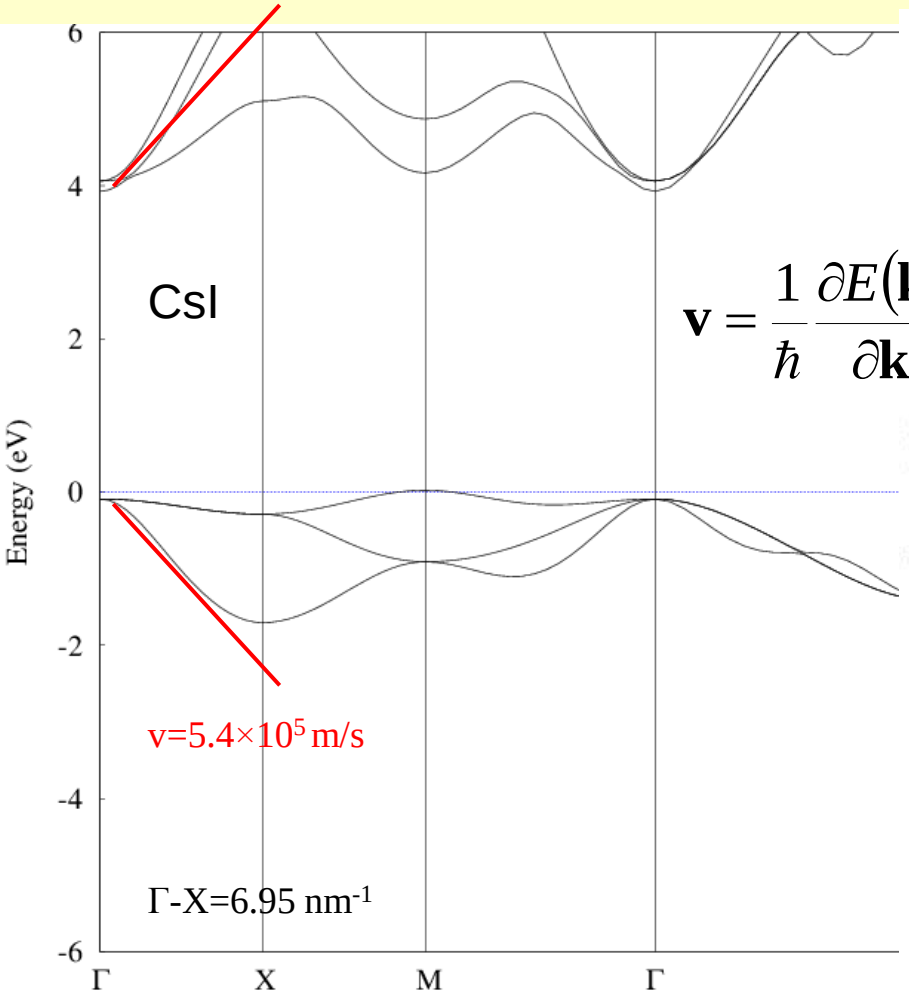

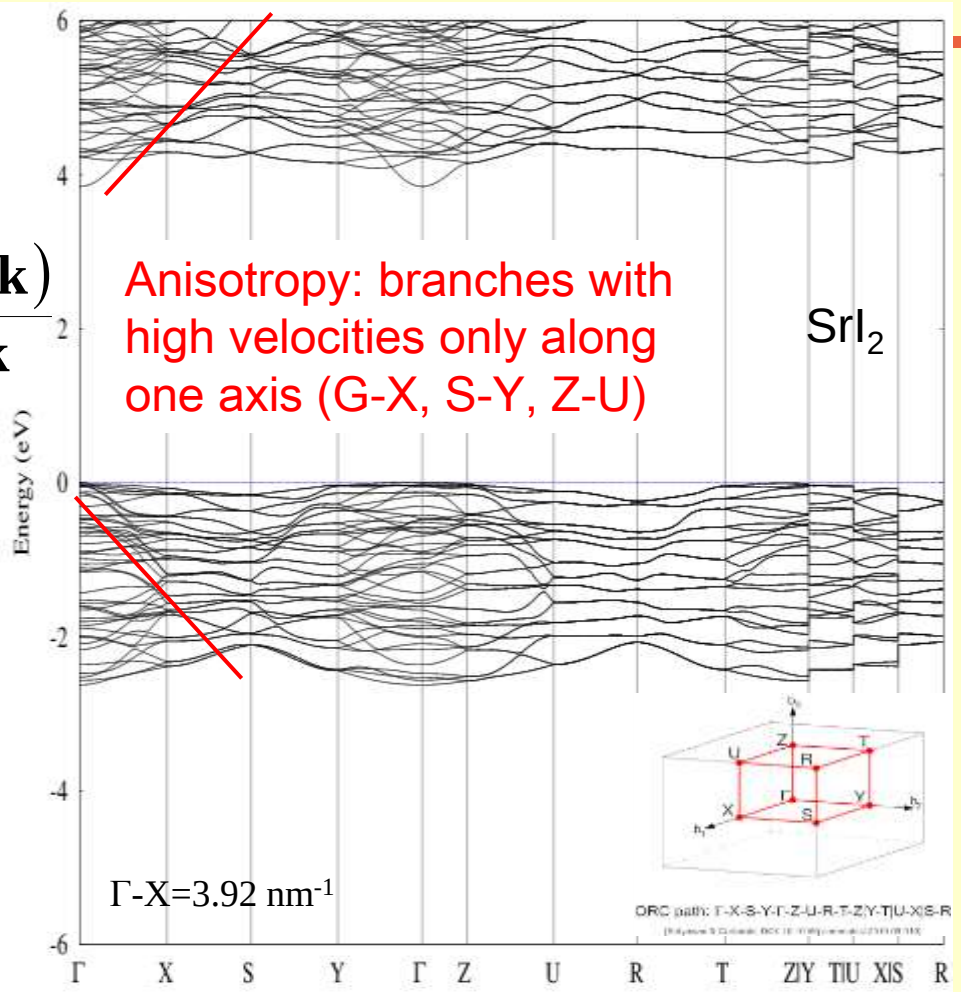

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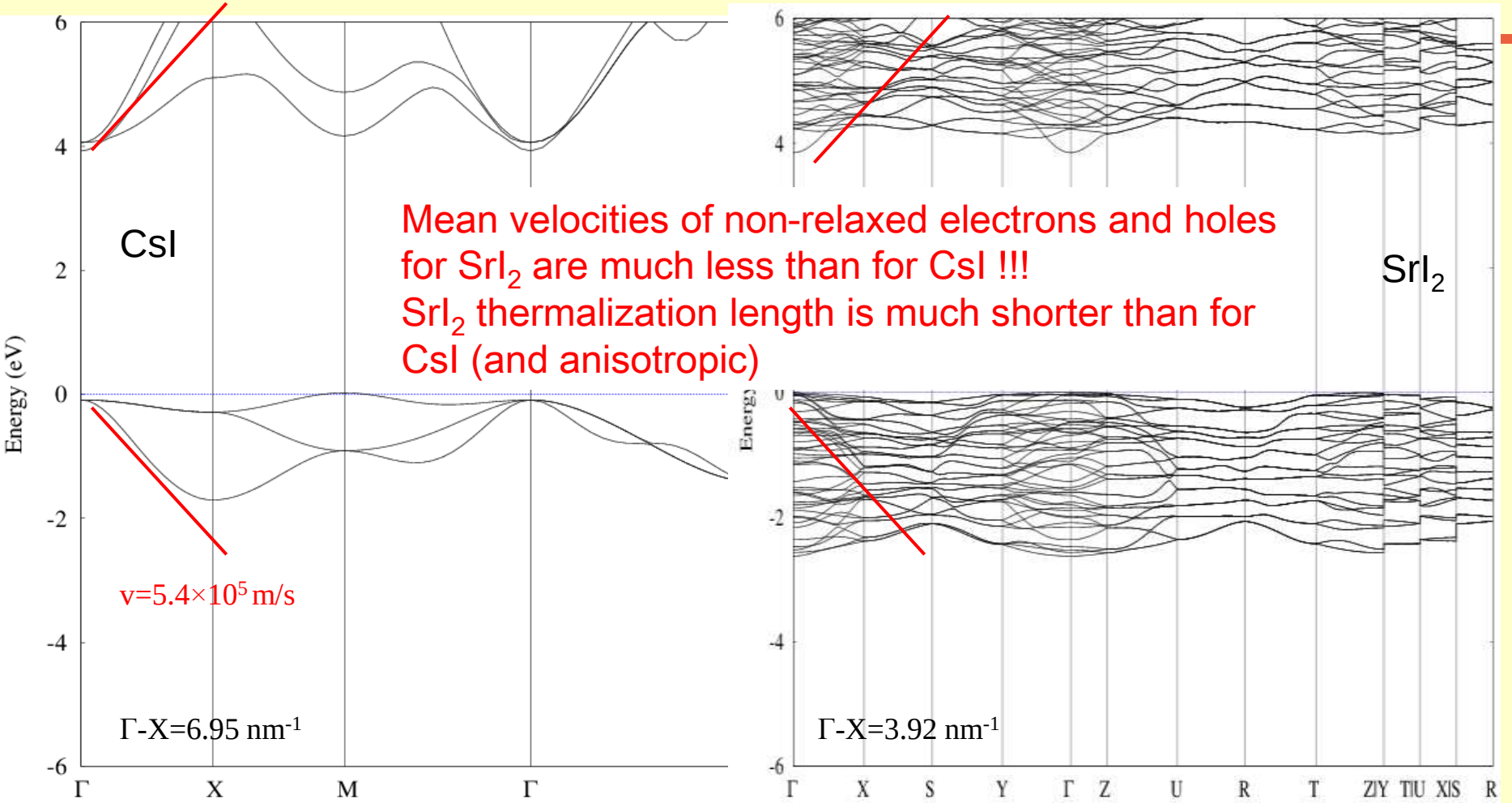

[1] W. Setyawan and S. Curtarolo, Comp. Mat. Sci. 49, 299 (2010).
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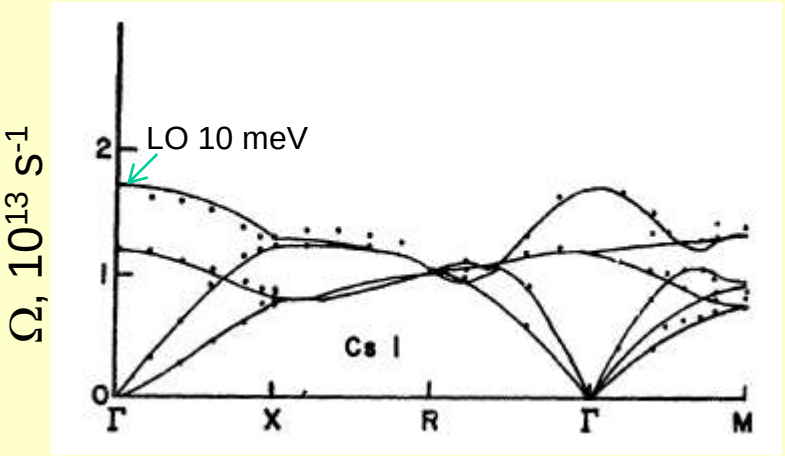
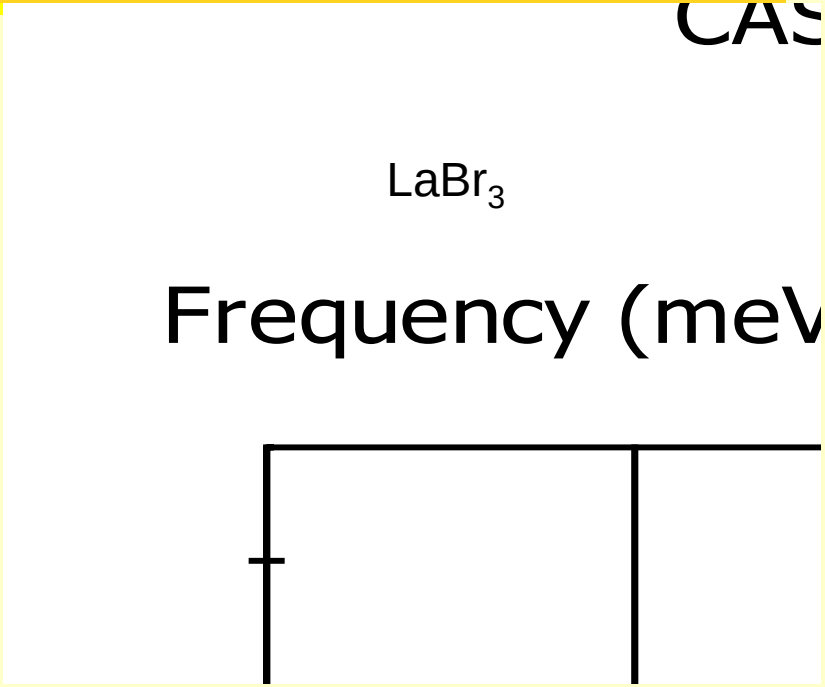
Comparison of phonon properties

(see Vasil'ev, Kirkin, SORMA West 2012 12C-2)



J.F. Vetelino, K. V. Namjoshi and S. S. Mitra, Phys. Rev. B 7, 4001–4004 (1973)



Phonons dispersion for $LaBr_3$.
I.Iskandarova, private communication

Only one LO phonon frequency for CsI (no energy relaxation below 10 meV)

7 LO phonon modes for $LaBr_3$, 23 LO modes for SrI_2 (full and faster thermalization due to LO emission/absorption, *detailed discussion in 12C-2 presentation)*

The reduced thermalization yield result in higher exciton production due to recombination in geminate pairs and in increased excitonic energy transfer in complex halides ($SrI_2:Eu^{2+}$, $LaBr_3:Ce^{3+}$)

Presence of trapped exciton (TE) emission even for high Eu concentrations

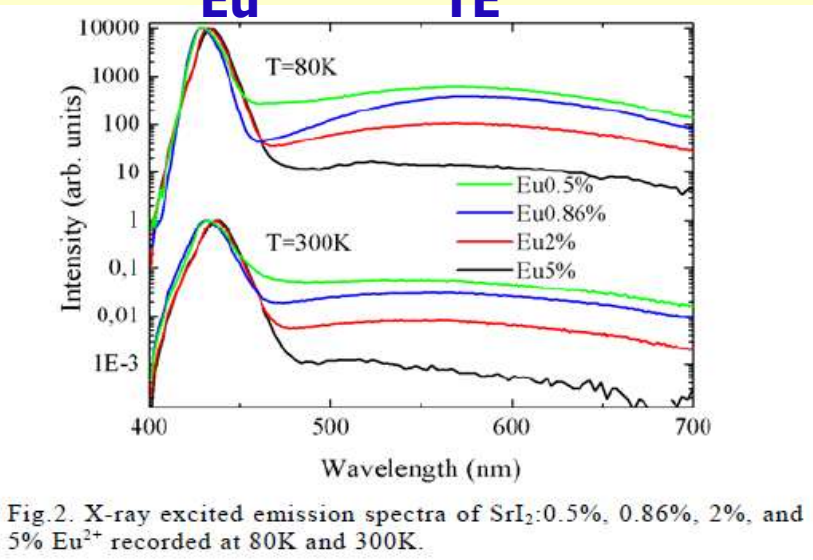
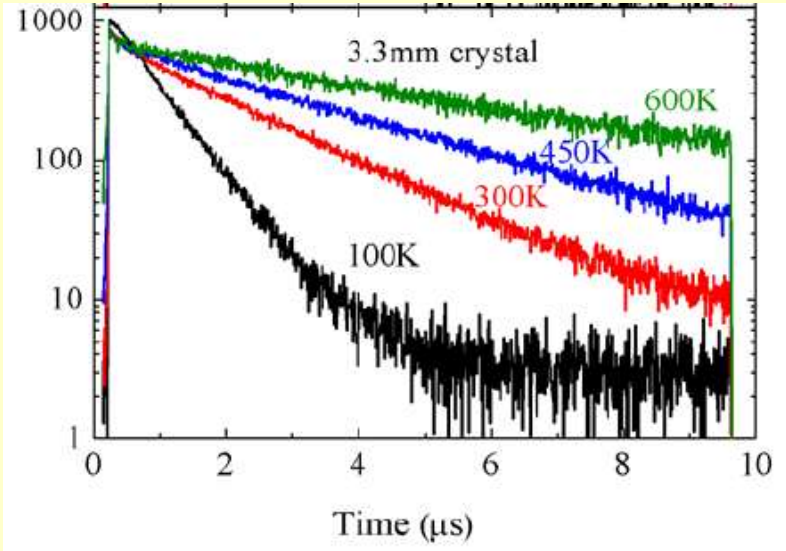


Fig.2. X-ray excited emission spectra of SrI_2:0.5%, 0.86%, 2%, and 5% Eu^{2+} recorded at 80K and 300K.

Exponential decay
(with effect of reabsorption)



M.S.Alekhin, J.T.M. de Haas, K.W. Krämer, P.Dorenbos, *IEEE TNS, vol. 58, issue 5, pp. 2519-2527, 2011*

The model resume

For all complex halides we can obtain high yield due to high yield of geminate recombination and small bimolecular effects in non-proportionality curves

Lower thermalization length (in comparison with alkali halides) is connected with flat bands in whole energy thermalization region ($E_{kin}<E_g$) and much more complicated LO phonon structure (and probably strongly anisotropic mobility due to layer structure)

(for more details see Vasil'ev, Kirkin, SORMA West 2012 12C-2)

Renaissance of Eu-doped scintillators
(history and reality)

Luminescence study 1948 - 1975	
LiCl :Eu	Lehmann,1975
LiI :Eu	Murray,1958
CaI_2:Eu	Hofstadter,1963 Lyskovich,1970
CaF_2:Eu	Butement,1948
$SrCl_2$:Eu	Lehmann,1975
$SrBr_2$:Eu	
SrI_2 :Eu	
SrI_2 :Eu *scintillator*	Hofstadter,1968, US Patent,3373279

New demands have led to discovery several new Eu-doped scintillators

New scintillators 2007 - 2011	
CaI_2:Eu	LLNL, LBNL, USA Cherepy, Moses et al. 2007 - 2009
SrI_2:Eu	
Ba_2CsI_5:Eu	
BaBrI:Eu	LBNL, USA Bourret, Derenzo et al. 2010
BaFI:Eu	
$SrCsI_3$:Eu	SMRC, Tennessee, USA, Zhuravleva, Melcher et al.2010
$CsEuI_3$	
Cs_3EuI_5	

Families of AE halides for scintillation applications

Families of compounds for Eu^{2+}

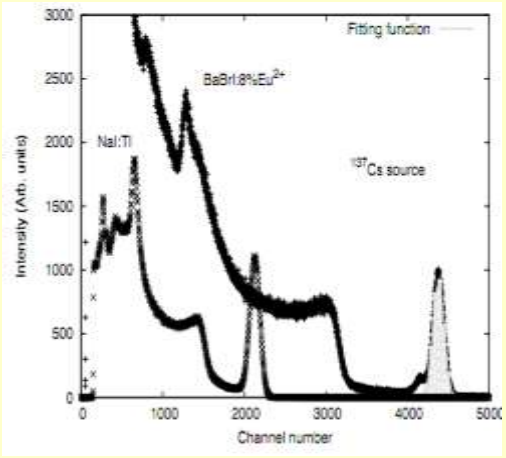
- Ba mixed halides BaXY, X and Y = F, Cl, Br, I
- Sr mixed halides SrXY, X and Y= F, Cl, Br, I
- Cs alkali-earth halides CsI-BaX_2 X = F, Cl, Br, I
- Cs alkali-earth halides CsI-SrX_2 X = F, Cl, Br, I

Families of compounds for Ce^{3+}

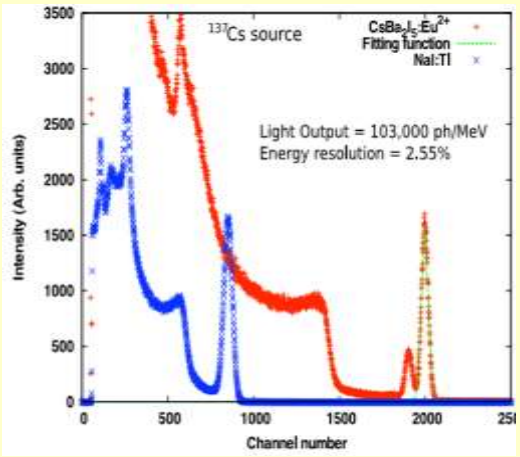
- A^{3+} mixed halides ($A_xX_{x(3-y)}Y_y$)
- A^{3+} complex halides ($CsAX_4$, etc...)

E. Bourret at al 2009-2011

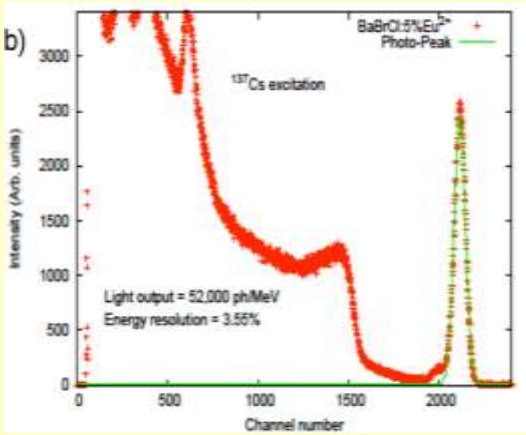
Pulse height spectra of record scintillators under γ ^{137}Cs excitation



BaBrI:Eu



$CsBa_2I_5$:Eu



BaBrCl:Eu

LBNL, USA
Bourret,Derenzo, Bizarri et al. 2009-2012

AE scintillator performance progress (2007→2012)

Crystal	2007 - 2009		2011 - 2012	
	LY ph/Mev	R, % Cs^{137}	LY ph/Mev	R, % Cs^{137}
SrI_2:Eu	115.000	2.6	115.000	2.6
Ba_2CsI_5:Eu	97.000	3.8	102.000	2.55
$SrCsI_3$:Eu	65.000	5.2	73.000	3.9
BaBrI:Eu	81.000	4.8	97.000	3,4

Many AE halides possess with efficiency about fundamental limit

Selection of one (best) scintillator has to base on the technology advantages

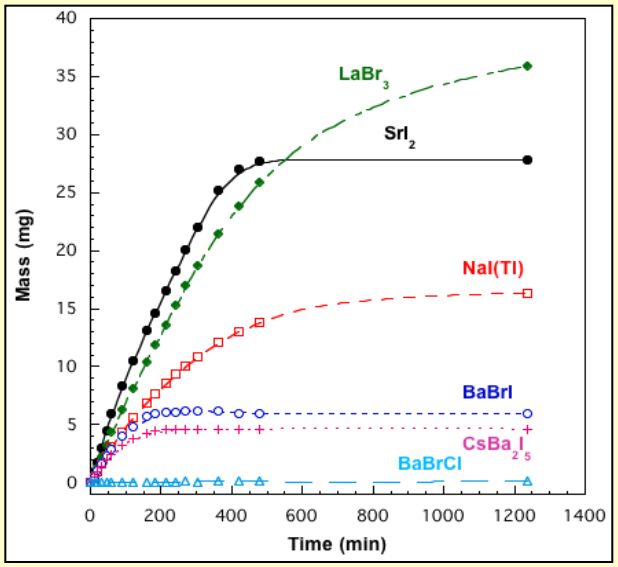
CRYSTAL GROWTH ,

RAW MATERIAL,

TARGET PRICE

FOR ALKALI-EARTH HALIDES

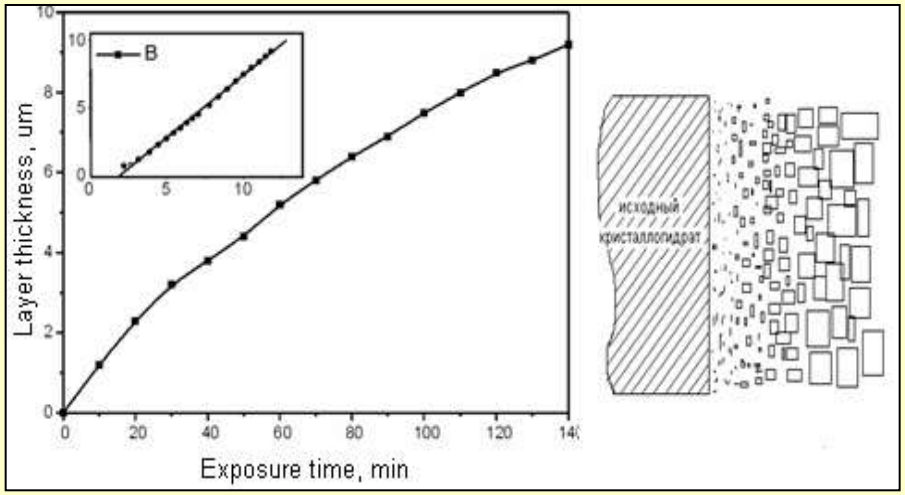
Hygroscopicity of halides



Weight gain of powdered scintillators exposed to air *(T=22˚C, Rel. Hum. 35-36%, 63-106 microns sieved particles).*

E.Bourret at al, 2012, private communication

X-ray study of hydrated layer growth on NaI(Tl) surface

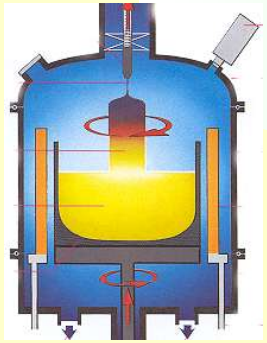


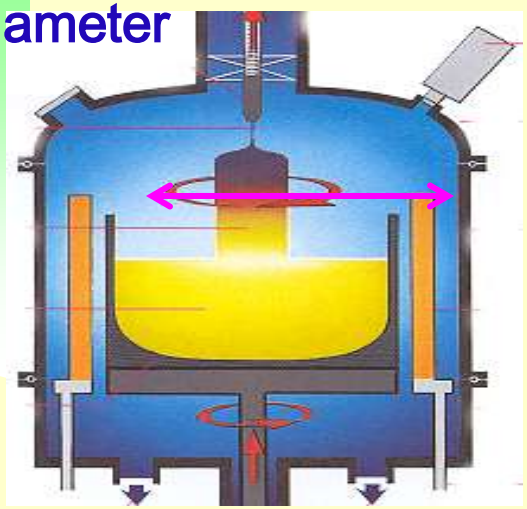
A.Kudin, ISMA, 1999

Note: new AE based scintillators have the same or the lower hygroscopicity as compared with NaI(Tl)

Two ways to increase industrial output

1. Increase of crystal / crucible diameter

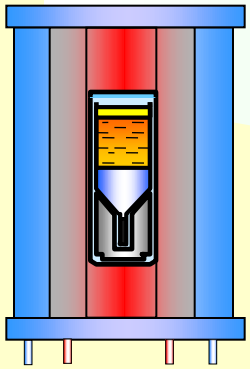


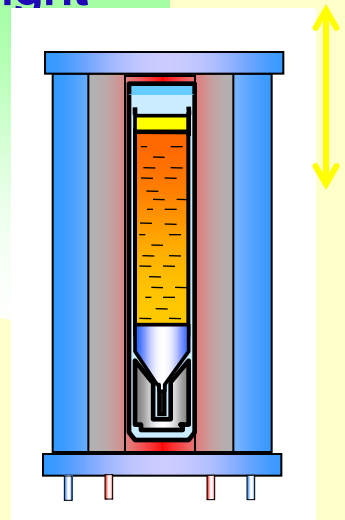


Czochralski

- ✓increased power input
- ✓melt turbulences

2. Lengthening of crystal / melt height



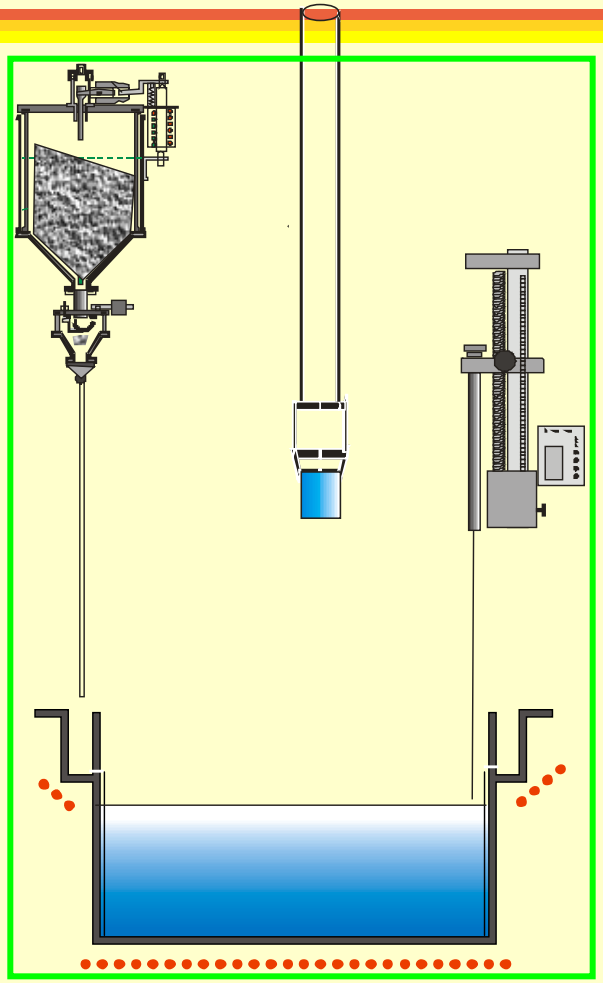


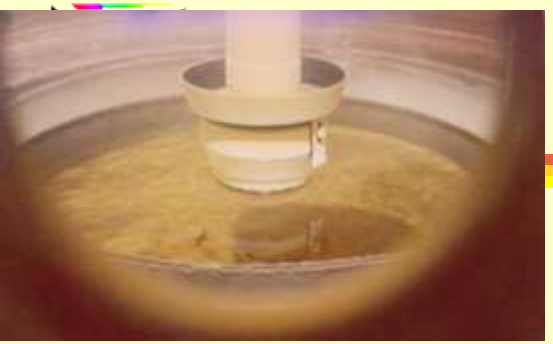
VGF

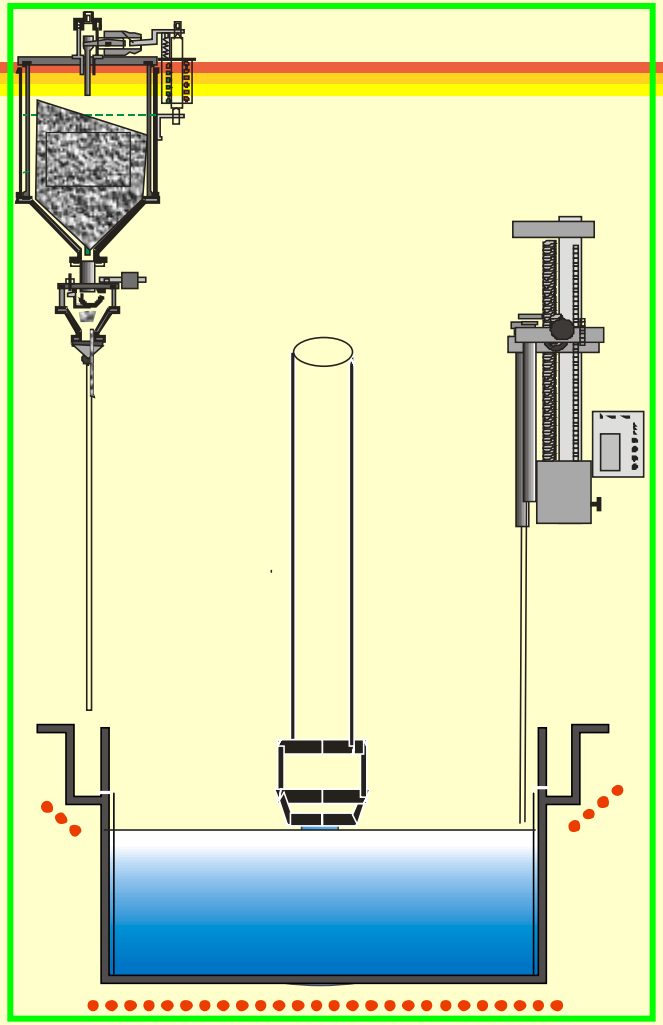
- ✓increased interaction with ampoule
- ✓increasing melt convection

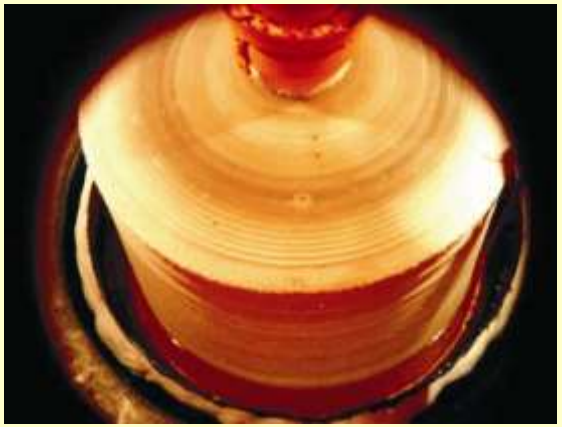
P.Rudolf, IWCGT 2008

Continuous growth procedure

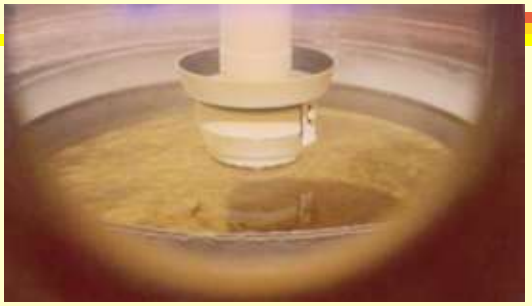


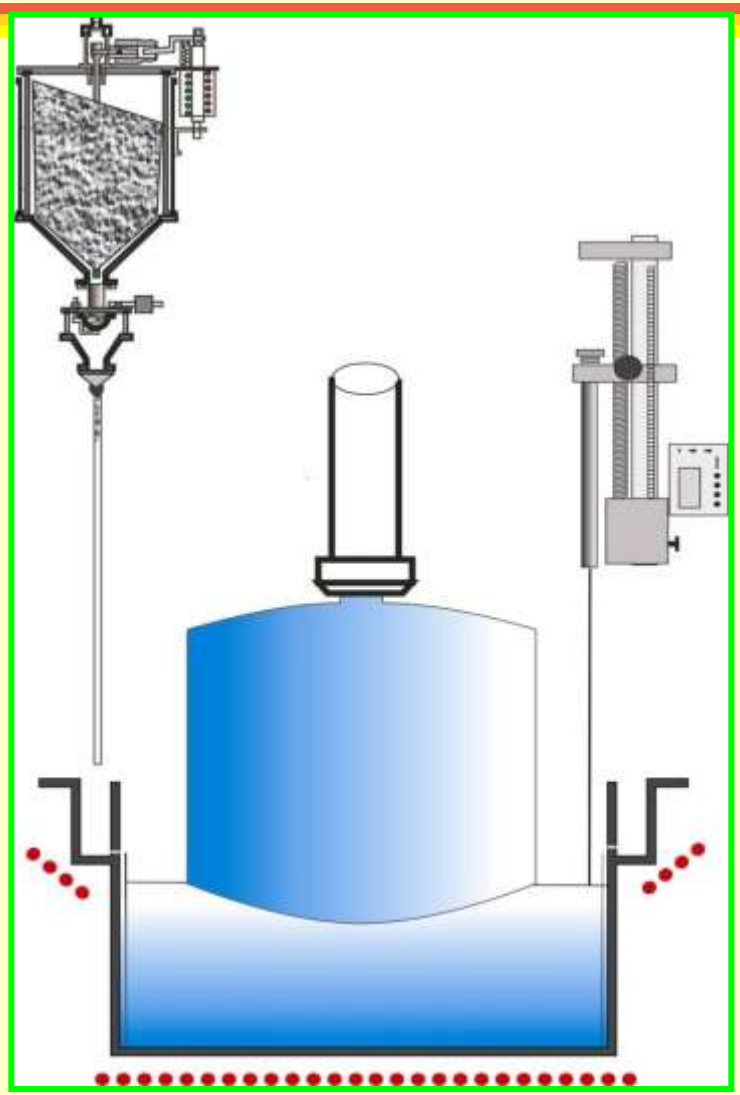


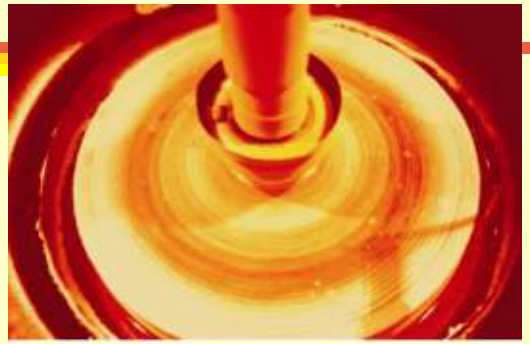


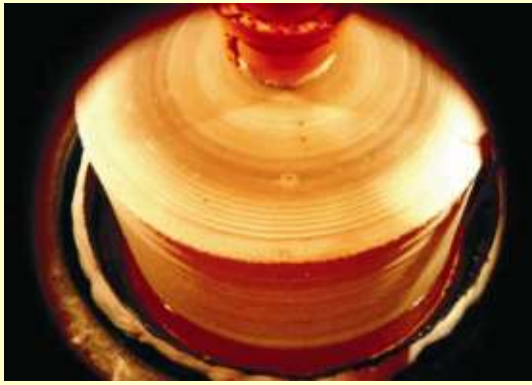


NaI(Tl) crystal continuous growth

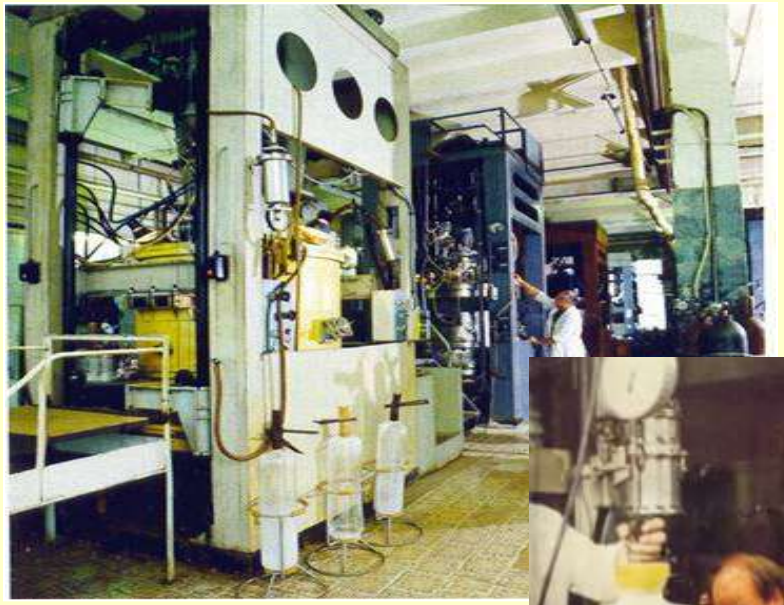








From Principles to Practice



NaI(Tl)
Industrial growth

Si – large size crystal growth

Si - industry is an example of efficient and cost reasonable crystals production

***Hygroscopicity is not a problem*!**

Raw material chemical chain

$$SrO + 2HI = SrI_2 + H_2O$$
$$SrCO_3 + 2HI = SrI_2 + H_2O + CO_2\uparrow$$

+ simple technology
– Need in high purity HI
– Some organics in HI potentially dangerous for SrI_2
– Pure HI cost

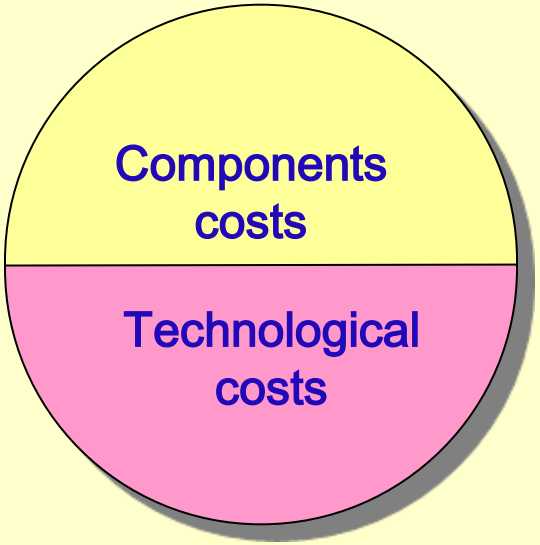
$$SrCO_3 + I_2 + 5N_2H_4 = SrI_2 + H_2O + CO_2\uparrow + N_2\uparrow$$
$$SrO + I_2 + 0{,}5N_2H_4 = SrI_2 + H_2O + N_2\uparrow$$

$$Sr(OH)_2 \bullet 8H_2O + I_2 + 0{,}5N_2H_4 = SrI_2 + H_2O + N_2\uparrow \ (\blacklozenge)$$

+ stable pure components is a good base for high quality RE iodides (SrI_2 in particular)
+ low components cost
– Toxicity

Target price for alkali-earth halides powder !?

Alkaline earth halides price



✓Sr and Ba price less then Cs one
✓Halide component is the same

✓Same or not so higher for alkali halides production

Lab level of production dictates the problems:

- ✓High price
- ✓Low purity level
- ✓Hydration problem

Current prices for halides powder

Product	*Producer*	*Price*
SrI_2	Russia USA India	4N $1200/kg 4N $3500/kg 2N $1300/kg
EuI_2 *	Russia USA	4N ~ $8000/kg 4N ~ $20000/kg
$BaBr_2$	Russia	4N ~$1000/kg
BaI_2	Russia	4N ~$1000/kg
CsI	USA Germany Ukraine	5N $150/kg 5N $160/kg 5N $150/kg

*Eu_2O_3 price $3500-4500/kg (base for EuI_2)

Current prices

Target price estimation for hydrated AE halides

Product name	*Price per anhydrous*
SrI_2 hydrate	$220-270/kilo
$BaBr_2$ hydrate	$150-200/kilo
BaI_2 hydrate	$150-200/kilo

Some reaction deteriorated scintillation crystal performance

$SrI_2 \cdot nH_2O = SrI_2 + nH_2O\uparrow$ … dehydration

$SrI_2 \cdot nH_2O = SrO$ or $Sr_5(IO_6)_2$ + … wrong dehydration technology

$SrI_2 + H_2O = SrO + 2HI$ … hydration

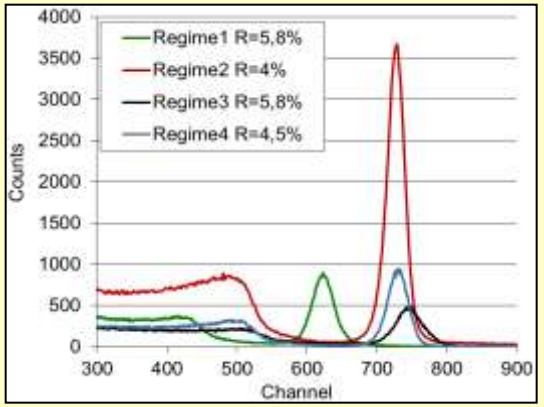
$2SrI_2 + O_2 = 2SrO + 2I_2$

$5SrI_2 + 6O_2 = Sr_5(IO_6)_2 + 4I_2$

$2SrI_2 + O_2 + 2CO_2 = 2SrCO_3 + 2I_2$

$2SrI_2 + 3O_2 + 2C = 2SrCO_3 + 2I_2$

C - as the trace of organics

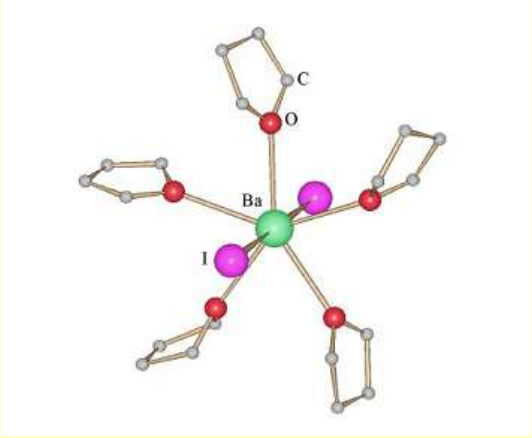


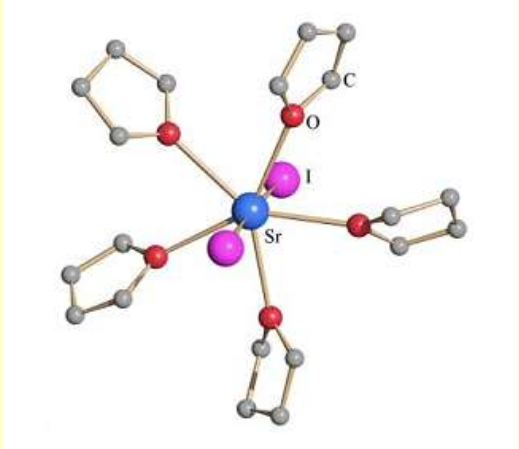
SrI_2 quality for the same raw material (3-4N) and different dehydration conditions

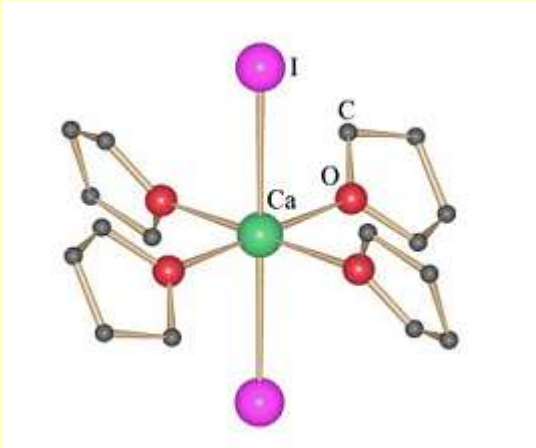
Potential structures on the AE halides

Table 1 X–M–X angles (°) of MX_2 in the gas phase[2]

MX_2	X = F	X = Cl	X = Br	X = I
BeX_2	180	180	180	180
MgX_2	180	180	180	180
CaX_2	133–155	180	173–180	180
SrX_2	108–135	120–143	133–180	161–180
BaX_2	100–117	100–127	95–135	102–105

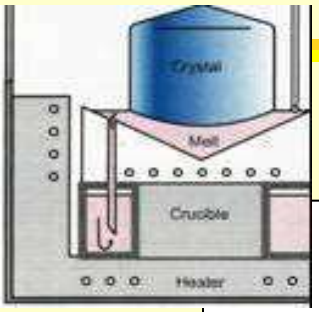


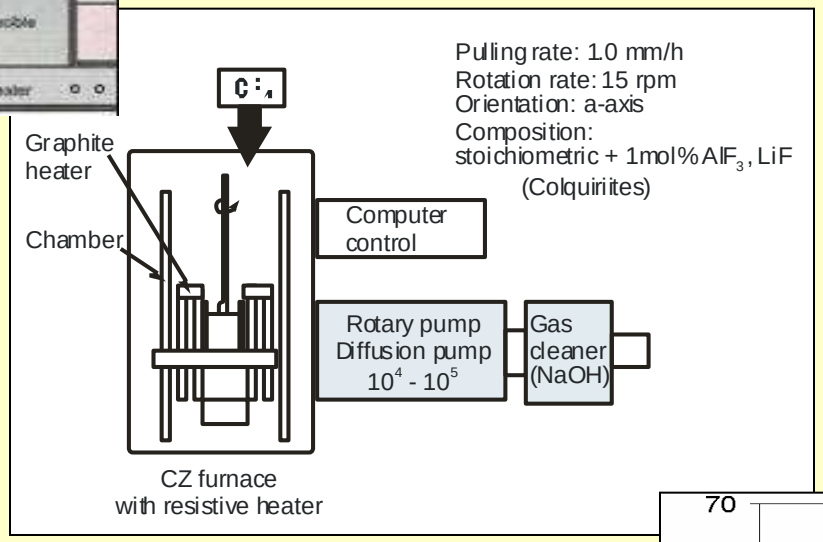




K. Fromm, 2002

Crystal purity – crystal quality





Growth "chemistry"

$MeO + 2HI \Leftrightarrow MeI_2 + H_2O$

$2MeO + C_2I_4 \Leftrightarrow 2MeI_2 + 2\,CO$

$2MeO + CI_4 \Leftrightarrow 2MeI_2 + CO_2$

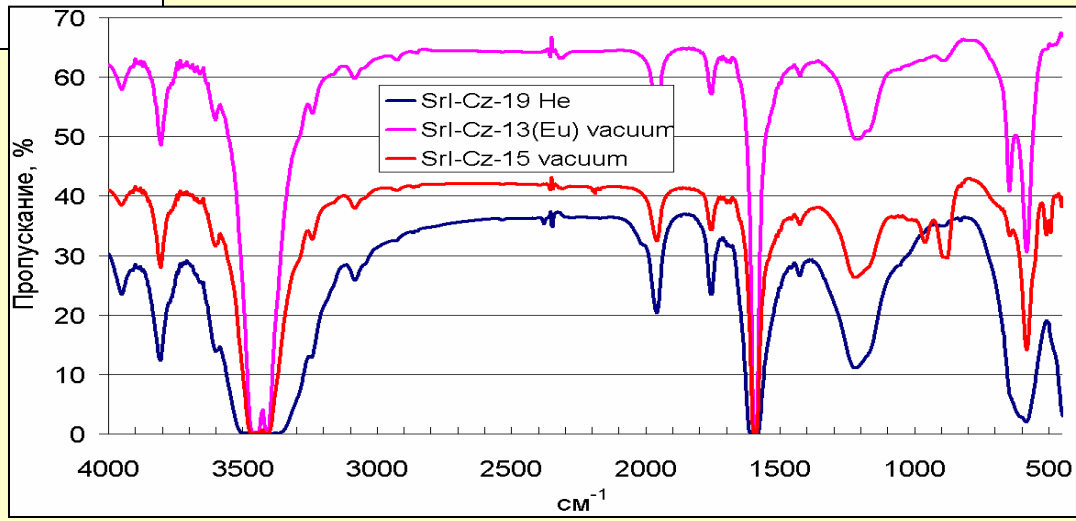
$2MeO + 2I_2 \Leftrightarrow 2MeI_2 + O_2$

$MeO + CI_4 \Leftrightarrow MeI_2 + CO + I_2$

$MeO + I_2 + CO \Leftrightarrow MeI_2 + CO_2$

IR spectra of SrI_2:Eu

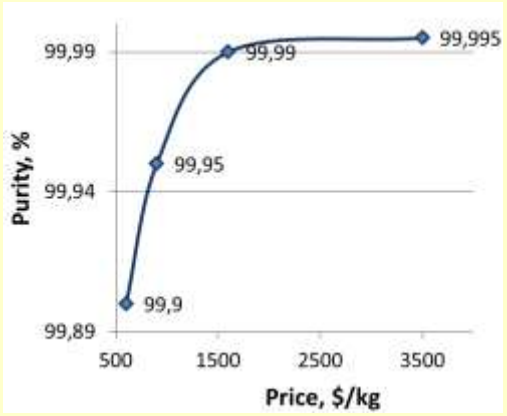
Peaks demonstrate oxygen impurities inside

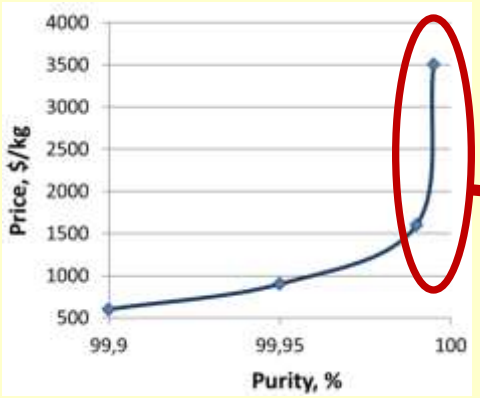


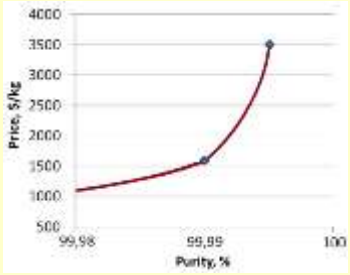
SrI_2:Eu
performance and cost vs. raw material purity

SrI_2. Raw material cost depending on purity

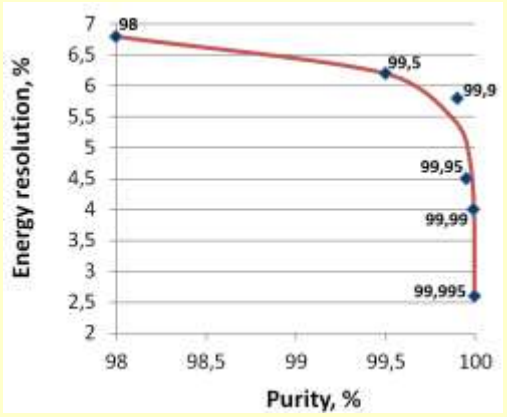
(Lab level)

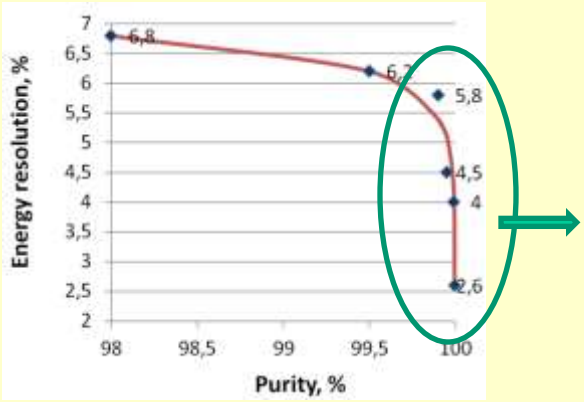


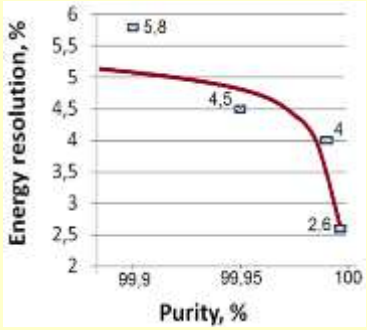




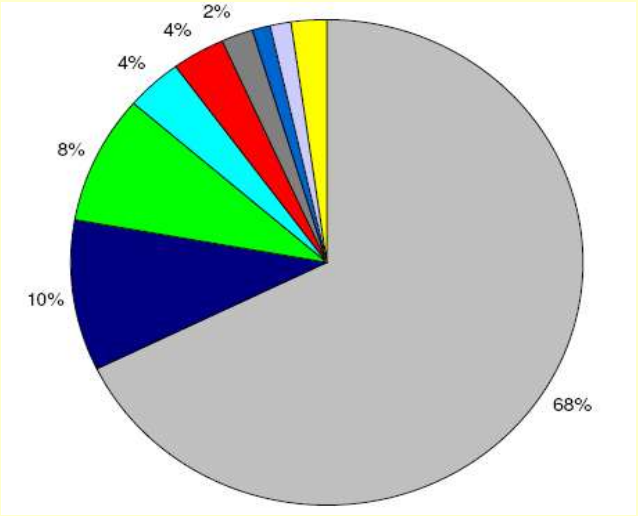
SrI_2:Eu. Energy resolution vs raw material purity

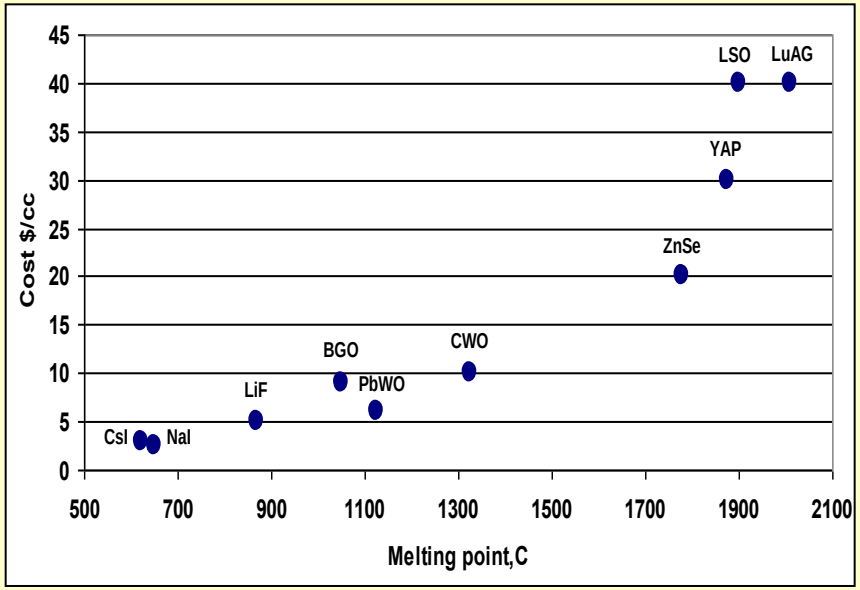






Cost structure for single crystal growth





2010 prices

Crystal cost structure (Si)

68% - raw material
10% - crucible
8% - system cost
4% - labor cost
4% - power
6% - other

Oxides

20% - crucible
17% - power

- Natural “bottle neck” (self-absorption)

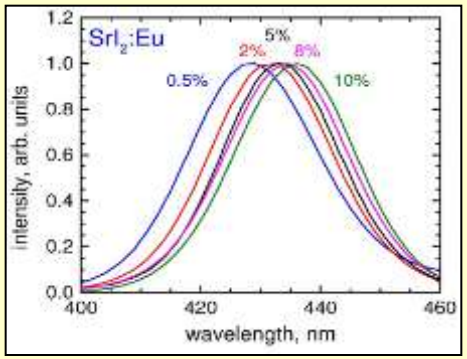
  and *overpass ways*

Self-absorption

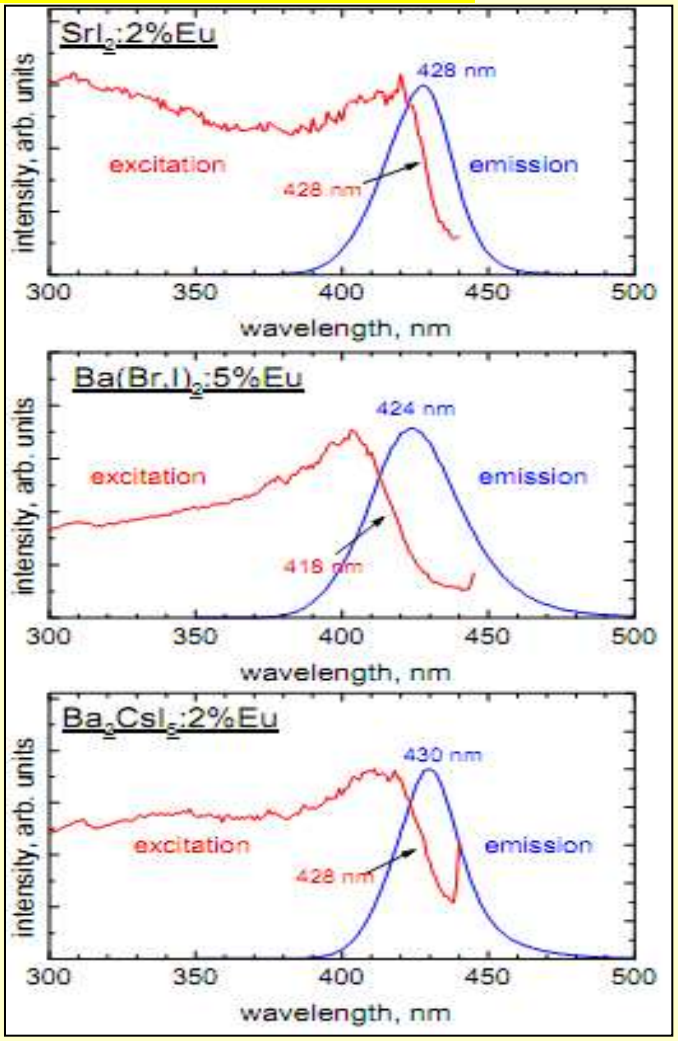
Self-absorption due to small Stokes shift is the key problem for large bulk Eu doped scintillator use

This is a typical for all Eu doped crystals !!!

Self-absorption lead to the low transparency and scintillator efficiency loss



J.Glodo et al. 2010

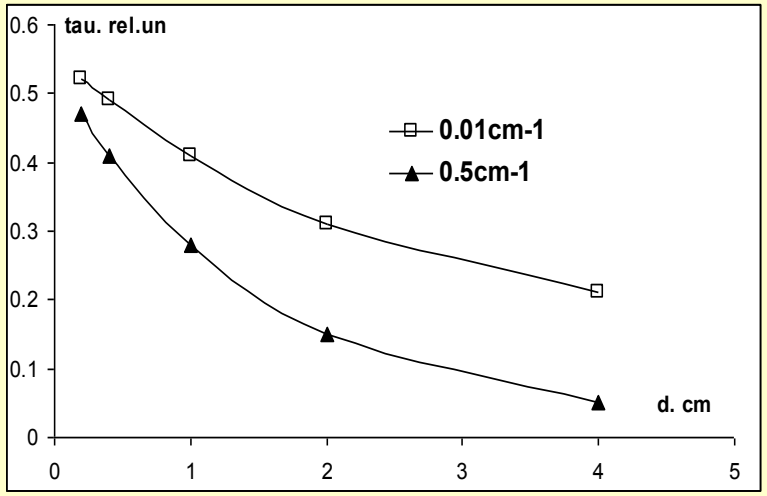


E. Bourret, S. Derenzo et al., 2009, 2010, 2011

Stokes shifts in Eu-doped scintillators

Crystal	Stokes shift, eV
Alkali halides	
NaI (Tl)	1.35
NaI (Eu)	0.8
CsI (Tl)	1.93
CsI (Na)	2.07
CsI (In)	1.83
CsI (Eu)	0.8
Alkali-earth halides	
SrI_2 (Eu)	0.15
CaI_2 (Eu)	0.30
Ba_2CsI_5 (Eu)	0.15
$CsSrI_3$ (Eu)	0.55
BaBrI (Eu)	0.40

AE scintillator have a small Stokes shift and low transparency



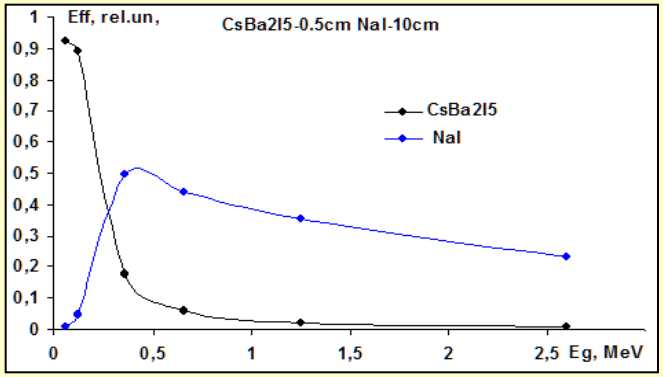
Light collection for high (0.01 cm^{-1}) and low (0.5 cm^{-1}) transparent crystals

V.A. Tarasov, ISMA, 2011

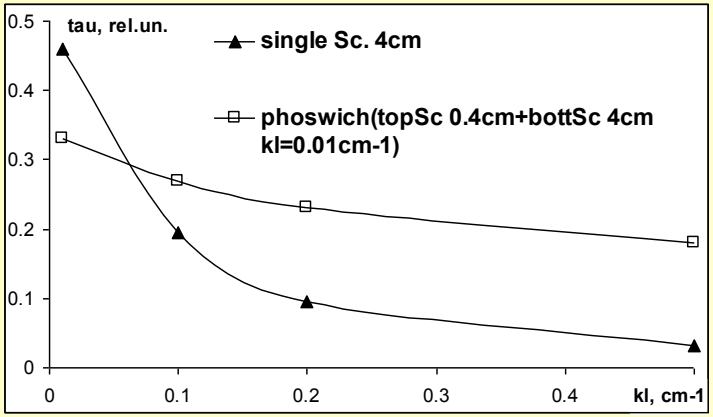
Resume:

Bulk Eu-doped scintillator could not be efficient scintillators

Combined (phoswich) detectors as a way to increase scintillator efficiency

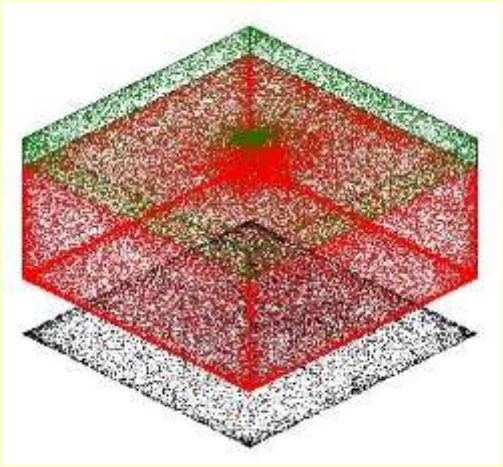


Gamma registration efficiency at 0.06 – 2.65 MeV for 0.5 cm thick $SrI_2(Eu)$ combined with 10 cm NaI(Tl)



Light collection coefficient for SrI_2:Eu and $SrI_2(Eu)$+NaI(Tl) phoswich detectors *4 cm thickness*

Phoswich detector scheme



Signal separation due to decay time difference

SrI_2 :Eu	1200ns
NaI : Tl	230ns
BaBrI :Eu	500ns
$CsBa_2I_5$:Eu	383; 1200ns
CsI : Tl	980ns

V.A. Tarasov, ISMA, 2012

Conclusions

✓The maximal CsI or NaI scintillation yield corresponds to STE relaxation at LNT and less then fundamental limit

✓Thermalization length is much higher than Onsager radius in alkali halides – therefore geminate recombination yield is much less then unity. This is a key issue for the high yield limitation

✓Alkali-earth halides are the best choice for the efficient scintillator development

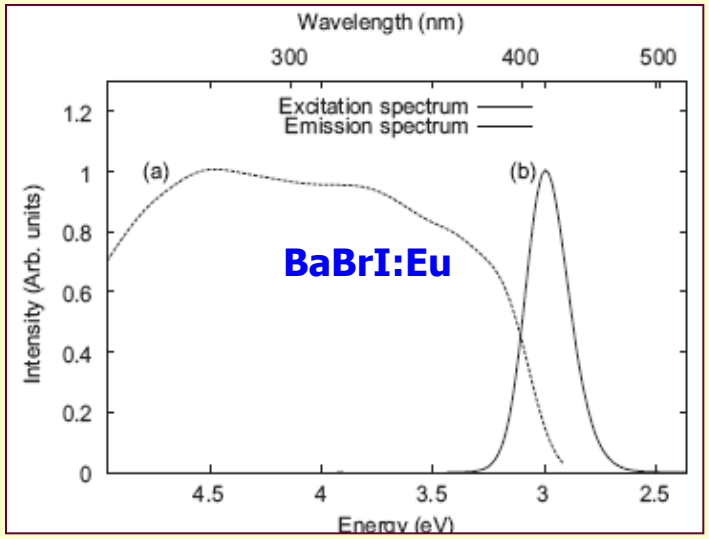
✓AE scintillator obtain claim for the chemical and crystal growth R&D before transfer to industrial technology. The target price for new scintillator has to be reasonable

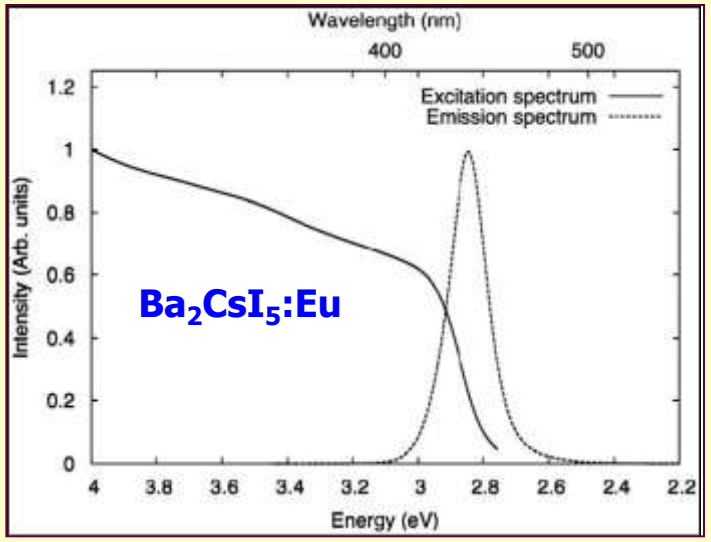
THANK YOU FOR ATTENTION!

Self-absorption in BaBrI:Eu and Ba_2CsI_5:Eu crystals

Crystal	ρ g/cm³	Lum, nm	LY ph/Mev	R, % Cs^{137}	Decay, ns
BaBrI :Eu	5.3	~413	81000	4,8	~500
Ba_2CsI_5:Eu	4.8	435	97000	3.8	383; 1500

Excitation and luminescence. Re-absorption





[E. Bourret, S. Derenzo et al., 2009, 2010, 2011]

Thermalization length is much higher than Onsager radius in alkali halides – therefore geminate recombination yield is much less then unity, other electrons and holes recombine in bimolecular way with large unavoidable losses and afterglow, and high non-proportionality at both ends of the curve