ISMA

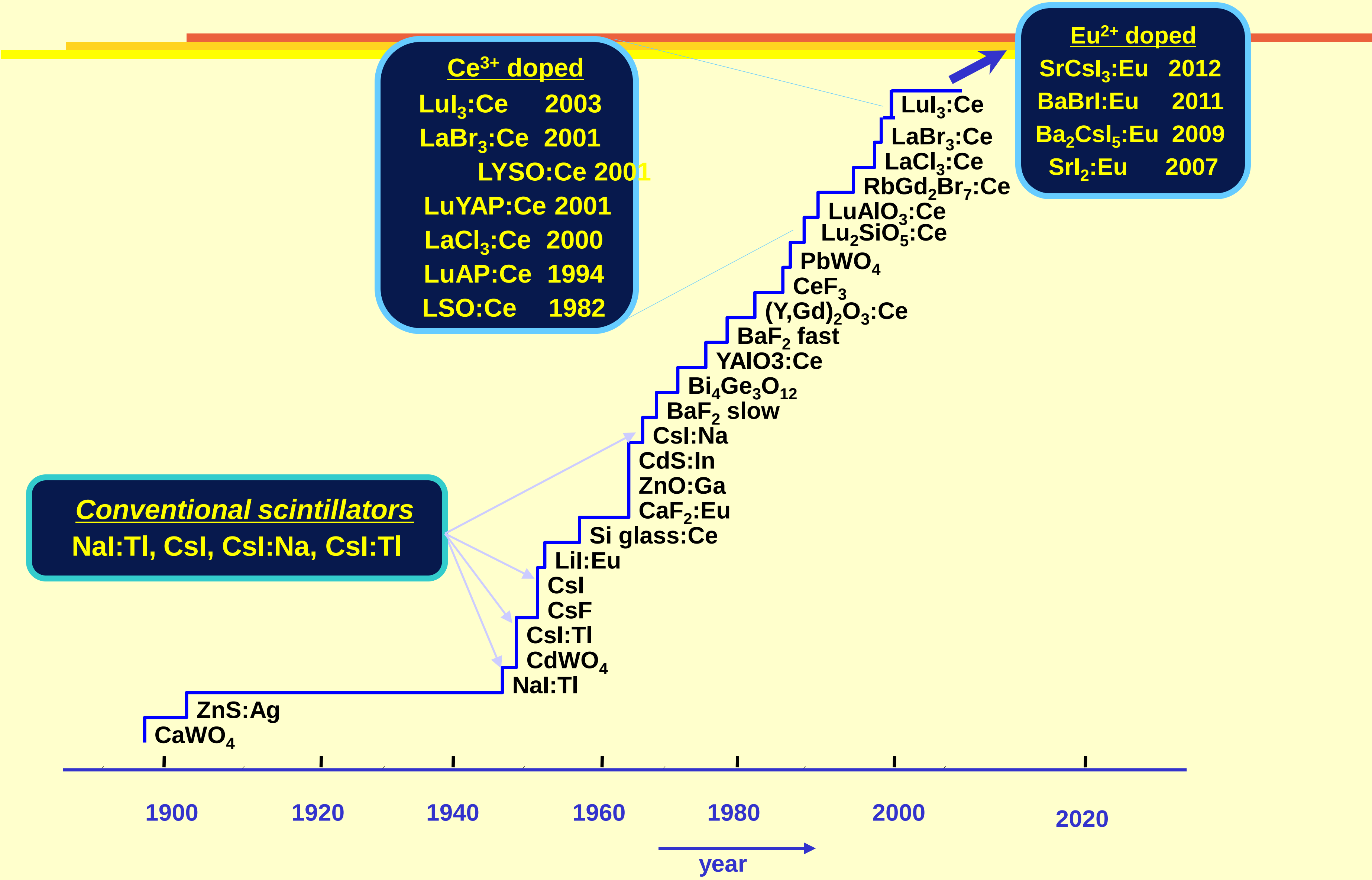
Last trends in scintillators development; theory and practice

<u>A. Gektin,</u>   **A.Vasil'ev**

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

Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University, Leninskie Gory 1(2), 119991, Moscow, Russia

Scintillation discovery



Ce^{3+} doped

LuI_3:Ce 2003

$LaBr_3$:Ce 2001

LYSO:Ce 2001

LuYAP:Ce 2001

$LaCl_3$:Ce 2000

LuAP:Ce 1994

LSO:Ce 1982

Eu^{2+} doped

$SrCsI_3$:Eu 2012

BaBrI:Eu 2011

Ba_2CsI_5:Eu 2009

SrI_2:Eu 2007

Conventional scintillators

NaI:Tl, CsI, CsI:Na, CsI:Tl

LuI_3:Ce

$LaBr_3$:Ce

$LaCl_3$:Ce

$RbGd_2Br_7$:Ce

$LuAlO_3$:Ce

Lu_2SiO_5:Ce

$PbWO_4$

CeF_3

$(Y,Gd)_2O_3$:Ce

BaF_2 fast

YAlO3:Ce

$Bi_4Ge_3O_{12}$

BaF_2 slow

CsI:Na

CdS:In

ZnO:Ga

CaF_2:Eu

Si glass:Ce

LiI:Eu

CsI

CsF

CsI:Tl

$CdWO_4$

NaI:Tl

ZnS:Ag

$CaWO_4$

NaI(Tl) way to Crystal Ball

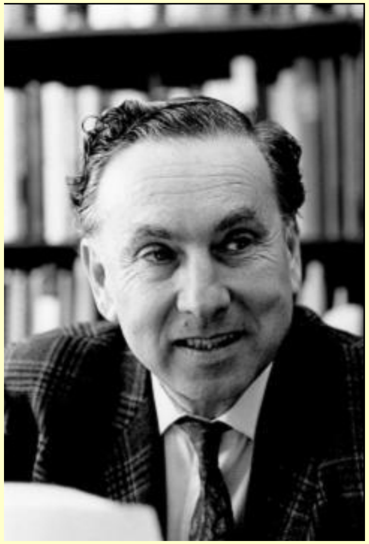
1949 – NaI(Tl) invention
1963 – Gamma-camera prototype

↓

Large NaI(Tl) needs

Harshaw Chemical Company

1952 – 0,5“ dia growth
1974 – 21” dia growth



Dr.Carl Swinehart
In Harshaw from
1932 to 1990

R&D supervisors !!! :
Prof. R.Hofstadter (Stanford)

and Dr. D.Stockbarger (MIT)

Scanned at the American Institute of Physics

ISMA, Scintillator Developments

New scintillator ? **New projects?**

2011-12 LPS

2007 LGSO

2004 dedicated imaging system

2000 SPECT

1994 CsI(Tl) CRYSTALS of 525 kg WEIGHT

1992 PWO

1989 CsI(CO_3)

1987 UNDOPED CsI SINGLE CRYSTALS

1986 $CdWO_4$, $BiGe_3O_{12}$

1985 "CRYSTAL" TECHNOLOGY

1978 "ROST" TECHNOLOGY

1974 ZnSe(Te)

1964 CsI(Na)

1961 PMMA

1959 NaI(Tl)

1955 ISC WAS FOUNDED

2012 – CALIFA (FAIR)

2008 GLAST (Int. NASA)

2007 AGILE (EC)

2005 NEMO (Int. NASA)

2005 OPERA (EC)

2000 PiBeta (Switzerland)

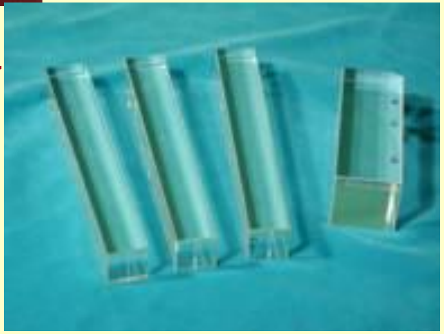
1998 BaBar (USA)

1996 BELLE (Japan)

1992-2008 LHC (CERN)

PWO - INNOVATION AT HIGH ENERGY PHYSICS CRYSTAL

L.Nagornaya



Material: PWO
Invention: 1991

PWO milestones:

1992 : Crystal-2000; PWO promotion

1994 : Choice of PWO for CMS e-cal

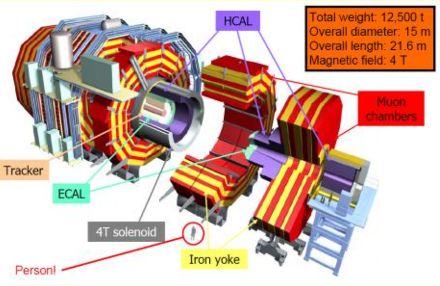
1994-1998 : extensive R&D on PWO

1998-2000 : Preproduction of 6000 crystals

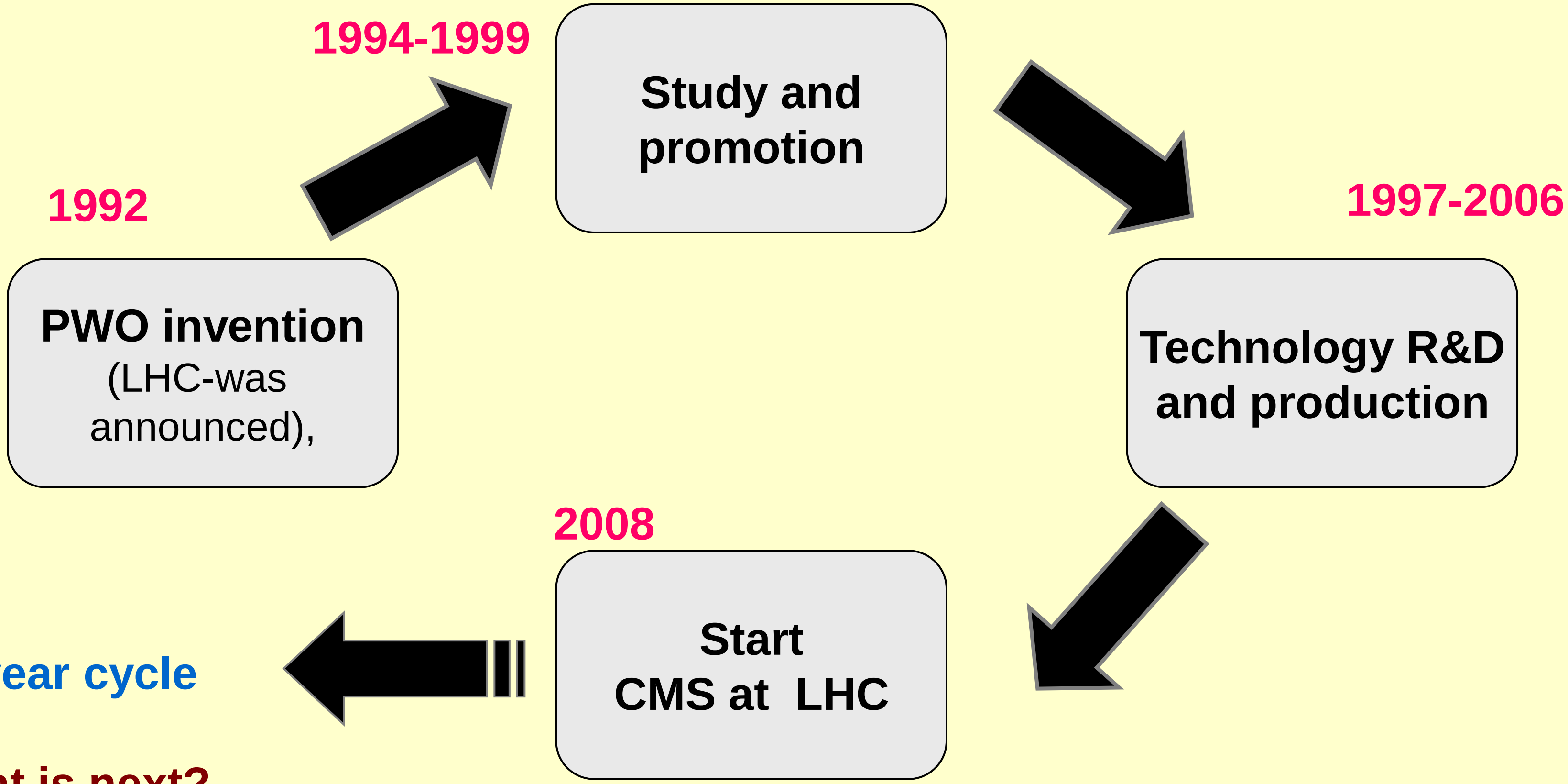
2001 : Start of the production

2008: E-cal complete

LHC - CERN



PbWO$_4$(PWO) cycle. From invention to LHC use



1992

PWO invention
(LHC-was announced),

1994-1999

Study and promotion

1997-2006

Technology R&D and production

2008

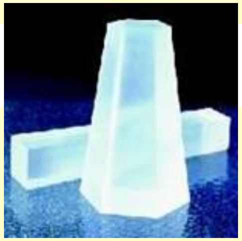
Start
CMS at LHC

17 year cycle

What is next?

ISMA for International Collaborations

High Energy and Nuclear Physics



CMS

PANDA

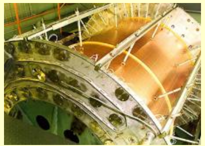
NEMO

OPERA

BELLE (Japan)

BaBar (USA)

PiBeta (Switzerland)

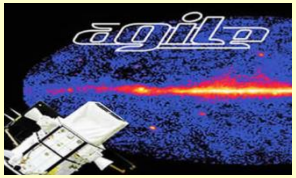


KEDR

CALIFA (FAIR)

Space Missions

GLAST (USA, Sweden…)



AGILE (Italy)

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:

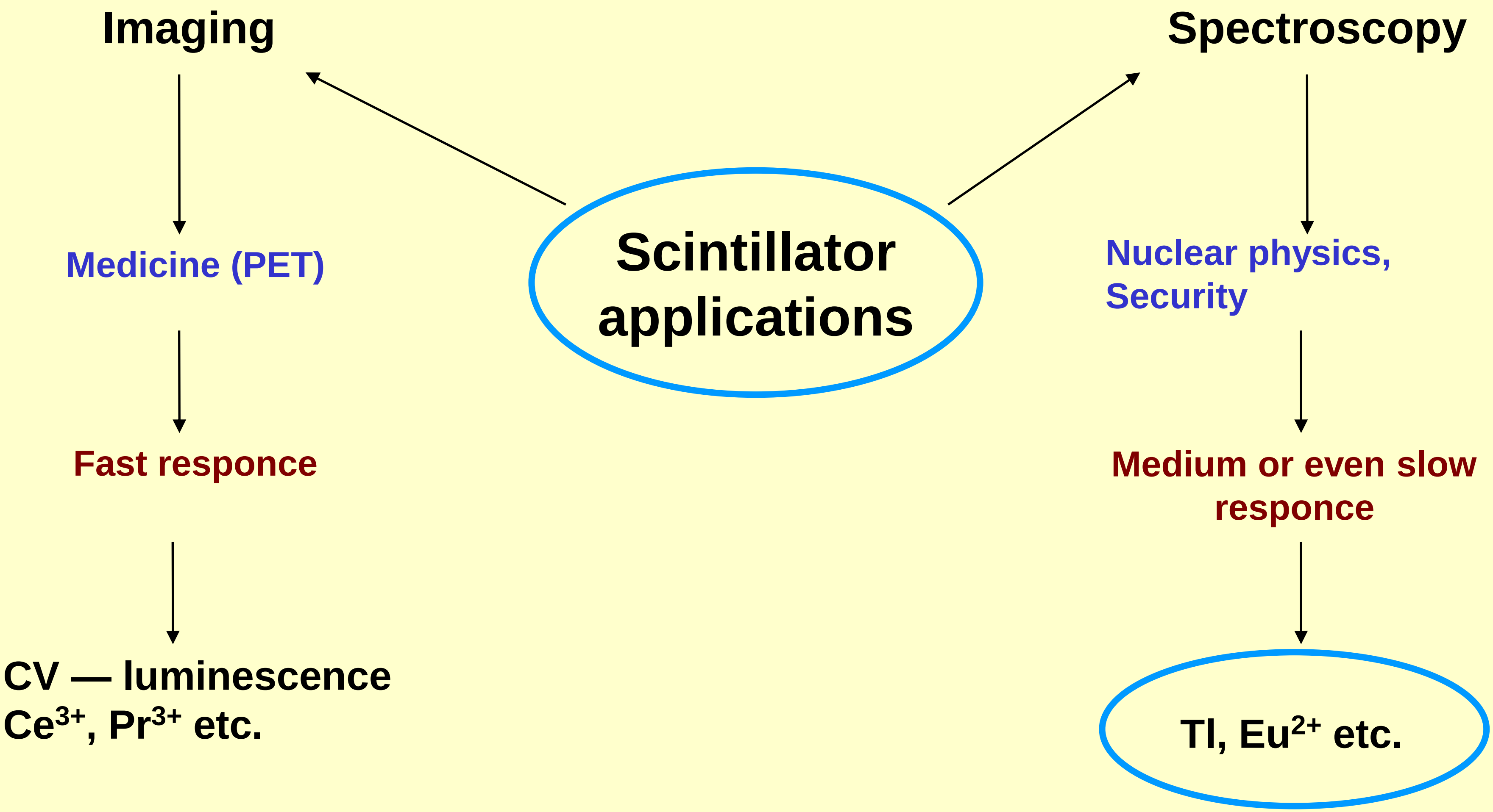
A - search of new compounds (Successfully done!)

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

B - modification of conventional scintillators

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

Logics and motivation



Scintillator applications

Imaging

Medicine (PET)

Fast responce

CV — luminescence
Ce^{3+}, Pr^{3+} etc.

Spectroscopy

Nuclear physics,
Security

Medium or even slow responce

Tl, Eu^{2+} etc.

Most efficient new scintillators

Crystal	ρ g/cm^3	Lum λ, nm	LY ph/Mev	R, % Cs^{137}	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	

Maximal scintillator light yield

Scintillator efficiency:

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

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

E_γ *quantum energy*

$E_{e\text{-}h}$ $= \sim 2.4\, E_g$

S *energy transfer efficiency*

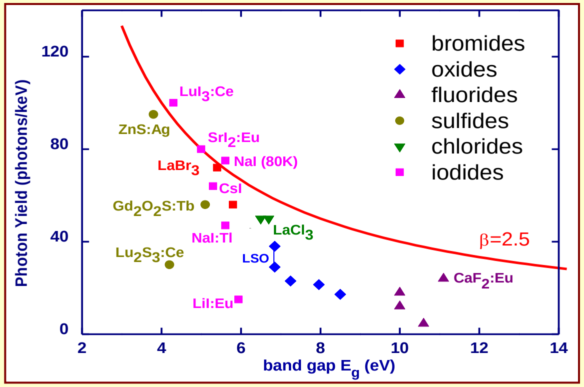
Q *luminescence center efficiency*

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

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). *Overpass ways*

Cascade

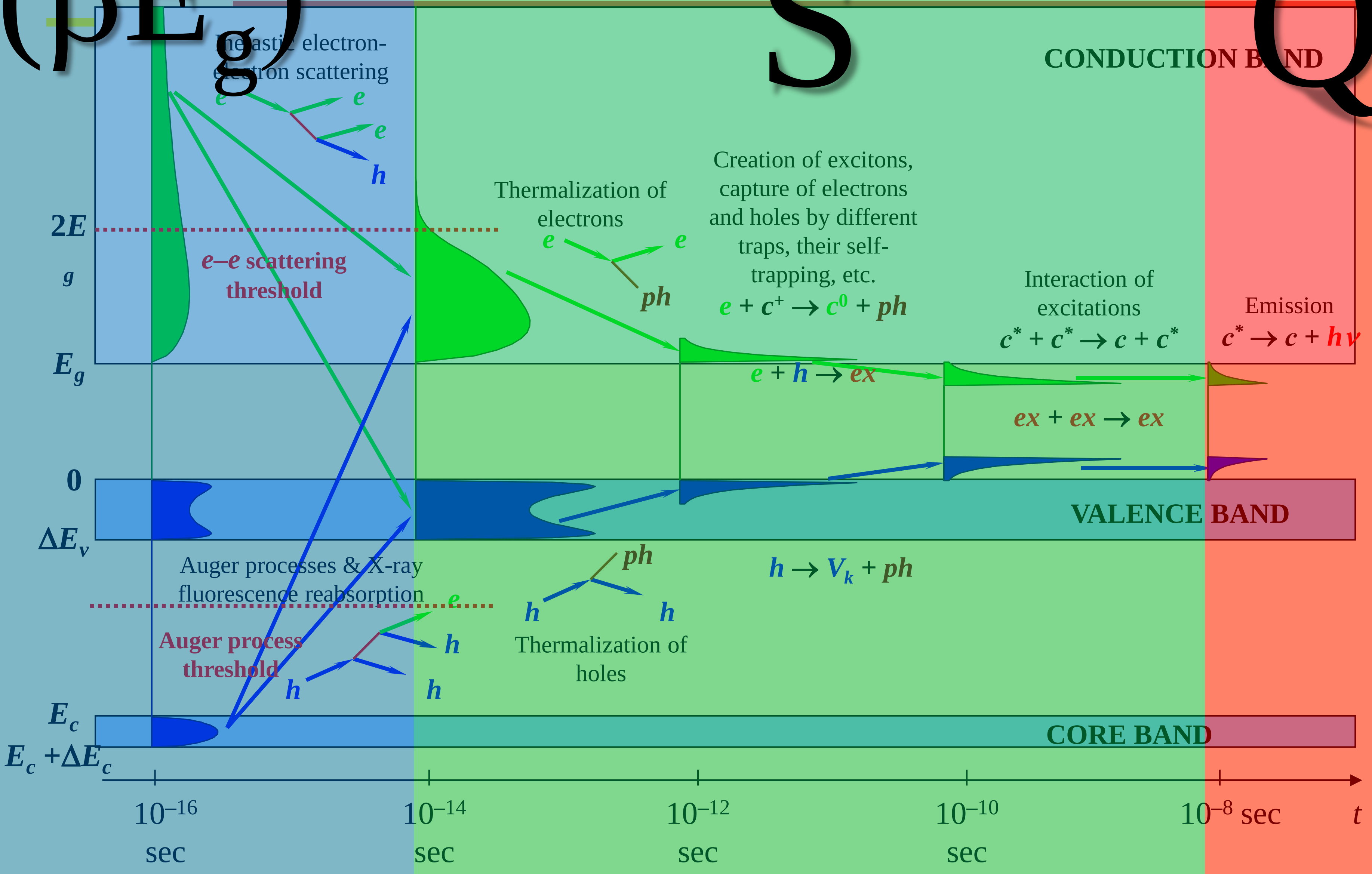
$$(\beta E_g)^{-1}$$

Transport

$$S$$

Center

$$Q$$



Inelastic electron-electron scattering

e–e scattering threshold

Auger processes & X-ray fluorescence reabsorption

Auger process threshold

Thermalization of electrons

Thermalization of holes

Creation of excitons, capture of electrons and holes by different traps, their self-trapping, etc.

$e + c^+ \to c^0 + ph$

$e + h \to ex$

$ex + ex \to ex$

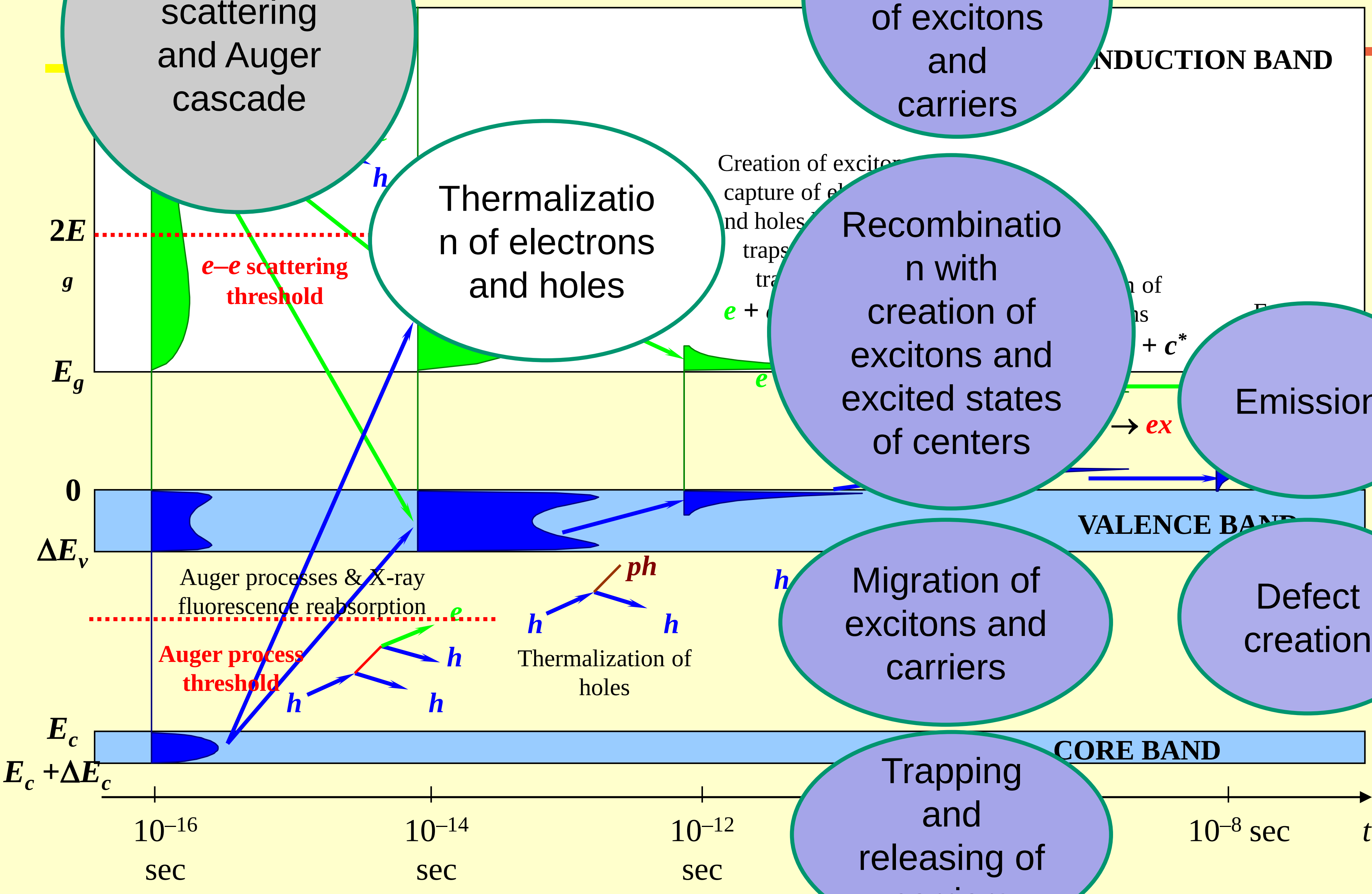
$h \to V_k + ph$

Interaction of excitations

$c^* + c^* \to c + c^*$

Emission

$c^* \to c + h\nu$



Electron scattering and Auger cascade

Thermalization of electrons and holes

Interaction and quenching of excitons and carriers

Recombination with creation of excitons and excited states of centers

Emission

Migration of excitons and carriers

Defect creation

Trapping and releasing of carriers

Electron scattering and Auger cascade

Thermalization of electrons and holes

Interaction and quenching of excitons and carriers

Recombination with creation of excitons and excited states of centers

Emission

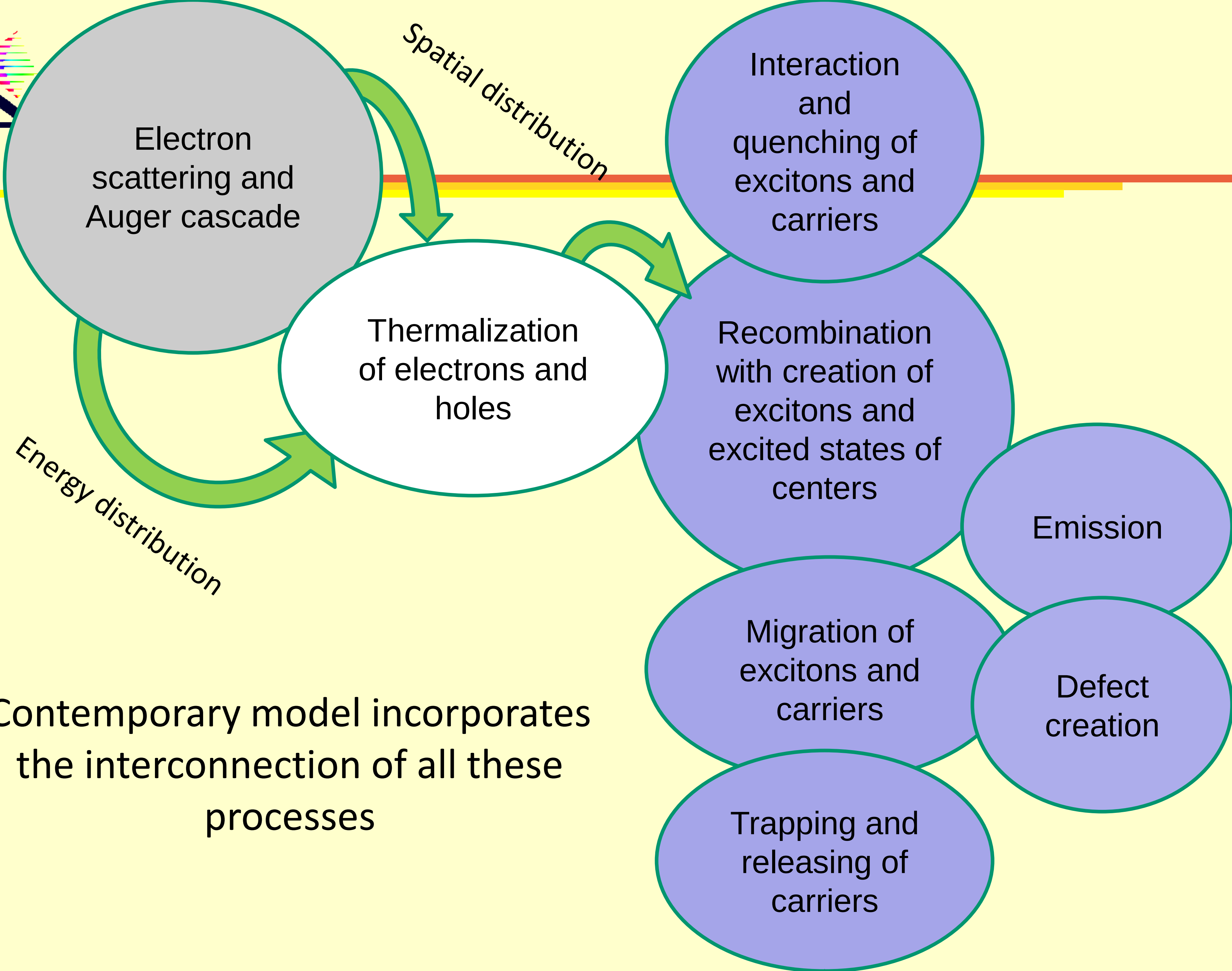
Migration of excitons and carriers

Defect creation

Trapping and releasing of carriers

Are these processes independent?

NO!



Electron scattering and Auger cascade

Spatial distribution

Energy distribution

Thermalization of electrons and holes

Interaction and quenching of excitons and carriers

Recombination with creation of excitons and excited states of centers

Emission

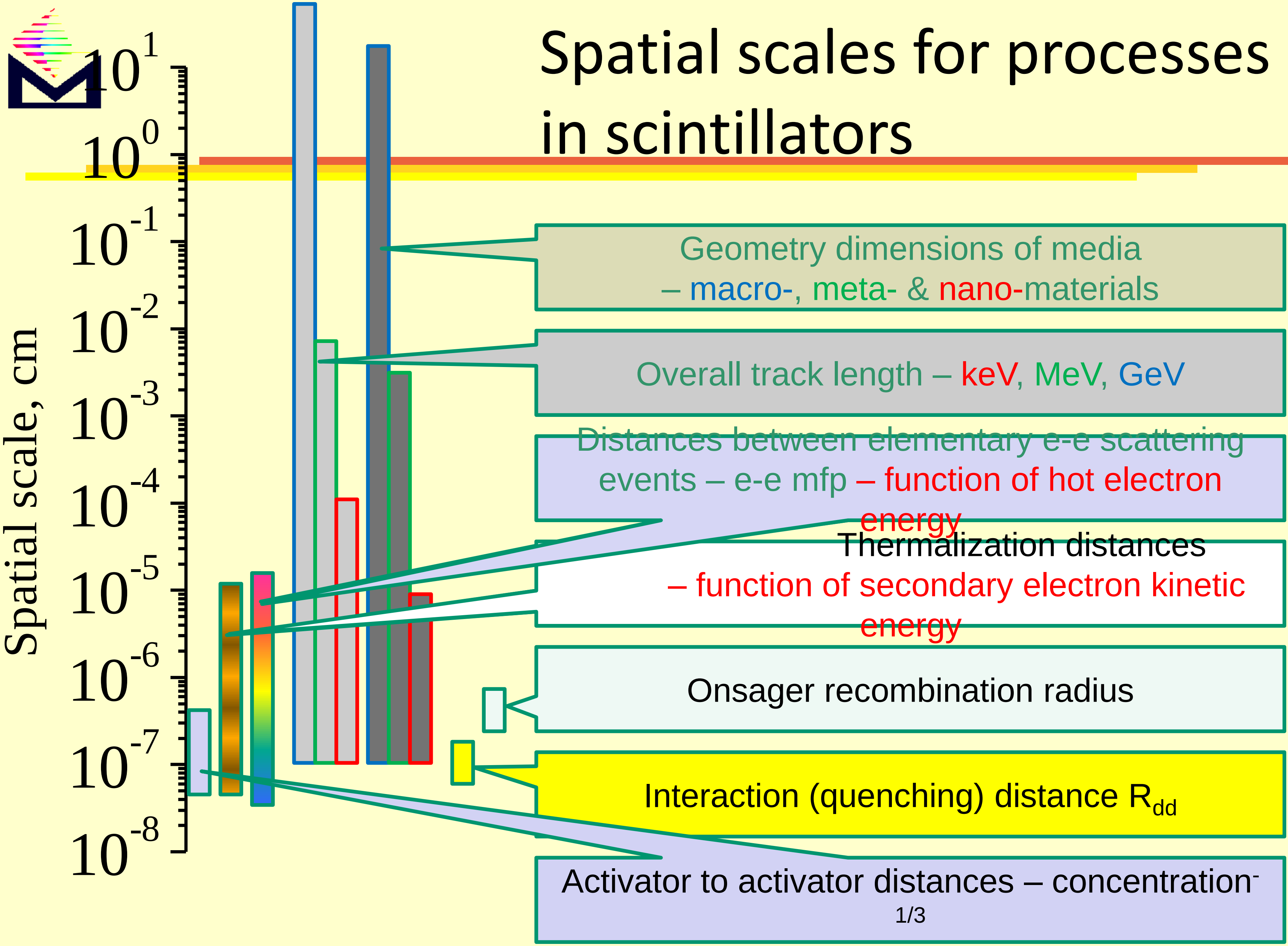
Migration of excitons and carriers

Defect creation

Trapping and releasing of carriers

Contemporary model incorporates the interconnection of all these processes

Spatial scales for processes in scintillators



Geometry dimensions of media – macro-, meta- & nano-materials

Overall track length – keV, MeV, GeV

Distances between elementary e-e scattering events – e-e mfp – function of hot electron energy

Thermalization distances – function of secondary electron kinetic energy

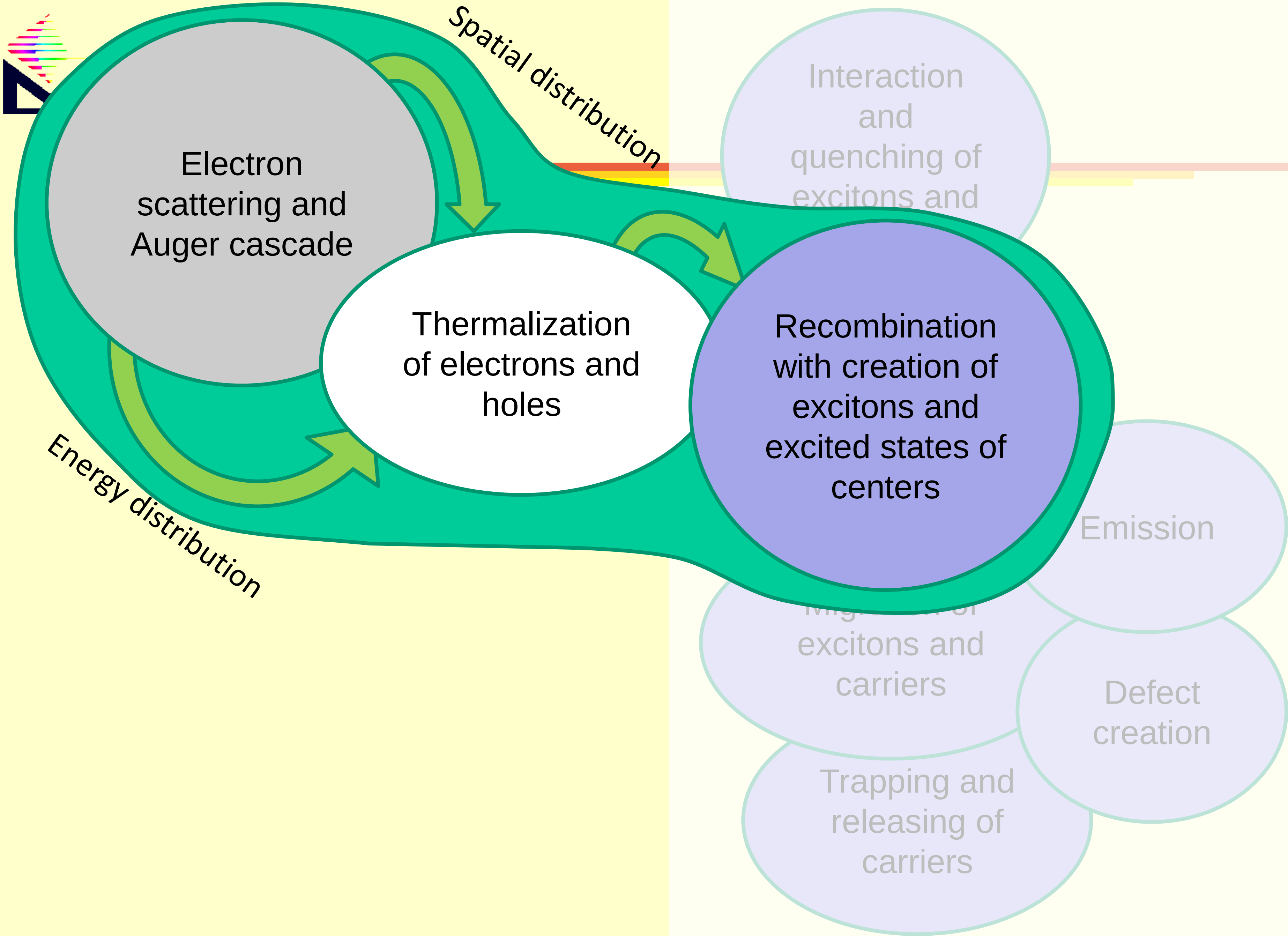
Onsager recombination radius

Interaction (quenching) distance R_{dd}

Activator to activator distances – concentration$^{-1/3}$

Outline

- Spatial scales for processes in scintillators
- Nanoparticles as scintillators
- Cascade, thermalization and recombination
- Different types of mobilities
- Thermalization length for different types of crystals
- Interconnection of cascade, thermalization and recombination stages in binary iodides
- Why cascade is so effective in CsI?
- Thermalization length and impurities
- Concluding remarks



Electron scattering and Auger cascade

Thermalization of electrons and holes

Recombination with creation of excitons and excited states of centers

Spatial distribution

Energy distribution

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Emission

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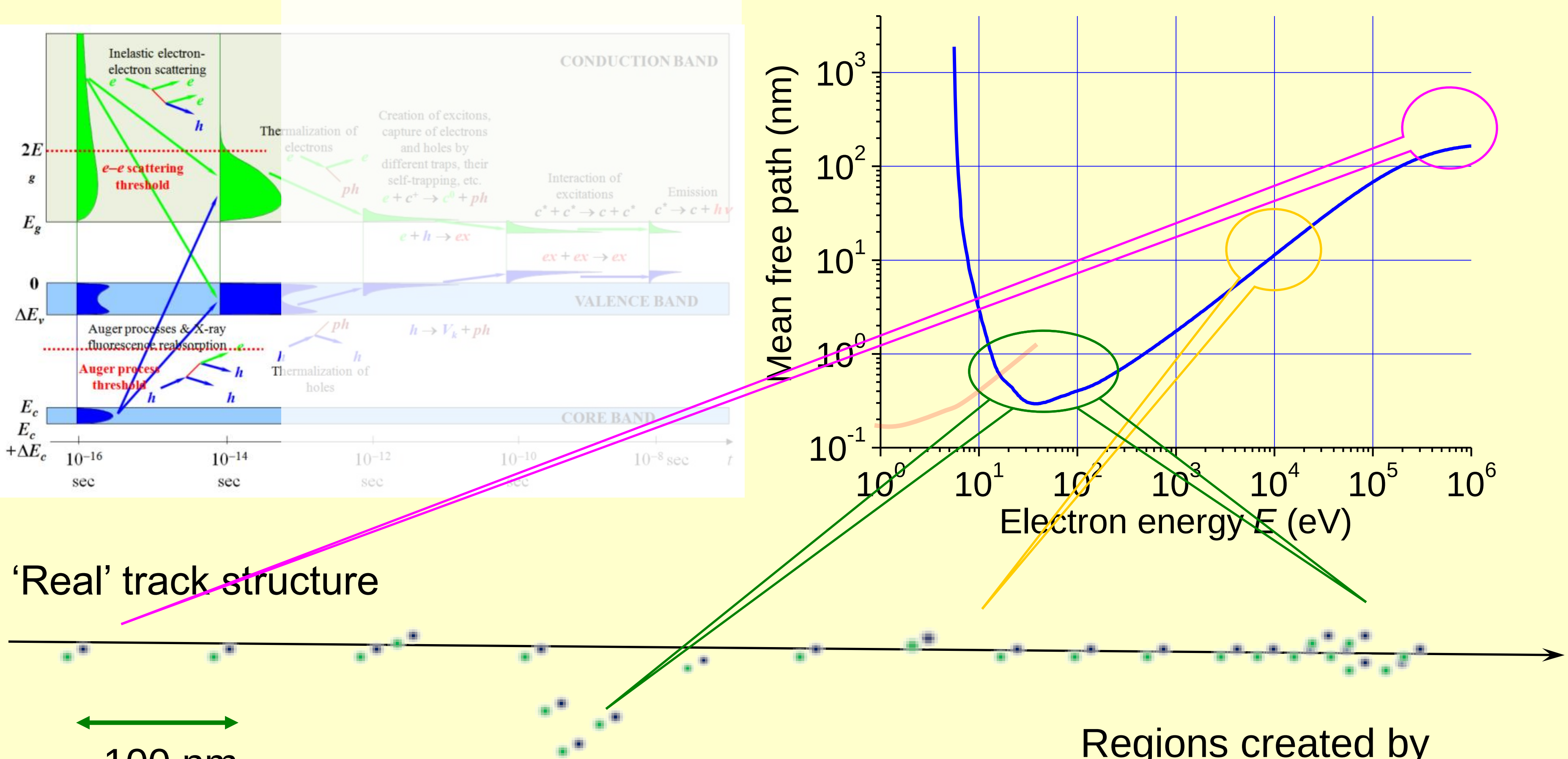
Spatial track structure for e-e scattering stage

(prior to thermalization)

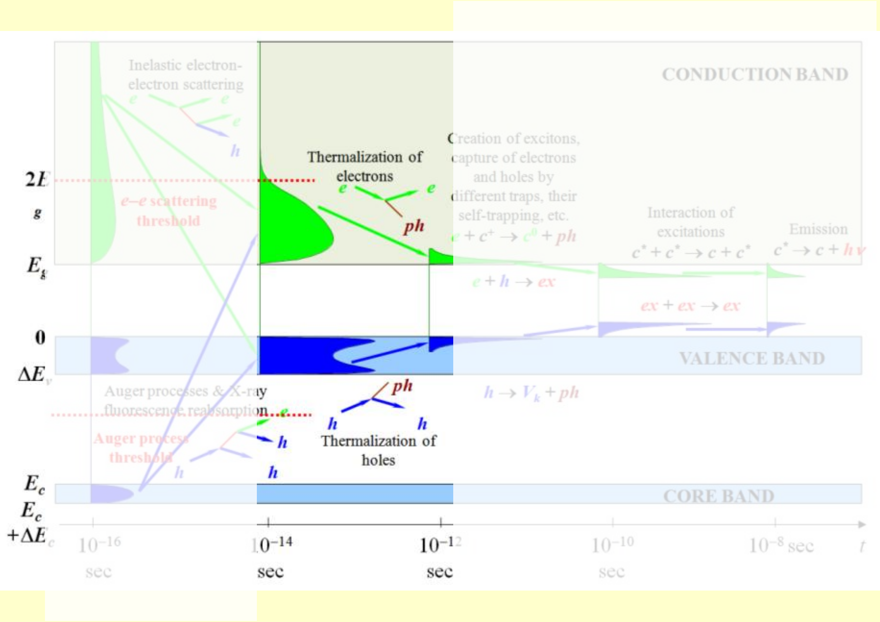


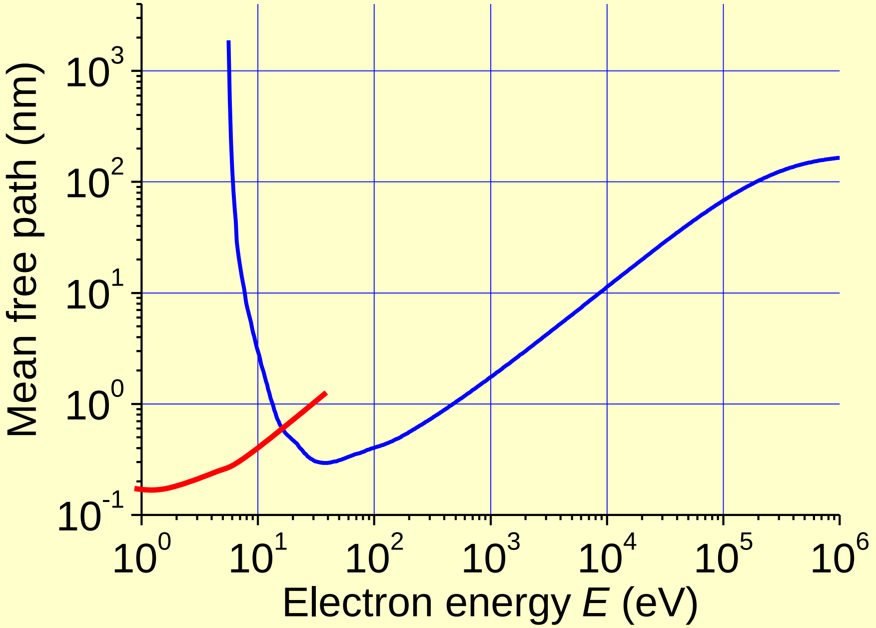
‘Real’ track structure

100 nm

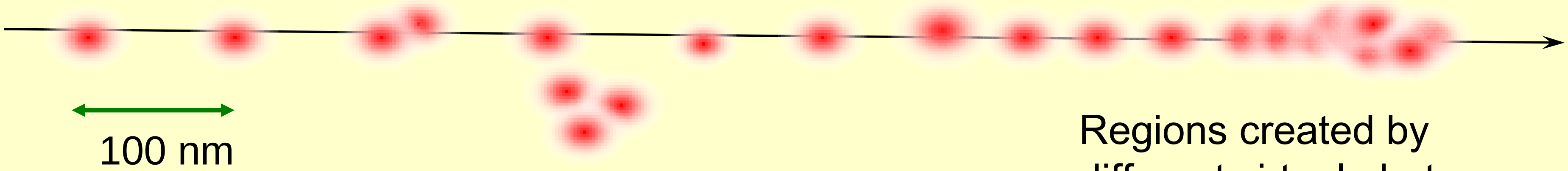
Regions created by different virtual photons are overlapped

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



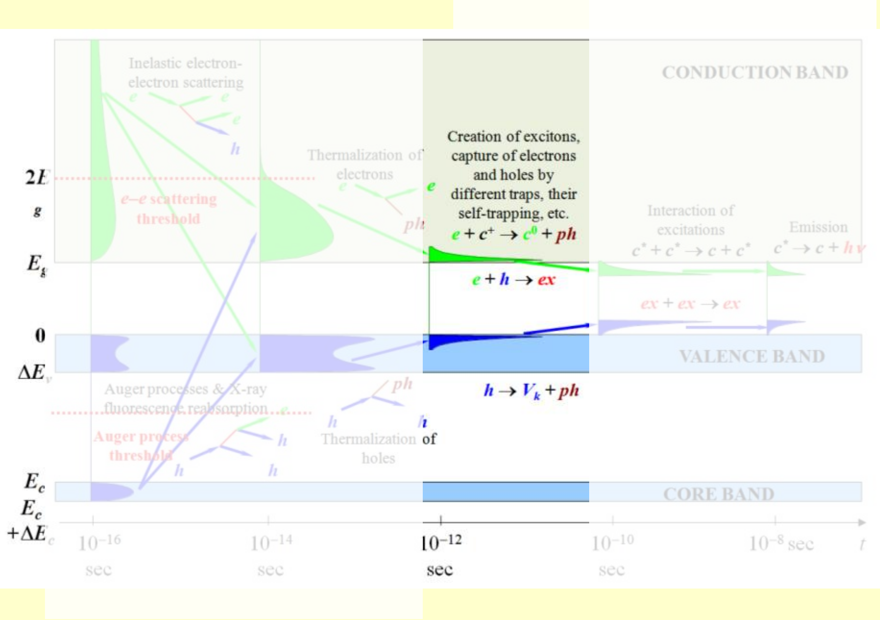


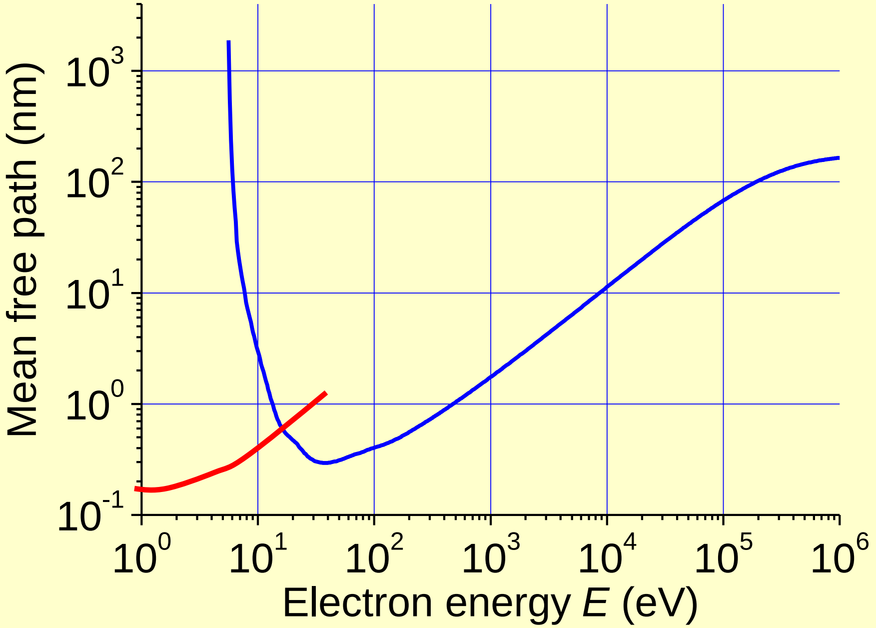
‘Real’ track structure



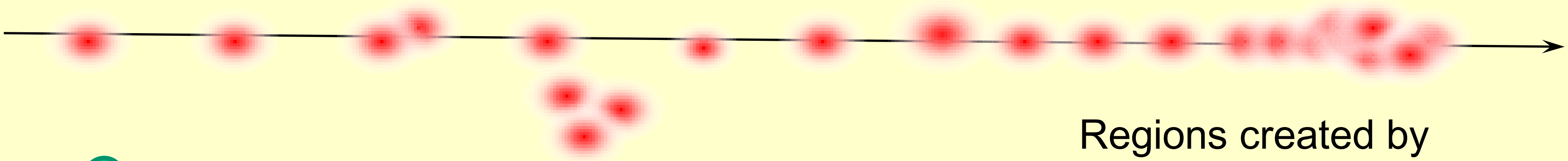
Regions created by different virtual photons are overlapped

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





‘Real’ track structure

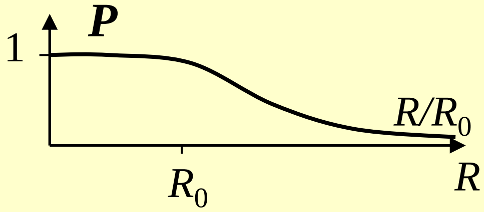


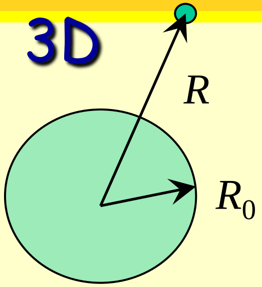
● Onsager radius10 nm

Regions created by different virtual photons are overlapped

3D diffusion-controlled recombination

Recombination probability





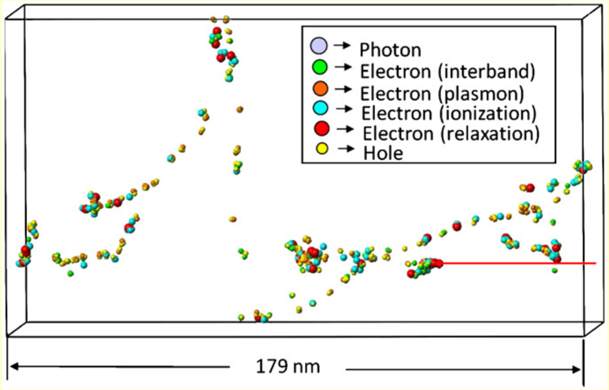
Black sphere $P = \begin{cases} 1, & r_{eh} < R_0 \\ R_0/r_{eh}, & r_{eh} > R_0 \end{cases}$

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

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

ε=5.7	T=300K	R_{Ons}=10 nm
	T=77K	R_{Ons}=38 nm
	T=10K	R_{Ons}=300 nm ???

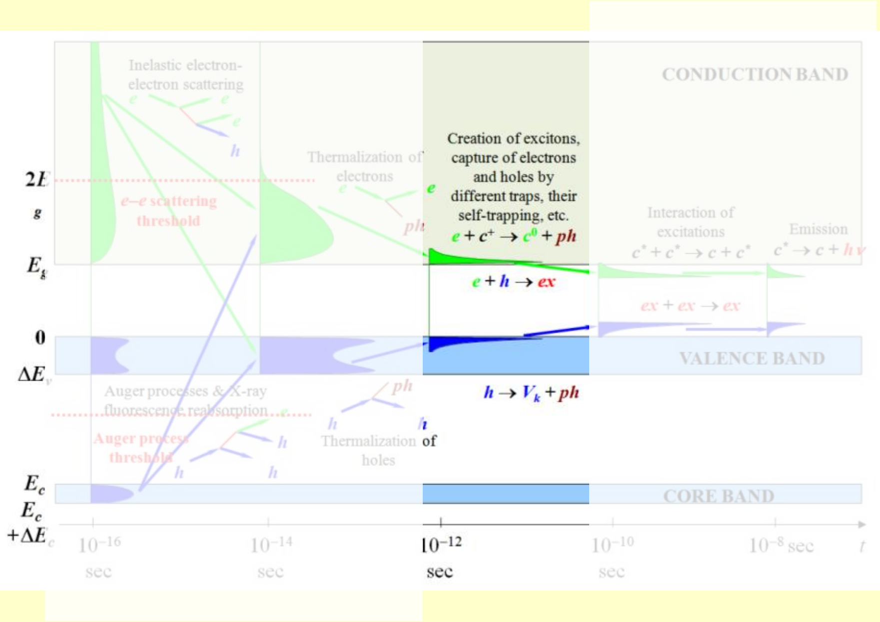
For thermalized excitations $R_{Ons}/r_{eh} << 1$
– exciton yield after thermalization should be low

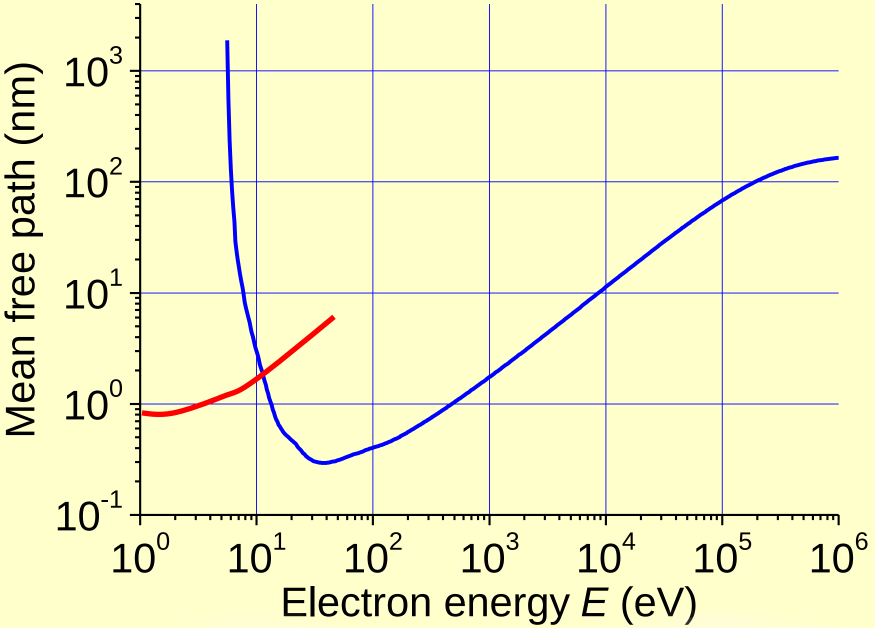


Simulated spatial distribution of e–h pairs for a 10 keV photon event in CsI,
where electrons and holes are distinguished by size and color, as indicated in legend.
NWEGRIM code.

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

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

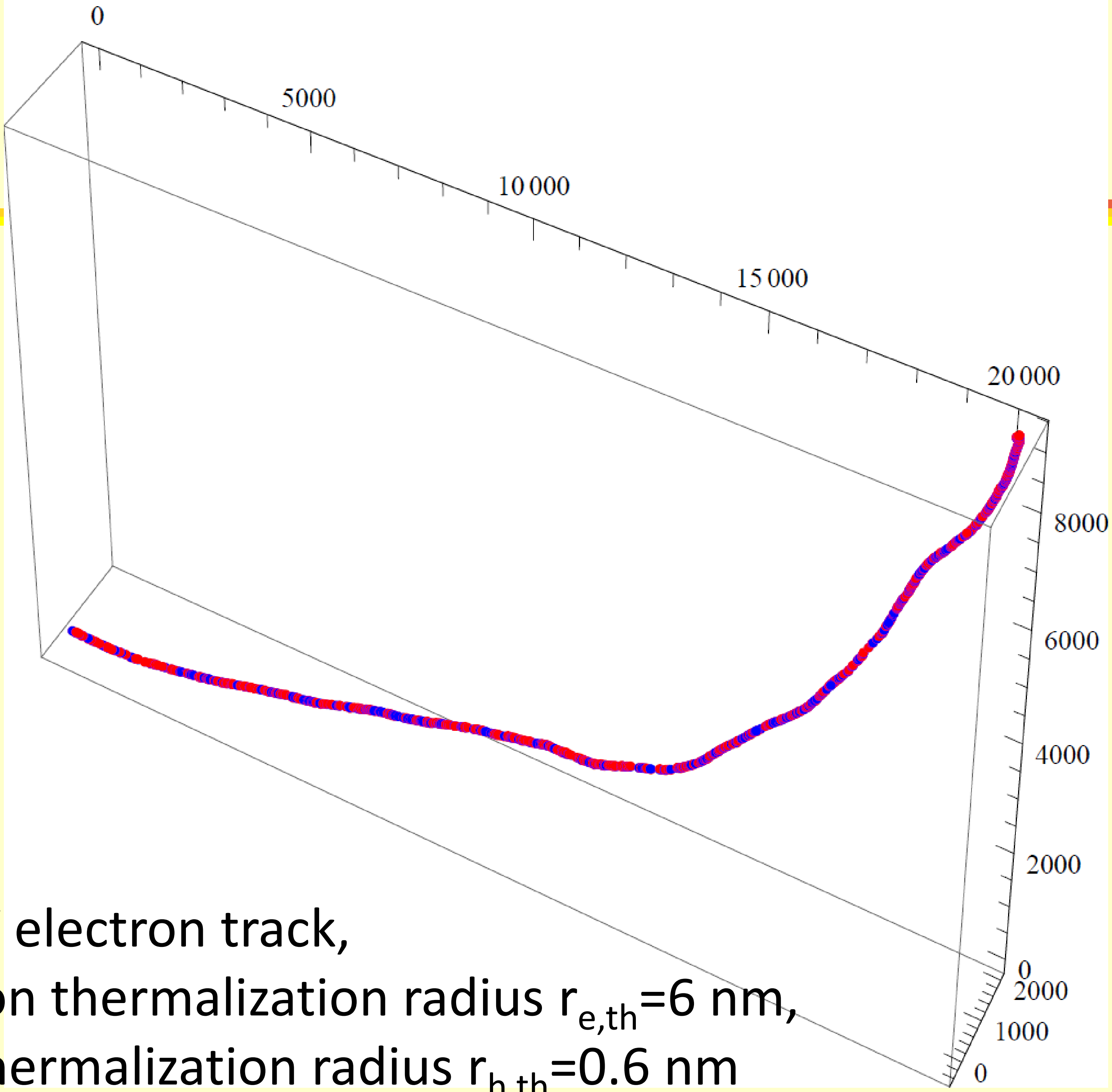




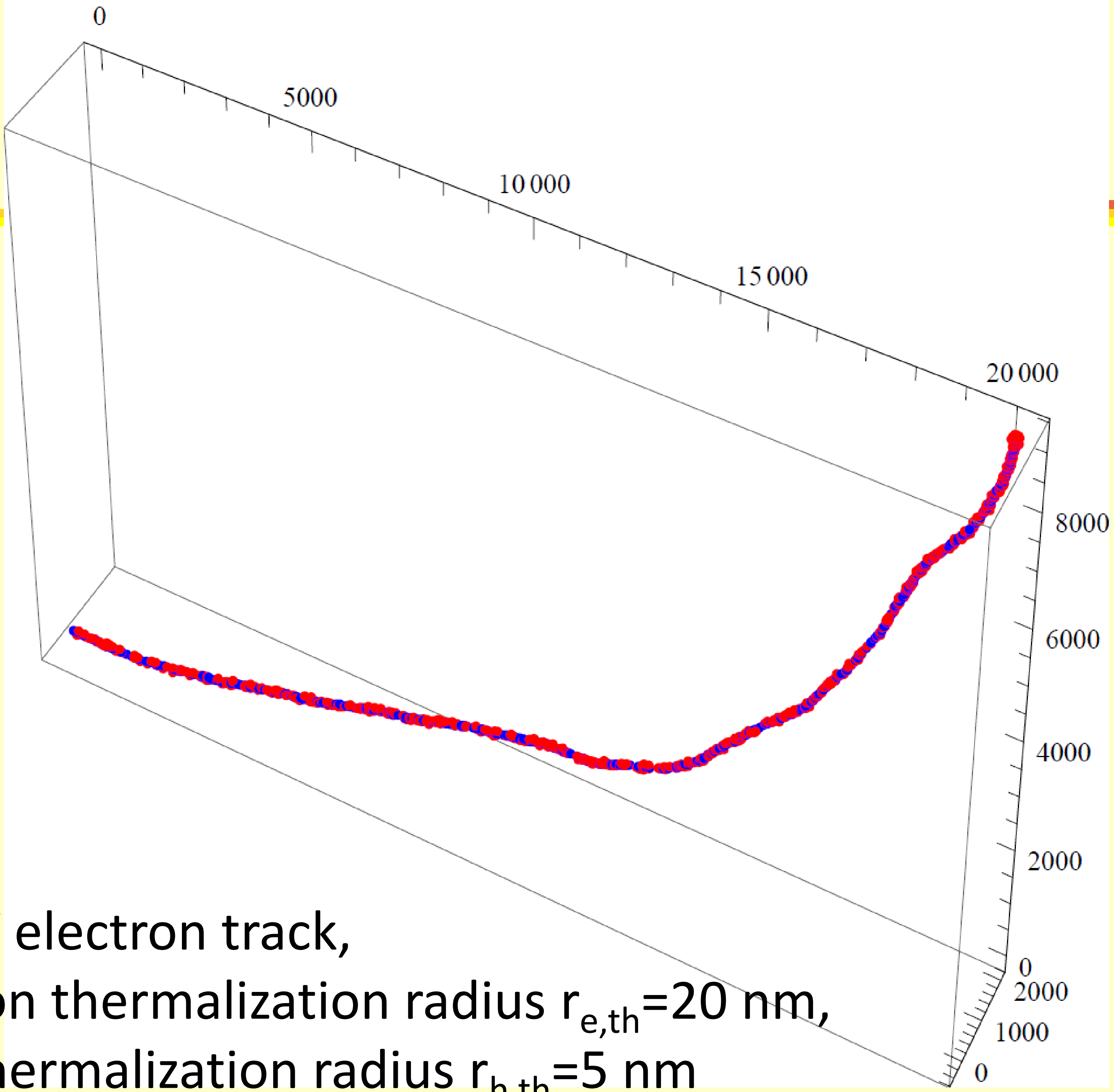
‘Real’ track structure

● Onsager radius10 nm

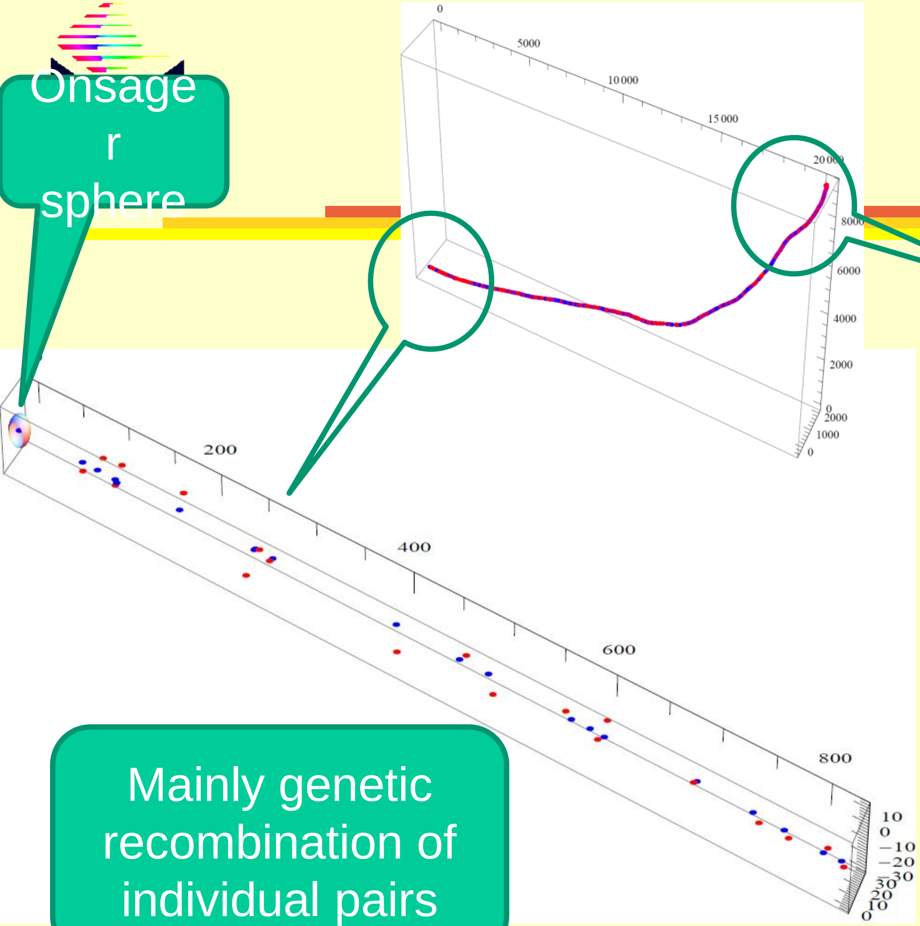
Example of structure of excited region after 30 keV electron passage



30 keV electron track,
electron thermalization radius $r_{e,th}$=6 nm,
hole thermalization radius $r_{h,th}$=0.6 nm

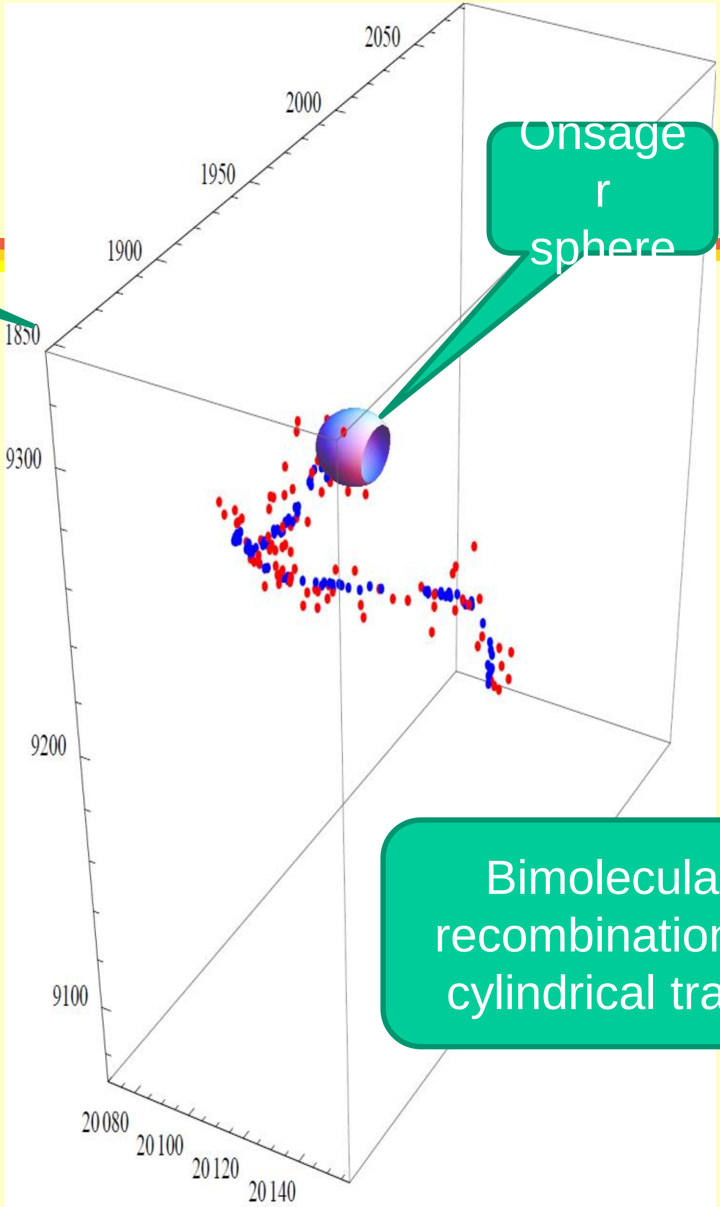


30 keV electron track,
electron thermalization radius $r_{e,th}$=20 nm,
hole thermalization radius $r_{h,th}$=5 nm



Onsager sphere

Mainly genetic recombination of individual pairs



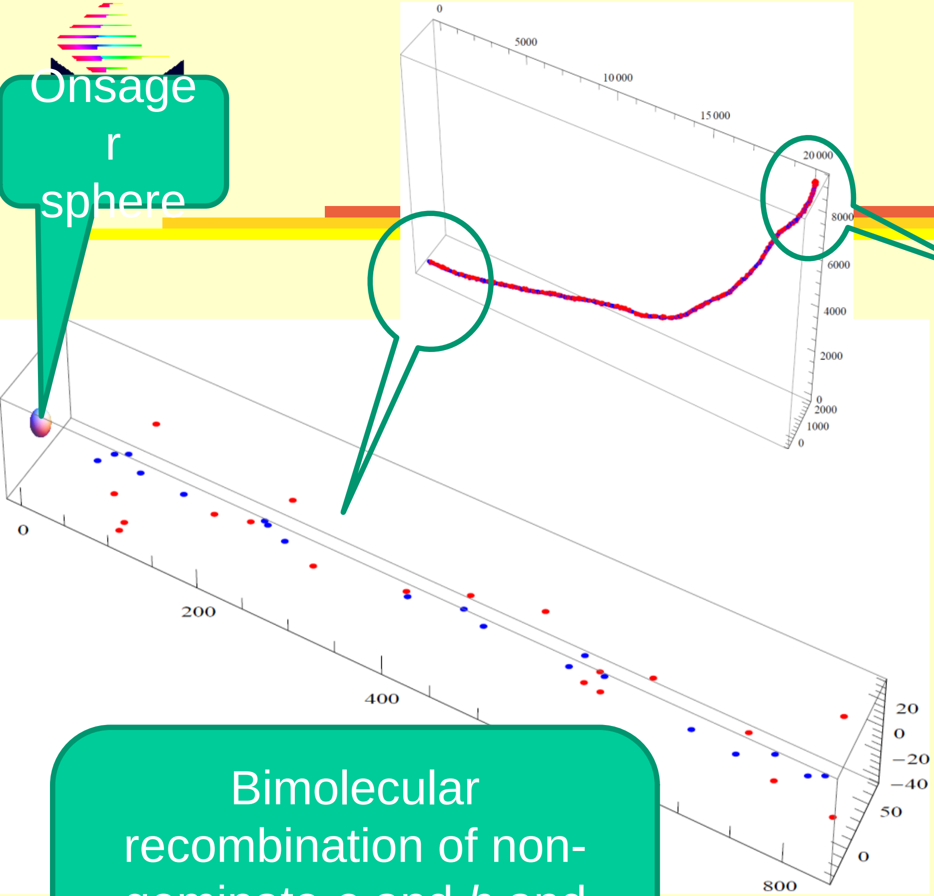
Onsager sphere

Bimolecular recombination in cylindrical track

30 keV electron track,

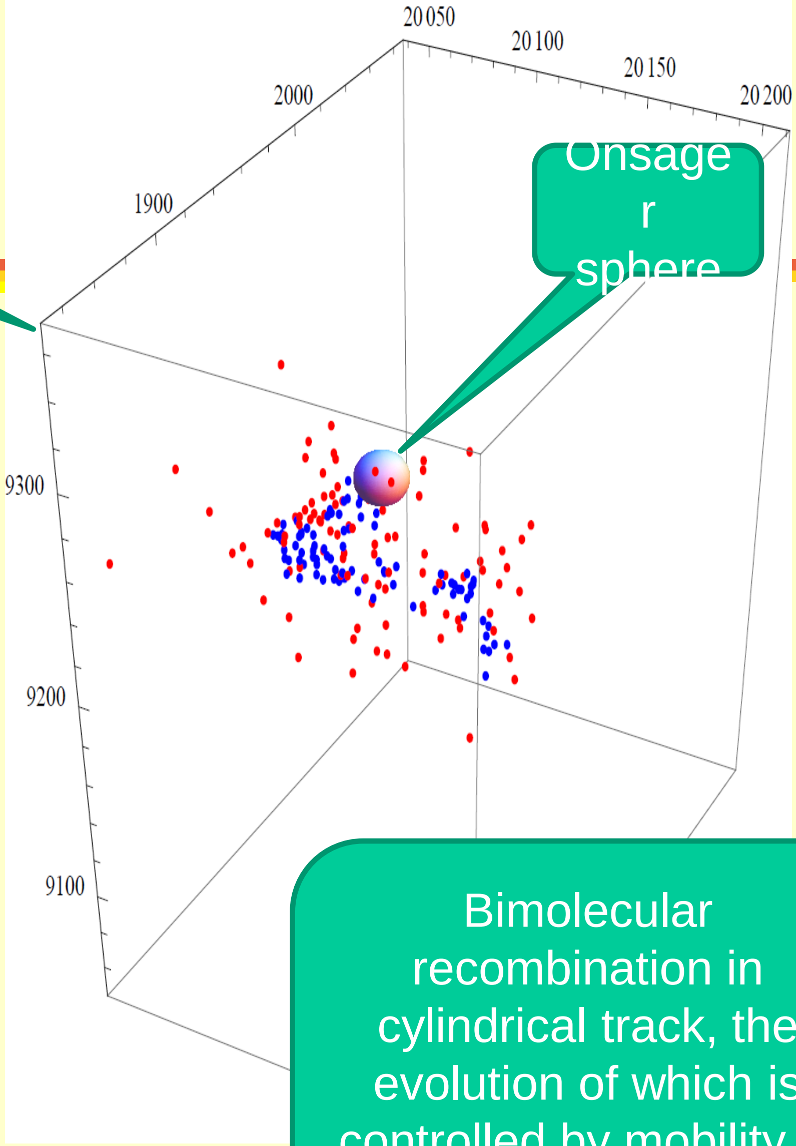
$r_{e,th}$=6 nm,

$r_{h,th}$=0.6 nm (red=e, blue=h)



Onsager sphere

Bimolecular recombination of non-geminate *e* and *h* and genetic recombination of individual pairs



Onsager sphere

Bimolecular recombination in cylindrical track, the evolution of which is controlled by mobility in strong electric fields

30 keV electron track,

$r_{e,th}$=20 nm,

$r_{h,th}$=5 nm (red=e, blue=h)

Outline

Spatial scales for processes in scintillators

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Cascade, thermalization and recombination

Different types of mobilities

Thermalization length for different types of crystals

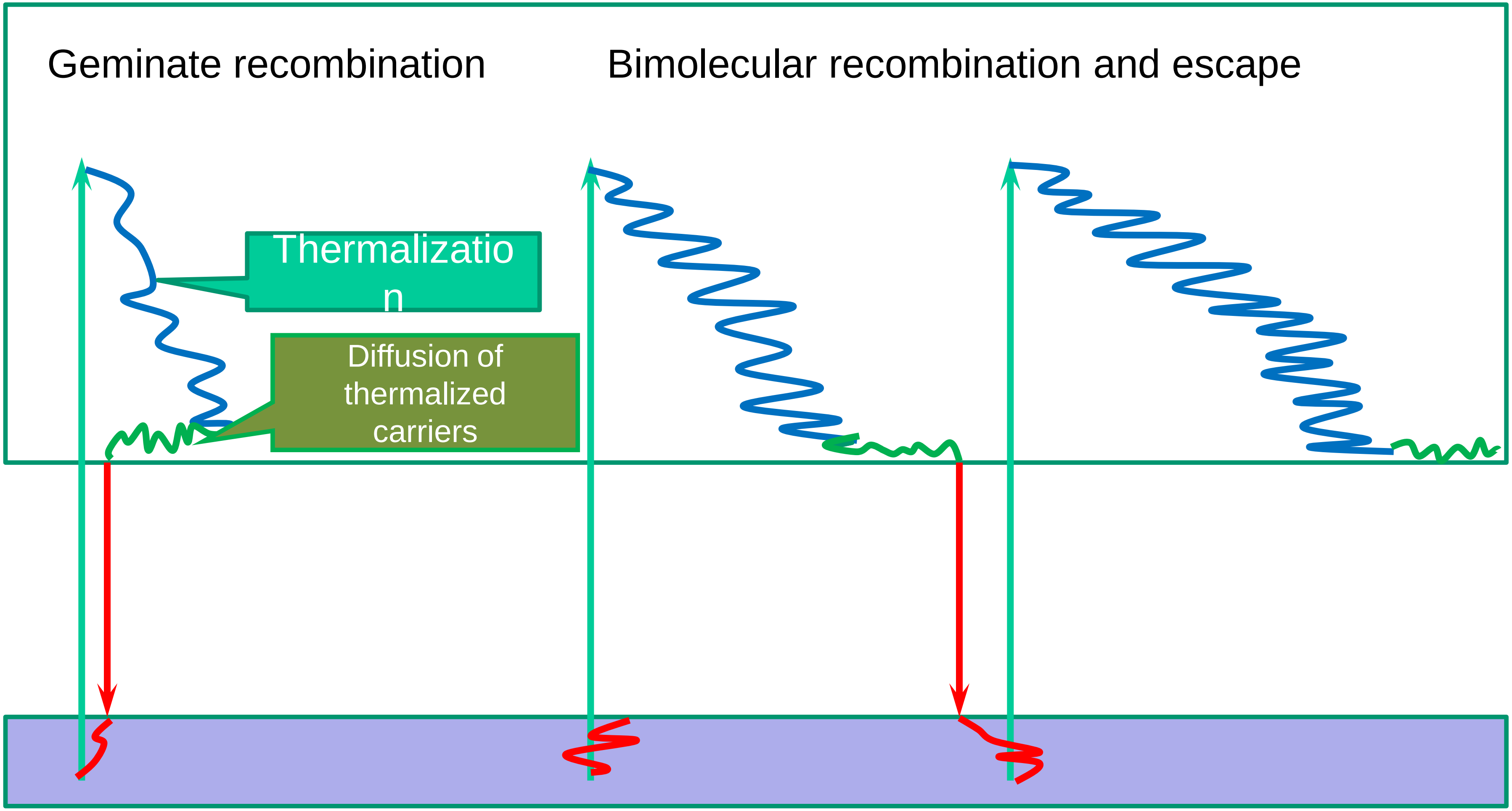
Interconnection of cascade, thermalization and recombination stages in binary iodides

Why cascade is so effective in CsI?

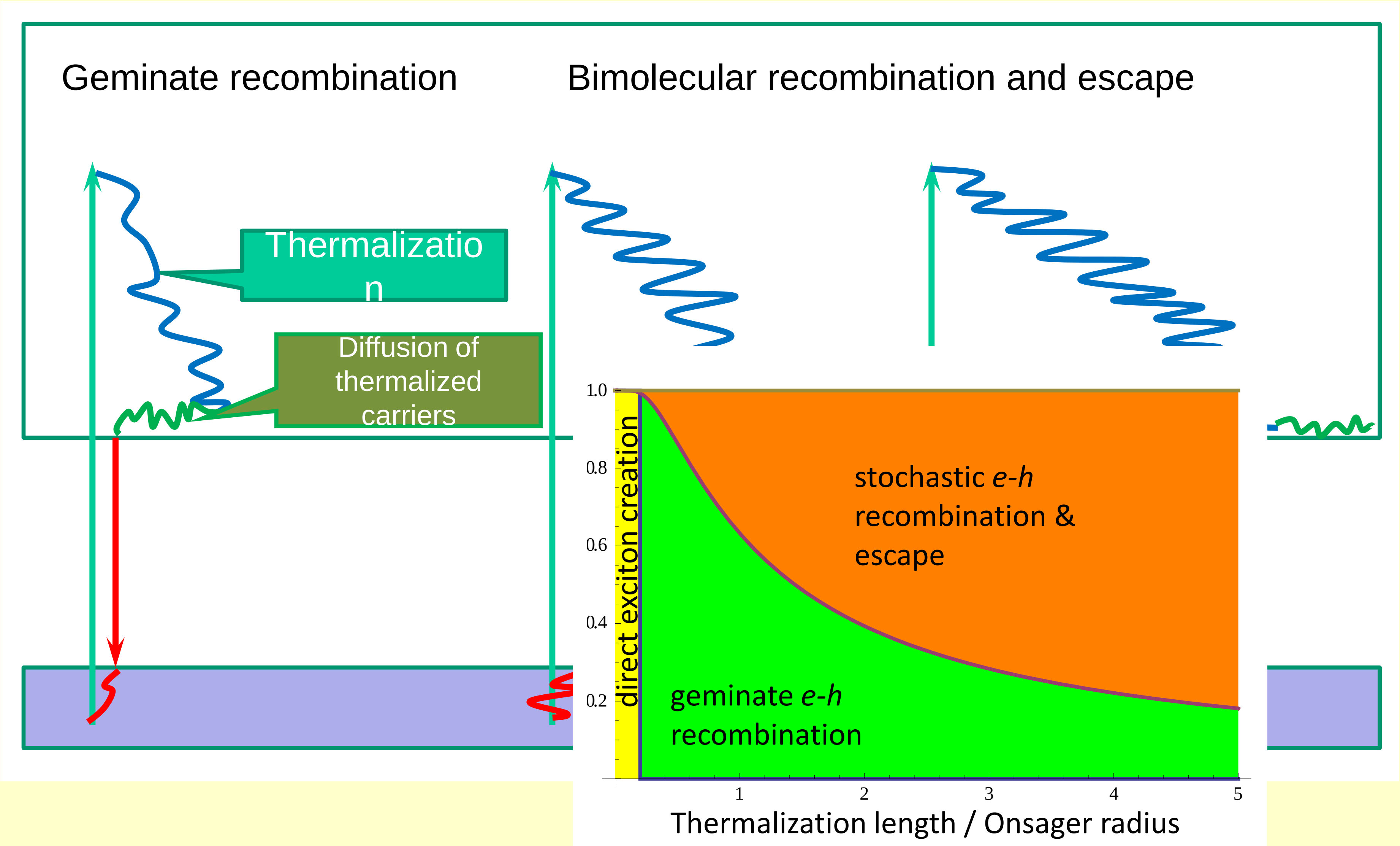
Thermalization length and impurities

Concluding remarks

Electron-hole separation and recombination



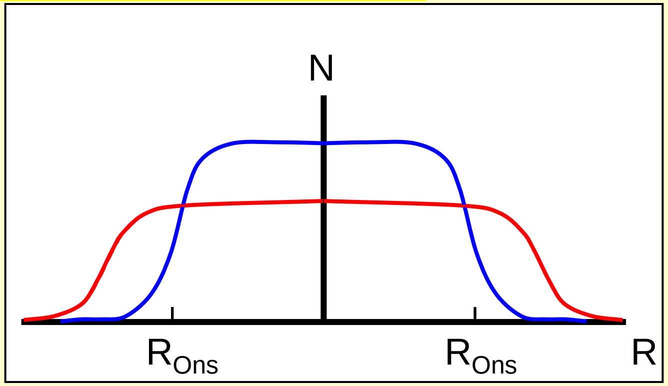
Electron-hole separation and recombination



How we can manage thermalization length?

What we have to do to improve the yield?

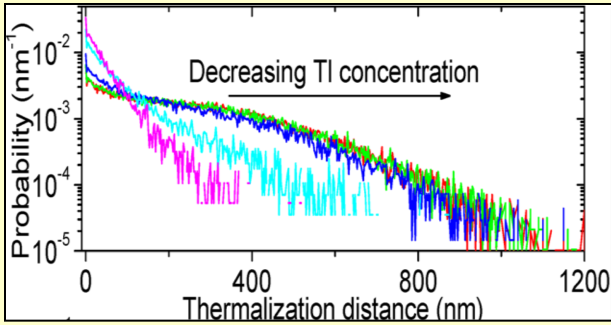
The goal is to concentrate e-h pairs at the distance less then Onsager radius, to minimize the volume of stochastic recombination and escape losses.



Two ways for e-h separation management

Doped/activated crystals (rare solutions)

Mixed crystals (hard solutions)



Z. Wang, Y. Xie, B. D. Cannon… 2011

Coupled processes of thermalization and spatial diffusion

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

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

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

Thermalization length for one LO phonon branch

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

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

We have to choose/engineer materials with

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

- higher LO phonon energies

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.

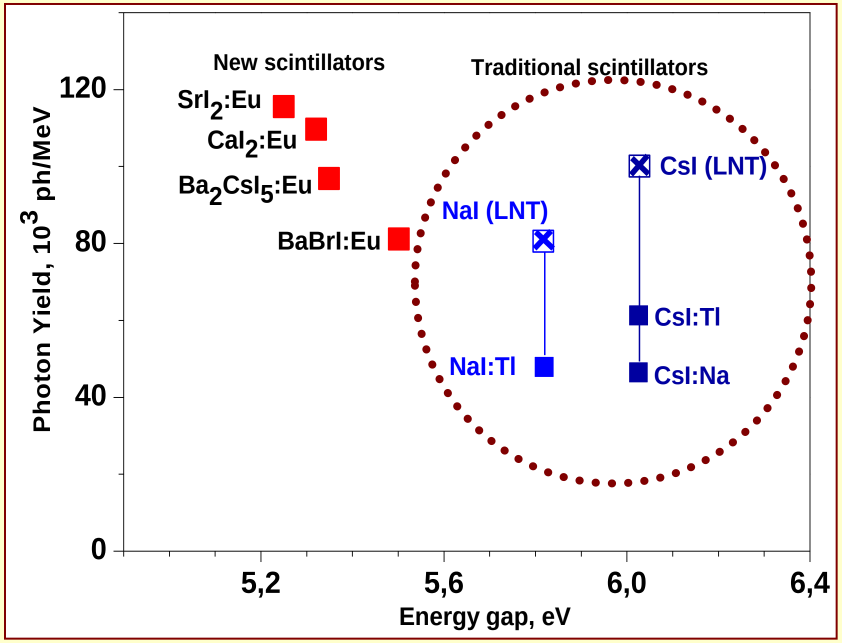
“Ideal” scintillator: Low hot mobility (high yield of excitons) and high thermalized mobility (low interaction).

Binary alkali halides:

Can the yield achieve theoretical limit?

Can we improve conventional alkali halide scintillators?

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



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

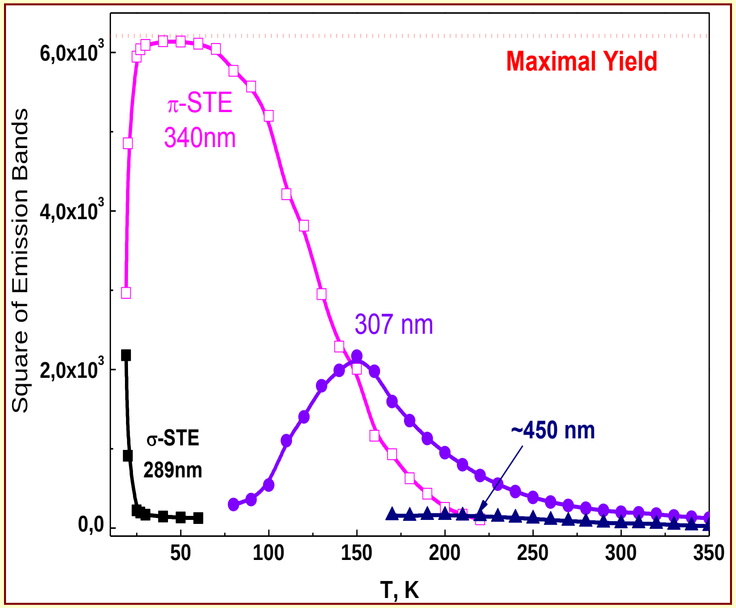
Experimental data are far from theoretic limit for NaI and CsI based crystals

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

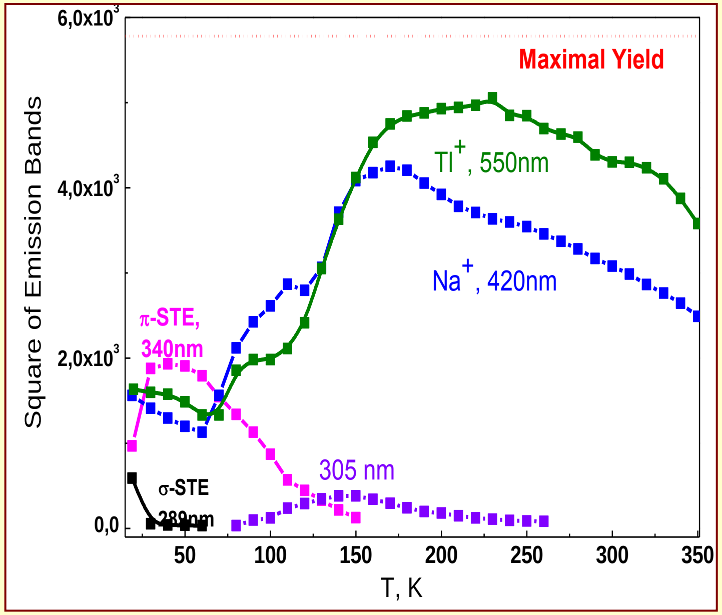
[V.Sciver,1958; Persyk,1980; Moszynski et al, 2010]

Exciton based luminescence

Pure CsI emission

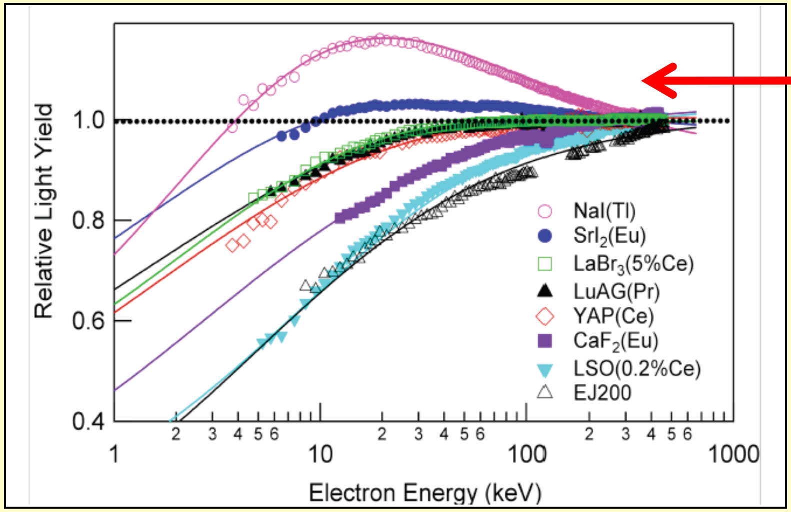


CsI:Na and CsI:Tl emission



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



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

Electron response of some scintillators

[S. A. Payne, W. W. Moses et al., *IEEE TNS, 2011*]

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

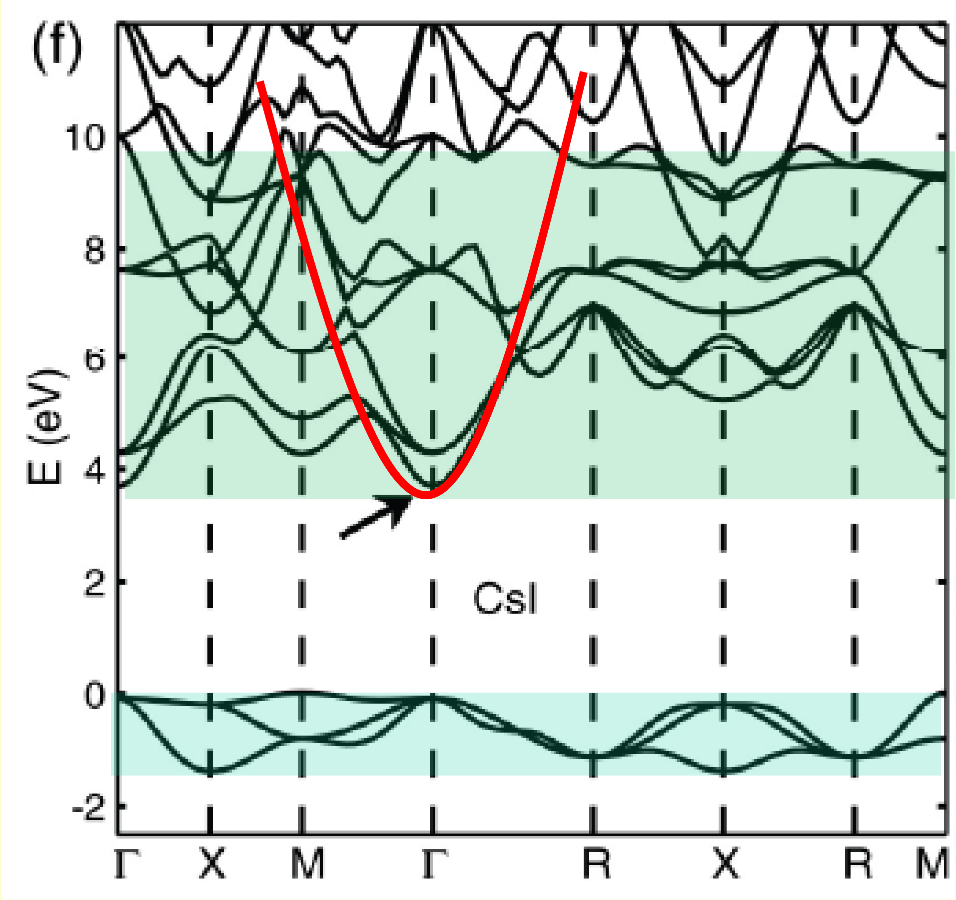
$$\frac{e^2}{\varepsilon R_{Ons}} = k_B T$$

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 ($E_{kin}<E_g$)



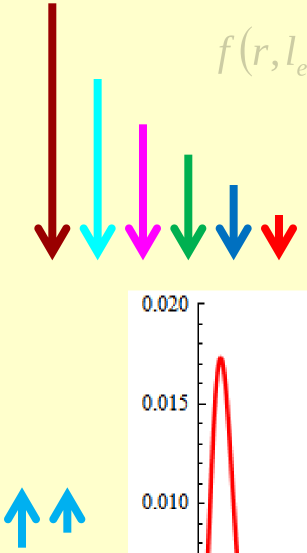
Band structure calculations

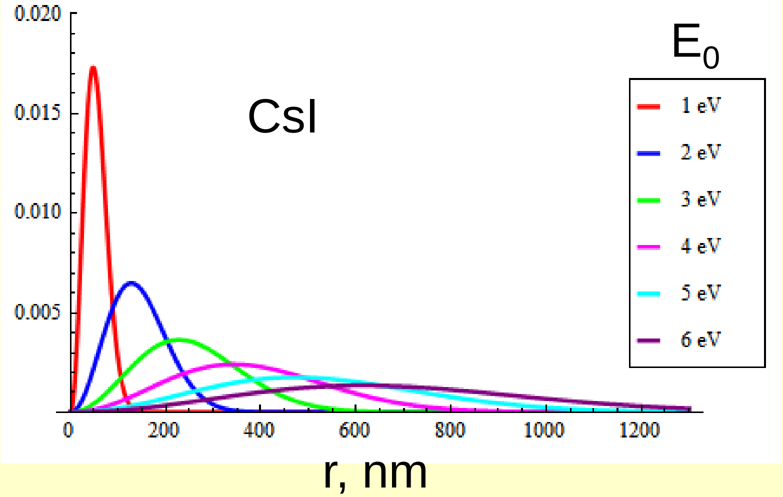
from W. Setyawan, R. M. Gaume et al. *IEEE TNS*, 2009

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

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

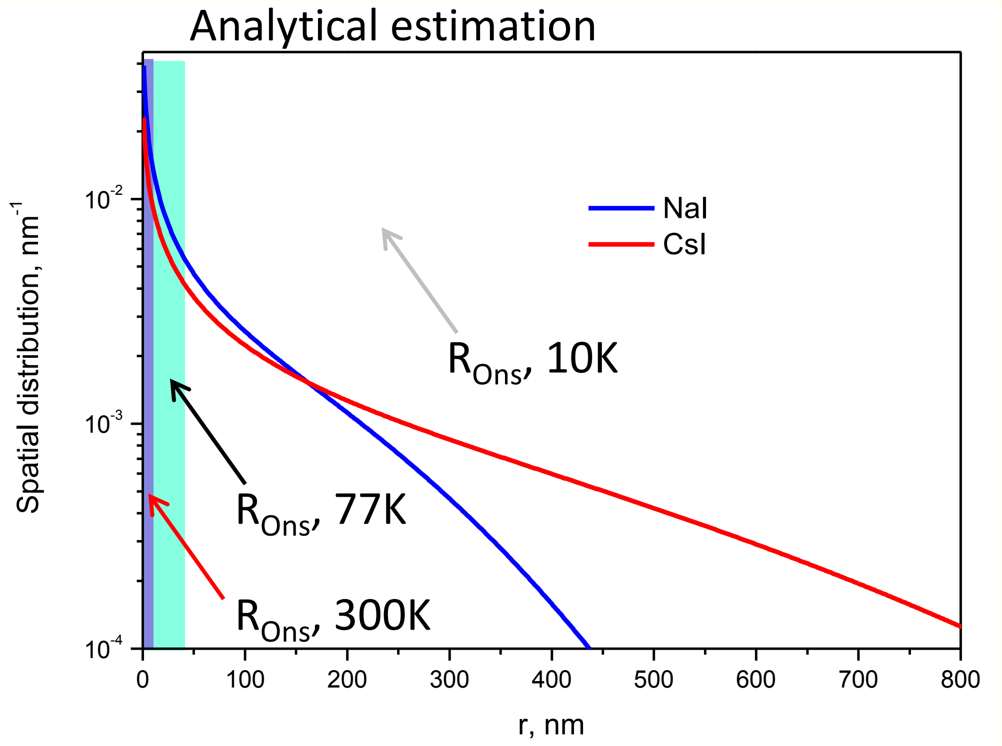
$$f(r, l_e(E_{e0})) = \frac{3\sqrt{6}\, r^2}{\sqrt{\pi}\, l_e^3(E_{e0})} \exp\left(-\frac{3r^2}{2 l_e^2(E_{e0})} \right)$$

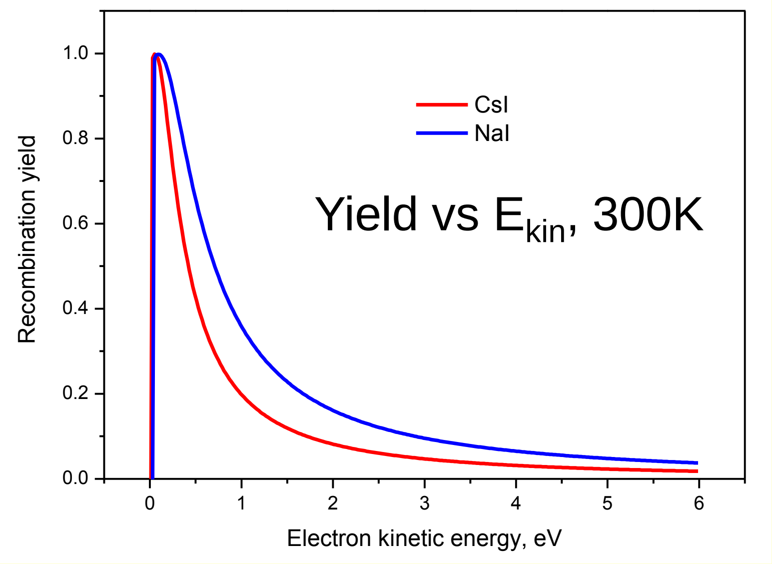




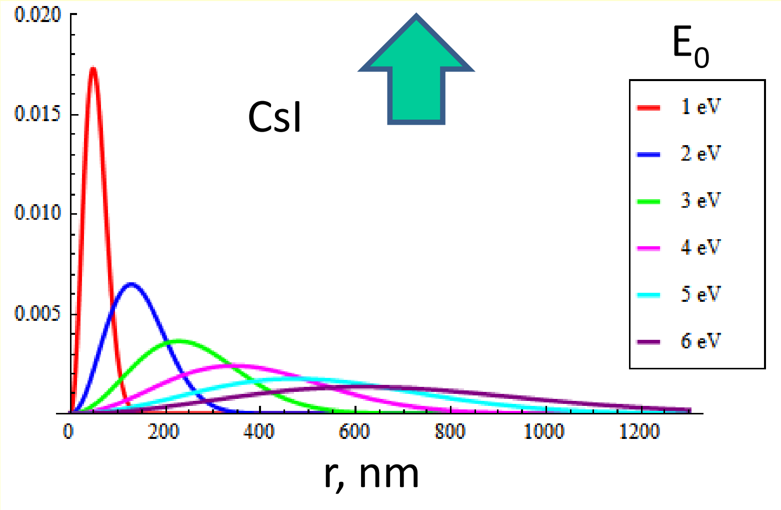
Spatial distribution of thermalized electrons (binary crystals)

Analytical estimation





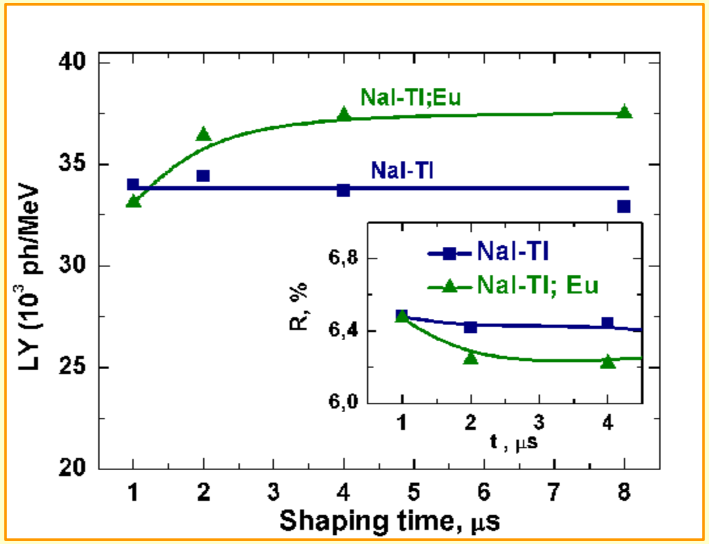
Yield vs E_{kin}, 300K



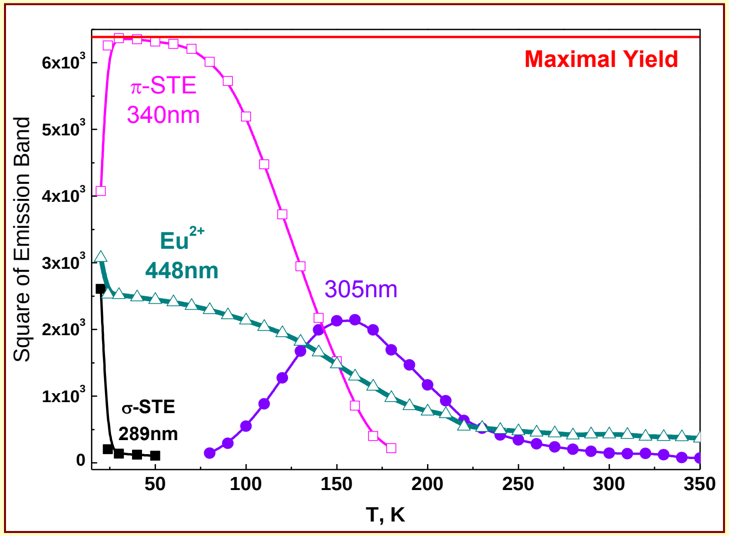
	R_{Ons}, 300K	Yield, 300K	Yield, 77K
CsI	9.87 nm	0.24	0.44
NaI	9.05 nm	0.34	0.58

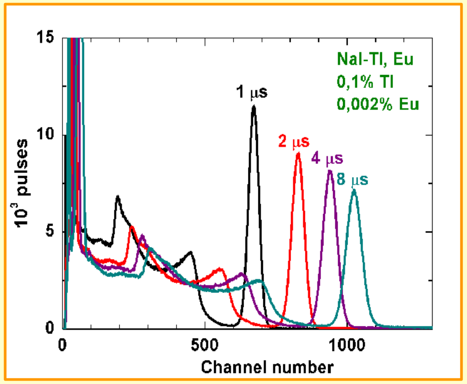
Can we use co-doping to collect more excitations?

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	$1\cdot10^{-1}$		415	230	100	6.4
NaI-Tl, Eu	**$1\cdot10^{-1}$**	**$1\cdot10^{-3}$**	**445**	**230 (26%)** **1000 (74%)**	**110**	**6.2**
NaI-Eu		**$1\cdot10^{-1}$**	**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?

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

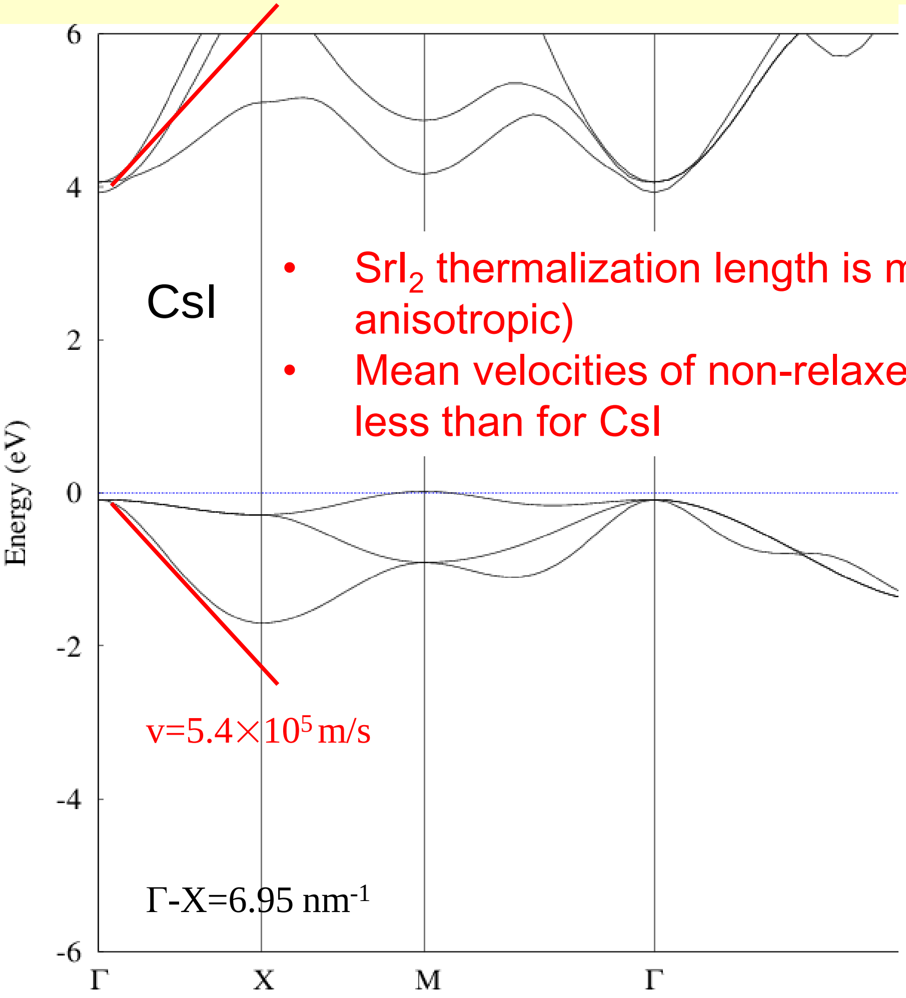
We should choose materials with

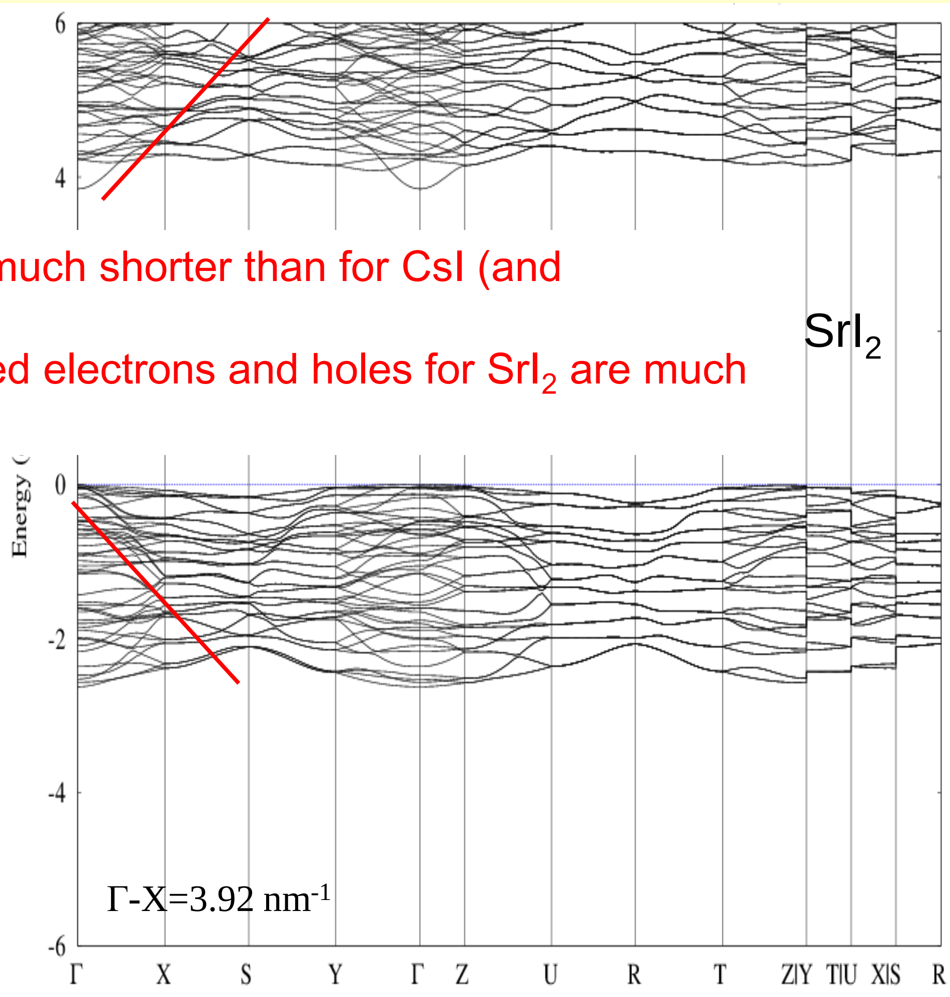
- **higher effective masses** in the whole relaxation region $E_{kin} < E_g$ and
- higher LO phonon energies

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





- SrI_2 thermalization length is much shorter than for CsI (and anisotropic)
- Mean velocities of non-relaxed electrons and holes for SrI_2 are much less than for CsI

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

Renaissance of Eu-doped scintillators

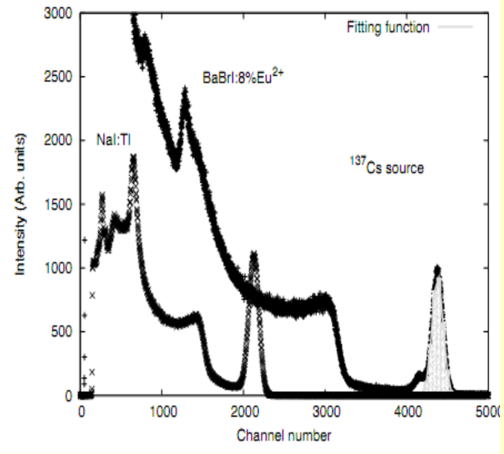
(history and reality)

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

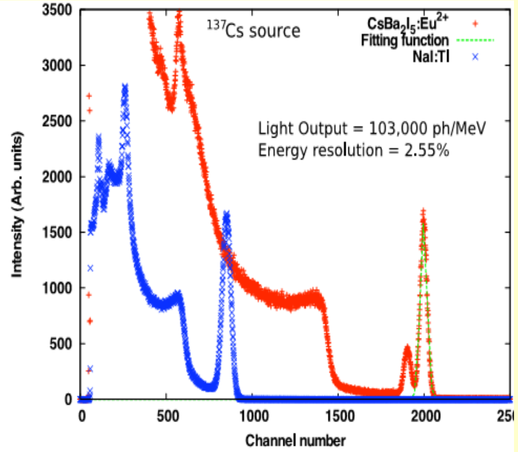
New demands have led to discovery several new Eu-doped scintillators

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	

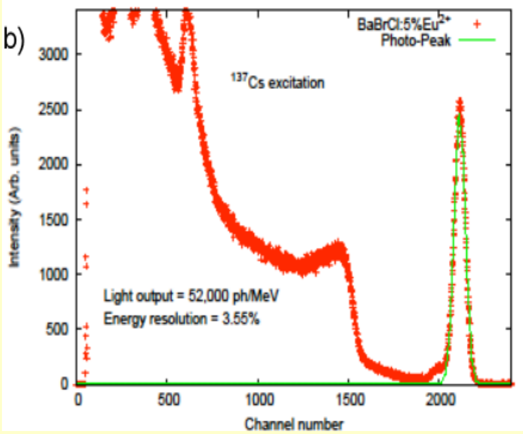
Pulse height spectra of record scintillators under γ ^{137}Cs excitation



BaBrI:Eu



CsBa$_2$I$_5$: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

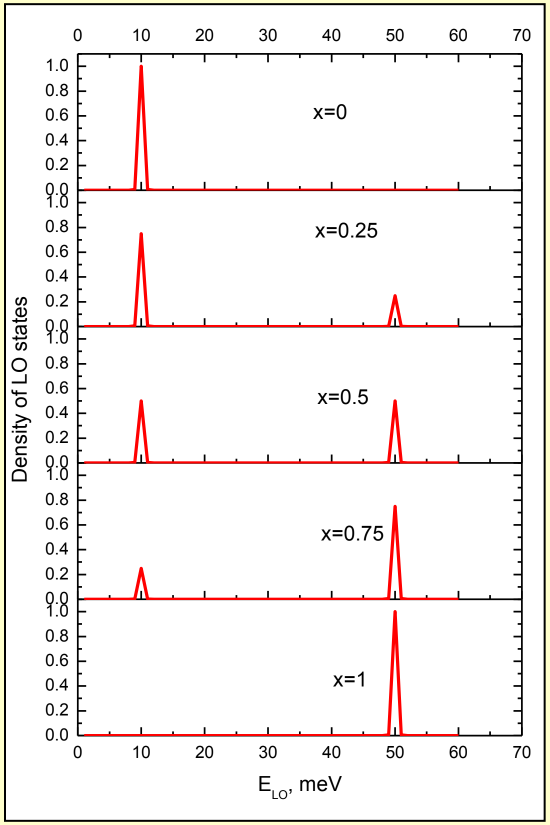
Many AE halides possess with efficiency about fundamental limit

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

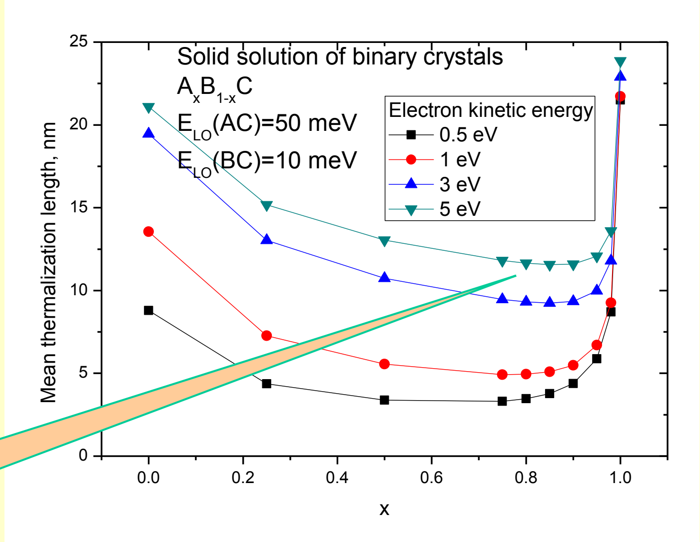
Modification of phonon spectrum (additional phonon branches)

Mixed – $A_xB_{1-x}C$ crystal model

Density of LO states

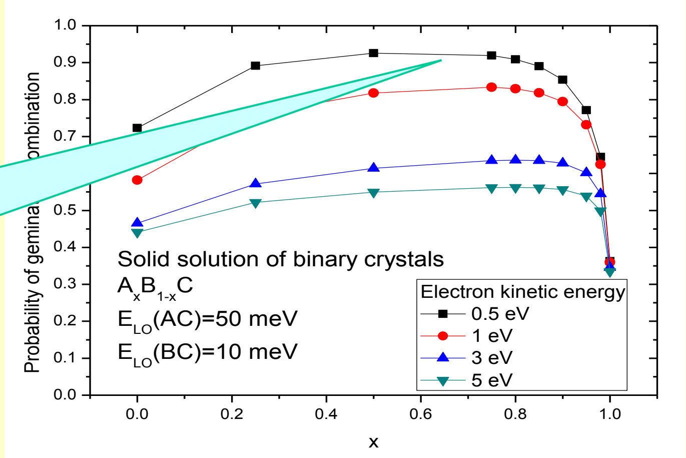


Mean thermalization length vs X concentration



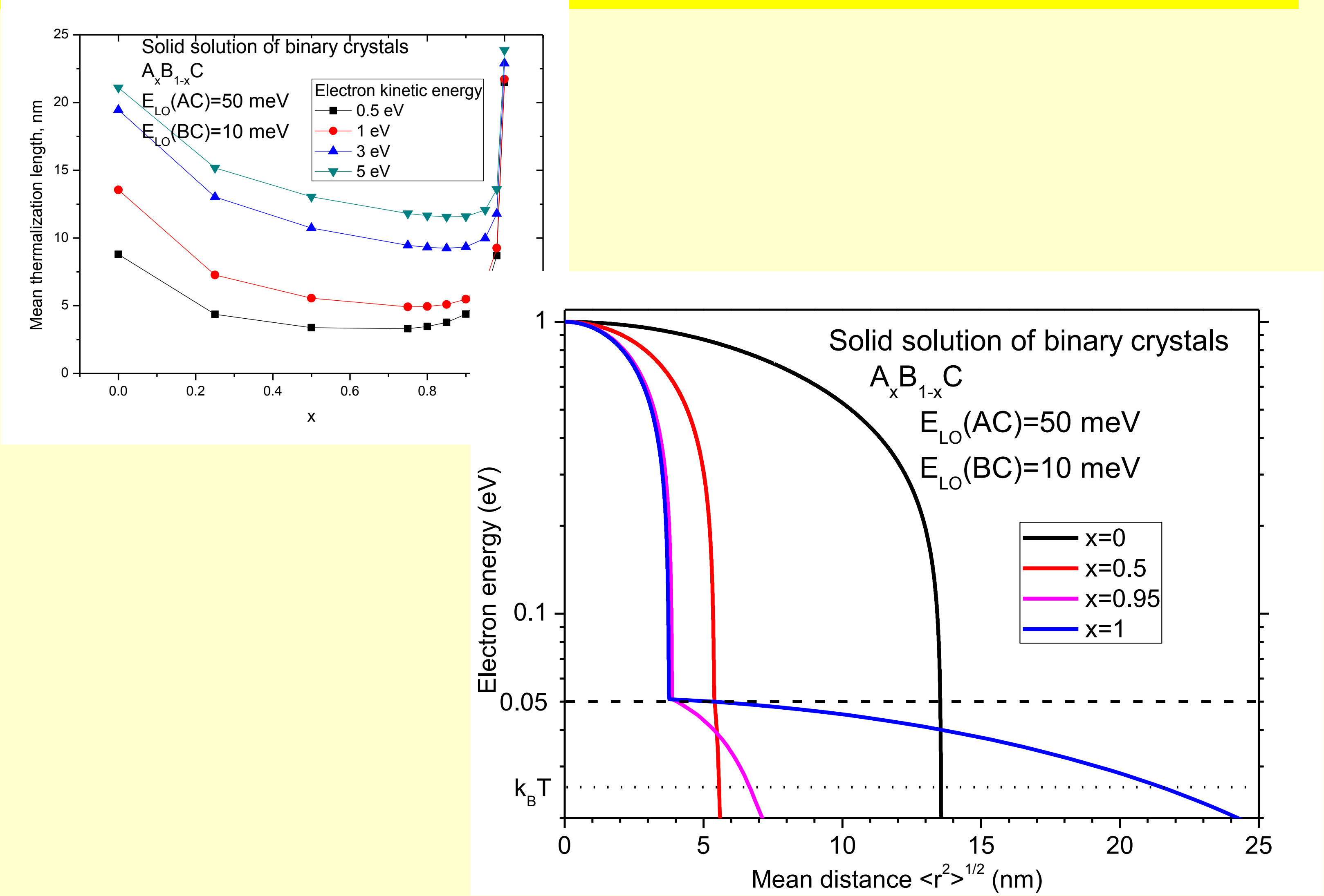
Thermalization length decrease

Probability of geminate recombination

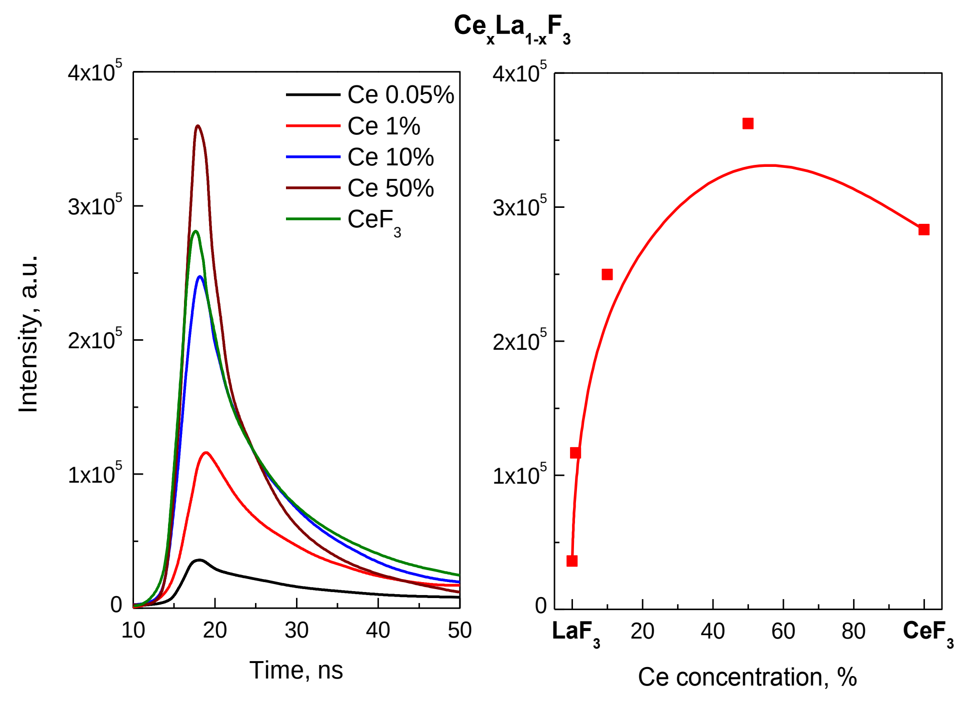


Recombination probability increase

Modification of electron spectrum – increasing of elastic scattering



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

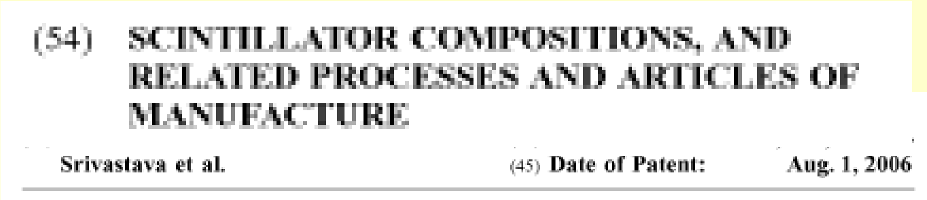


A.N. Belsky, A.V. Gektin et al., Proceedings of SCINT'95, Delft, 1995

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

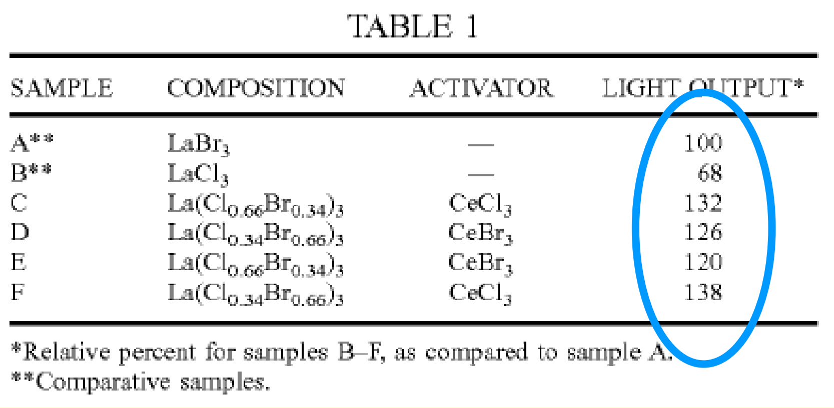
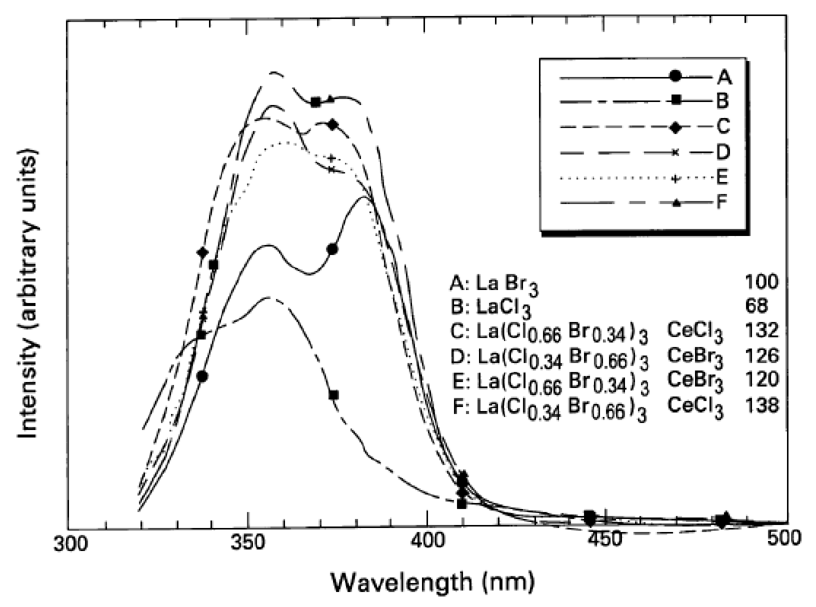


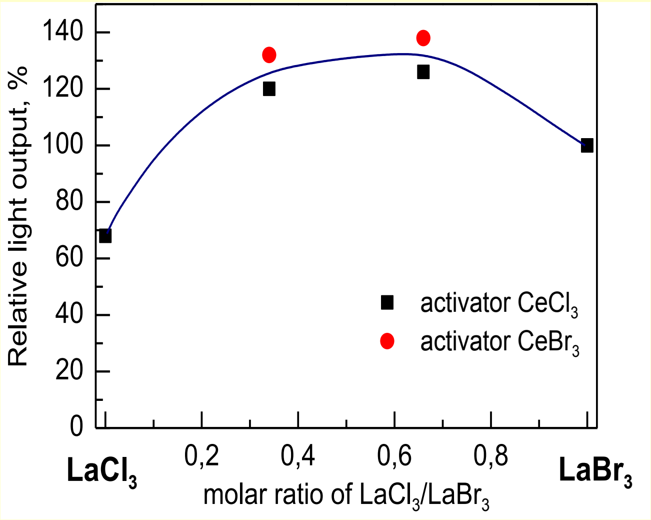
TABLE 1

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.

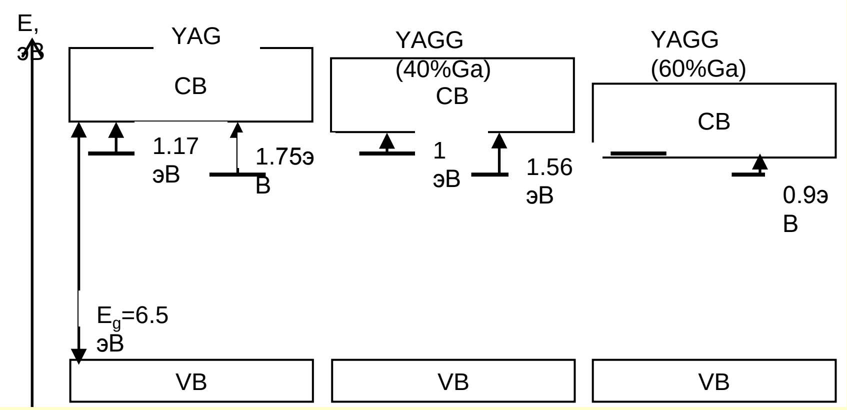


Emission spectra under UV excitation



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

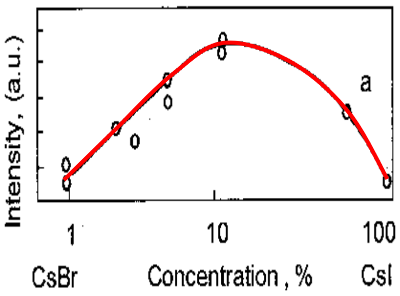
** Crystal performance, initial purity and activator concentration are crucial for the experimental study of phenomena

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

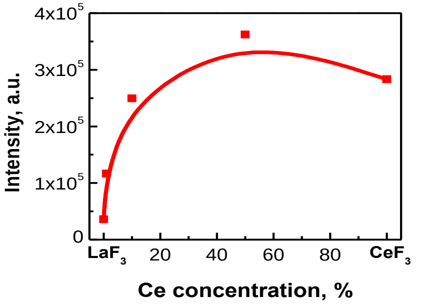
**** We need in more detailed theoretical estimations for doped and mixed crystals

CONCLUSIONS

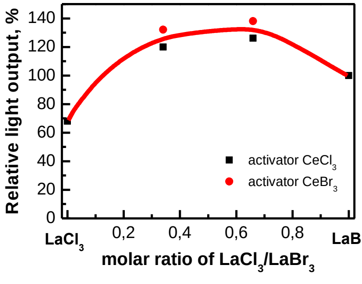
CsI-CsBr



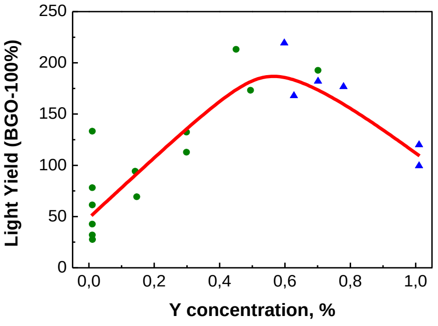
$Ce_xLa_{1-x}F_3$



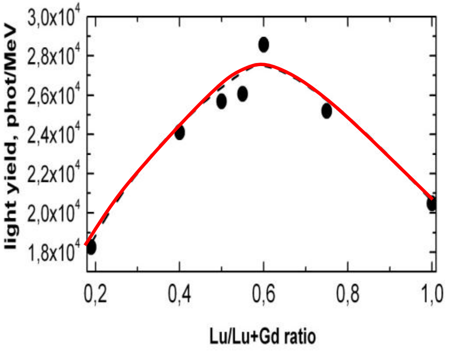
$LaCl_3$-$LaBr_3$



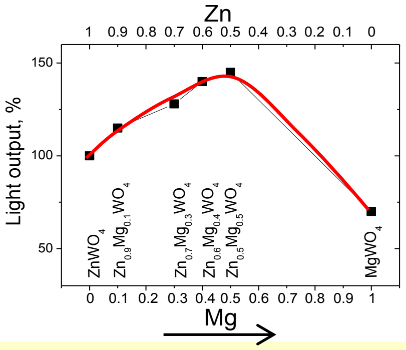
(Lu, Y)AlO_3: Ce



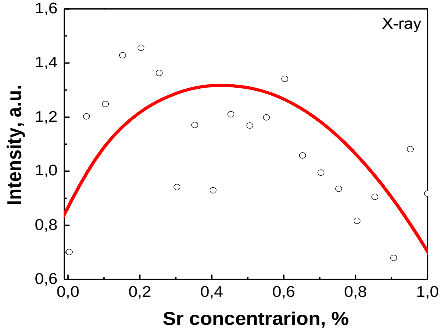
LGSO:Ce



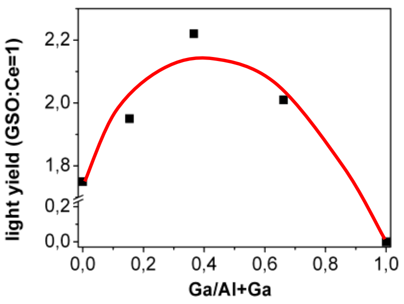
$Zn_xMg_{1-x}WO_4$



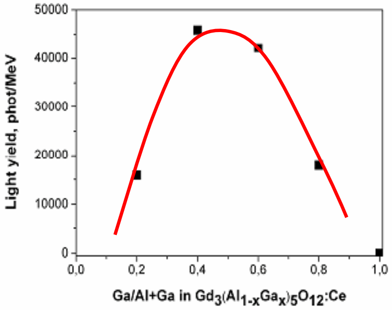
$Ca_{1-x}Sr_xS$



YAGG:Ce

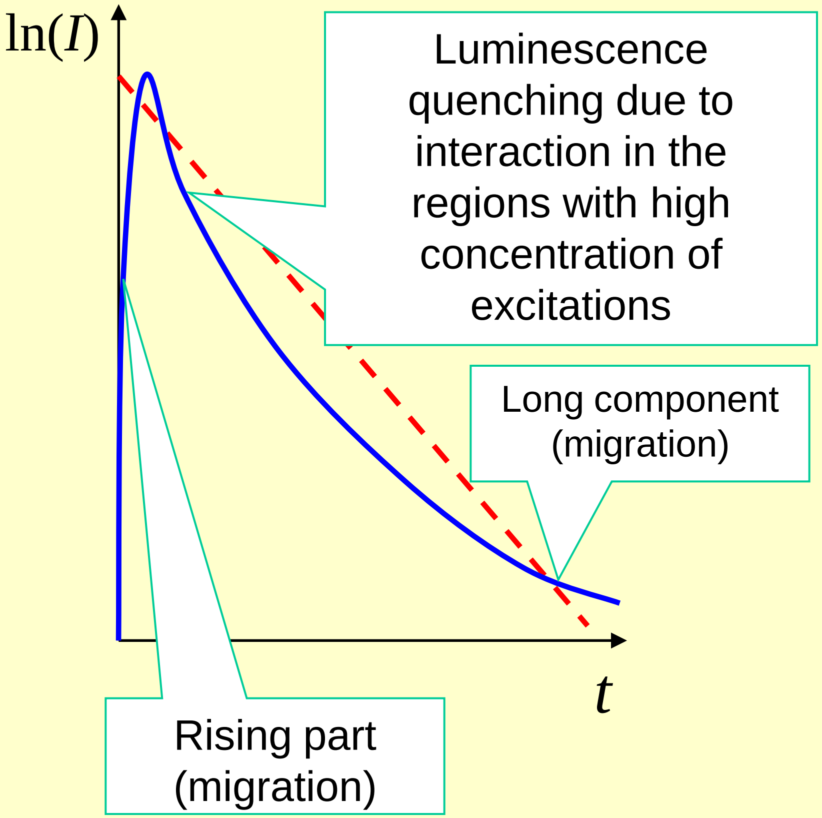


$Gd_2(Al_xGa_{1-x})_5O_{12}$:Ce



Modification of kinetics in scintillators

Scintillator kinetics

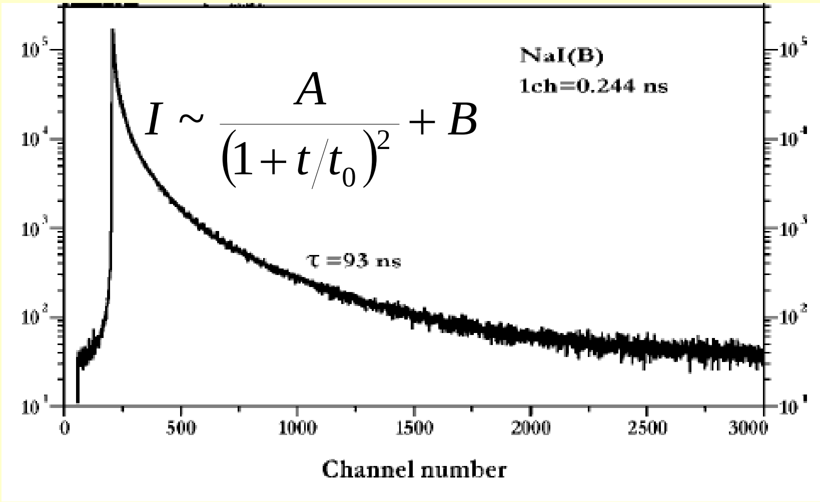


Luminescence quenching due to interaction in the regions with high concentration of excitations

Long component (migration)

Rising part (migration)

Essentially non-exponential decay kinetics for pure NaI



$$I \sim \frac{A}{\left(1+t/t_0\right)^2} + B$$

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

CRYSTAL GROWTH ,

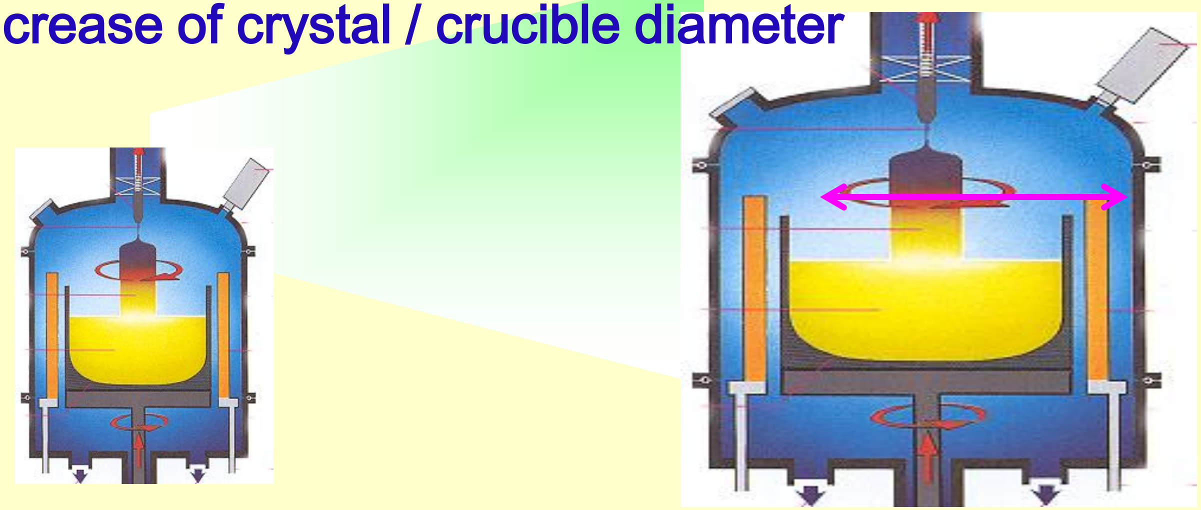
RAW MATERIAL,

TARGET PRICE

FOR ALKALI-EARTH HALIDES

Two ways to increase industrial output

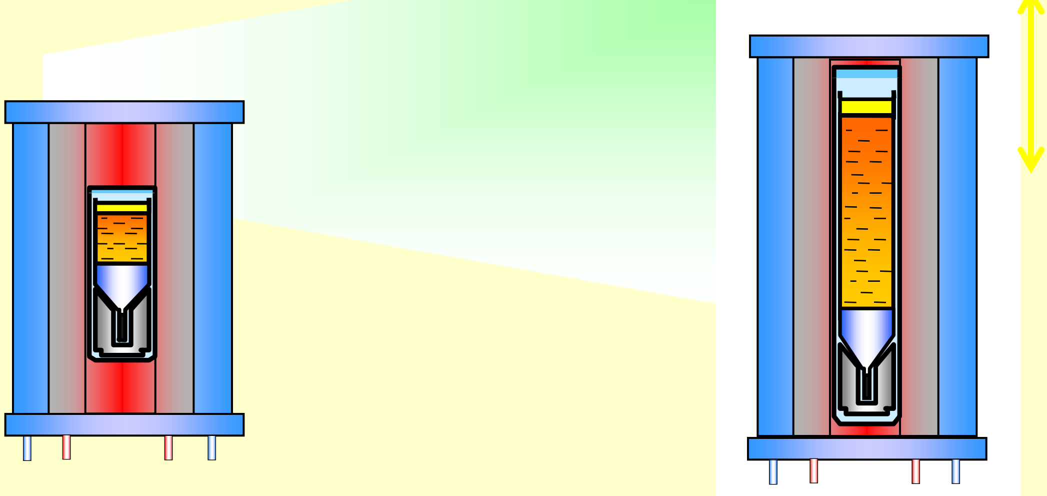
1. Increase of crystal / crucible diameter



Czochralski

- ✓ increased power input
- ✓ melt turbulences

2. Lengthening of crystal / melt height

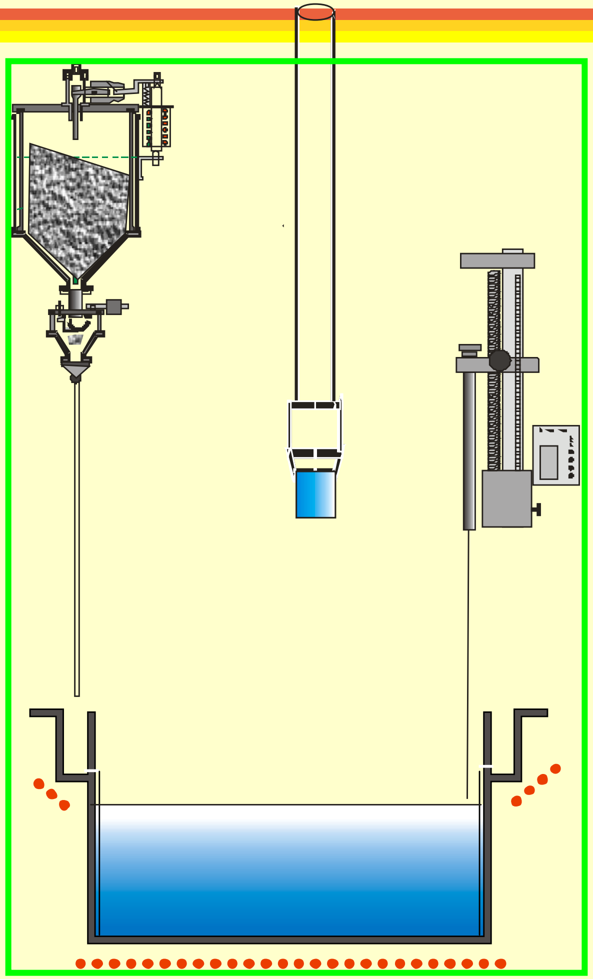


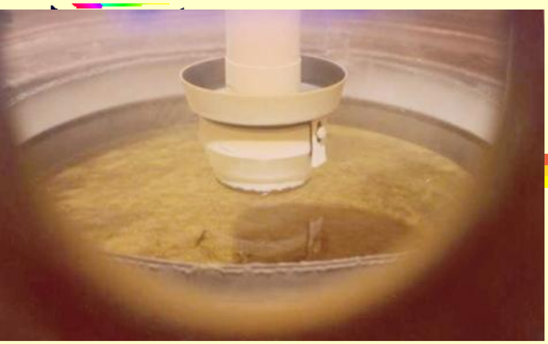
VGF

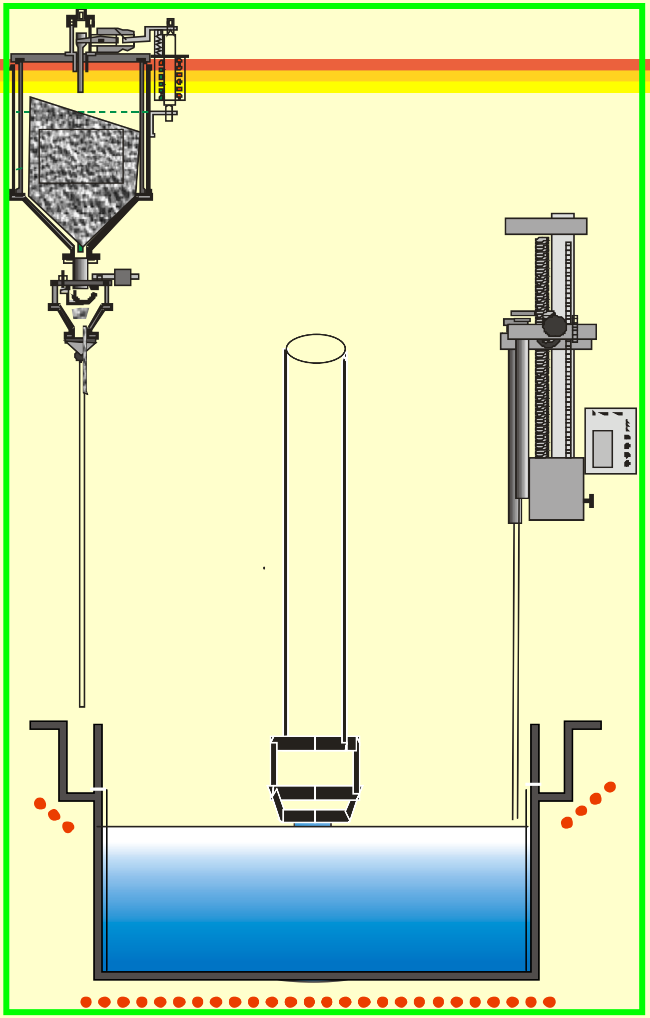
- ✓ increased interaction with ampoule
- ✓ increasing melt convection

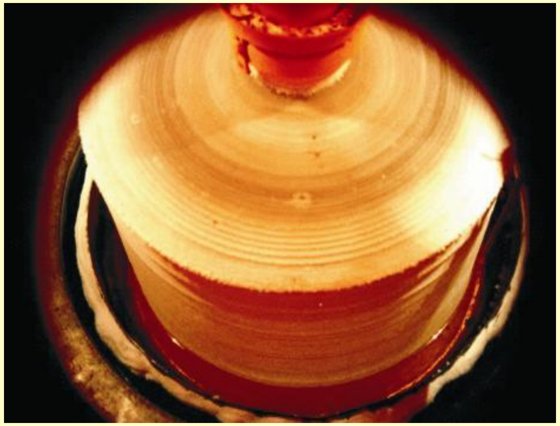
P.Rudolf, IWCGT 2008

Continuous growth procedure

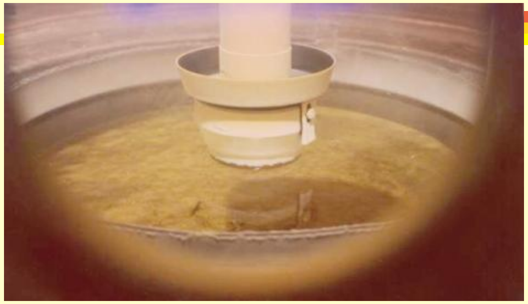


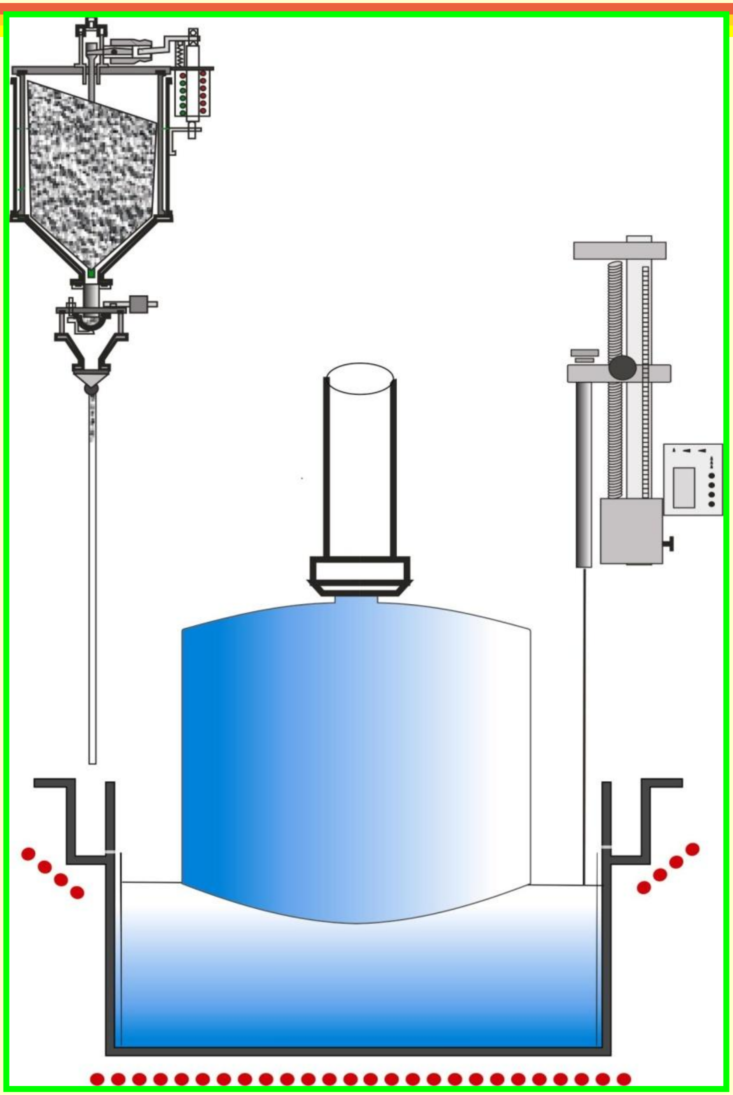


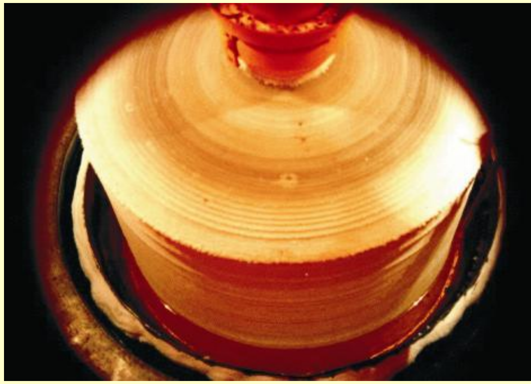




NaI(Tl) crystal continuous growth







From Principles to Practice

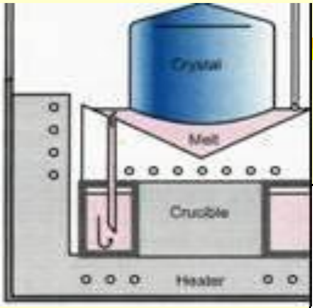
NaI(Tl)
Industrial growth

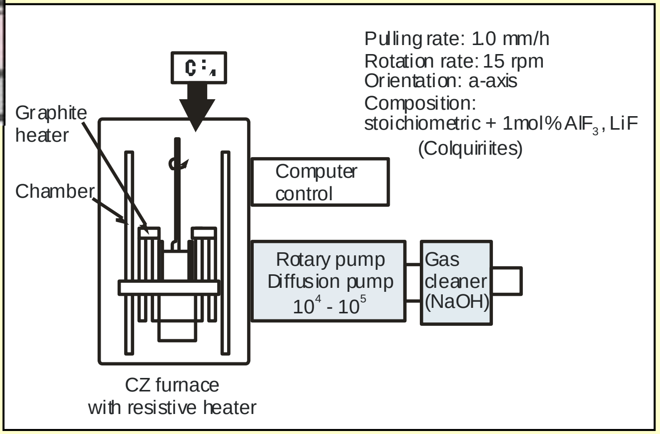
Hygroscopicity is not a problem!

Si – large size crystal growth

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

Crystal purity – crystal quality





Growth “chemistry”

$MeO + 2HI \iff MeI_2 + H_2O$

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

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

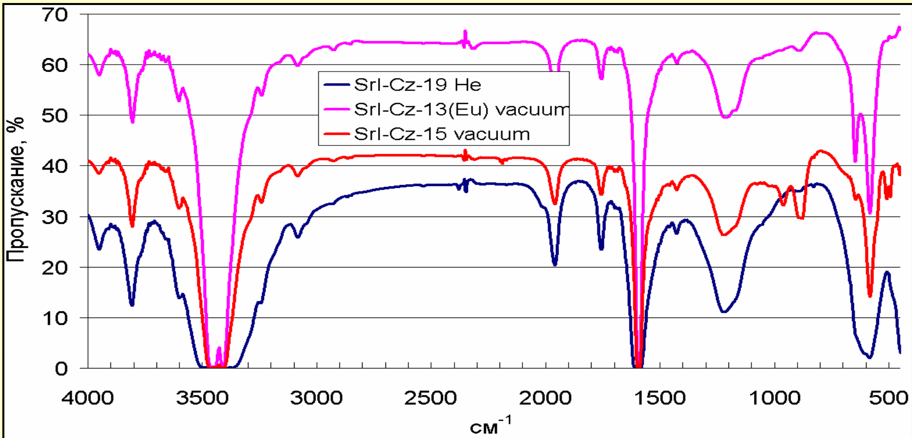
$2MeO + 2I_2 \iff 2MeI_2 + O_2$

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

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

IR spectra of SrI_2:Eu

Peaks demonstrate oxygen impurities inside



Current prices for halides powder

Current prices

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)

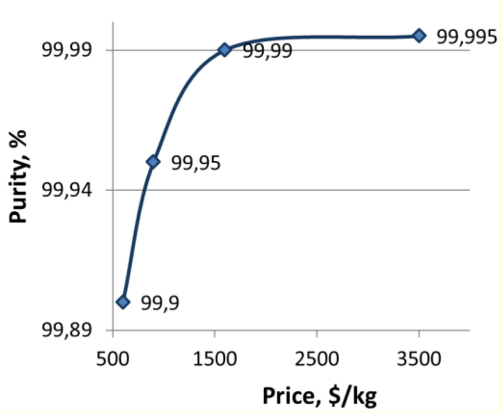
Target price estimation
for hydrated AE halides

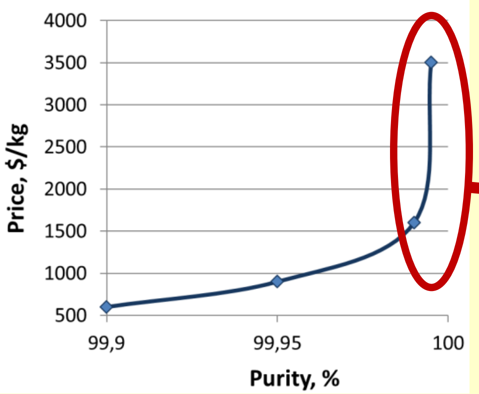
Product name	*Price per anhydrous*
SrI_2 hydrate	$220-270/kilo
$BaBr_2$ hydrate	$150-200/kilo
BaI_2 hydrate	$150-200/kilo

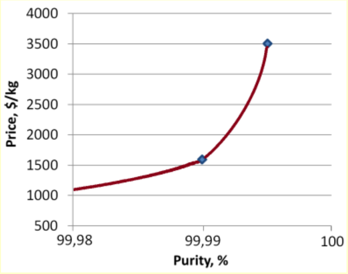
SrI_2:Eu
performance and cost vs. raw material purity

(Lab level)

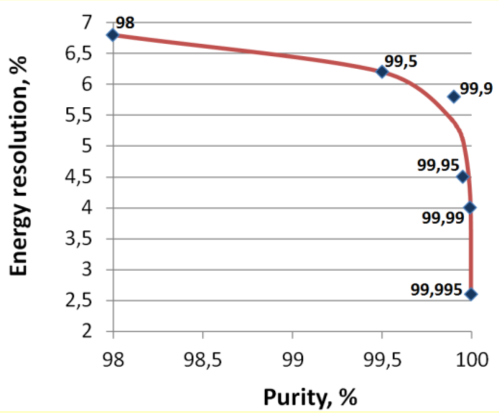
SrI_2. Raw material cost depending on purity

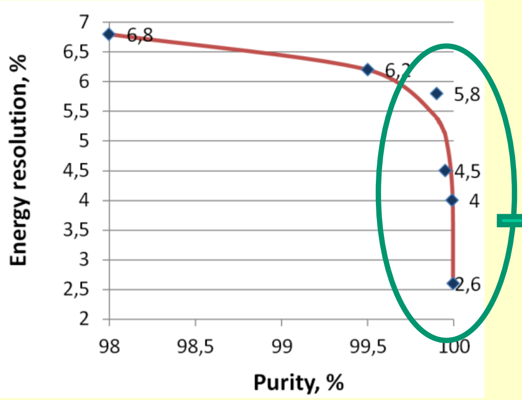


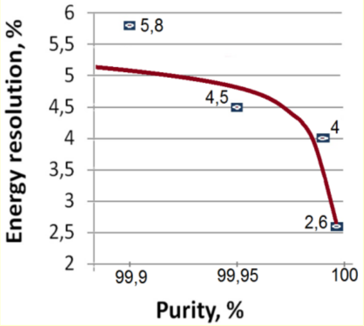




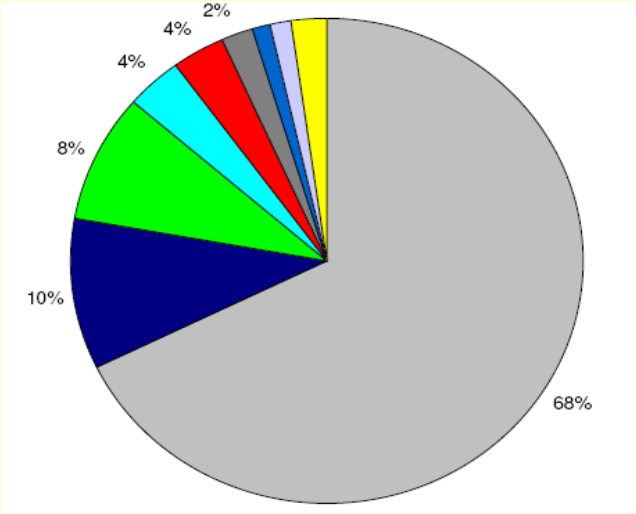
SrI_2:Eu. Energy resolution vs raw material purity

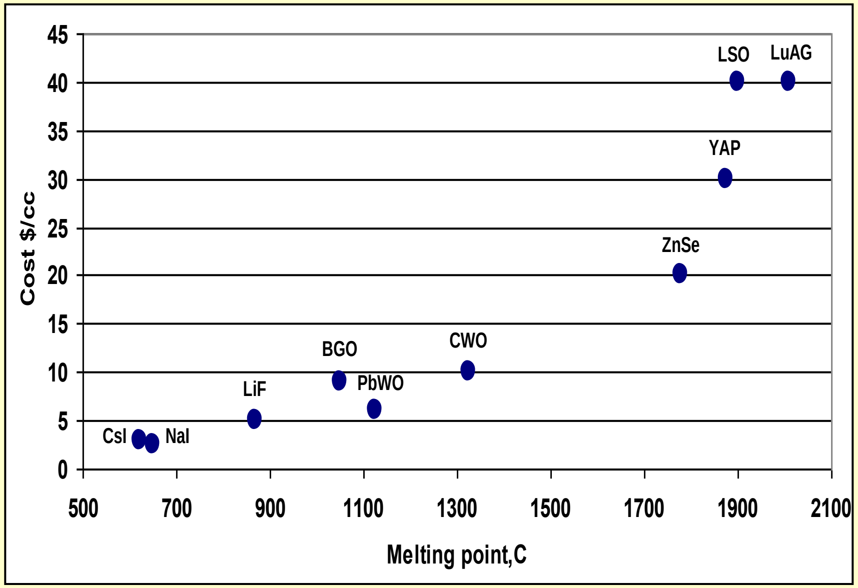






Cost structure for single crystal growth





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

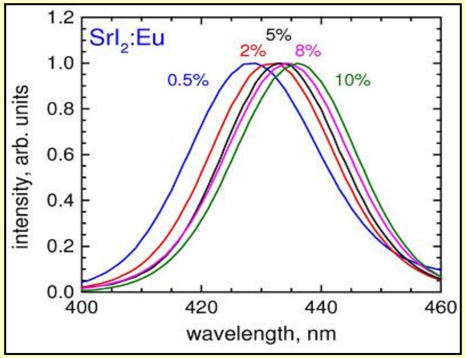
- Natural “bottle neck” (self-absorption) and *overpass ways*

Self-absorption

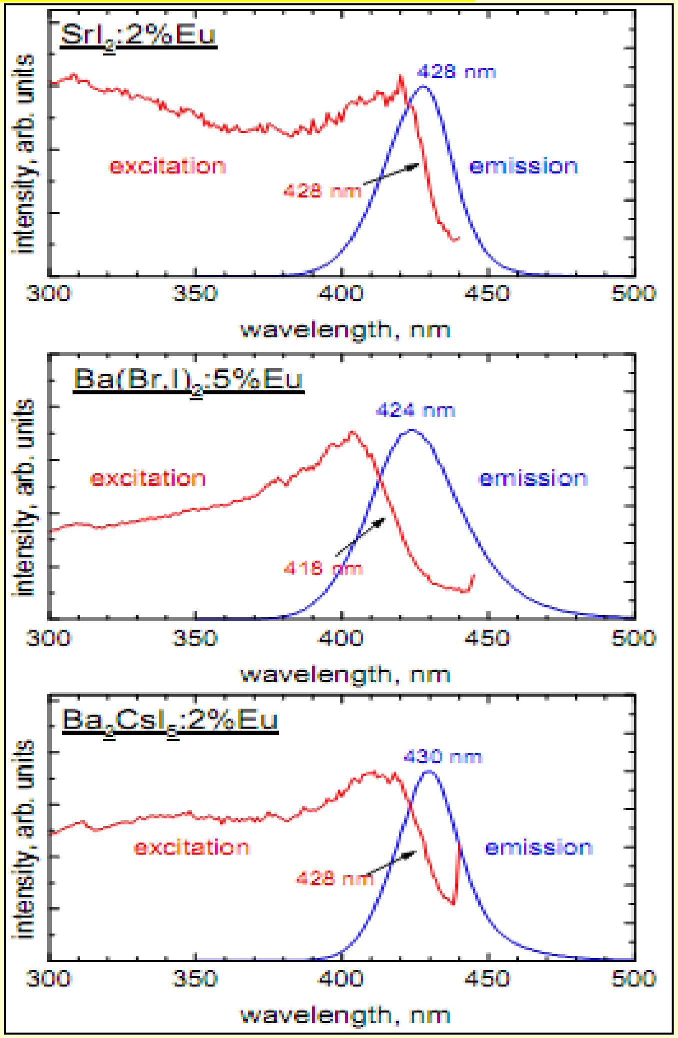
Self-absorption due to small Stokes shift is the key problem for large bulk Eu doped scintillator use

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

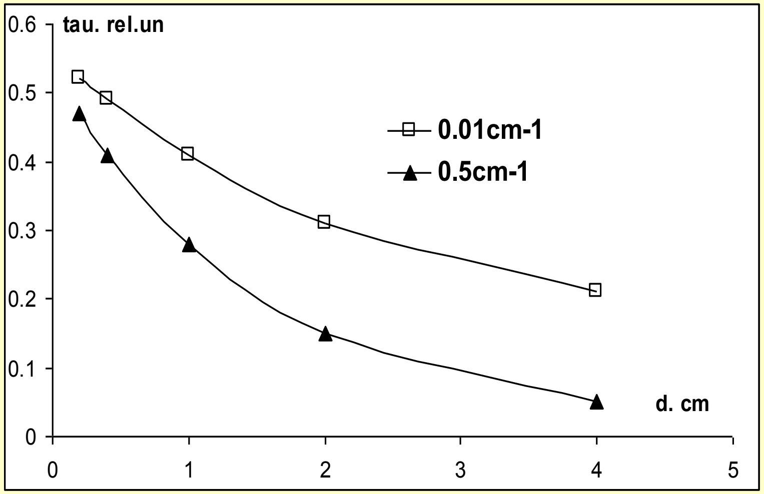


E. Bourret, S. Derenzo et al., 2009, 2010, 2011

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



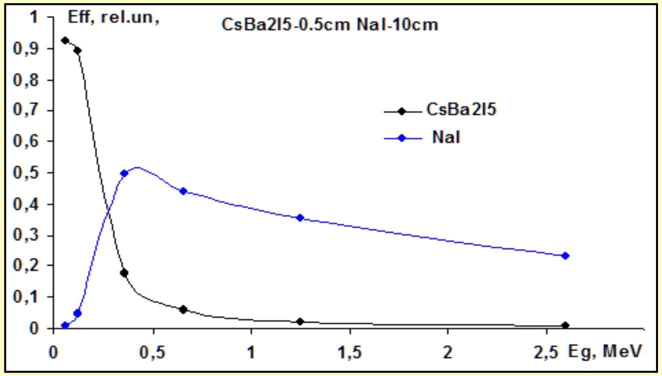
Light collection for high (0.01 cm^{-1}) and low (0.5 cm^{-1}) transparent crystals

V.A. Tarasov, ISMA, 2011

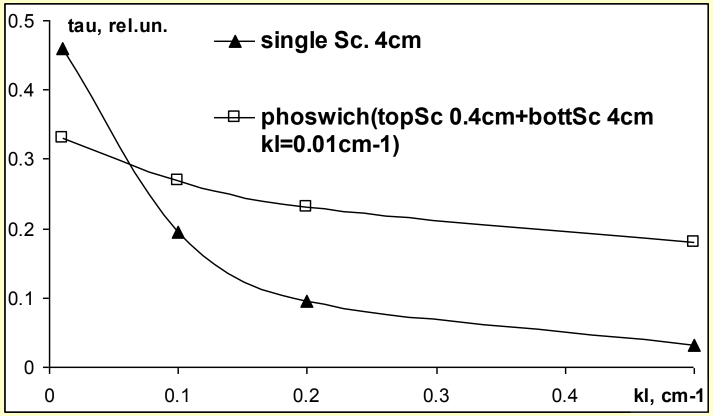
Resume:

Bulk Eu-doped scintillator could not be efficient scintillators

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

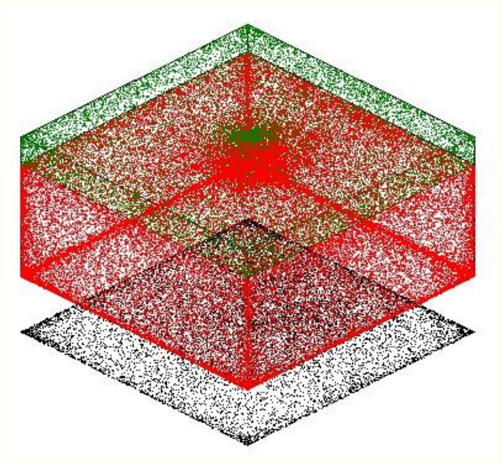


Gamma registration efficiency at 0.06 – 2.65 MeV for 0.5 cm thick SrI_2(Eu) combined with 10 cm NaI(Tl)



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 last years scintillators developments significantly upscale our vision of the perfect scintillator.

✓ Practical needs rise up theoretical studies and view to the fundamental process in radiation absorptions and primary stages of excited states relaxation (evolution).

✓ Theoretical simulations allow to select the process “skeleton” to make new material search more predictable.

✓ Next years forecast –

- community has to select two-three best candiated for the technology development
- we need in criteria for the best scintilaltors selection

THANK YOU FOR ATTENTION!