Inorganic scintillation materials: R&D state-of-art and trends

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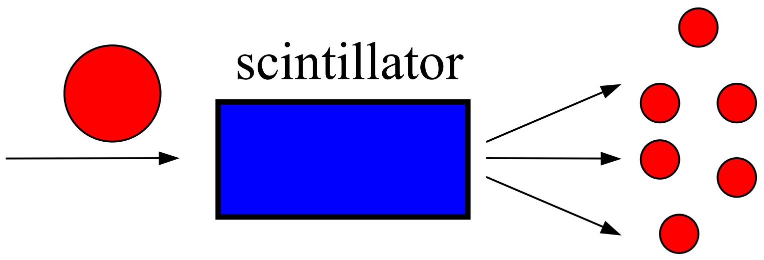
Principle of a scintillator

Spectral transformer

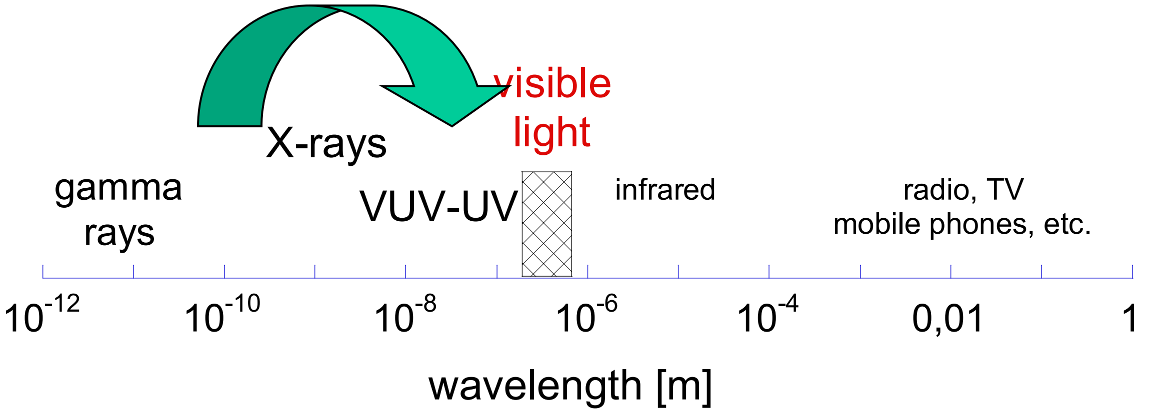


1 photon
(keV - GeV)

n photons
(2 - 4 eV)

Counting of
HE photons!

Fast response
needed !

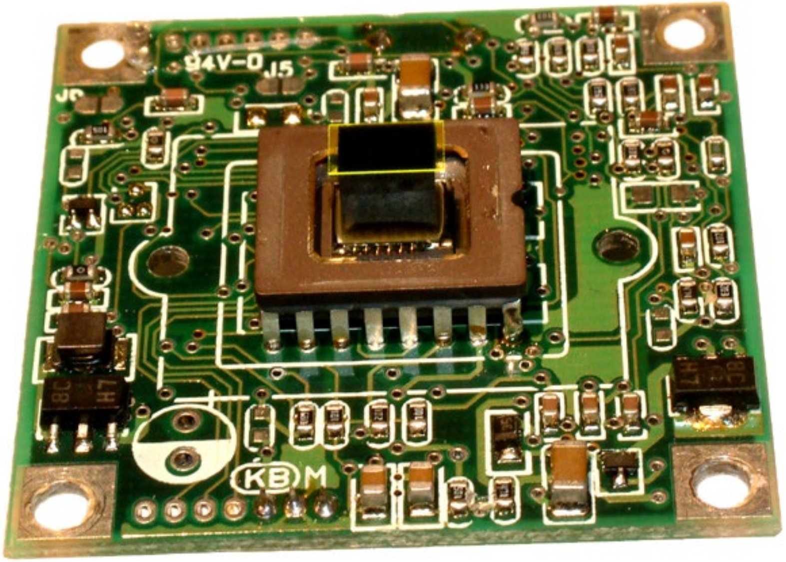


Why we need them – there are no direct sensitive detectors for photons with energy above a few keV

Scintillation detector = scintillator+photodetector

⇒ registration of X-rays or γ-radiation, energetic particles or ions.

Scintillator TRANSFORMS high-energy photons into photons in UV/VIS spectral region, which one can easy and with high sensitivity register by the conventional detectors.

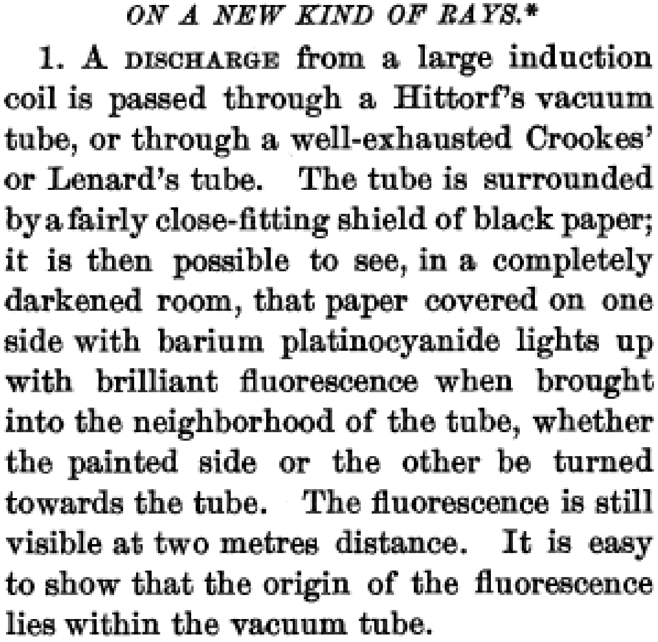


PD, APD, CMOS, CCD …
Si, GaAs, GaN, AlN, InGaN, SiC, diamond

W.C. Roentgen, Science 3, 227 (1896)

History of scintillators starts short after the discovery of X-rays at the end of 19th century

…



*ON A NEW KIND OF RAYS.**

1. A DISCHARGE from a large induction coil is passed through a Hittorf's vacuum tube, or through a well-exhausted Crookes' or Lenard's tube. The tube is surrounded by a fairly close-fitting shield of black paper; it is then possible to see, in a completely darkened room, that paper covered on one side with barium platinocyanide lights up with brilliant fluorescence when brought into the neighborhood of the tube, whether the painted side or the other be turned towards the tube. The fluorescence is still visible at two metres distance. It is easy to show that the origin of the fluorescence lies within the vacuum tube.

Film

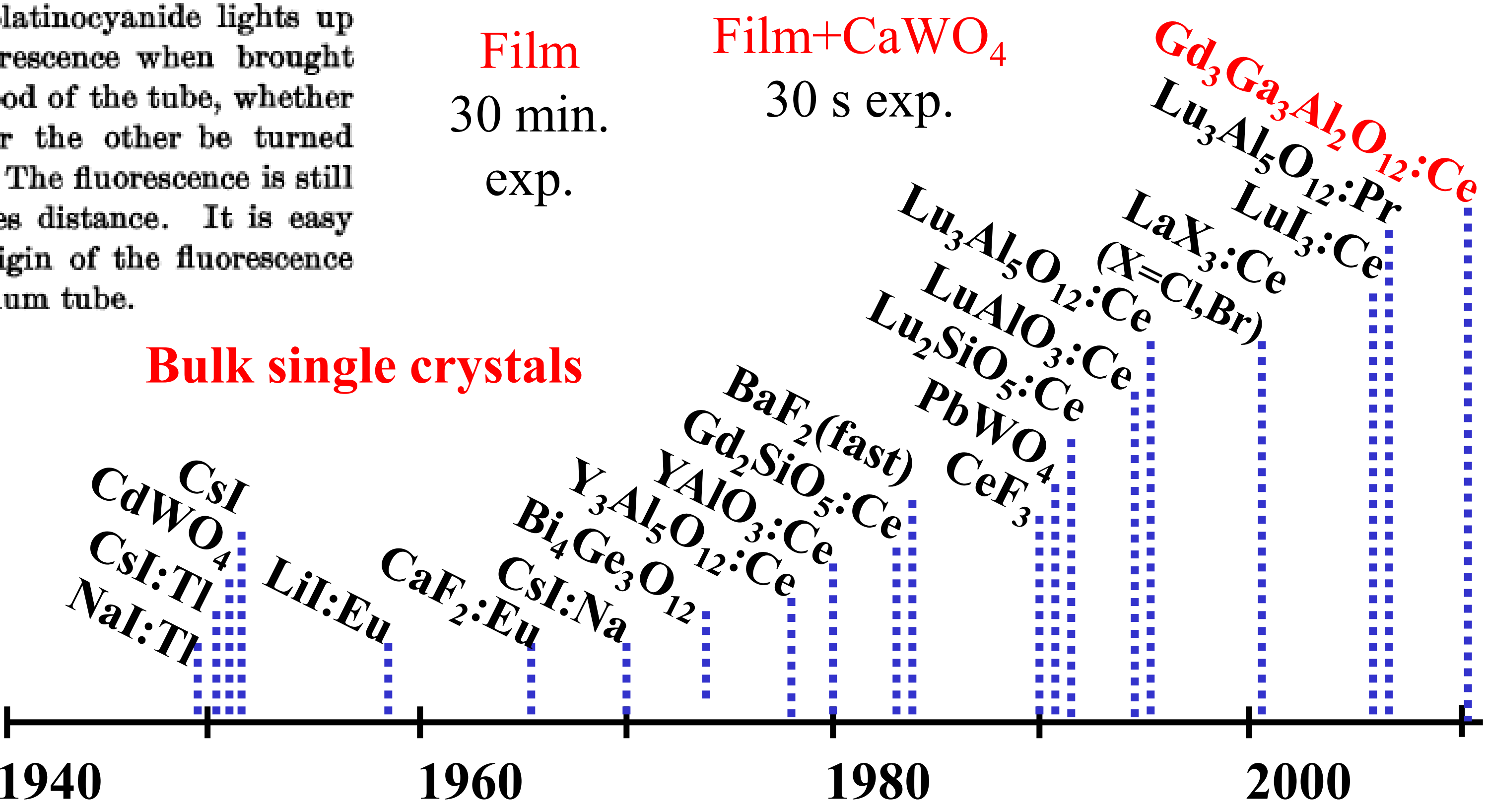
30 min. exp.

Film+$CaWO_4$

30 s exp.

$CaWO_4$ powder in 1896

Bulk single crystals



Year of introduction of a scintillation material

Parameters and characteristics

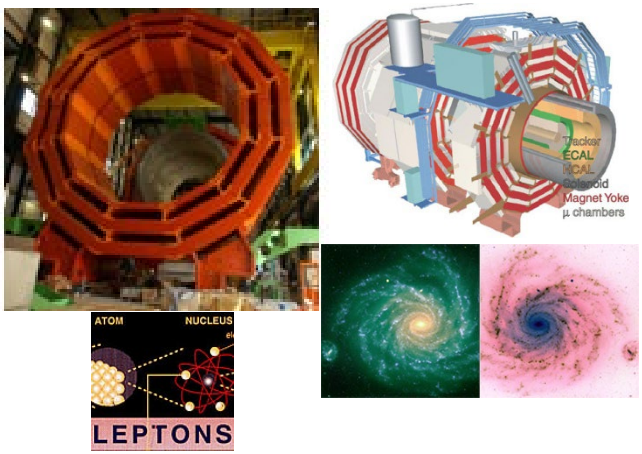
- Integral efficiency and **Light yield**
- **Energy resolution** and nonproportionality
- Emission wavelength
- **Speed of scintillation response**
- **Density** (La, Lu, Gd frequently used)
- Radiation resistance
- Chemical composition
- Price

Applications of scintillators

Medical application

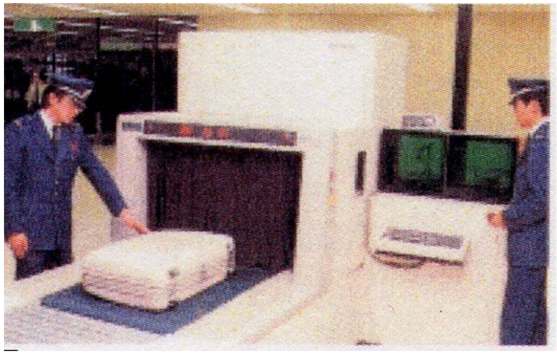
PET, SPECT, CT

High energy physics



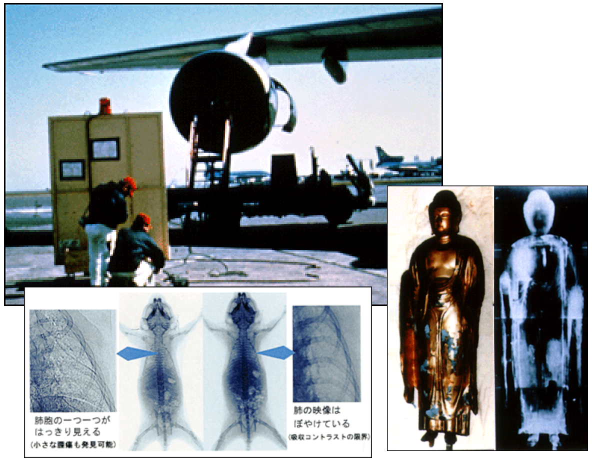
Particle physics, …

Security check



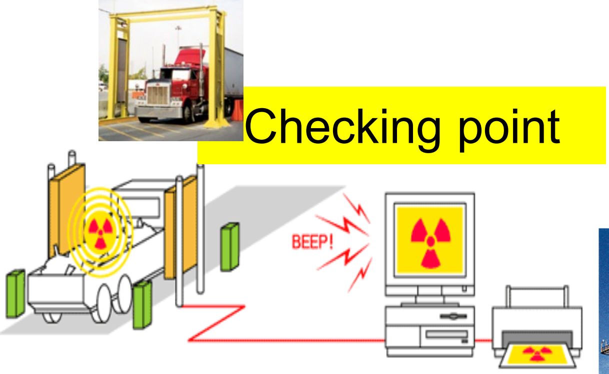
X-ray scanning

Nondestructive analysis



Computed tomography

X&Neutron-based



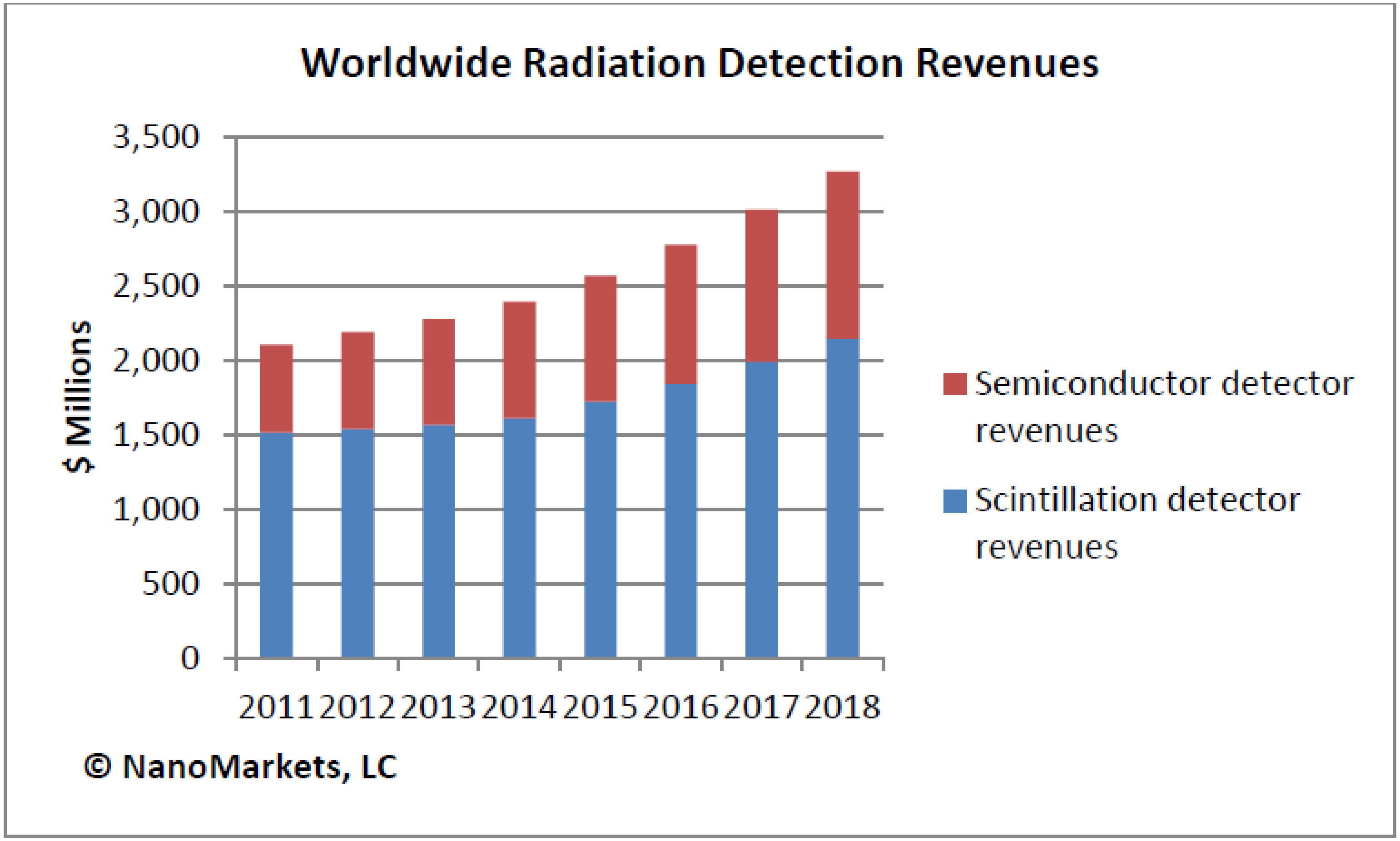
Checking point

Remote detection

Other applications

Hazards,disasters, geology

Radiation detectors - Revenues worldwide



70-75% of revenues comes from scintillation detectors

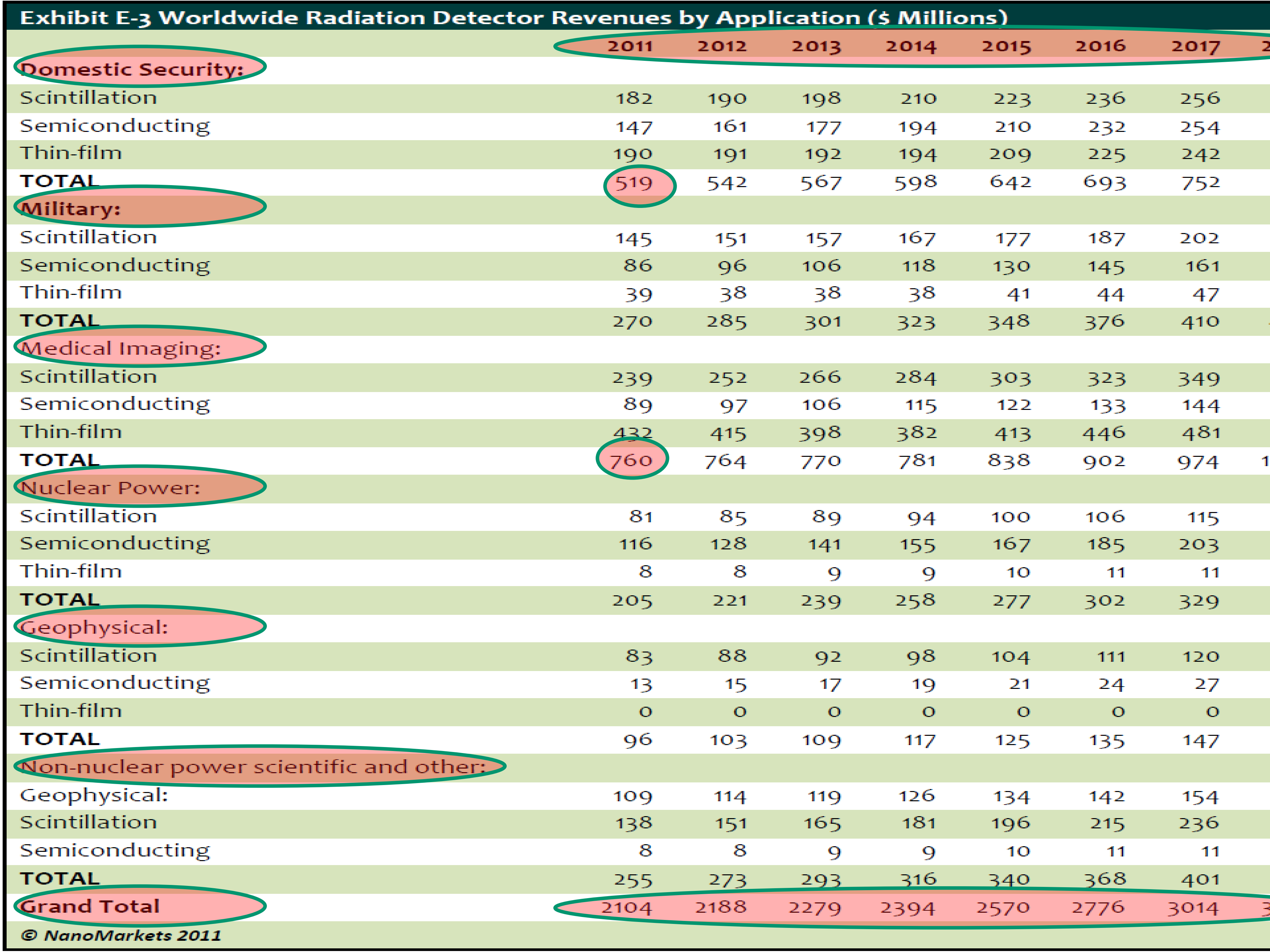


Exhibit E-3 Worldwide Radiation Detector Revenues by Application ($ Millions)

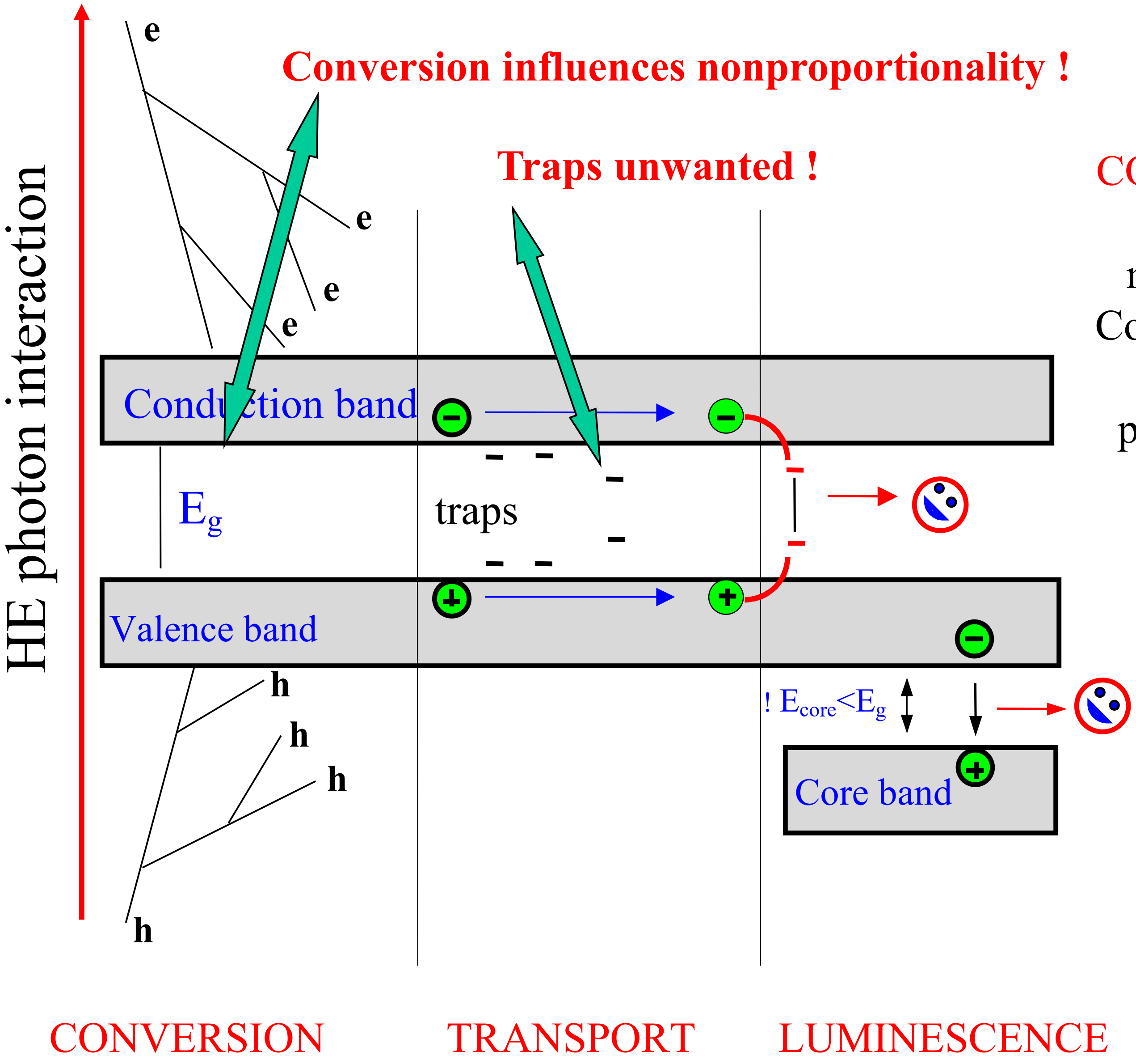
	2011	2012	2013	2014	2015	2016	2017
Domestic Security:							
Scintillation	182	190	198	210	223	236	256
Semiconducting	147	161	177	194	210	232	254
Thin-film	190	191	192	194	209	225	242
TOTAL	519	542	567	598	642	693	752
Military:							
Scintillation	145	151	157	167	177	187	202
Semiconducting	86	96	106	118	130	145	161
Thin-film	39	38	38	38	41	44	47
TOTAL	270	285	301	323	348	376	410
Medical Imaging:							
Scintillation	239	252	266	284	303	323	349
Semiconducting	89	97	106	115	122	133	144
Thin-film	432	415	398	382	413	446	481
TOTAL	760	764	770	781	838	902	974
Nuclear Power:							
Scintillation	81	85	89	94	100	106	115
Semiconducting	116	128	141	155	167	185	203
Thin-film	8	8	9	9	10	11	11
TOTAL	205	221	239	258	277	302	329
Geophysical:							
Scintillation	83	88	92	98	104	111	120
Semiconducting	13	15	17	19	21	24	27
Thin-film	0	0	0	0	0	0	0
TOTAL	96	103	109	117	125	135	147
Non-nuclear power scientific and other:							
Geophysical:	109	114	119	126	134	142	154
Scintillation	138	151	165	181	196	215	236
Semiconducting	8	8	9	9	10	11	11
TOTAL	255	273	293	316	340	368	401
Grand Total	2104	2188	2279	2394	2570	2776	3014

© NanoMarkets 2011

An Outline …

- Introduction to scintillator physics and composition&defect engineering approach
- Examples of R&D in :
    - LaX_3 (X=Cl,Br)
    - Eu-doped halides
    - aluminum garnets
    - aluminum perovskites
    - silicates
- Role of Ce^{4+} in scintillation mechanism of oxide scintillators
- Nanoscintillators – why?
- Conclusions

Physics of scintillators



Conversion influences nonproportionality !

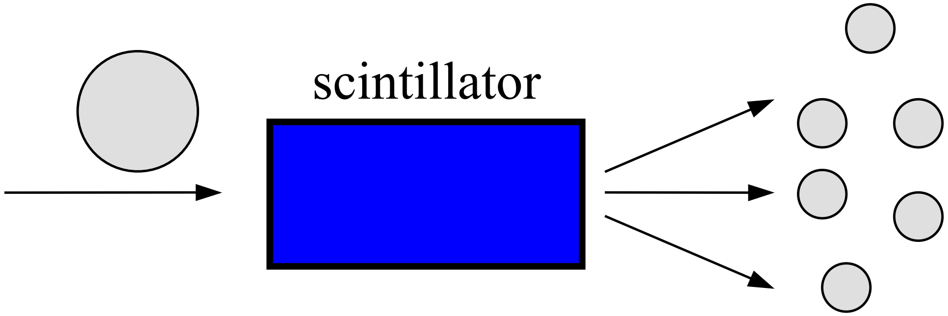
Traps unwanted !

CONVERSION -interaction of a high-energy photon with a material through photoeffect, Compton effect, pair production, appearance of electron-hole pairs and their ther-malization

TRANSPORT - diffusion of electron-hole pairs (excitons) through the material, possible (repeated) trapping at defects, nonradiative recombination

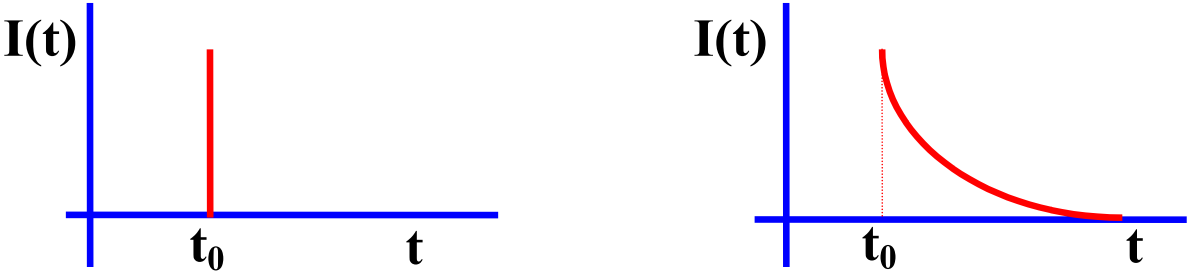
LUMINESCENCE -trapping of charge carriers at the luminescence centre and their radiative recombination

Speed of scintillation response



1 photon
(keV - GeV)

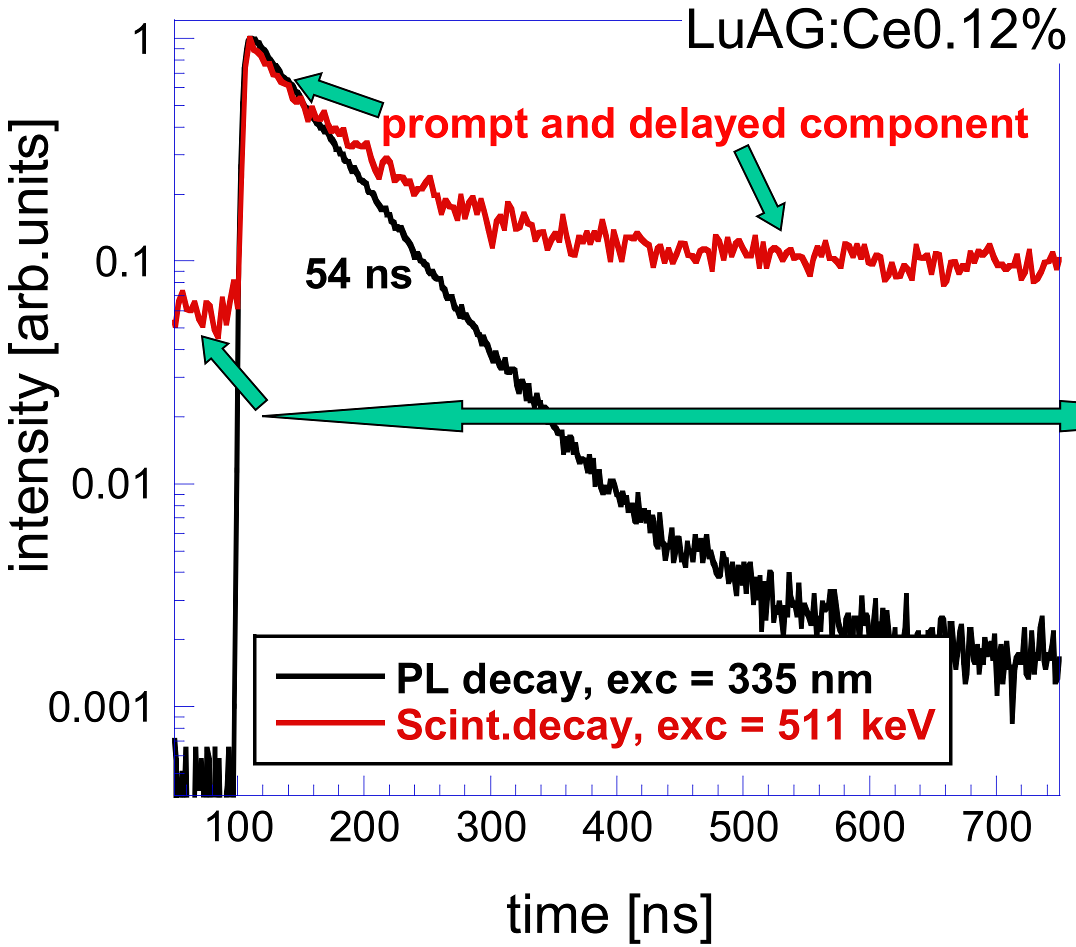
n photons
(1 - 6 eV)



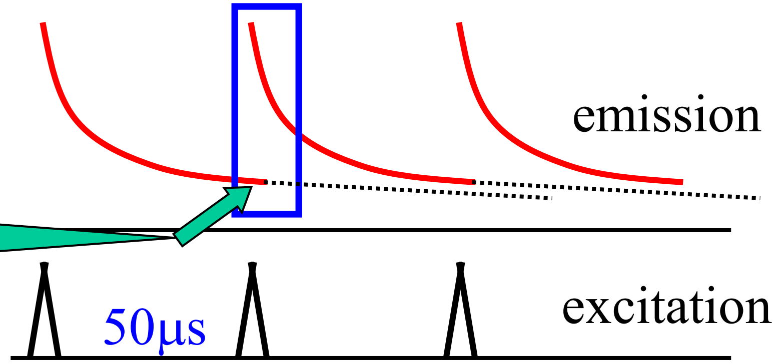
$I(t) = \Sigma A_i \exp[-t/\tau_i]$

Duration of the output light pulse is determined by the luminescence decay time of the emission centers, but also by the timing characteristics of the transport stage !

Scintillation and photoluminescence decay



“Background increase” due to slow decay components in scint. decay



Usually the decay approximation is made by $I(t) = \Sigma A_i \exp(-t/\tau_i)$

Prompt (fast) component is due to the decay time of the emission center (Ce^{3+}), while the **delayed (slower)** decay processes arise in the transport stage.

Strategies in the material engineering

- **Defect engineering (DE)** – targeted codoping (cations) or annealing (anions) to disbalance "natural" defect/trap occurrence and concentration in the material structure
- **Band-gap engineering (BGE)** – more profounded changes in the material electronic band structure due to admixing (alloying) of another chemical component, which is usually possible only in the solid solutions

Defect occurrence is always related to technological recipe!

Strategy for point defect study in scintillator materials

Correlation of several techniques at specifically prepared sample set under well-defined technological conditions:

- ➢Thermoluminescence – to visualize trapping states, which take part in the radiative processes, spectra can advise on recombination sites
- ➢Thermally stimulated currents – to visualize complementary nonradiative processes
- ➢Electron paramagnetic (spin) resonance – to understand location and nature of unpaired-spin-containing trapping centers
- ➢Time-resolved emission spectroscopy – to interconnect the luminescence (scintillation) kinetics with the occurrence or non of the defects visualized by the above techniques

These techniques are correlated with the evaluation of practical scintillator characteristics mentioned before ….

Ce-doped LaX_3 (X=Cl,Br) single crystals

LaBr3:Ce: *Van Loef et al, APL 79,1573 (2001)*

LaCl3:Ce: *van Loef et al, IEEE TNS 48, 341 (2001)*

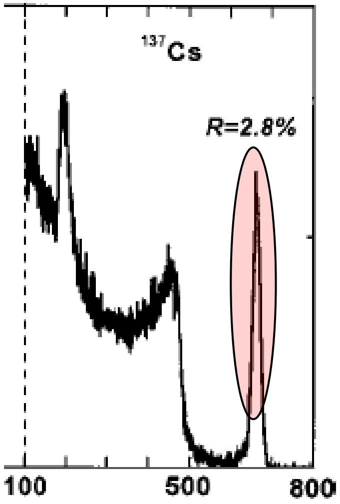
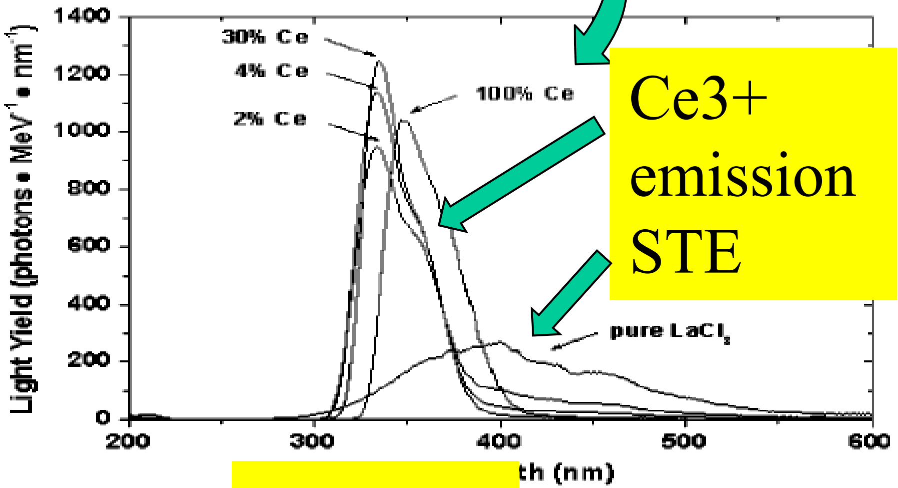
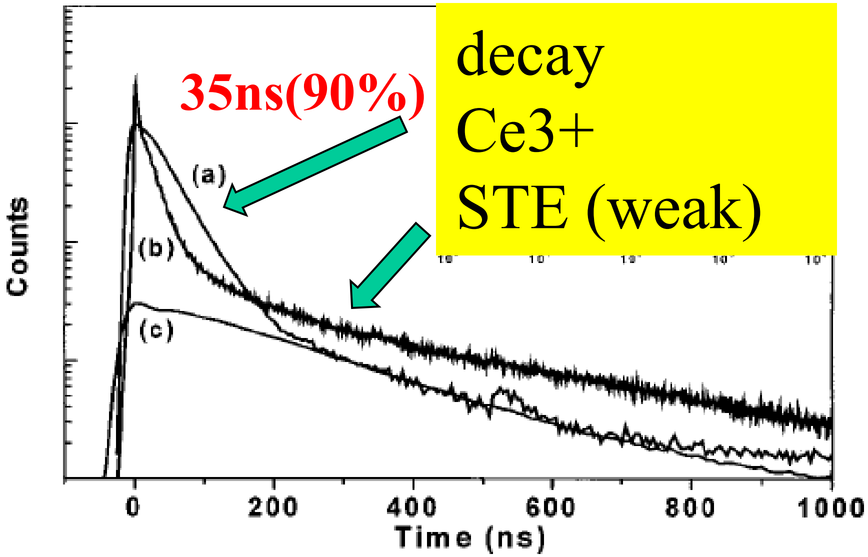


Figure of merit of $LaBr_3$:Ce higher
LY:60-70 000phot/MeV
En.res. 2.8%@667keV

Very hygroscopic!!

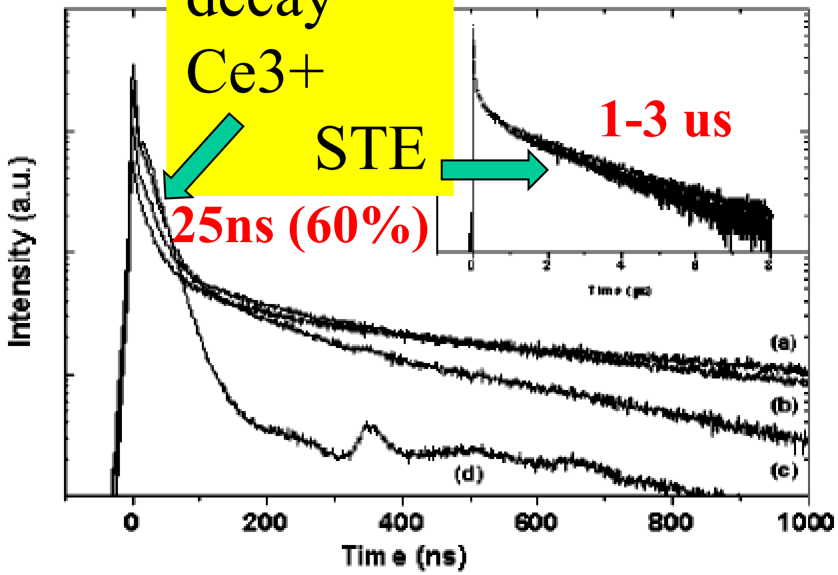


Ce3+
emission
STE



35ns(90%)

decay
Ce3+
STE (weak)



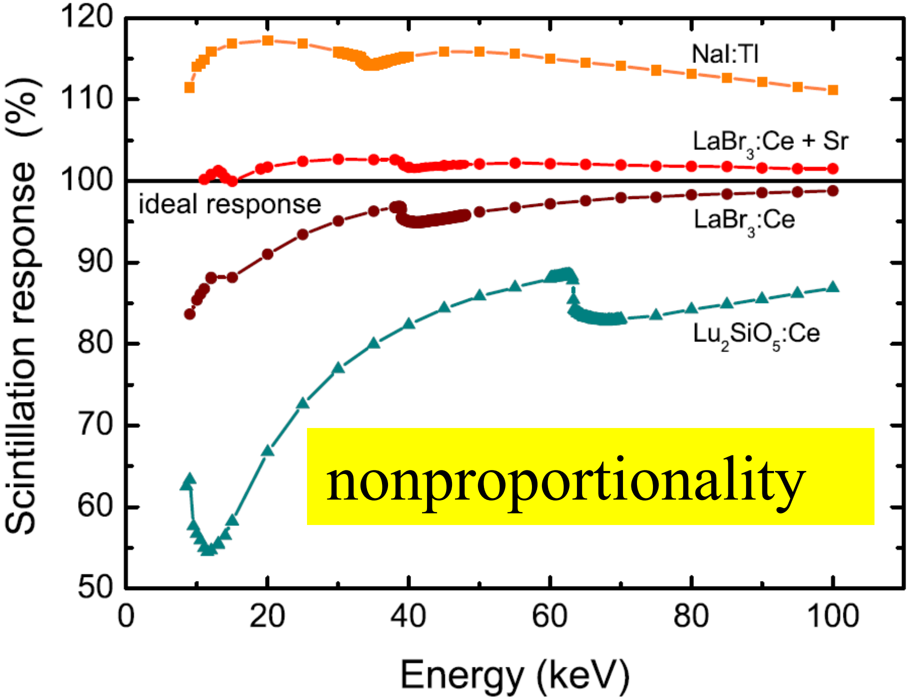
decay
Ce3+
STE

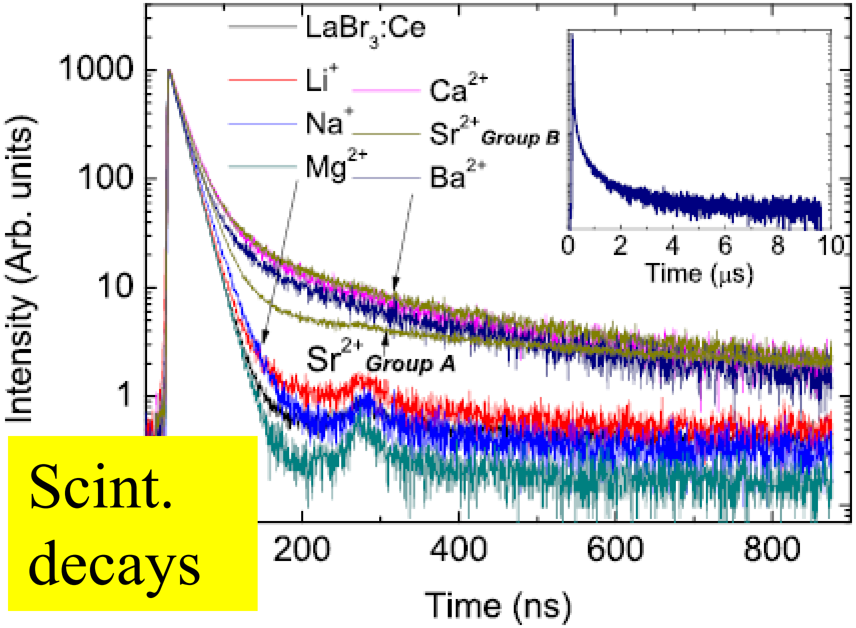
25ns (60%)

1-3 us

Optimization of $LaBr_3$:Ce by codoping

$LaBr_3$:Ce5%,Sr^{2+}0.03%: *Alekhin et al, APL 102, 161915 (2013)*
$LaBr_3$:Ce, A^+(Me^{2+}): *Alekhin et al, JAP113, 224904 (2013)*



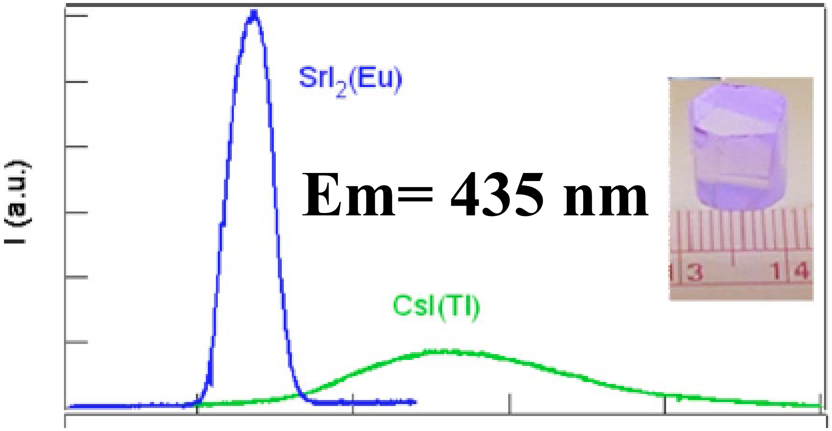


Improved LY up to 78 000 phot/MeV and en.res. up to 2.0%@667keV Energy resolution improvement explained by smaller nonproportionality, but decay shows slower components, TSL intensity increased, etc., i.e. codoping introduces traps, optimization principle is not clear

Eu-doped binary halides

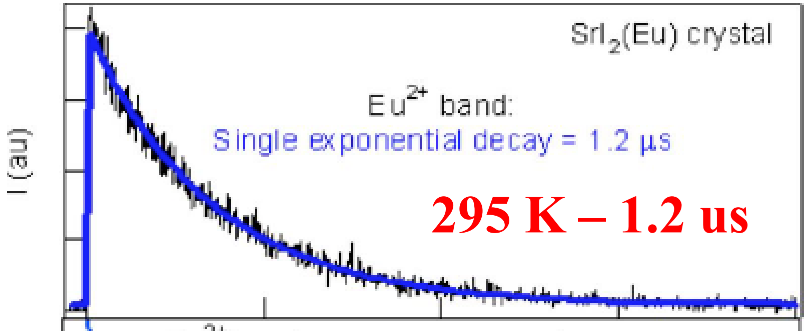
New security measures: need for mid density, ultrahigh LY and excellent energy resolution scintillators, to distinquish radioactive isotopes ⇒ **SrI_2:Eu** re-invented (**Hofstadter, U.S. Pat. 3,373,279 2 (1968)**

Cherepy et al, APL 92, 083508 (2008)
Yang et al, J.Lumin. 132,1824 (2012)

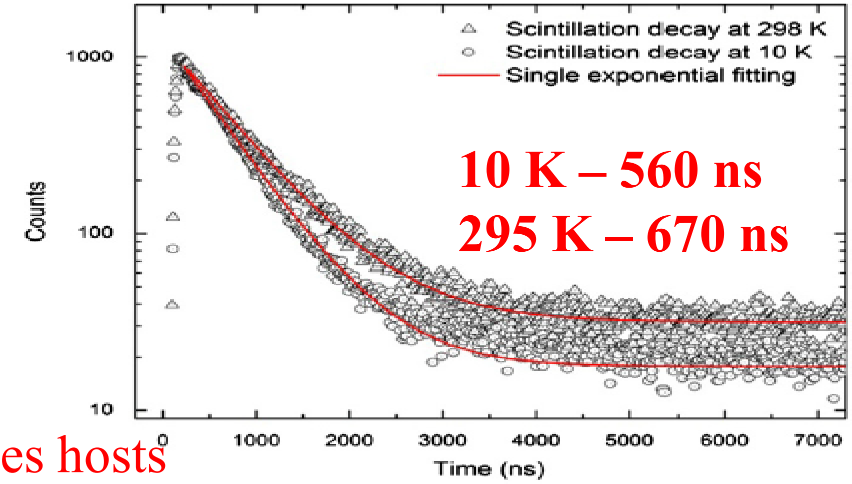


Em= 435 nm

LY>80 000 phot/MeV, en.resolution 3.7%@667keV, however, hygroscopic, **small Stokes shift** results in reabsorption, DT size dep.



295 K – 1.2 us

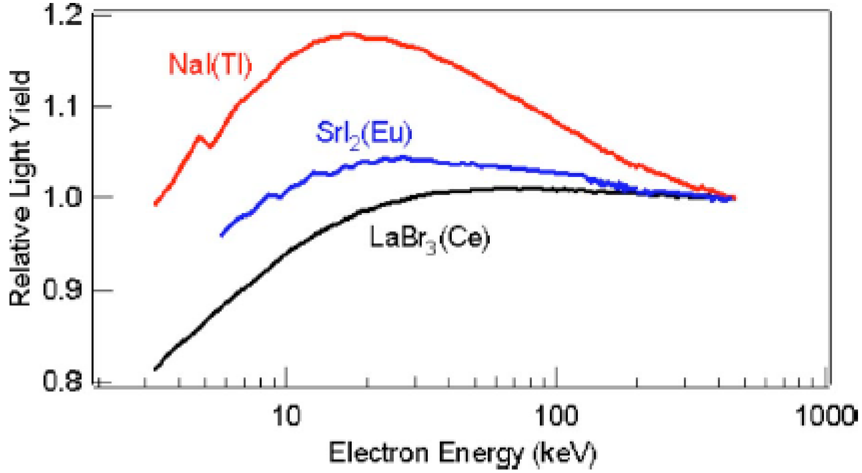


10 K – 560 ns
295 K – 670 ns

Initiated search for Eu-doped new ternary halides hosts

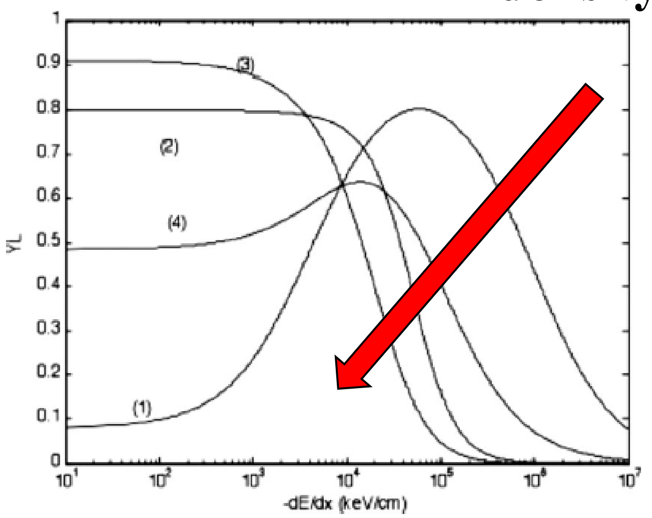
Scintillator nonproportionality

Bizarri et al, JAP 105, 055507 (2009)
Grim et al, pss (a) 209,2421 (2012)
Wang et al, pss (b) 250, 1532 (2013)

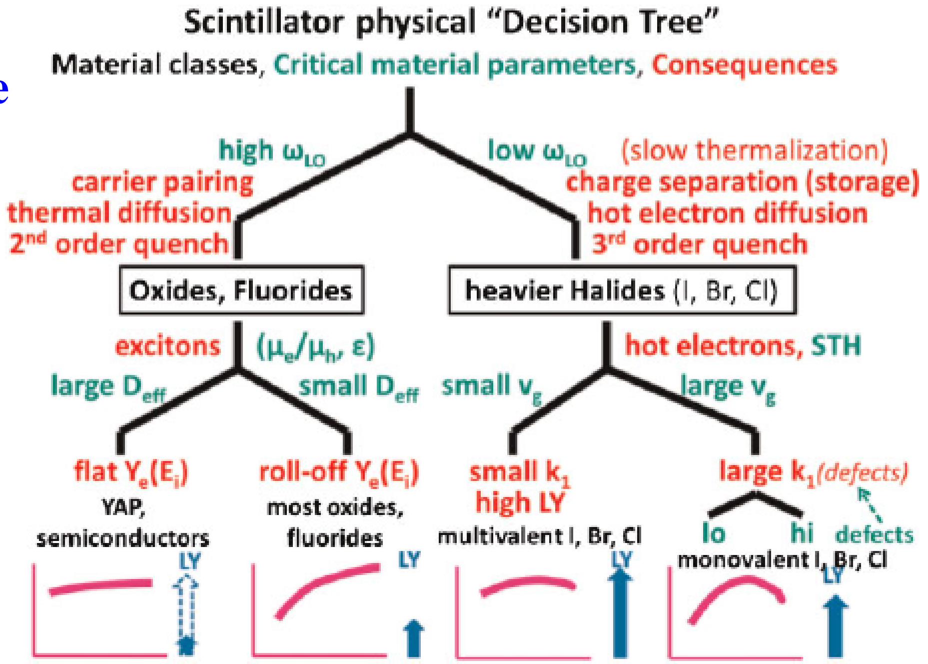


$$Y_L = \frac{a_1 + a_2 n(x)}{1 + a_3 n(x) + a_4 n(x)^2},$$

Local yield YL versus density of excitations n



1) **NaI:Tl**
2) **BaF$_2$:Ce**
3) **GSO:Ce**
4) **LaCl$_3$:Ce**



Scintillator physical "Decision Tree"

Material classes, Critical material parameters, Consequences

high ω_{LO}
carrier pairing
thermal diffusion
2nd order quench

low ω_{LO} (slow thermalization)
charge separation (storage)
hot electron diffusion
3rd order quench

Oxides, Fluorides

excitons (μ_e/μ_h, ε)
large D_{eff}
small D_{eff}

flat $Y_e(E_i)$
YAP, semiconductors
LY

roll-off $Y_e(E_i)$
most oxides, fluorides
LY

heavier Halides (I, Br, Cl)

hot electrons, STH
small v_g
large v_g

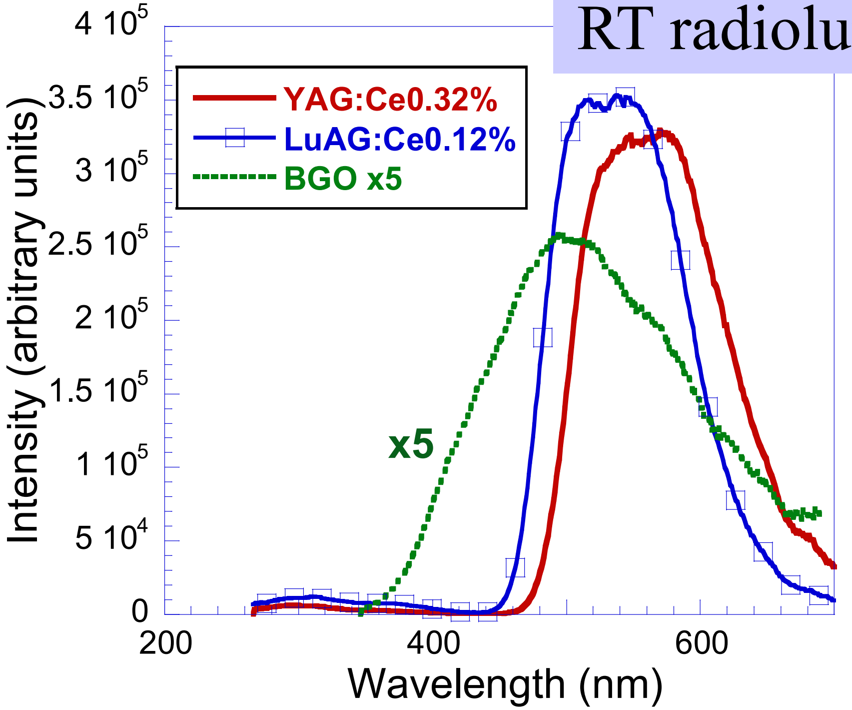
small k_1
high LY
multivalent I, Br, Cl
LY

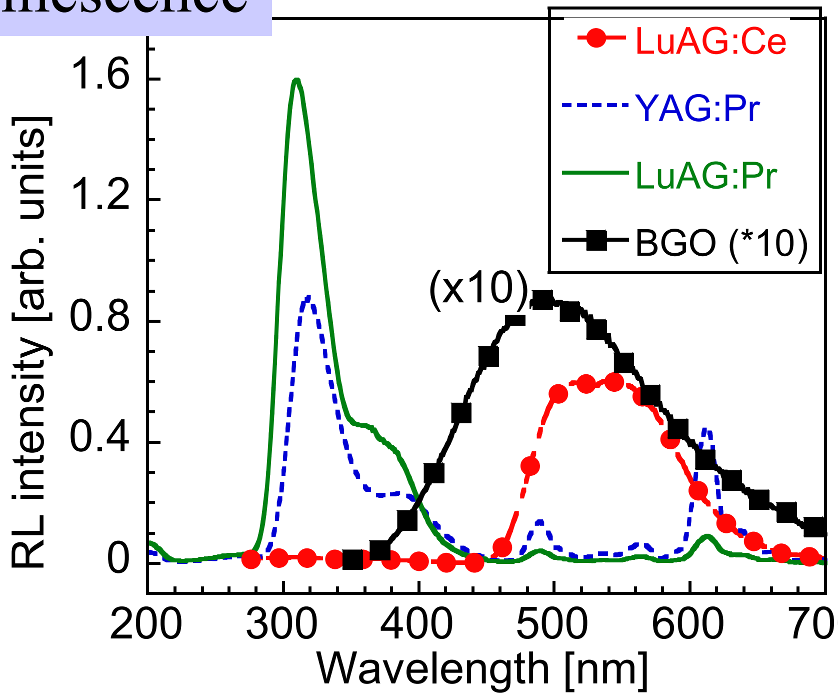
large k_1 *(defects)*
lo
hi
defects
monovalent I, Br, Cl
LY

At high enough density of elementary excitations LY ALWAYS decreases, but the onset is compound-specific !

BGE strategy: Ce^{3+} and Pr^{3+}-doped $Lu_3Al_5O_{12}$

RT radioluminescence





Light yield (1 μs time gate)

Best YAG:Ce ~ only 3x BGO

Best LuAG:Ce ~ 60% of YAG:Ce

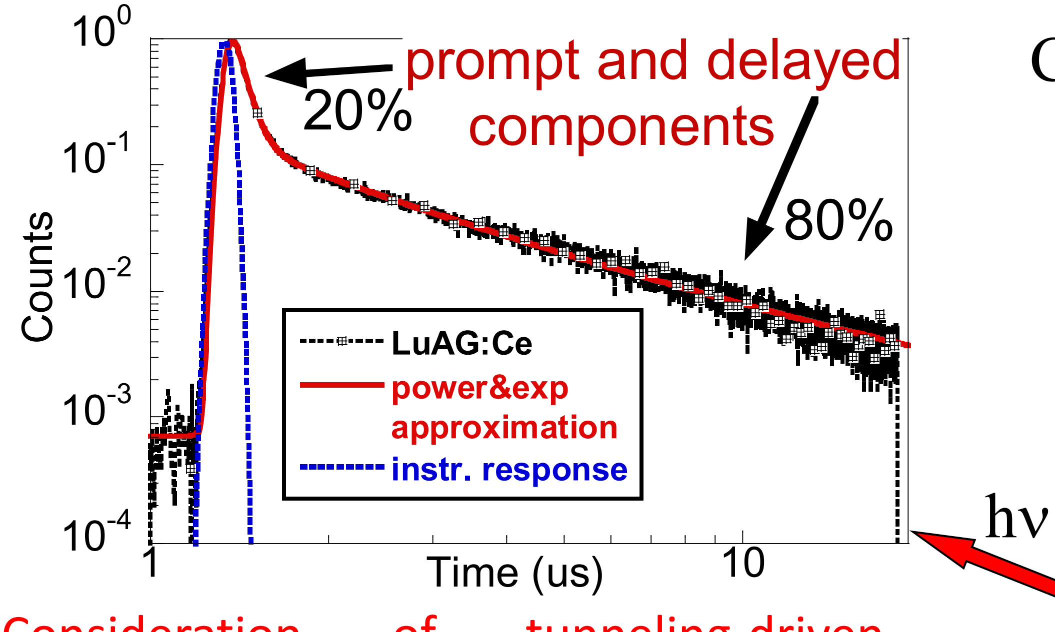
A lot of "slow light" !

The problem:

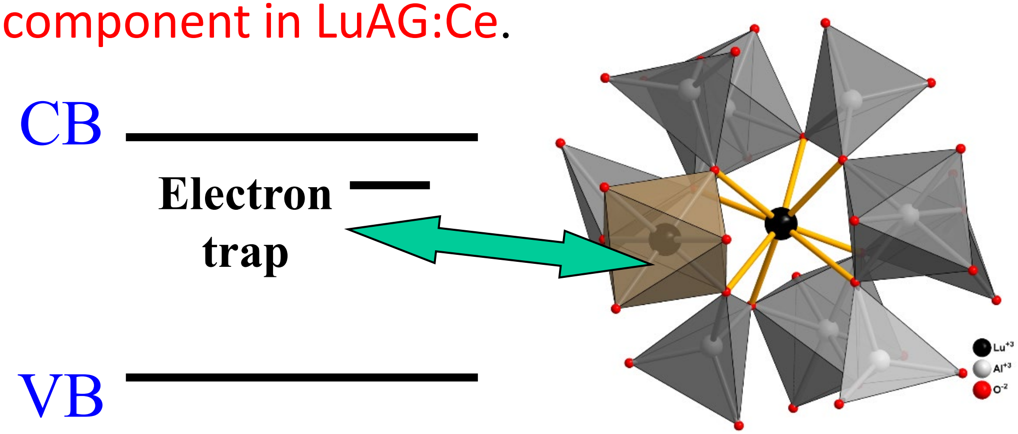
Retrapping of electrons at shallow traps before their radiative recombination at Ce^{3+} (Pr^{3+}) ions

Nikl, phys. stat.sol. (a) ***201****, R41 (2004)*

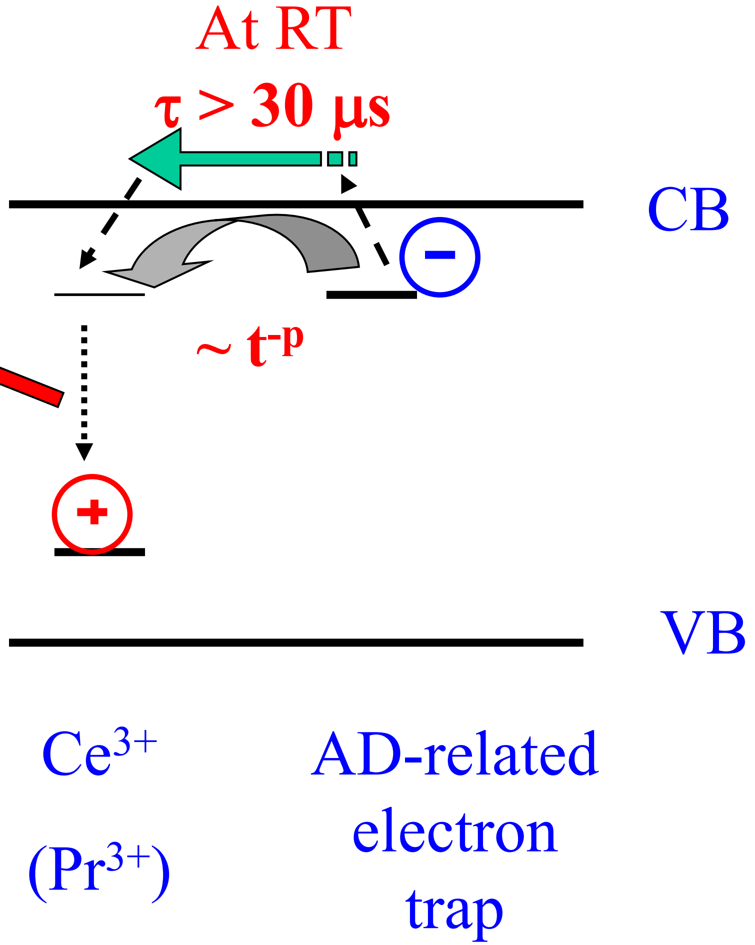
Scintillation decay of LuAG:Ce (Pr) at RT



Consideration of tunneling-driven recombination **provides a physical ground** for the slower scintillation decay component in LuAG:Ce.

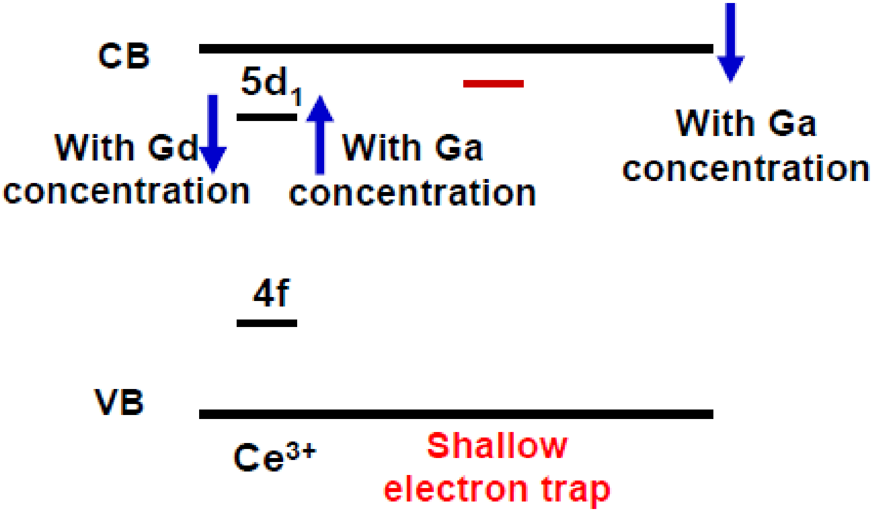


Correlated TSL and EPR study designed the key processes:



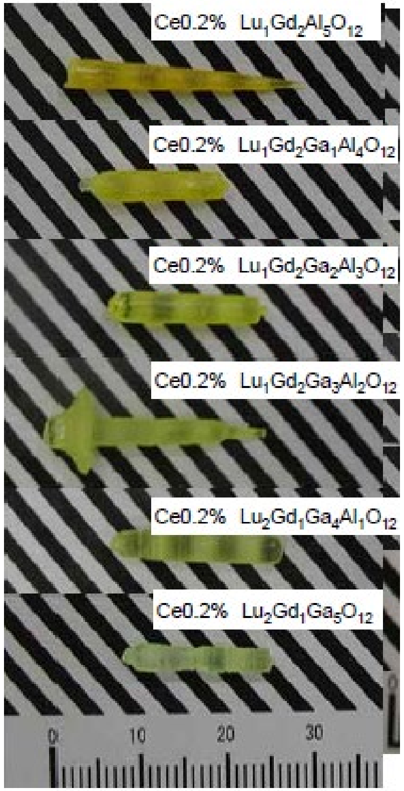
Nikl et al, Phys. Rev. B ***76****,195121(2007)*

Multicomponent garnets $Gd_yLu/Y_{3-y}Ga_xAl_{5-x}O_{12}$

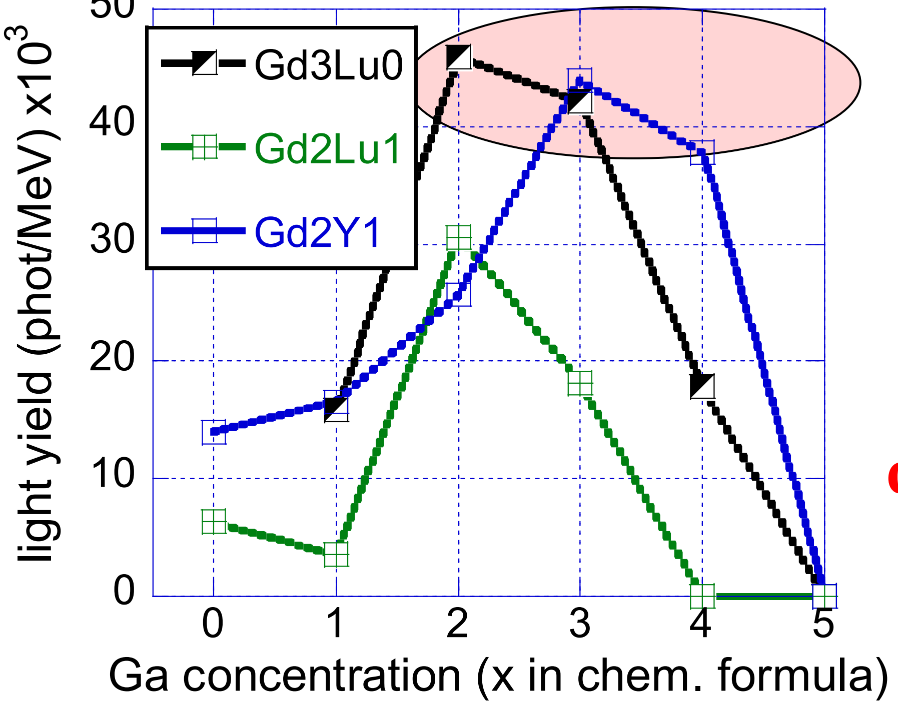


In Ga-admixed LuAG the $5d_1$ level of $Ce(Pr)^{3+}$ gets closer to CB edge ⇒ thermally induced ionization&LY loss

The Gd admixture can help!



Light yield

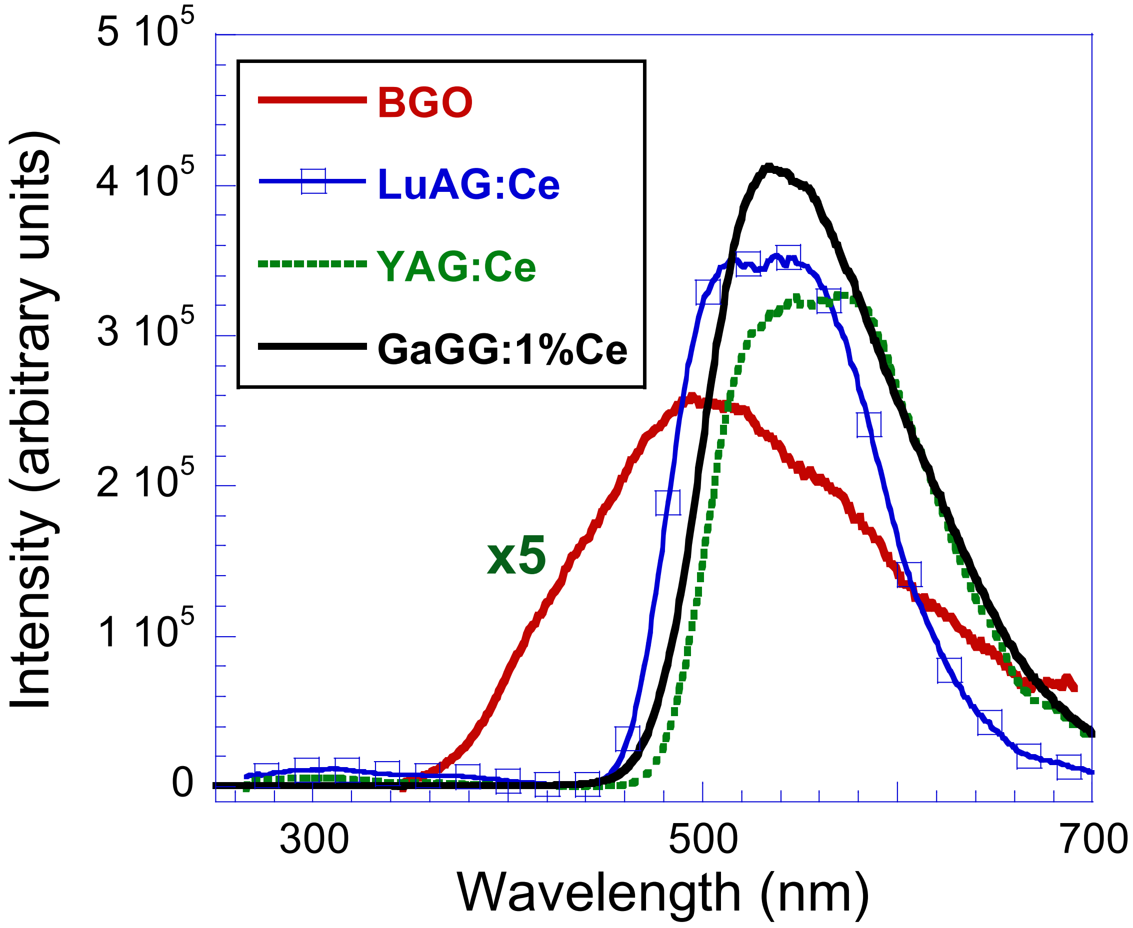


Kamada et al, Crystal Growth& Design **11**, 4484 *(2011)*

LY increase more than twice for x=2-3

Scint. decay dominated by PL decay time for x=3, though weak slow comp. remains

RL spectra of Ce-doped YAG, LuAG and GAGG



Kamada et al, . J. Phys. D ***44,*** *505104 (2011)*
Prusa et al, Rad. Meas. ***56****, 62 (2013)*

Scintillation efficiency (integral of RL spectrum) of GAGG:Ce is only about 10-20% higher than that of YAG:Ce and LuAG:Ce, i.e. **huge LY increase shows that the slow part of scintillation response was transformed into fast one**.

The highest LY of GAGG:Ce (spectrally corrected) measured so far is approaching 60 000 phot/MeV (close to theoretical limit, see *Dorenbos, IEEE TNS* ***57****, 1162 (2010))*

Kamada et al, Optical Materials ***36****, 1942 (2014)*

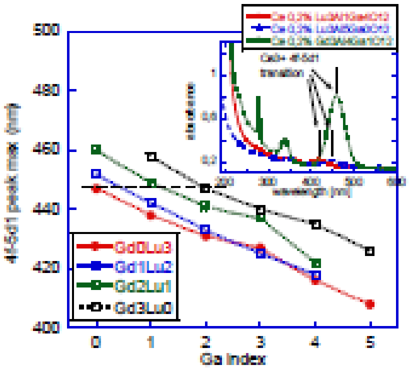
Development of Ce:GAGG and its application

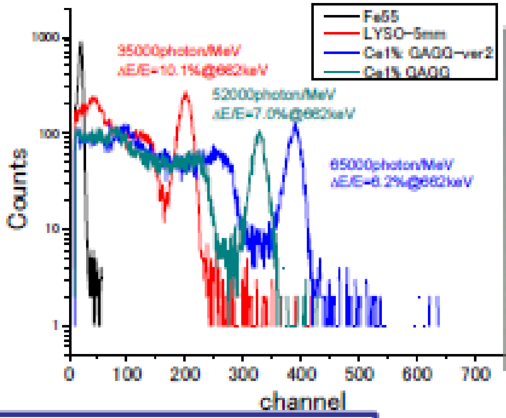
Courtesy of A. Yoshikawa

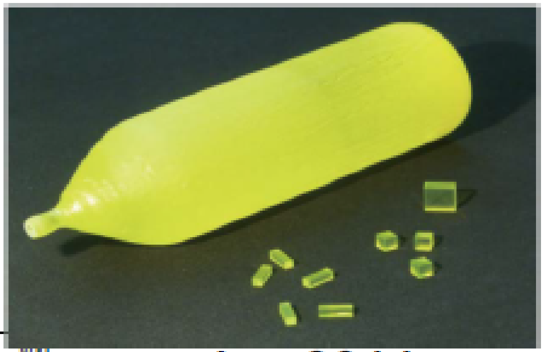
With Furukawa, JAEA, Univ. Tokyo

Nov. 2010

Ce:Gd$_3$ (Al,Ga) $_5$O$_{12}$







Jan. 2011

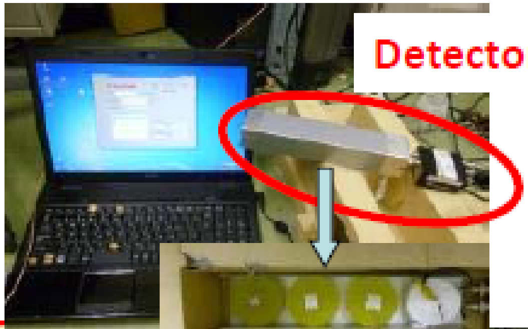
development

Luminescent study, LY,
Decay evaluation

2inch crystal !

Nov. 2011 in the market

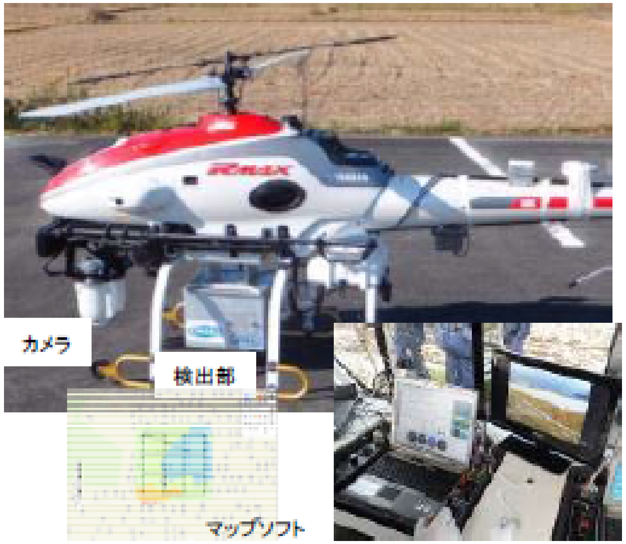
Just one year



Detector unit

GAGG
+APD

Sept. 2012

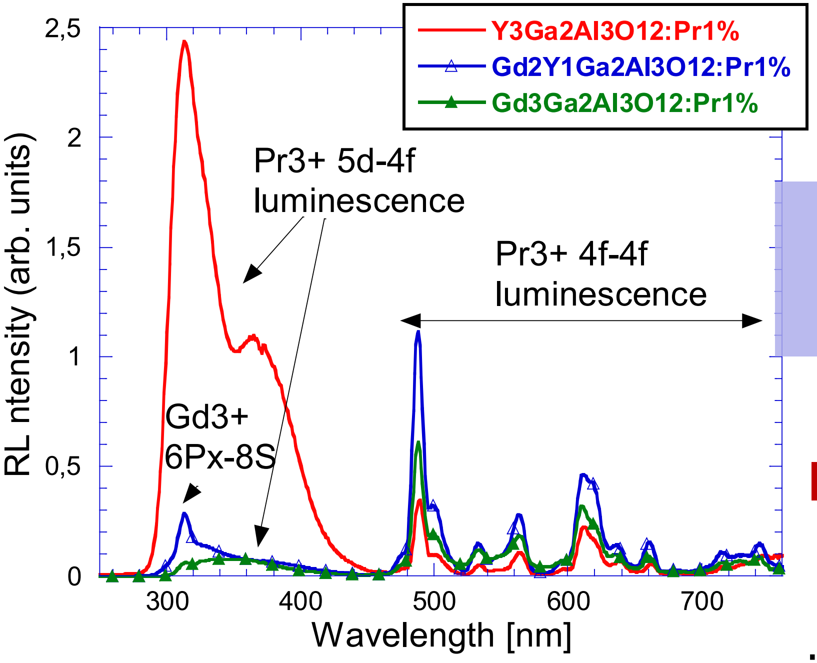


Compact & real time
Survey meter

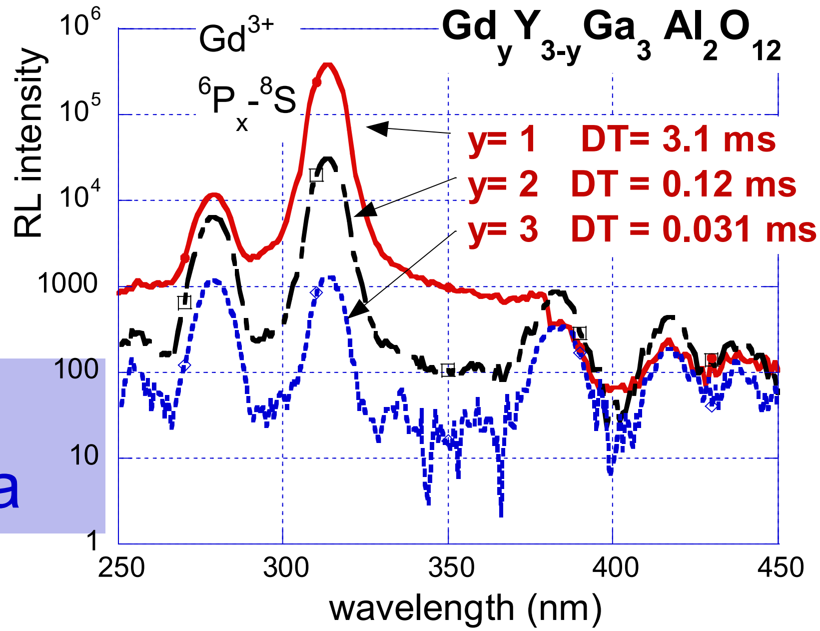
Food checking system

GAGG Compton camera
on the unmanned helicopter

Pr^{3+} doped $(Gd,Y)_3Ga_2Al_3O_{12}$

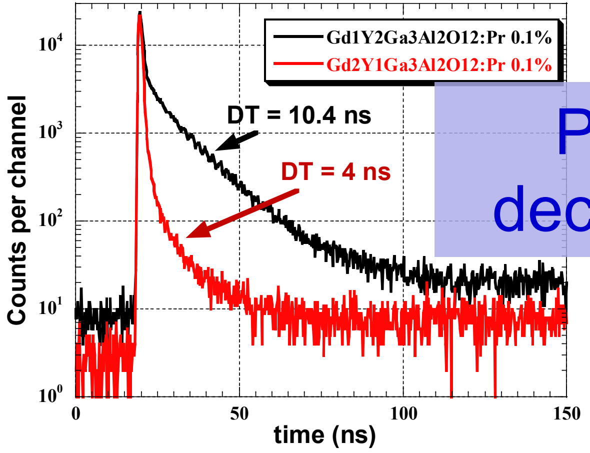


RL spectra



Introduction of Gd^{3+} into YGAG host result in dramatic decrease of Pr^{3+} 5d-4f emission (LY only 4000 ph/MeV), 4f-4f intensity increases, scint. decay governed by 6 ns DT

GGAG:Pr 0.1%, decay kinetics (exc. nanoLED). Ex=281 nm; Em=325 nm; RT



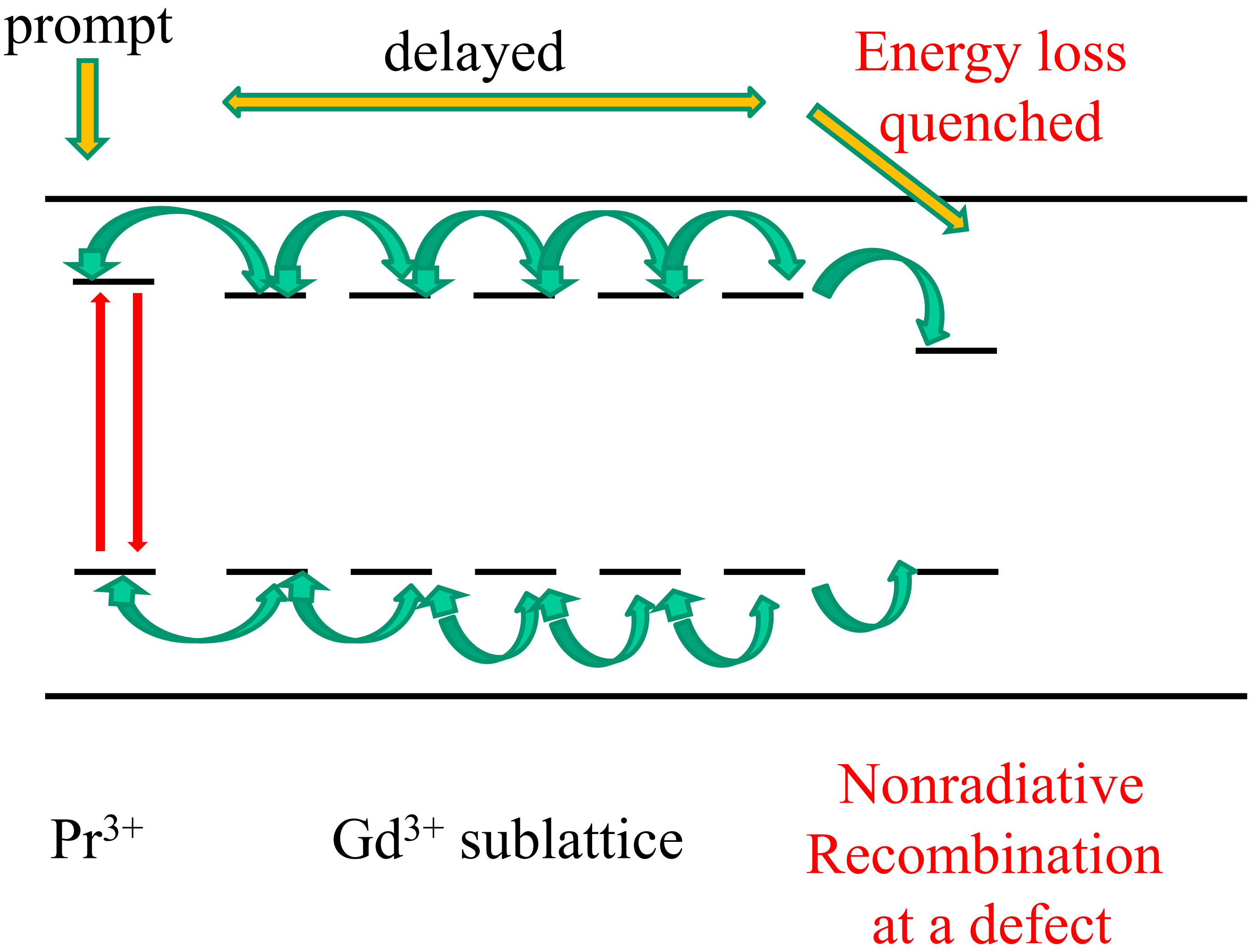
PL decays

Proposed interpretation:

- ❑ $5d_1$-$^3H_4$(Pr^{3+}) in resonance with ^8S-$^6P_{7/2}$ (Gd^{3+}) , reverse ET $Pr^{3+} \Rightarrow Gd^{3+}$&migration away in Gd-sublattice !

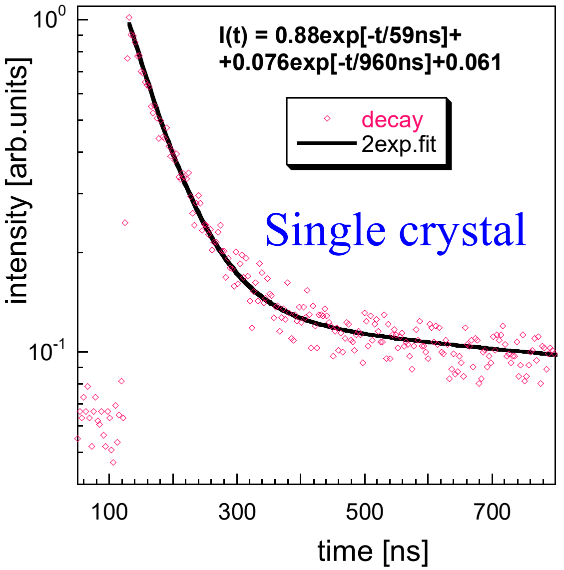
Babin et al, J. Phys. D: Applied Phys. ***46*** *(2013) 365303*
Wu, Ren, Optical Materials ***35****, 2146 (2013)*

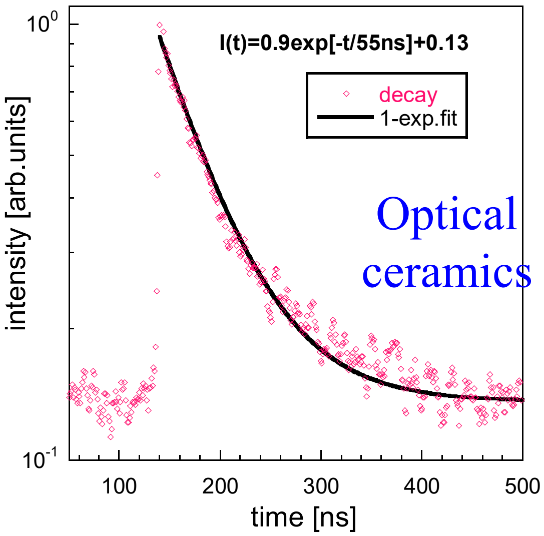
Energy transfer sketch in GAGG:Pr

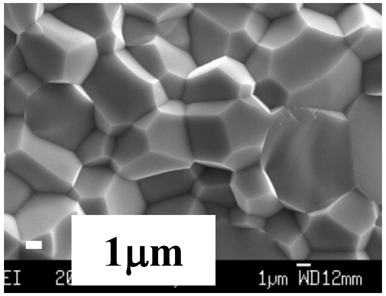


YAG:Ce and LuAG:Ce optical ceramics

Scint. Decay LuAG:Ce OC



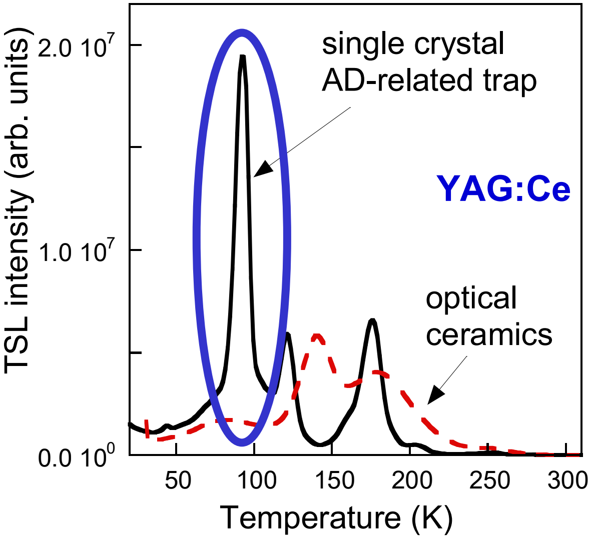


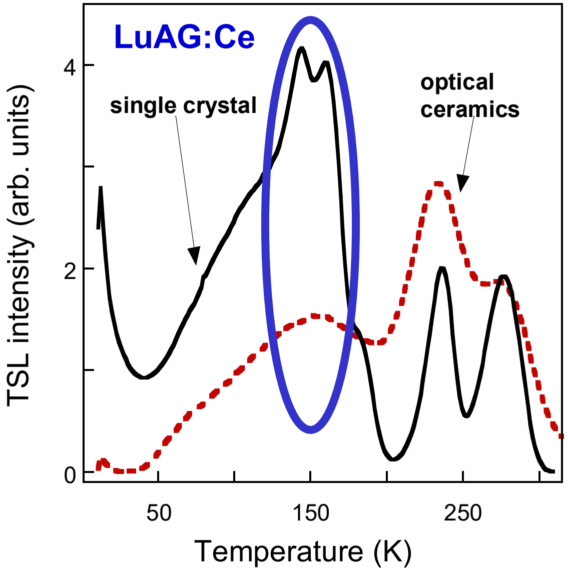


OC doesn’t show slower submicrosecond decay component as the AD's are absent, but does show enhanced slower processes at tens-hundreds of μs, which are most probably due to deeper traps at the grain interfaces

J.Lumin. ***126***, *77 (2007)*
J.Appl. Phys. ***101***, *033515 (2007)*

TSL glow curve
X-ray irr. at 10 K



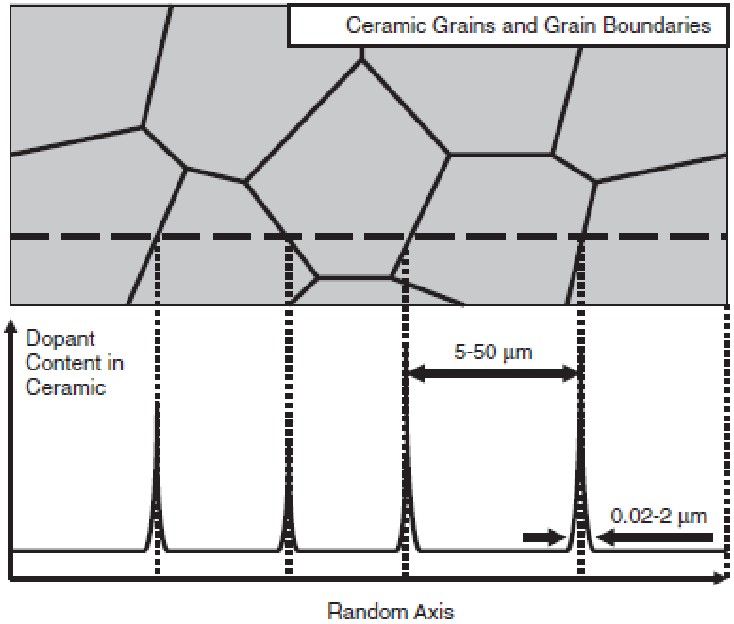


Dopant segregation at grain boundaries in OC

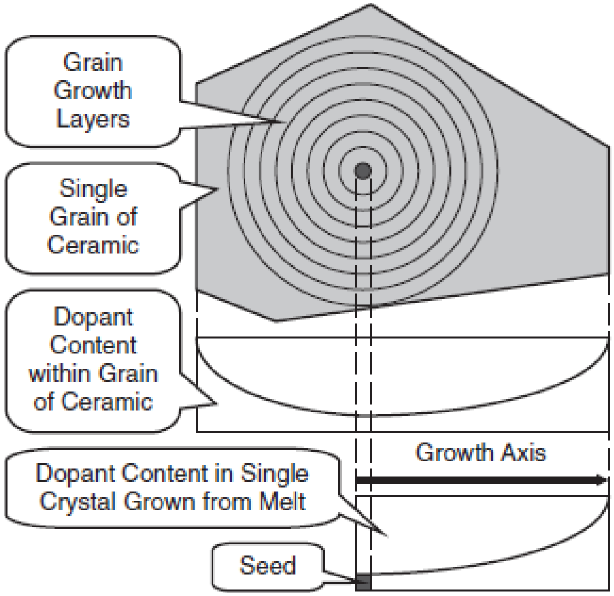
Japanese Journal of Applied Physics **49** (2010) 075601 **REGULAR PAPER**

Correlation between Segregation of Rare Earth Dopants in Melt Crystal Growth and Ceramic Processing for Optical Applications

Valery I. Chani[1]*, Georges Boulon[1,2], Wei Zhao[2,3], Takayuki Yanagida[1], and Akira Yoshikawa[1,4]



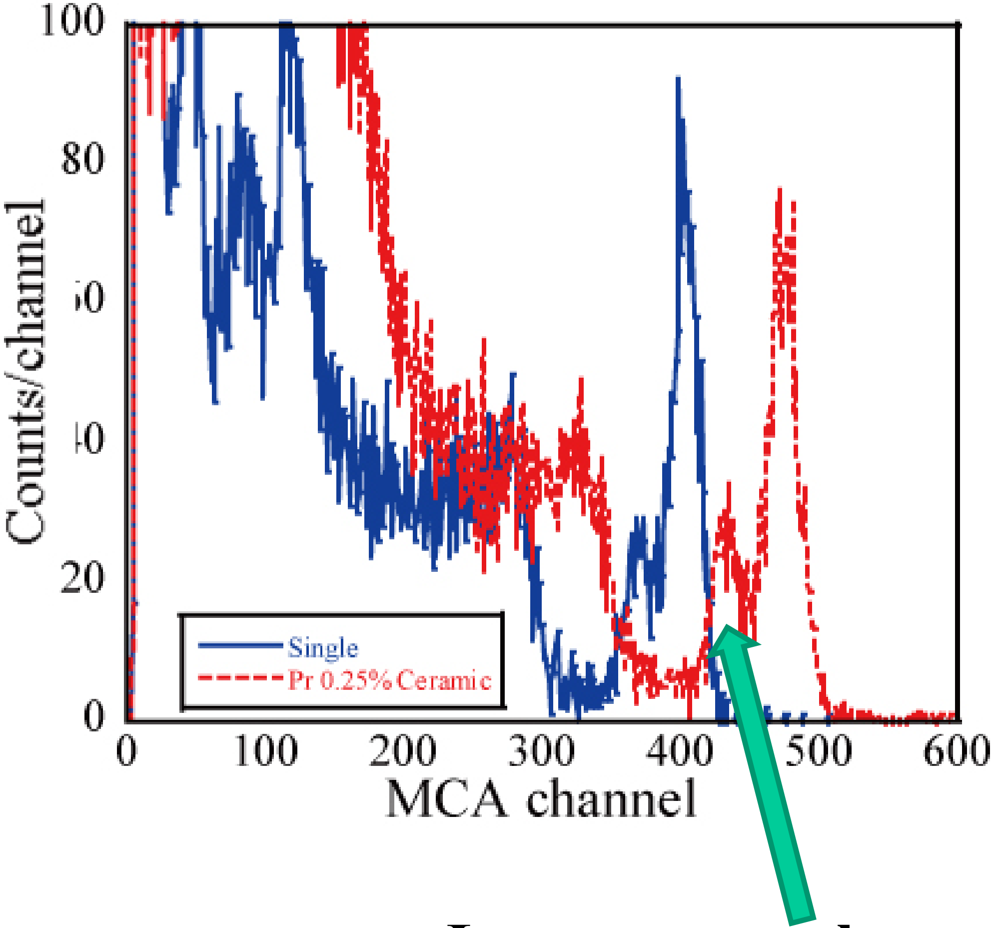
YAG:Ce – Ce concentration at grain boundaries increases !



This phenomenon is observed when segregation coef. in the melt growth of single crystal is < 1 !

The advanced LuAG:Ce(Pr) optical ceramics

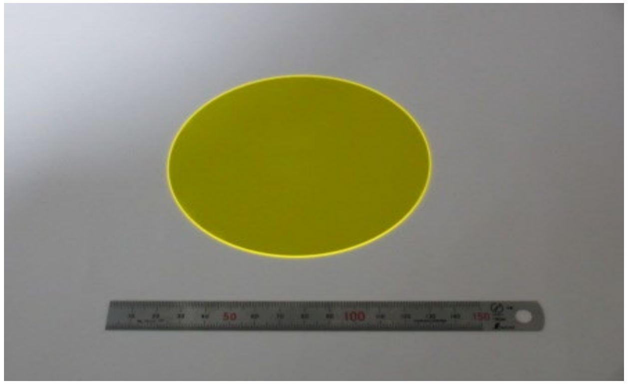
Energy spectra



Lu-escape peak

In the latest LuAG:Pr OC samples from Konoshima Co. the **LY of OC is 21% higher respect to SC**! (21800 ph/MeV, 4.6%@662 keV)

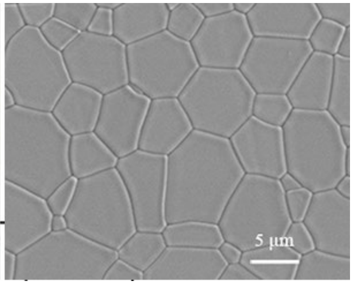
Yanagida et al, IEEE Trans.Nucl.Sci. **59**, 2146 (2012)



Ceramic Ce:YAG (Ø 120 mm) manufactured by Konoshima

S. Liu et al, ISLNOM-6, October 21-23, 2013, Shanghai

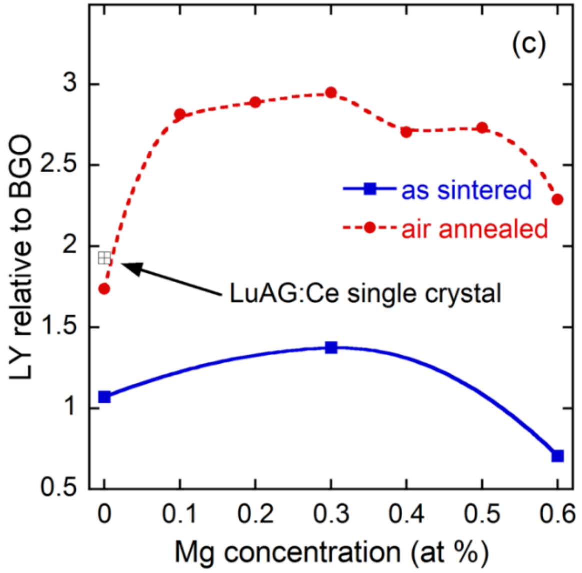
Light yield of LuAG:Ce,Mg ceramic



Sample	d(mm)	L.O.(1μs)(p.e./MeV)	L.O.(1μs)(ph/MeV)	L.O.(10μs)(p.e./MeV)	L.O.(10μs)(ph/MeV)	$LY_{1\mu s}/LY_{10\mu s}$ (%)
LuAG:Ce pixel*	2	2448	18000	3627	26669	67
LuAG:Ce ref	2.09	1549	13941	2284	20556	68
LuAG:Ce,Mg ceramic**	**2**	**1622**	**21897**	**2059**	**27800**	**79**

* *J.A. Mares, et al. IEEE. T. Nucl. Sci. 59, 2120(2012)*

After optimization - comparable with LSO:Ce!!!



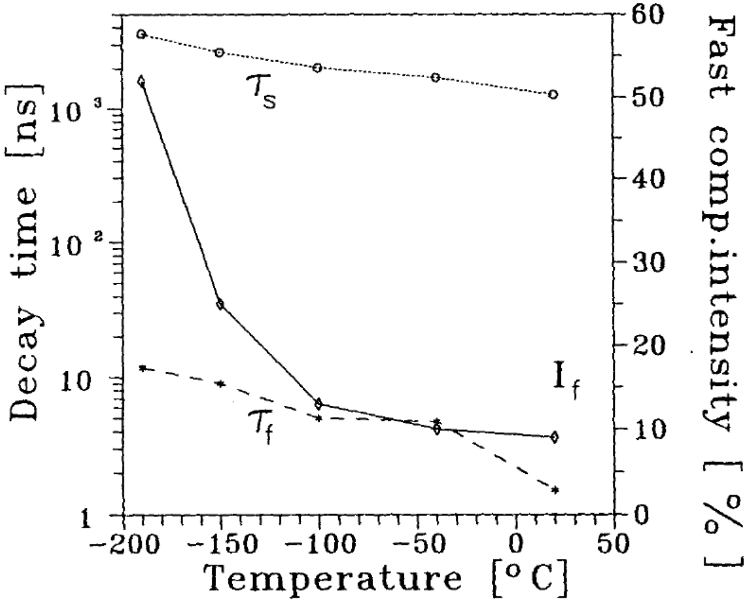
- Light yield of 25000ph/MeV@1μs shaping time has been achieved.
- 40% higher than the best LuAG:Ce single crystal pixel reported in literature

*Liu et al, Phys.stat. sol. RRL **8**, 105 (2014)*

*Liu et al, Adv. Opt. Mater. **4**, 731 (2016)*

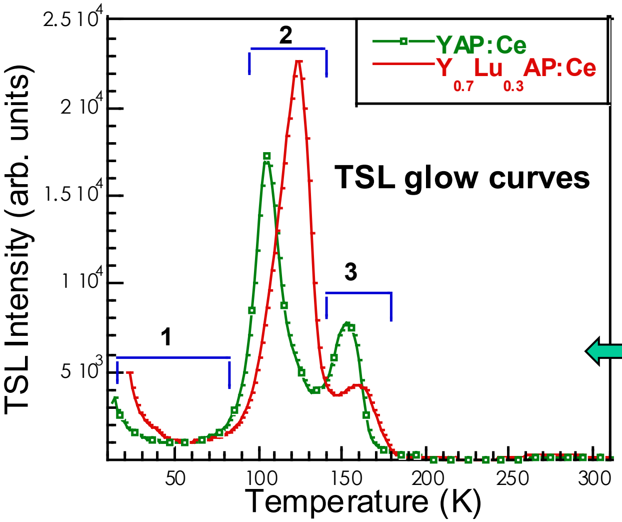
Aluminum perovskites

- ☐ Studied intensively in 1990's, Ce-doped (YAP-LuAP), (YAP-GdAP)
- ☐ Problem of Lu-rich LuYAP:Ce was unstable growth and decreasing LY due to increasing shallow trap depths (*Belsky et al, IEEE TNS 48, 1095 (2001), Fasoli et al, IEEE TNS* ***55****, 1114 (2008)*)
- ☐ Ce-doped GdAP studied comparatively less (*Dorenbos et al, REDS 135, 321 (1995), Mares et al, REDS 135, 369 (1995)*), back transfer Ce3+⇒Gd3+ evidenced !



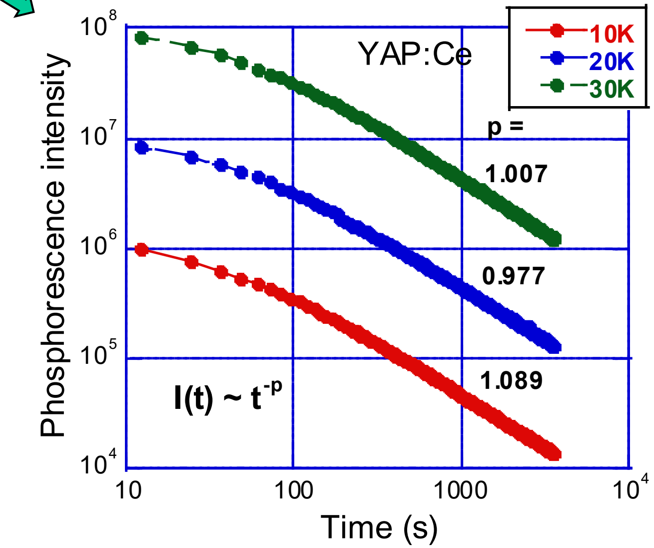
Back energy transfer is due to the overlap of the very side at high energy part of Ce^{3+} emission with 305-310 nm ^8S-^6P_x absorption lines of Gd^{3+} ....that is why it is so much temperature dependent

Thermoluminescence below RT: Complete analogy with (Lu,Y)AG:Ce!



Region 1 points again to a tunnelling process:

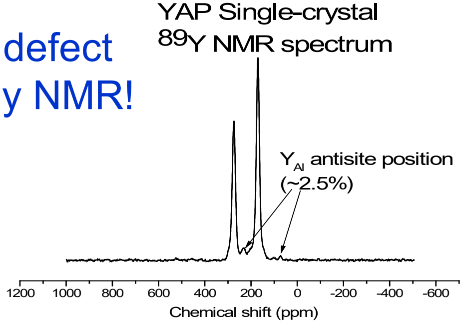
Fasoli et al, IEEE TNS 55 (2008) 1114



Is electron trap in region 2 based on the antisite Y_{Al} (Lu_{Al}) defect?? **YES** !

(Zhydachevskyy et al, J. *Phys. Chem. C* 125 (2021) 26698

Y_{Al} antisite defect evidenced by NMR!

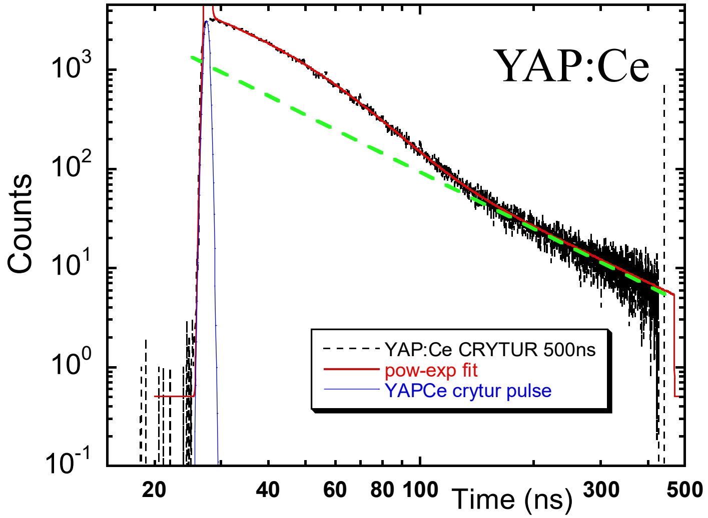


TSL peak in region 3 is due to the shallowest O^- center evidenced by EPR

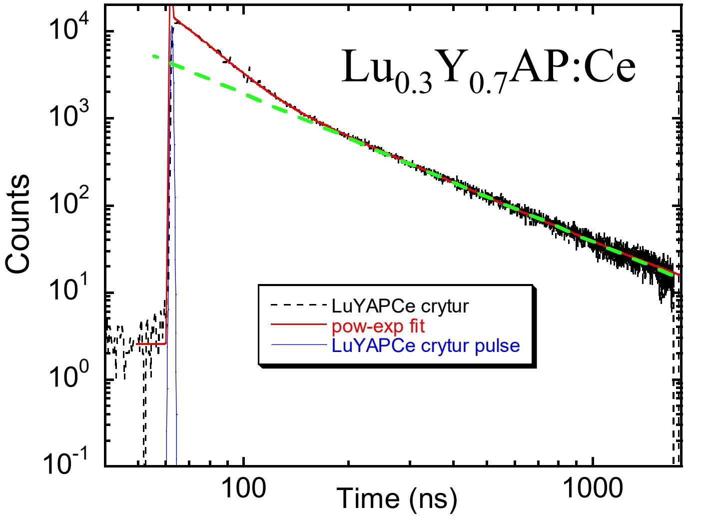
(*Laguta et al, Phys. Rev. B* ***80,*** *045114 (10 pp) (2009*)
Nikl et al, phys.stat.sol. (a) ***204****, 683 (2007)*

Scintillation decay of $(Lu,Y)AlO_3$:Ce Complete analogy with (Lu,Y)AG:Ce!

$I(t)=2465\exp(-t/\mathbf{18.7\,ns}) + 2963(1.9+0.05t)^{-2.007} + 0.5$



$I(t)=9070\exp(-t/\mathbf{17.6\,ns}) + 3207(0.77+0.01t)^{-1.73} + 2.541$



With increasing content of Lu the slower decay component becomes comparatively more intense and its course decelerate! It can be modelled by the sum of exp and inverse power function with coefficient p within 1.5-2 which is still within the limits of more recent theoretical model of tunneling driven luminescence decay (*Sahai et al, J. Lumin.* ***195*** *(2018) 240*)

Chewpraditkul, et al, Phys. Stat. Sol. (a) ***210*** *(2013) 1903*

We considered (Gd,Ln)AP:Ce, Ln=Lu,Y

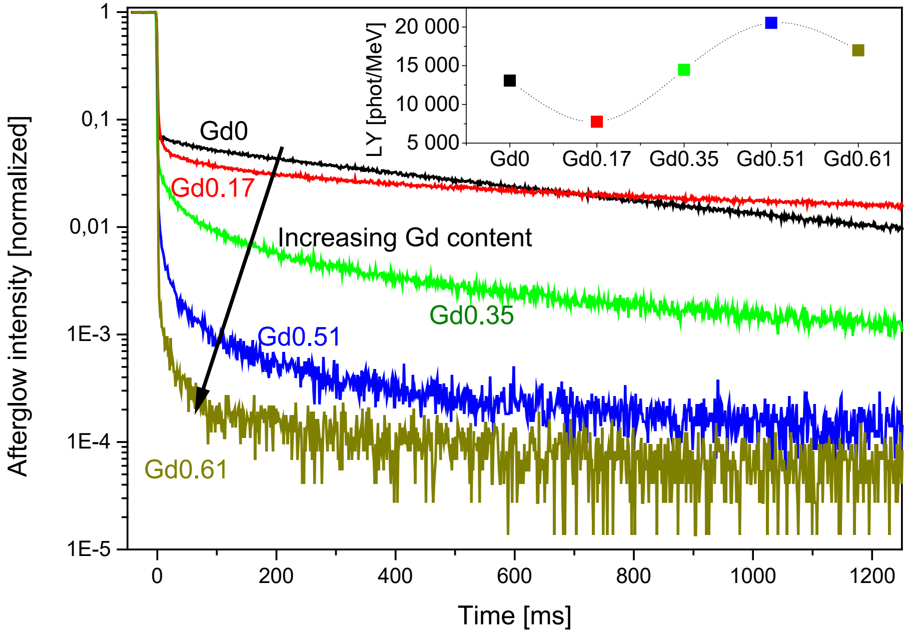
- ☐ **More stable growth** of perovskite phase compared to (Lu,Y)AP and **higher Z_{eff}** compared to YAP
- ☐ More than one order higher decrease of conduction band edge (more than 1.5 eV) compared to LuYAP (0.1-0.2 eV)
- ☐ The same structure, i.e. solid solution of YAP, LuAP and GdAP exists in full range
- ☐ Very few studies at lower quality samples have ben reported in literature *(Dorenbos et al, REDS 135, 321 (1995), Mares et al, REDS 135, 369 (1995))* which show **degrading Ce3+⇒Gd3+ reverse energy transfer** strongly Gd-concentration dependent with possible LY increase around Gd:Y ~ 1:1 composition *(Kamada et al, phys.stat.sol.(c)* ***9*** *(2012) 2263, mPD samples, max LY ~ 14000 phot/MeV)*

Is there a golden island of compositions where electron trapping gets suppressed and light yield increased?

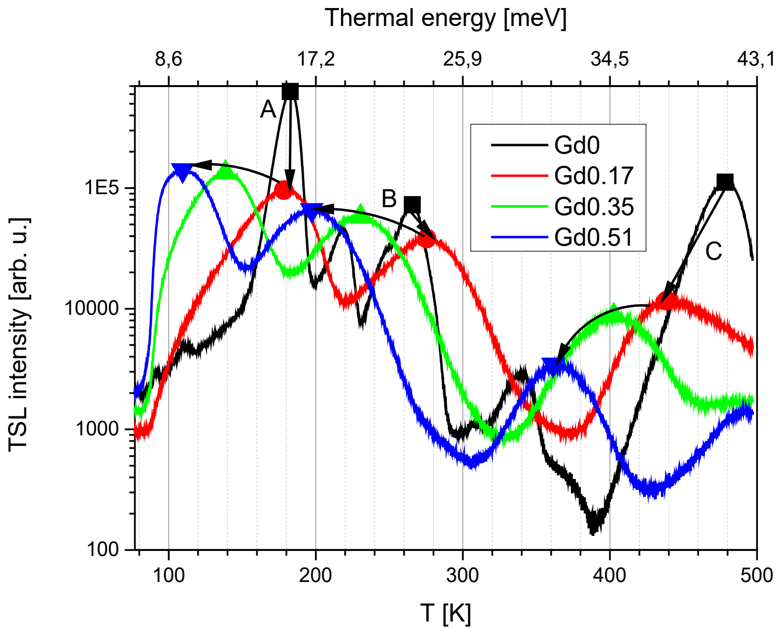
Breakthrough in (Lu,Gd)AP:Ce perovskite scintilators

The balanced Gd-admixture into the Lu cation sublattice in (Lu,Gd)AlO_3:Ce dramatically increases scintillation performance of **melt-grown bulk crystals**. In an optimized composition **the light yield approaches 21 000 phot/MeV,** the value which is close to that of classical, but much less dense, YAP:Ce and which is by **70-80% higher in comparison with the best LuYAP:Ce** reported so far.

Afterglow and light yield

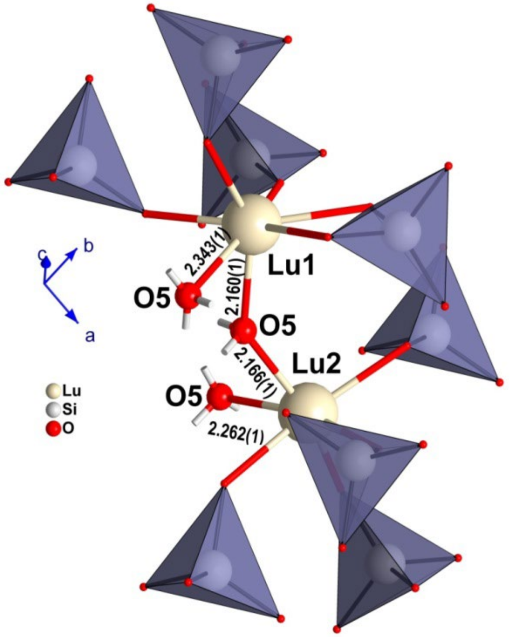


TSL glow curves



M. Pokorný, V. Babin, A. Beitlerová, K. Jurek, Jan Polák, J. Houžvička, D. Pánek, T. Parkman, V. Vaněček, M. Nikl, The Gd-admixed (Lu,Gd)AlO_3 single crystals: Breakthrough in heavy perovskite scintillators. NPG Asia Materials (2021) ***13****:66. DOI: 10.1038/s41427-021-00332-w*

Ce-doped orthosilicates (RE_2SiO_5) for PET

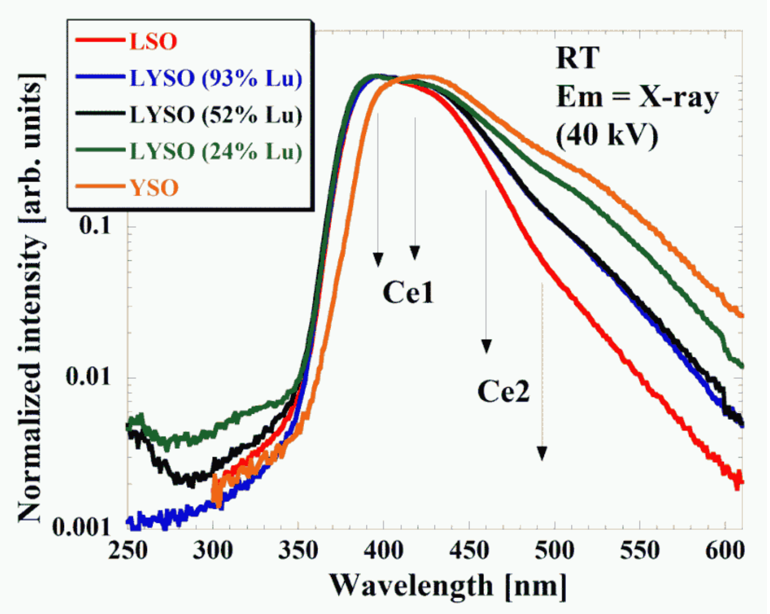


Ce-doped GSO already reported in 1980's *Takagi, Fukazawa, APL 42, 43 (1983)*
Ce-doped LSO entered scintillation community in early 1990's *(Suzuki et al, NIM A 320,263 (1992)*

Two Ce centers, strong afterglow and its mechanism, deep traps and weakly bonded oxygen giving easy rise to a vacancy, were the essential problems addressed

Mixed Ce-doped LSO-YSO reported in yr. 2000 *(Cook et al, JAP 88, 7360 (2000))*
and discussion arised, if it is "the same scintillator" as LSO:Ce

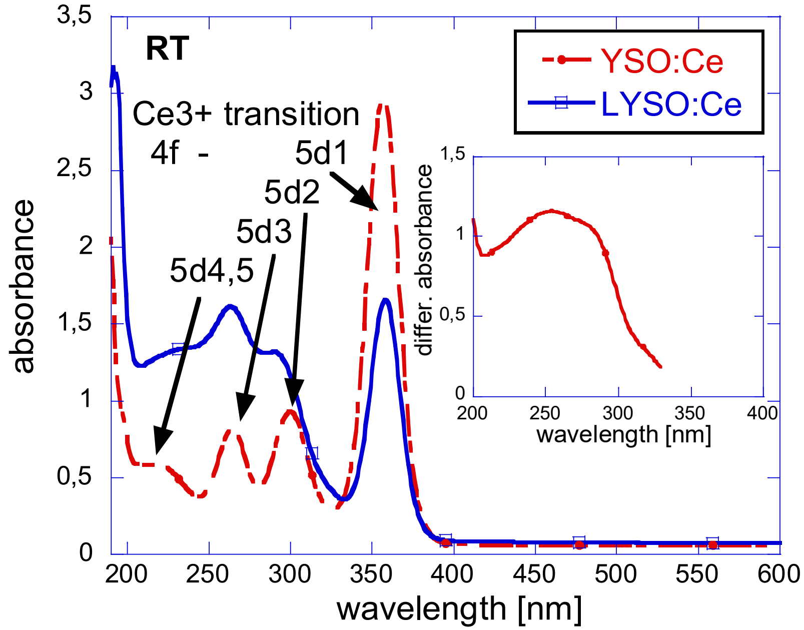
Radioluminescence spectra



Ca^{2+} codoping of Ce-doped orthosilicates

Series of papers from C. Melcher group showed for both the Ce-doped LSO and YSO hosts that Ca^{2+} codoping increases LY, accelerates scintillation response and reduces electron trapping-related effects observed in TSL glow curves *(Spurrier et al, IEEE TNS 55, 1178 (2008), Yang et al, IEEE TNS 56, 2960 (2009)*

In addition, there are **evident changes in the absorption spectra**:



Chewpraditkul et al, OM 35,1679(2013)

LYSO:Ce with 60 ppm of Ca in the crystal shows noticeable presence of Ce^{4+} (peak at 270 nm, *Visser et al, IEEE TNS 41, 689 (1994)*) and at the same time its LY is of about 32 000 phot/MeV ⇒ Ce^{4+} is certainly not scintillation killer and its role in scintillation mechanism should be clarified ...

Solid solution fashion

The long thermalization length comparing to Onsager radius is the main reason for geminate pair concentration decrease and later luminescence losses. The easiest way for thermalization length decrease is the scintillation crystal doping or even transfer to the mixed crystals (solid solution).

Gektin et al, IEEE Trans. Nucl. Sci. ***61***, 262 *(2014)*

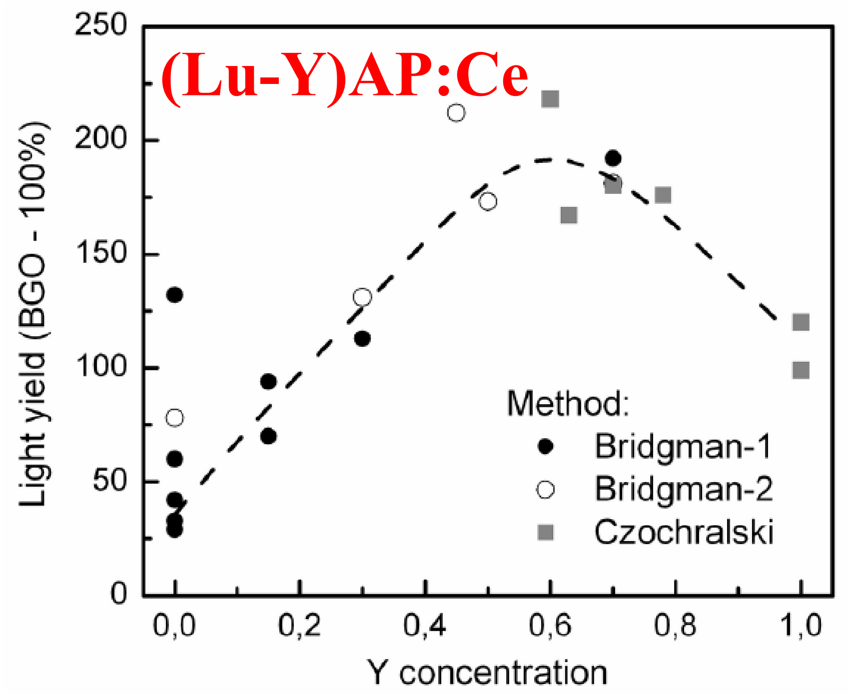


Fig.7. Light output of $Lu_xY_{1-x}AlO_3$:Ce crystals depending on Y concentration.

Belsky et al, IEEE Trans. Nucl. Sci.48, 1095 (2001)

The point is that mixed cations energy levels should influence the very bottom of conduction band to limit out-diffusion of thermalized electrons …

Mixed pyrosilicates $(Gd,La)_2Si_2O_7$:Ce

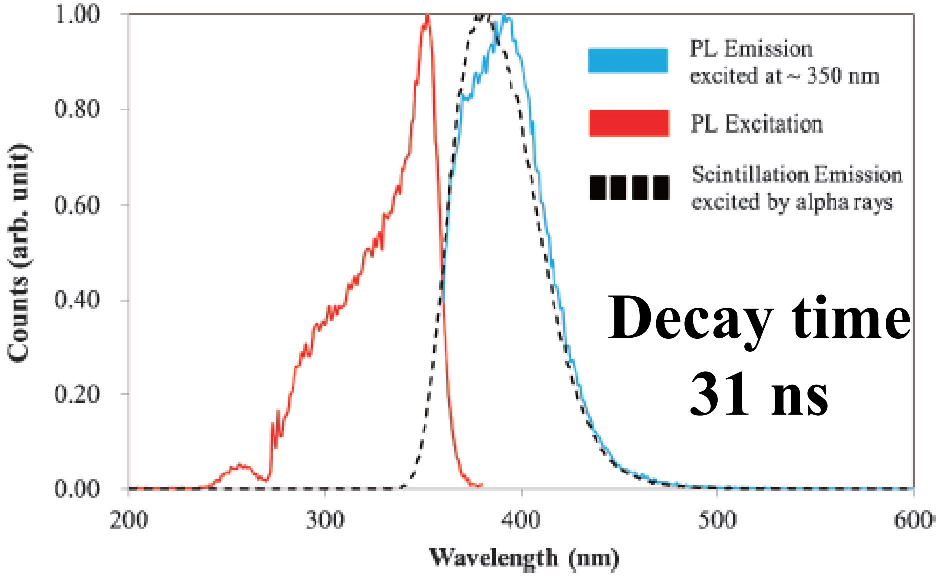
LPS:Ce :Pauwels et al, IEEE TNS 47, 1787, (2000)
Powder GPS:Ce :Kawamura et al, NIM A 583, 356 (2007)
GPS:Ce : Gerasymov et al, JCG 318, 805 (2011)
ScPS:Ce : Feng et al, Optical materials 34, 1003 (2012)
GPS:Ce : Feng et al, Physica B 411, 114 (2013)
(La,Gd)PS:Ce : Suzuki et al, Appl. Phys. Expr. 5 (2012) 102601

Though LPS:Ce was prepared more than decade ago and might have similar scintillation performance compared to LSO:Ce, it can’t probably compete with LYSO:Ce and does not offer any clear advantage (density, speed of response, en.res., LY, intrinsic radioactivity) so that it did not find practical application.

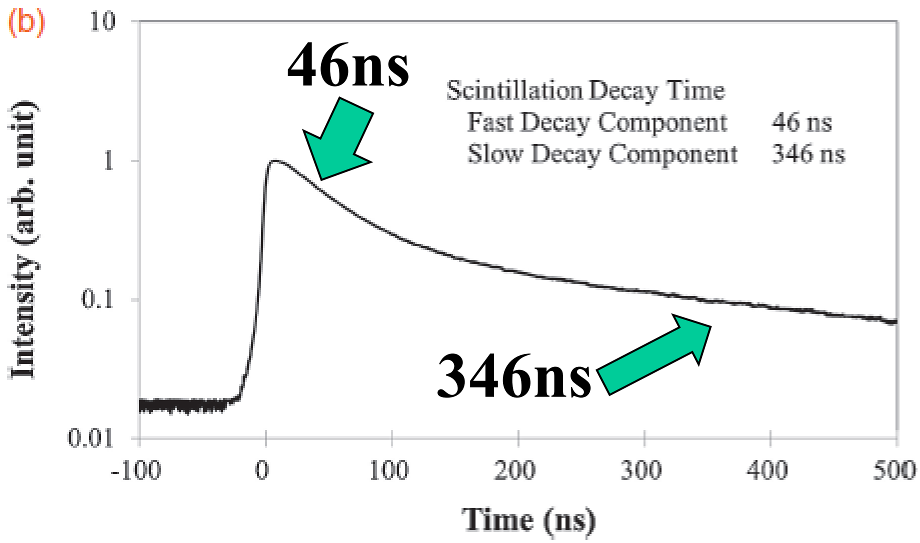
Interestingly, **GPS:Ce performs much better compared to GSO:Ce** and is free of intrinsic radioactivity. Nevertheless, its growth by Czochralski method is troublesome. However, stabilization of the growth process was achieved by La-admixture.

$(Gd,La)_2Si_2O_7$:Ce characteristics

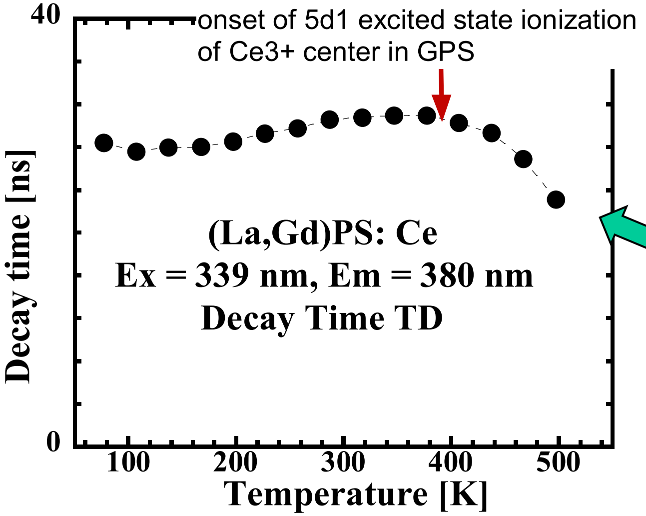
PL exc-em spectra&decay



Scintillation decay



Suzuki et al, Appl. Phys. Expres ***5*** *(2012) 102601*



LY of about 36 000 phot/MeV and energy resolution about 5 %.

Ce^{3+} is stable against quenching and ionization up to 400 K!

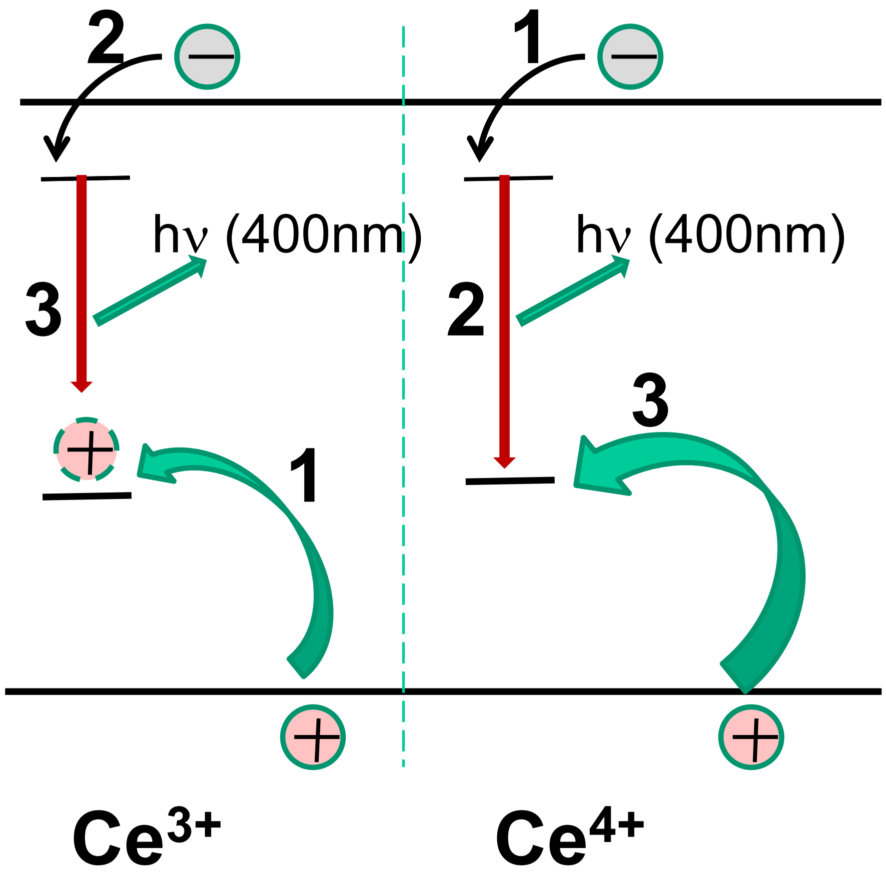
Jary et al, J. Phys. Chemistry C ***118*** *, 26521 (2014)*

DE strategy: Ce^{4+} role in scintillation mechanism in oxide scintillators

In 1990's it was general opinion that Ce^{4+} is scintillation killer in aluminum perovskite (YAP) host, but we have to change our mind now as far as its role in Ce-doped orthosilicates and garnets …

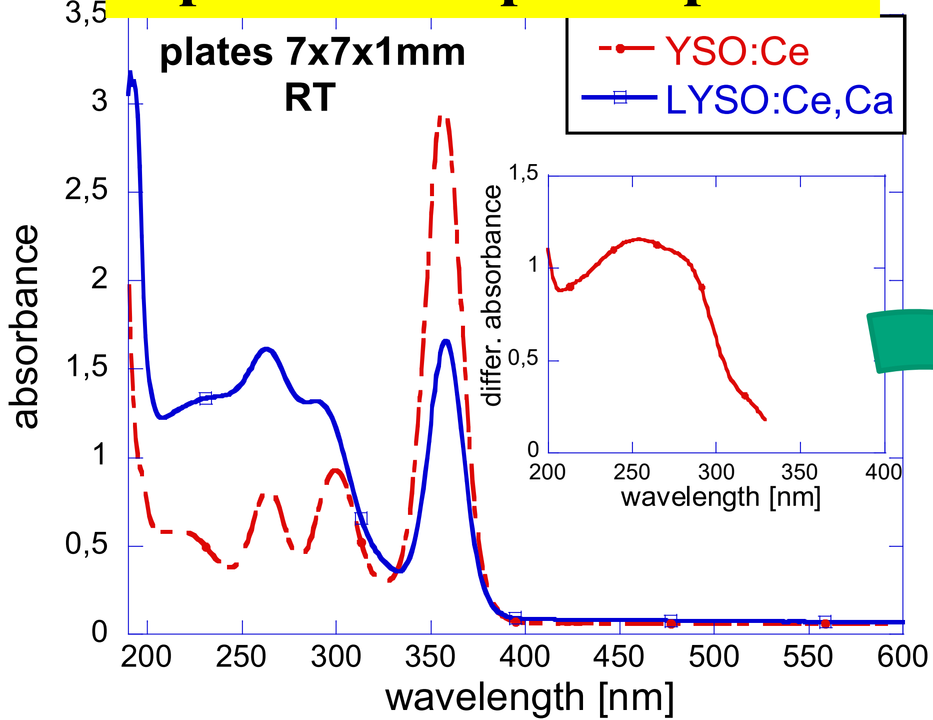
LYSO:Ce,Mg :Blahuta et al, IEEE TNS 61, 3134 (2013)

In LYSO:Ce,Mg, **the Mg^{2+} codoping and air annealing** induce the presence of Ce^{4+} (proved by XANES, optical absorption), **LY is enhanced and afterglow strongly diminished also because the oxygen vacancy concentration is diminished!**



Ce^{4+} center in LYSO:Ce,Me^{2+}

Optical absorption spectra



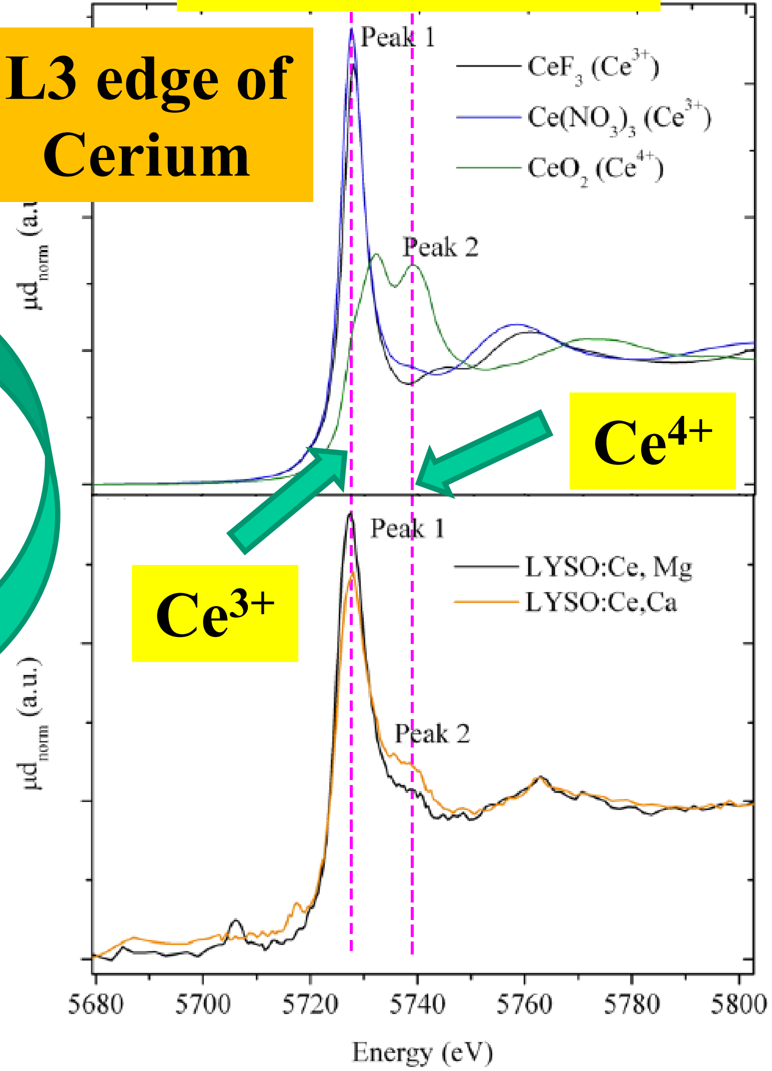
Charge transfer (CT) absorption of Ce^{4+}

The light yield of about 32,000 ph/MeV was obtained for LYSO:Ce,Ca, which is among the highest ones ever reported in literature. Ca content of about 60 at. ppm was confirmed by GDMS.

Chewpraditkul et al, OM 35, 1679 (2013)

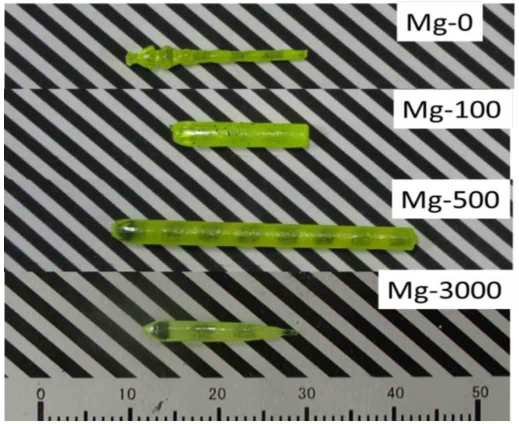
XANES spectra

L3 edge of Cerium

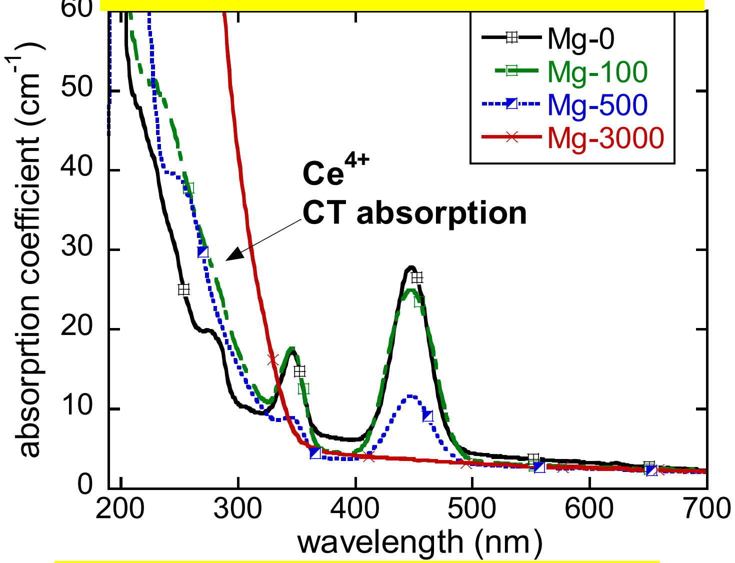


Up to 35% of Ce^{4+} in total Ce content

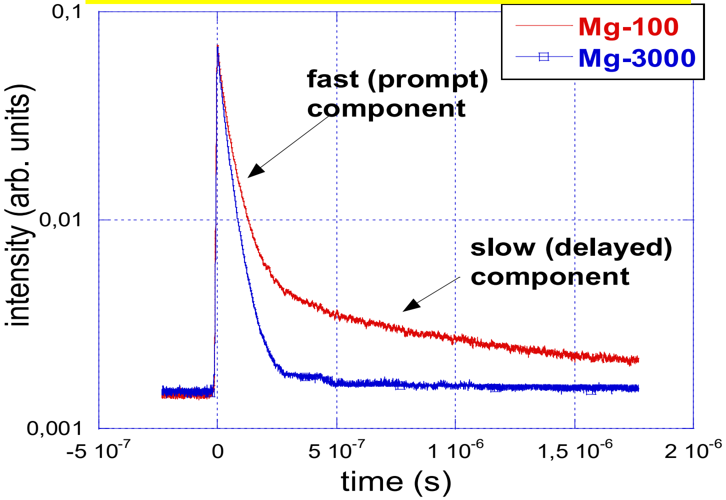
Mg^{2+} codoped LuAG:Ce: concentration dependence



Absorption spectra



Scintillation decay



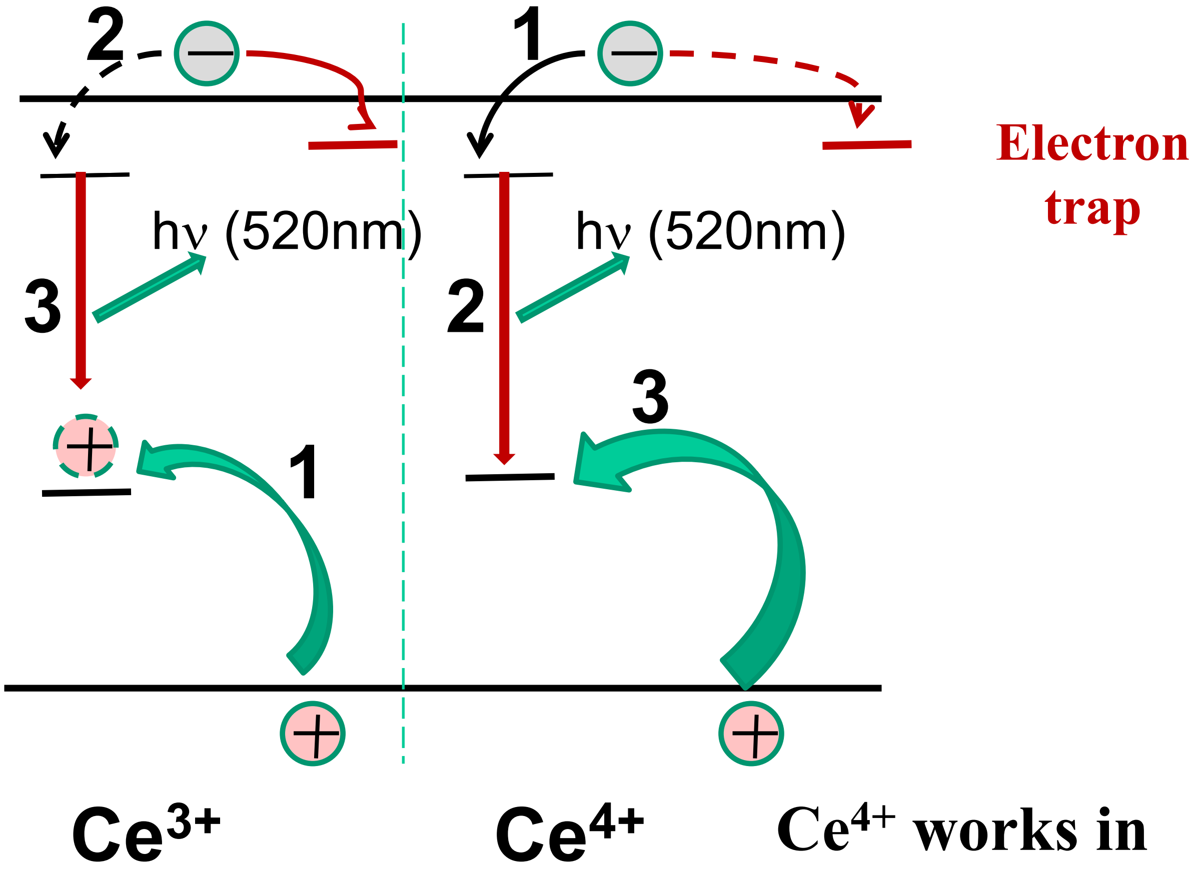
OC from SICCAS mPD crystals from A. Yoshikawa lab

Nikl et al, Cryst.Growth Des. **14**, 4827 (2014)
Liu et al, Phys.stat. sol. RRL **8**, 105 (2014)

Sample	Light yield (ph/MeV)	T1(ns)/ I1(%)	T2(ns)/ I2(%)	Afterglow at 4 ms(%)/400ms(%)
Mg-0	4850	58/48	300/52	**19/8.3**
Mg-100	**23100**	48/58	380/42	**1.3/0.08**
Mg-500*	18800	48/57	275/43	**2.5/0.07**
Mg-3000	14100	**15/11**	**51/89**	0.2/0.03
LuAG-Ce – Cz	**17200**	**58/42**	**958/58**	**2.9/0.4**

Why stable Ce^{4+} is that good for LY increase in oxide single crystal (ceramic) scintillators

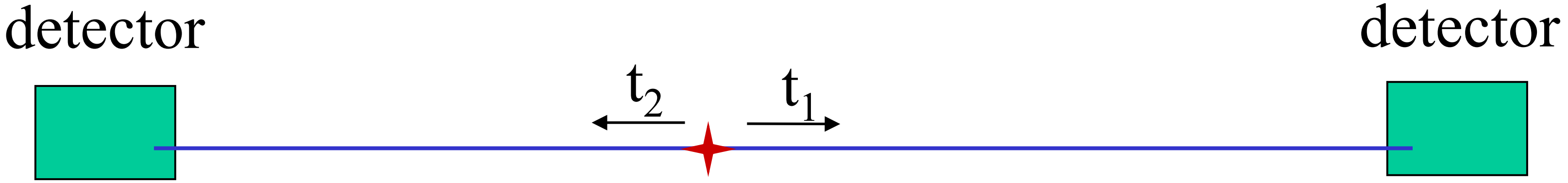
Ce^{4+} center can directly compete with any electron trap for electron capture in the first instants of scintillator mechanism so that **it will directly convert a fraction of slow part of scintillation response to the fast one**. **Ce^{3+} cannot make this as it must capture the hole first.**

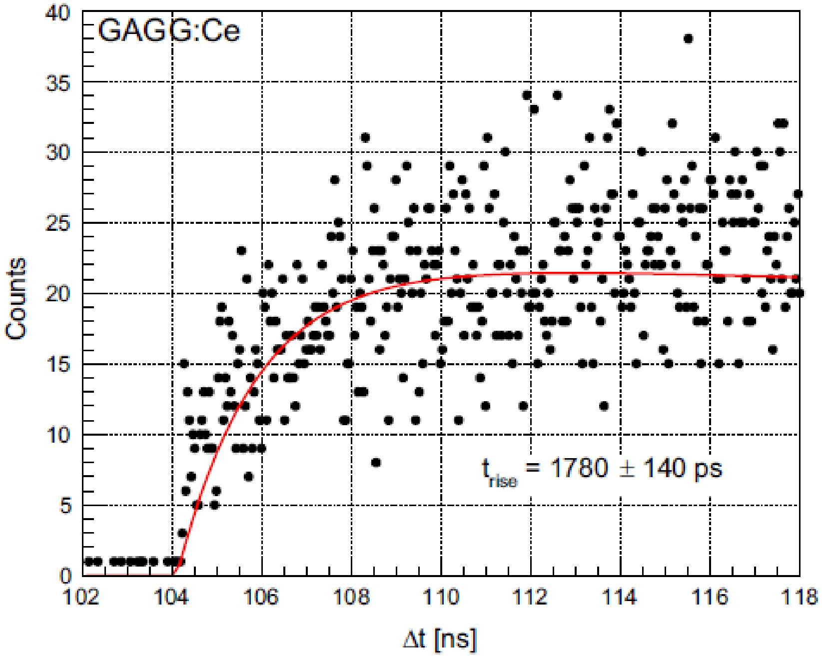


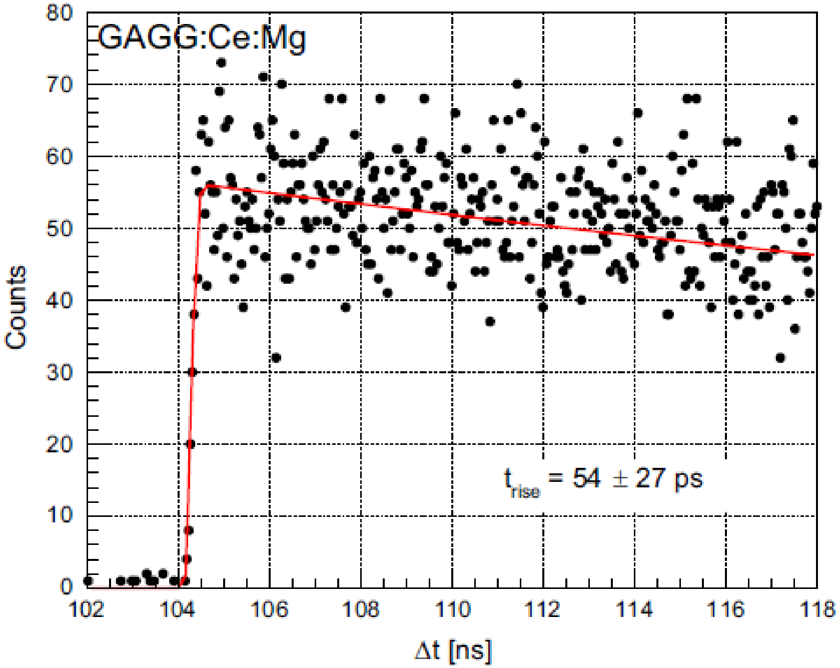
Ce^{4+} works in parallel with Ce^{3+} center, they are not competing!

Timing coincidence resolution - Mg^{2+} codoped GAGG:Ce

Critical parameter for usage of fast scintillators in time-of-flight measurements







Mg codoping in GGAG:Ce almost erase rise time in scintillation decay and TCR is improved from about 540 ps to 230 ps. Comparable values with LYSO:Ce,Ca ⟹ candidate for PET!!!

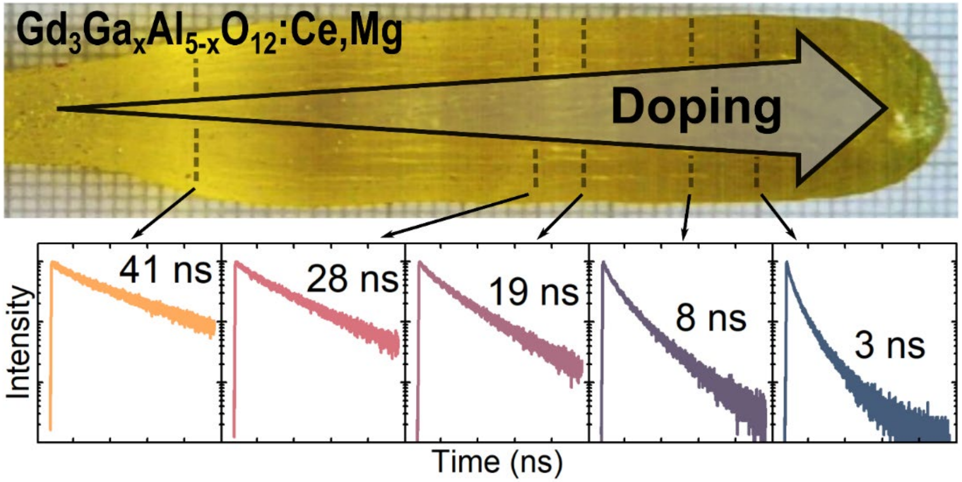
(*Lucchini et al, NIM A **816**, 176 (2016)*)

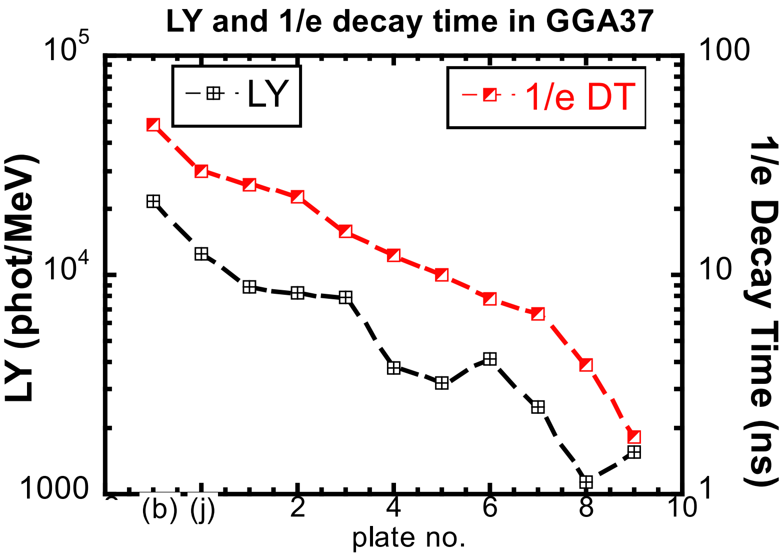
Better quality GAGG:Ce,Mg - TCR of 196 ps was achieved (Kamada et al, IEEE TNS 63,443 (2016)

Scintillation decay acceleration in heavily (Ce,Mg)-doped GGAG

Due to closely spaced Ce-Mg pairs

Babin et al, Optical Materials ***83*** *(2018) 290*

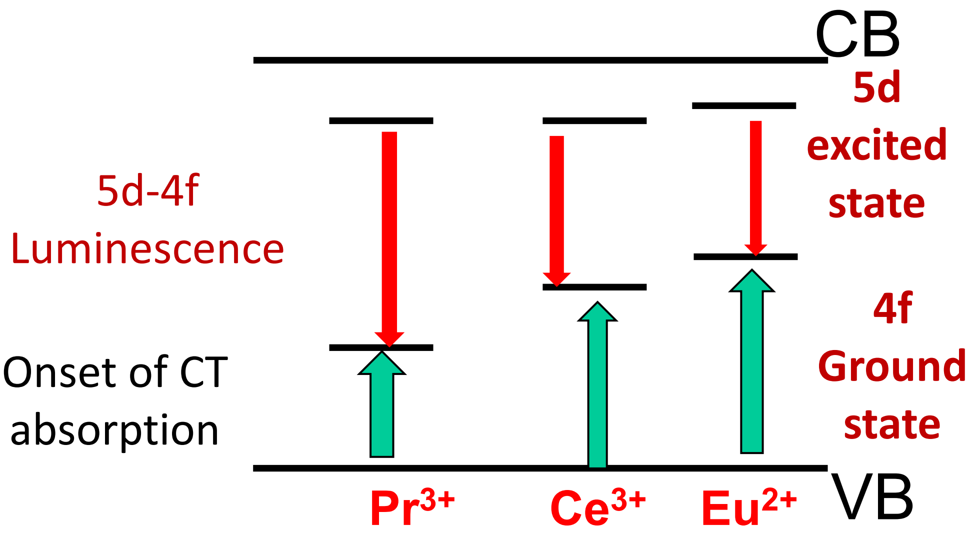




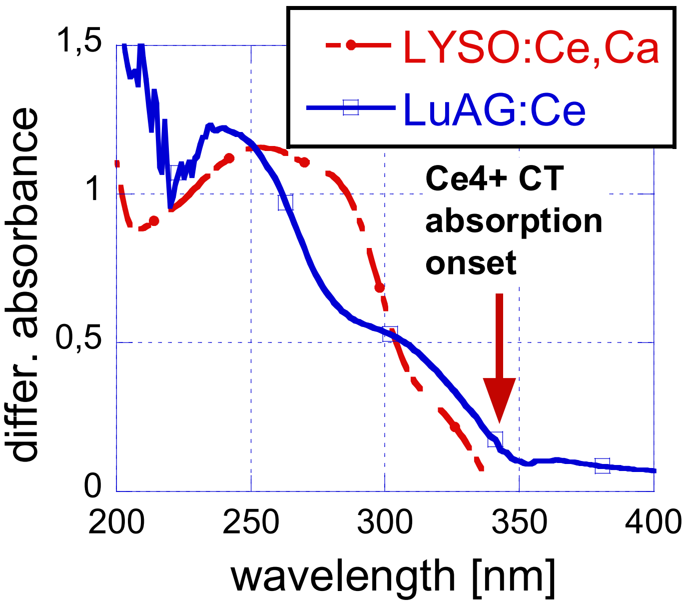
Despite the significantly lowered light yield towards the crystal end, the CTR values remain competitive to the fastest GAGG-based samples reported in literature so far. An ultralow afterglow on the ms time scale is also beneficial. Such combination of scintillation characteristics makes this material very competitive for fast timing, high-count-rate and high-speed X- and γ-ray imaging applications in high energy physics, industry, medical and military fields.

Martinazzoli et al, Materials Advances ***3*** *(2022) 6842*

Ce^{4+},Pr^{4+} in LuAG, YAP, LYSO hosts



Charge transfer absorption of Ce^{4+}

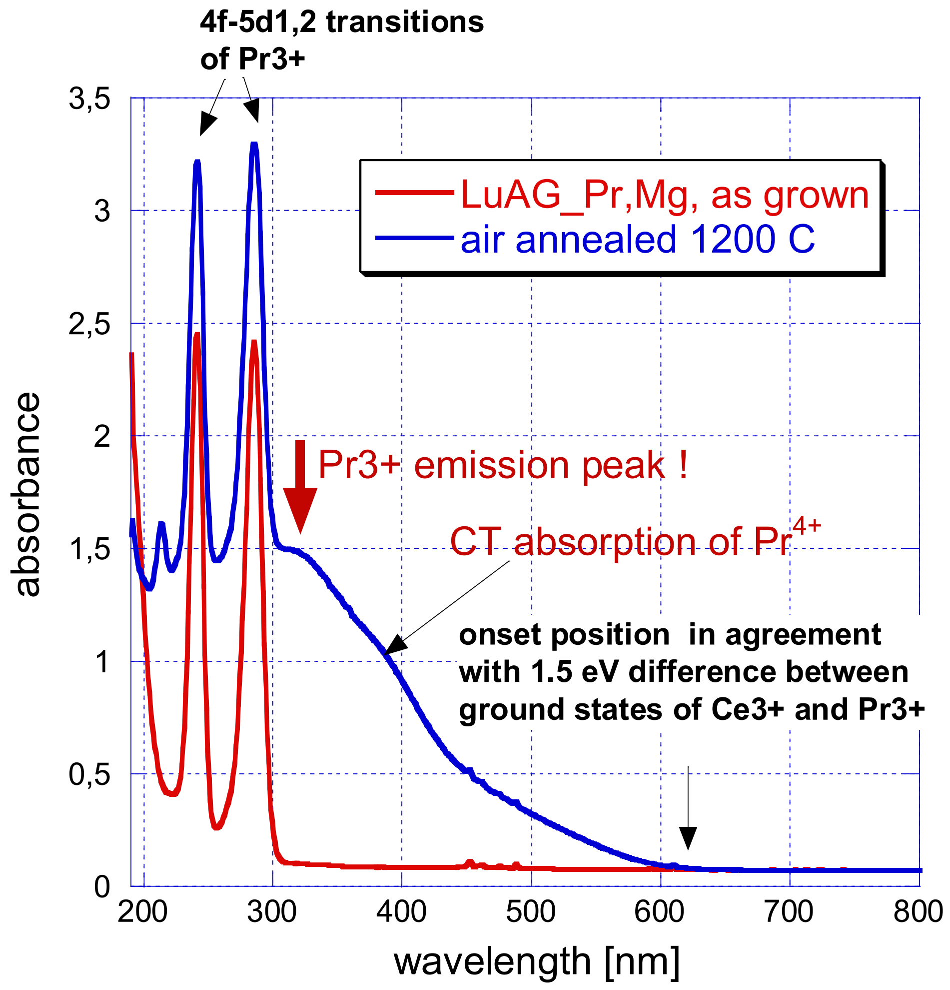


Nikl et al, Optical Materials **26**, *545* (2004)

CT absorption of Ce^{4+} (Pr^{4+},Eu^{2+}) is analogous to well-studied CT of Yb^{3+}. Within the class of materials constituted by the same anion (e.g. oxides, fluorides) its onset will be very similarly positioned. For the Ce^{4+} center in garnet, silicate and perovskite oxide hosts it will be positioned around 340-350 nm. **Thus it will re-absorb scintillation of Ce^{3+} in YAP, but will not in silicates and garnets**.

Does Pr^{4+} help?
Not in oxides!

Absorption spectra LuAG:Pr,Mg, 1 mm thick

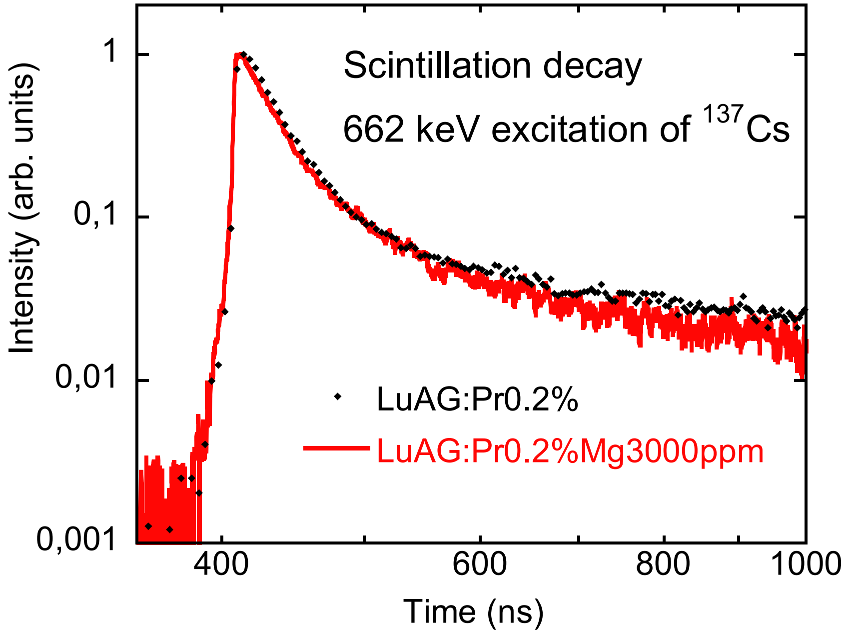

4f-5d1,2 transitions of Pr3+

Pr3+ emission peak !

CT absorption of Pr^{4+}

onset position in agreement with 1.5 eV difference between ground states of Ce3+ and Pr3+

Total overlap of Pr^{4+} CT absorption and Pr^{3+} emission spectra causes significant reabsorption of scintillation light and disable usage of this concept for the **bulk** Pr-doped oxide materials!



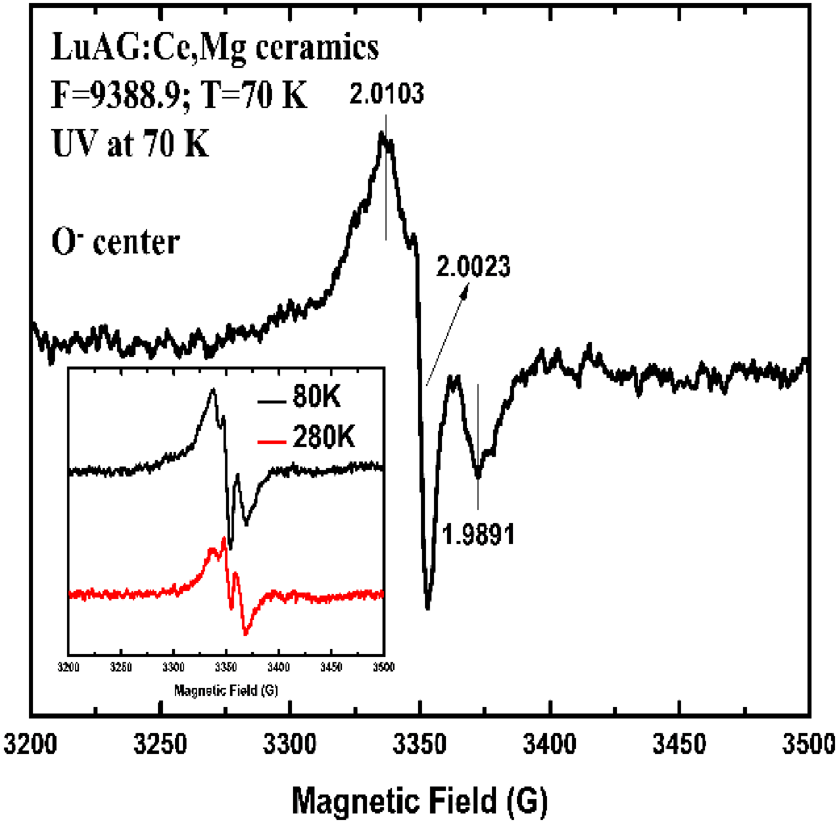
Trends in scintillation decay are the same as in Ce,Mg-doped LuAG

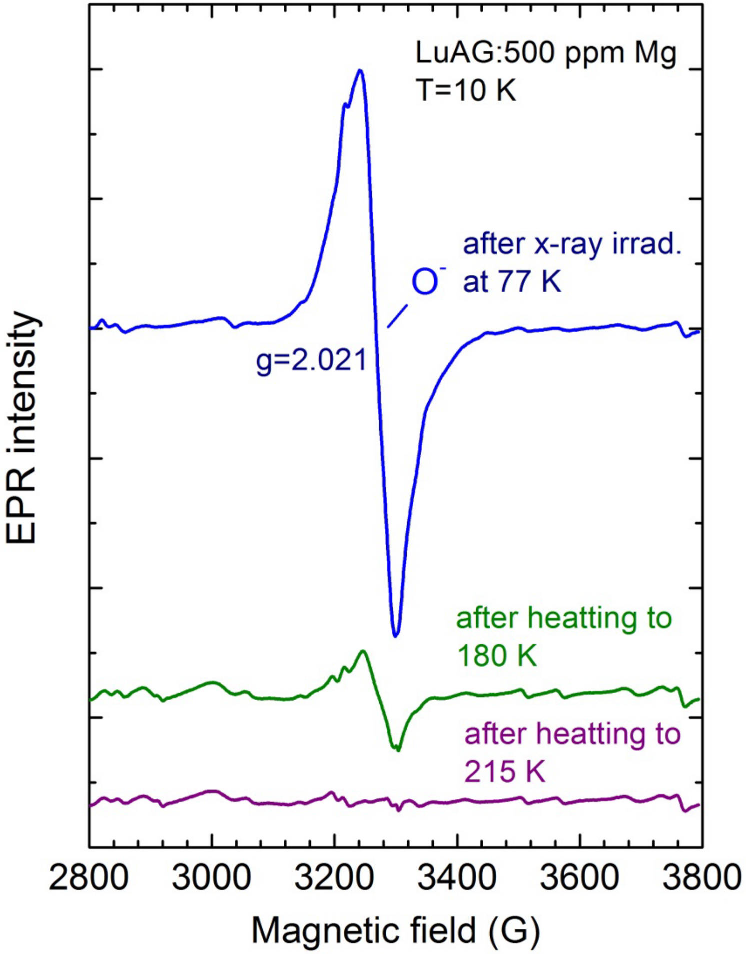
*Pejchal et al, **181**, 277 (2017)*

Another player in charge compensation game: O^- hole center – EPR experiment

In LuAG:Ce,Mg ceramics

In LuAG:Eu,Mg single crystal





Hu et al, Phys. Stat. Sol. RRL **9**, 245 *(2015)//*
Optical Materials ***45*** *(2015) 252*
Nikl et al, IEEE TNS **63**, 433 (2016)

EPR O^- signal can be correlated with TSL glow curves !

Conclusions – bulk scintillators

❑In recent years, new concepts of “defect” or “band-gap” engineering appeared, some of which noticeably improving the figure-of-merit of a scintillation material (LSO(LYSO):Ce, Ca^{2+}, $LaBr_3$:Ce,Sr^{2+}).

❑While defect engineering usually focuses on a specific defect to suppress its role in trapping processes, band-gap engineering involves more complex mechanism resulting in improvement of scintillation performance in a solid solution host or creating even new, unexpected material composition.

❑ Combining the effect of Ga and Gd admixture in the multicomponent Ce-doped $(Lu\text{-}Gd)_3(Al\text{-}Ga)_5O_{12}$ garnet, trapping processes due to Lu_{Al} antisite defects (AD) were diminished and the single crystal oxide scintillators with light yield exceeding 50 000 phot/ MeV were prepared (GAGG:Ce). Heavy codoping with Mg can accelerate its scintillation response below 10ns at the expense of LY.

❑$(Gd,Lu)AlO_3$:Ce appears a breakthrough in heavy aluminum perovskites with LY exceeding that of YAP:Ce with an advantage of much higher Zeff.

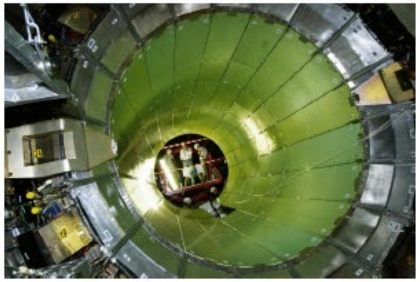
❑Admixture of La in GPS :Ce stabilizes the structure and provides new excellent scintillation material with very high LY, high temperature stability and no intrinsic radioactivity.

❑In Ce-doped orthosilicate and garnet scintillators the role of Ce^{4+} must be revisited. In these materials it contributes positively to fast scintillation response by providing new fast radiative recombination pathway.

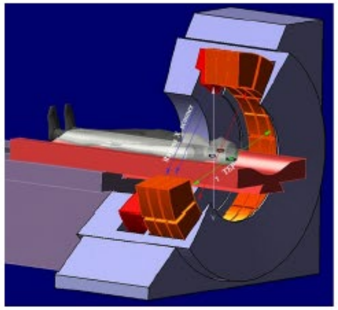
Fast **A**dvanced
Scintillator **T**iming
(2014-2018)

Scintillators in fast timing

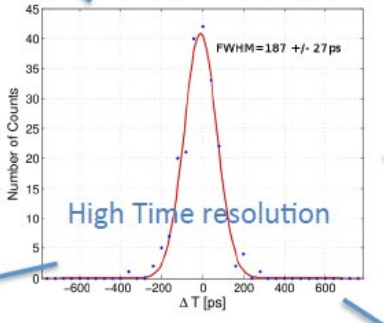
ASCIMAT



High Energy Physics Calorimetry

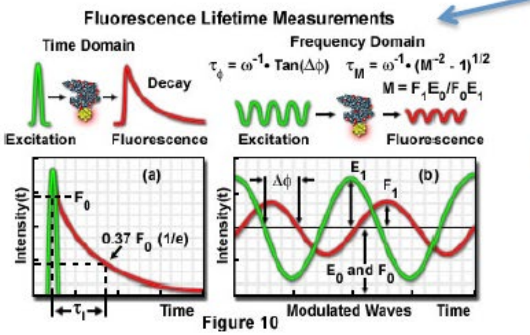


Positron Emission Tomography

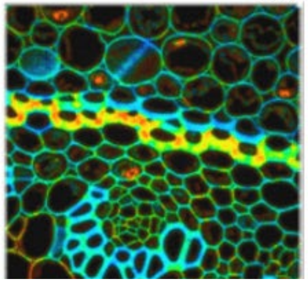


High Time resolution

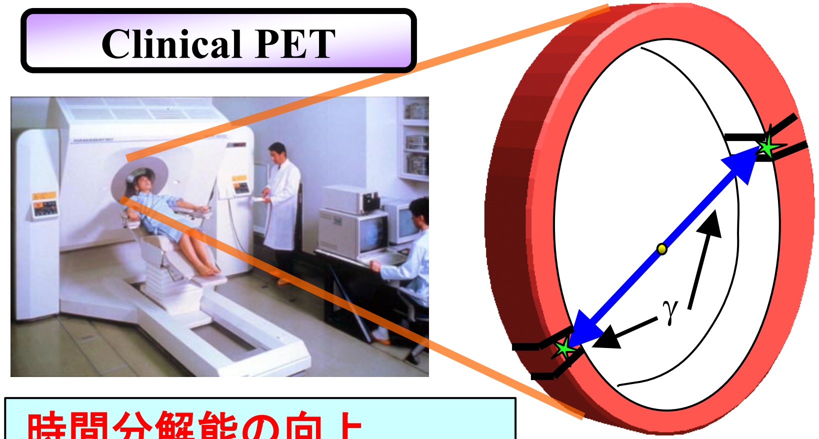
Quantum Cryptography



FLIM: Fluorescence Lifetime
Imaging Microscopy
&
FRET: Förster Resonance
Energy Transfer

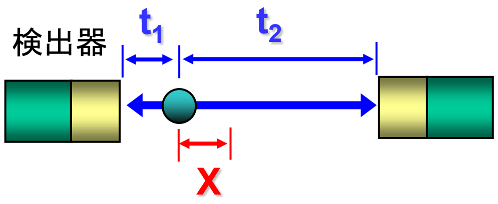


Time of Flight PET - determination of the interaction point along each of coincidence line detected



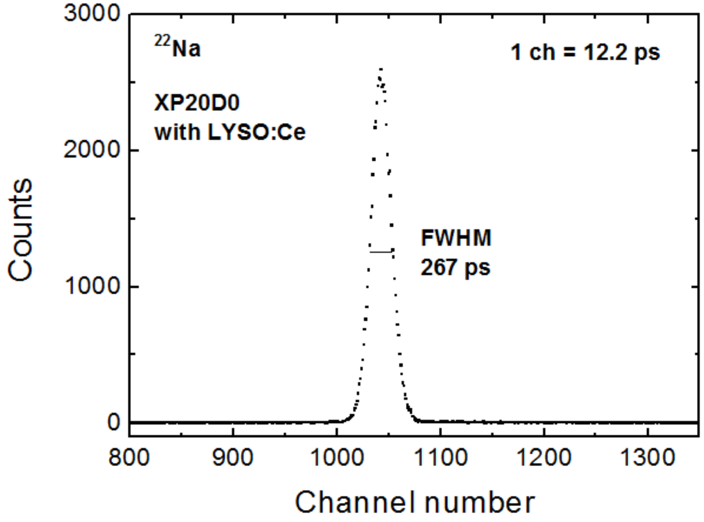
時間分解能の向上

Time of Flight (TOF) 型PET



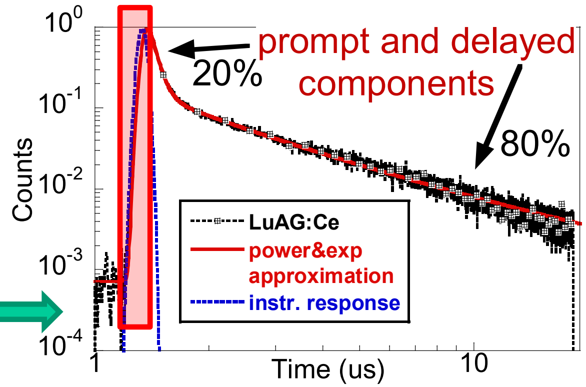
$X = (t_2 - t_1) \cdot (c/2)$

10 ps = 1.5 mm intrinsic position uncertainity in PET



Coincidence timing resolution (CTR) spectrum measured for LYSO:Ce,Ca

Ca codoping improves LY, speed of scintillation response and CTR!



Originally made by superfast scintillator (BaF2), today reconstructed from the **rising edge** of high LY scintillators used LYSO:Ce – measurement of CTR

Types of emission in scintillating crystals and delay between energy deposit and photon emission

- Excitonic emission (STE, excitations of anion complexes)
- Emission of activators (Ce, Pr, …)
- Crossluminescence
- Quantum confinement driven luminescence
- Intraband hot luminescence
- Cherenkov radiation

Slow

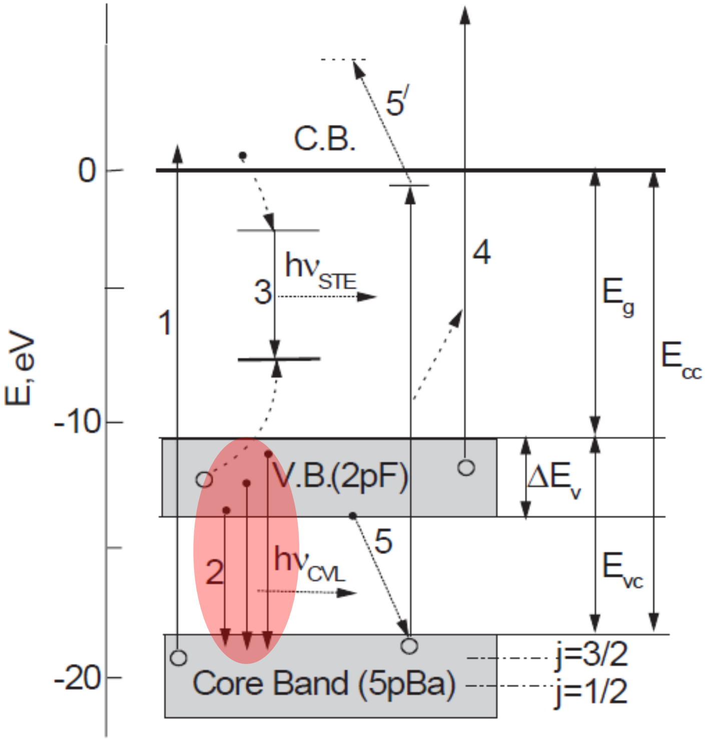
↓

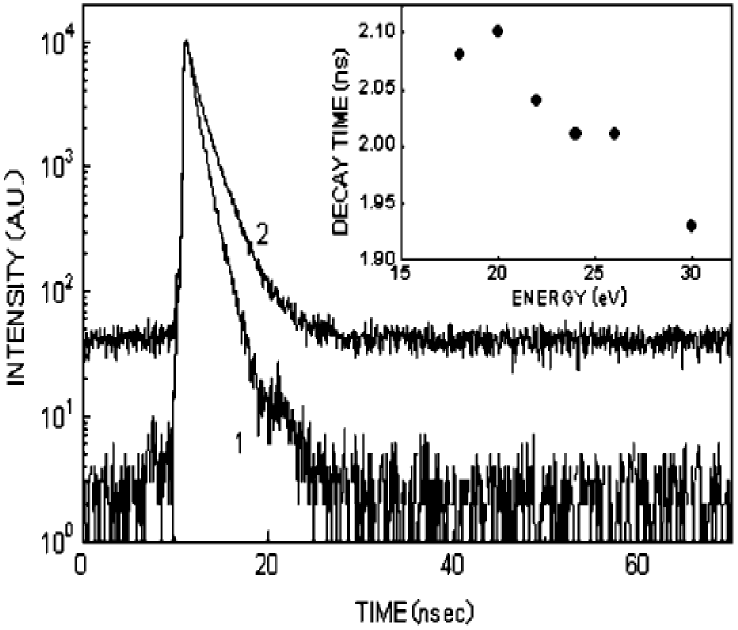
Fast

ELSEVIER Radiation Measurements 38 (2004) 343–352
www.elsevier.com/locate/radmeas

Core–valence luminescence in scintillators

Piotr A. Rodnyi*

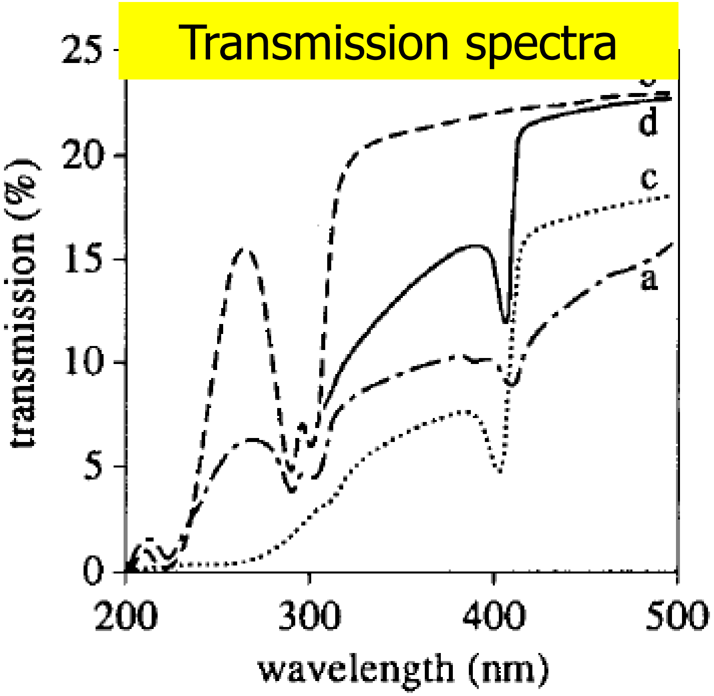




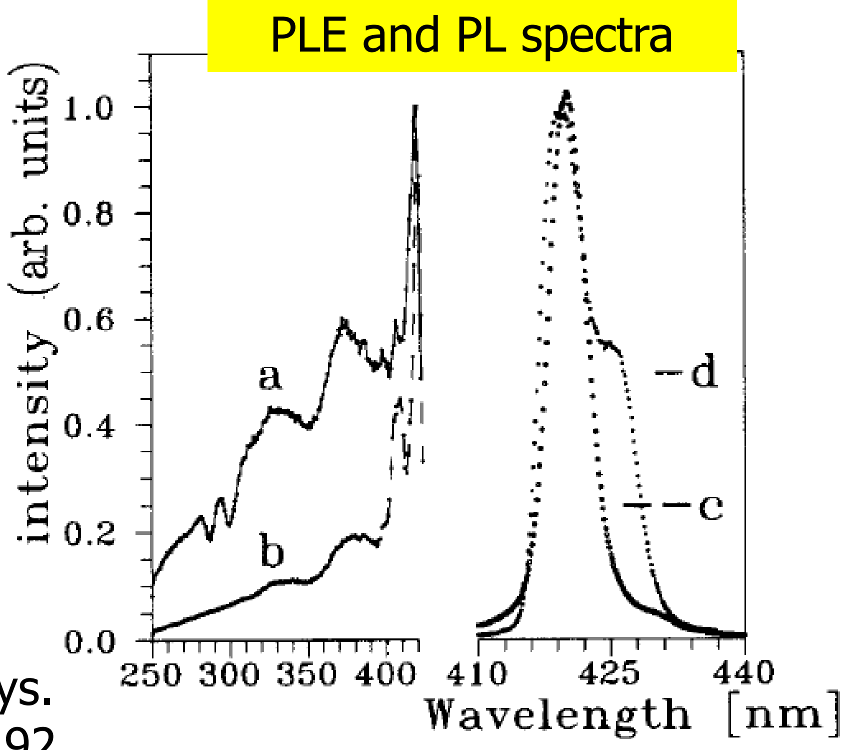
Crystal	$h\nu_{em}$ (eV)
BaF_2	5.6/6.4
CsF	3.1
CsCl	5.1
CsBr	6.0
RbF	5.25

Radiative lifetime of about 1 ns, spectrum VUV-UV, but LY low (BaF_2 best around 1000 ph/MeV) and accompanied often by slow STE emission, only halides so far …did we really explore enough this phenomenon???

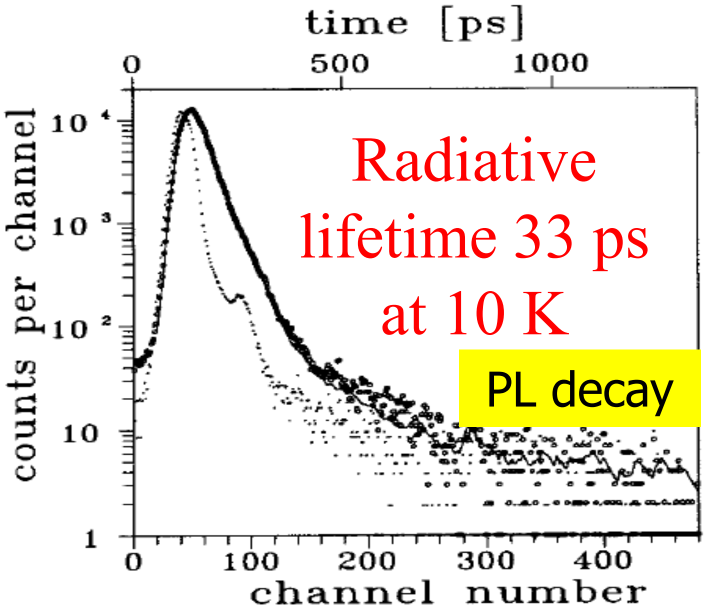
CsPbX$_3$ nanocrystals in CsX SC host (quantum dots)


Transmission spectra

Nikl et al, Phys. Rev. B 51, 5192 (1995).


PLE and PL spectra

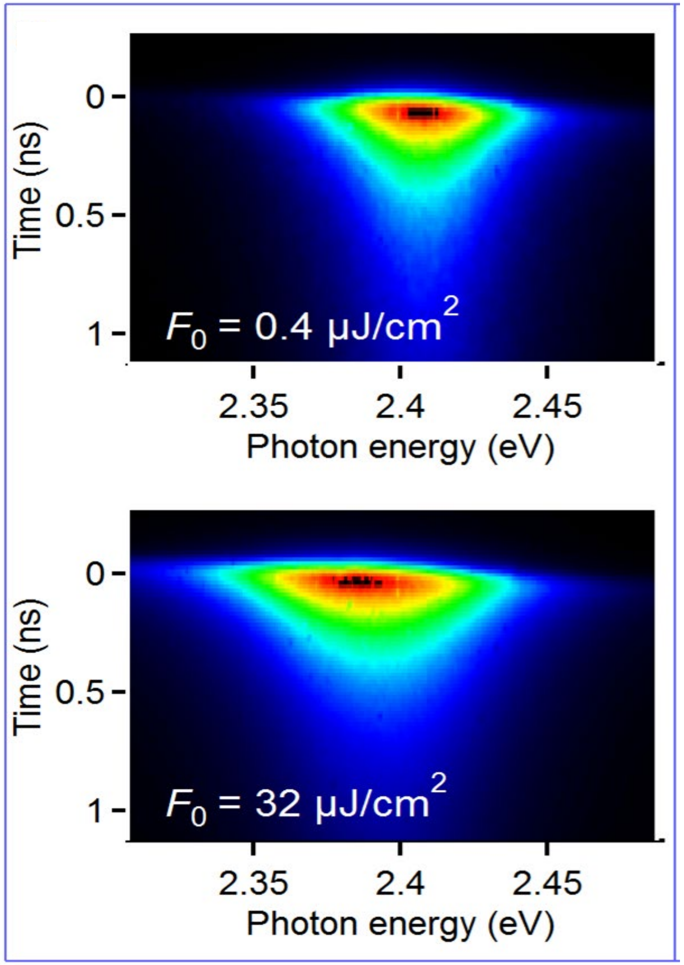
Thanks to strong quantum confinement of Wannier exciton (nanocrystals few nm size) and microscopic superradiance effect (multiplication of oscillator strength) radiative lifetime is shortened down to several tens of ps!


Radiative lifetime 33 ps at 10 K

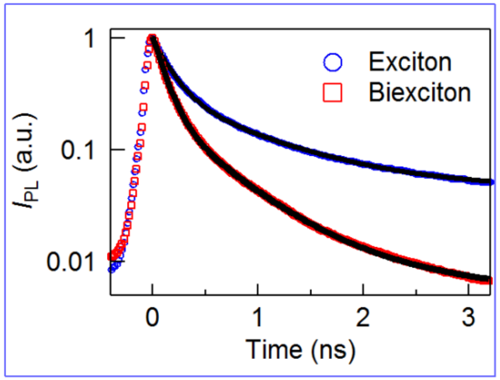
PL decay

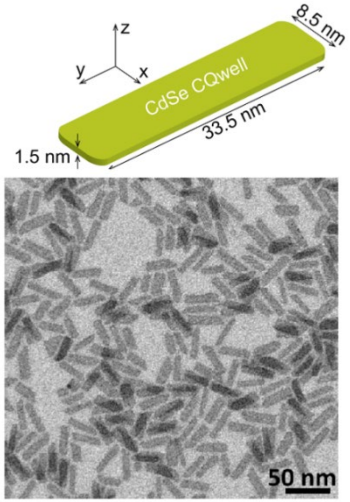
Problems: Wannier exciton strongly quenched RT, transport stage inefficient

Colloidal CdSe nanosheets (quantum wells)



Emission 500-520 nm
Exciton lifetime: **440 ps**
Biexciton lifetime: **125 ps**





J. Grim et al. *Nature nanotech.* **9**, 891–895 (2014)

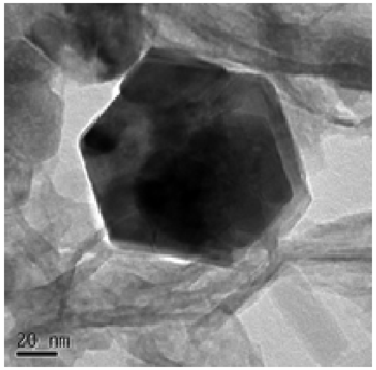
ZnO-based nanocrystals

V. Cuba, Wed, 9.00

- Hexagonal structure of wurtzite
- Usually non-stoichiometric $Zn_{1+x}O$; n-type semiconductor – naturally doped by O vacancies and Zn interstitials
- Advantageous properties–**high radiation stability**, absorbance in UV and transparency in visible spectral range
- Optoelectronic properties– wide band gap (3,4 eV), **high E_B of excitons (60 meV)**, low afterglow, **extremely short luminescence decay of excitons (sub-ns)**

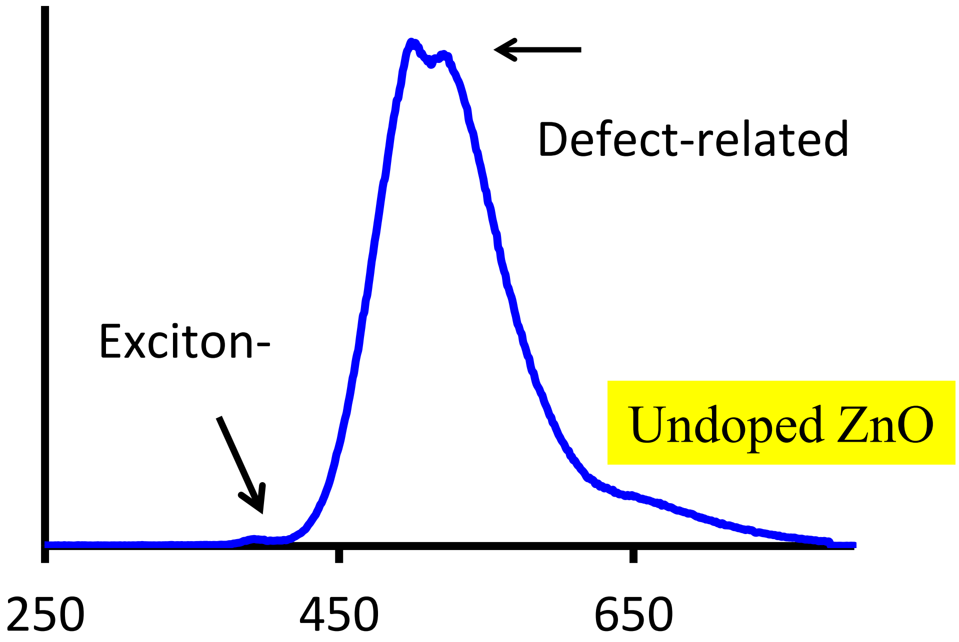
Radiation- or photo-induced precipitation:

Principle: reaction of dissolved precursors with products of radio/photolysis of water leading to the precipitation of solid phase (particle size~nm)



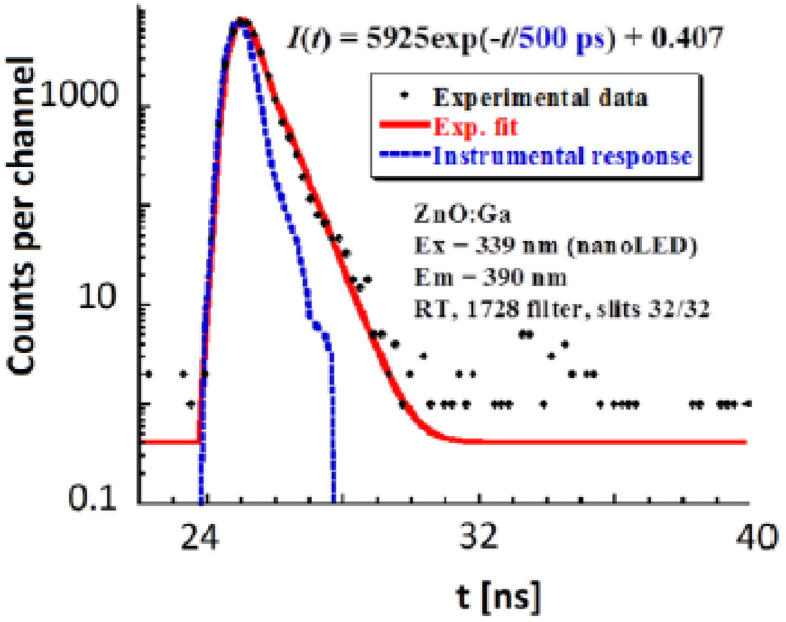
Luminescence characteristics of powder

Subnanosecond decay of exciton state is a suitable center for superfast scintillator!

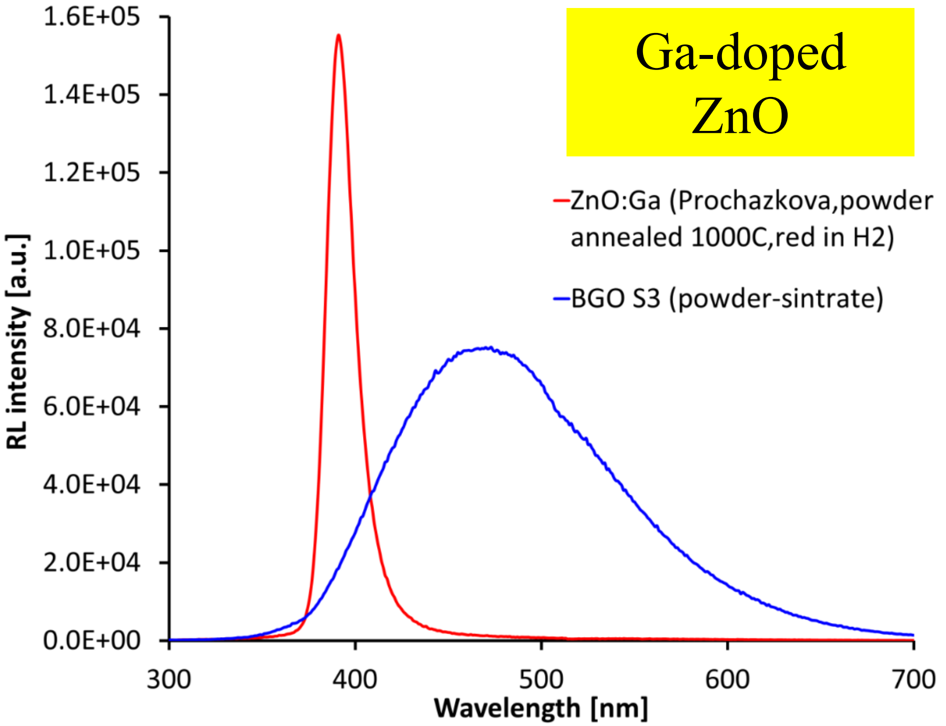


Undoped ZnO

PL decay of Ga-doped ZnO exciton emission



Bourret-Courchesne et al, NIM A 601, 358 (2009)

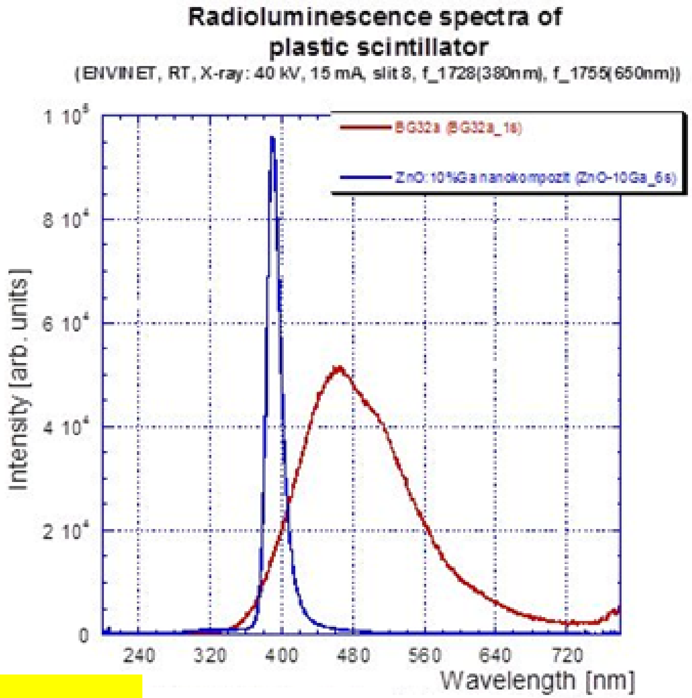


Ga-doped ZnO

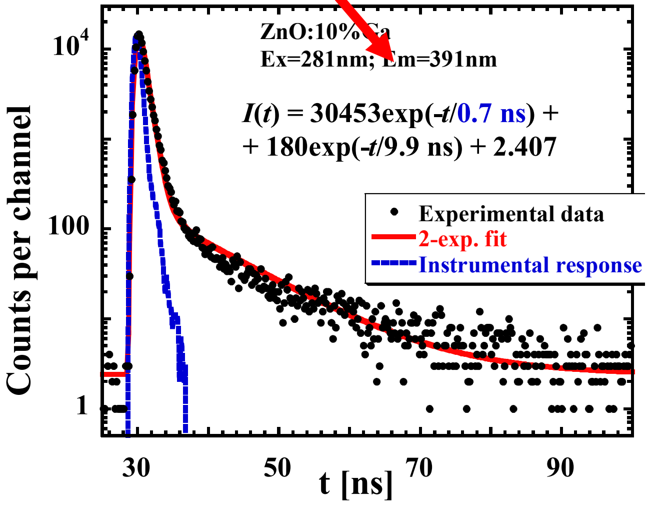
Composite materials

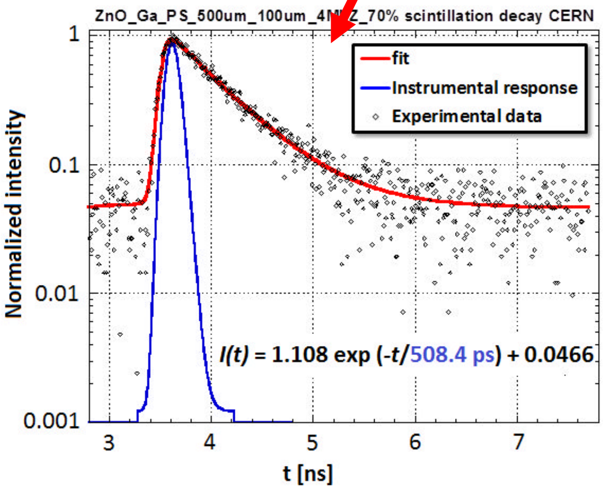
ZnO:Ga-PS (polystyrene matrix)

- 10 wt. % ZnO:Ga in PS matrix
- RL spectra – only ZnO:Ga emission
- PL decay - excited at 281 and 339 nm; nonradiative energy transfer ZnO:Ga – PS (~400 ps)



Decays under UV excitation into PS host and under X-ray





Rise time below the time resolution of the set-up (18 ps) !!!

Buresova et al, Opt. Express ***24****, 15289 (2016)*

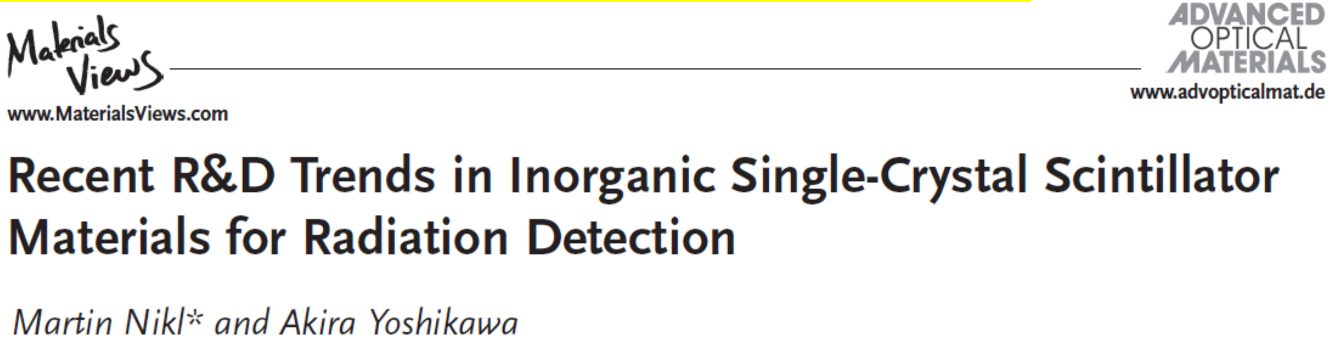
Conclusions - nanoscintillators

- Wannier exciton-based emission combined with quantum size effect can be used to create superfast nanoscintillators (decay time < 1 ns), reabsorption due to small Stokes shift and surface losses in nanocrystals are major problems to deal with.
- Embedding such nanocrystals (quantum dots) into a suitable host with efficient and (super)fast energy transfer host->nanocrystal and diminished surface/interface losses can open the way for their practical use in hybrid scintillators for fast timing

Financial&networking support acknowledged from:

Czech science foundation no. P202/12/0805, 15-18300Y and 16-15569S. MEYS LH14266 and SAFMAT LM2015088 and LO1409. EC FP7 no. 316906 (Luminet), H2020 no. 644260 (Intelum) and no. 690599 (Ascimat). Crystal Clear Collaboration, COST FAST TD1401.

Have a look at recent review papers:



Materials Views
www.MaterialsViews.com

ADVANCED OPTICAL MATERIALS
www.advopticalmat.de

Recent R&D Trends in Inorganic Single-Crystal Scintillator Materials for Radiation Detection

Martin Nikl and Akira Yoshikawa*

Adv. Opt. Mater. **3**, 463–481 (2015).

And:

C.Dujardin et al, NEEDS, TRENDS and ADVANCES IN INORGANIC SCINTILLATORS.
IEEE Trans.Nucl.Sciences **65**, 1977-1997 (2018).
DOI: 10.1109/TNS.2018.2840160)
(special issue of SCINT2017 conference)