Role of defects in the scintillation process

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ASCIMAT

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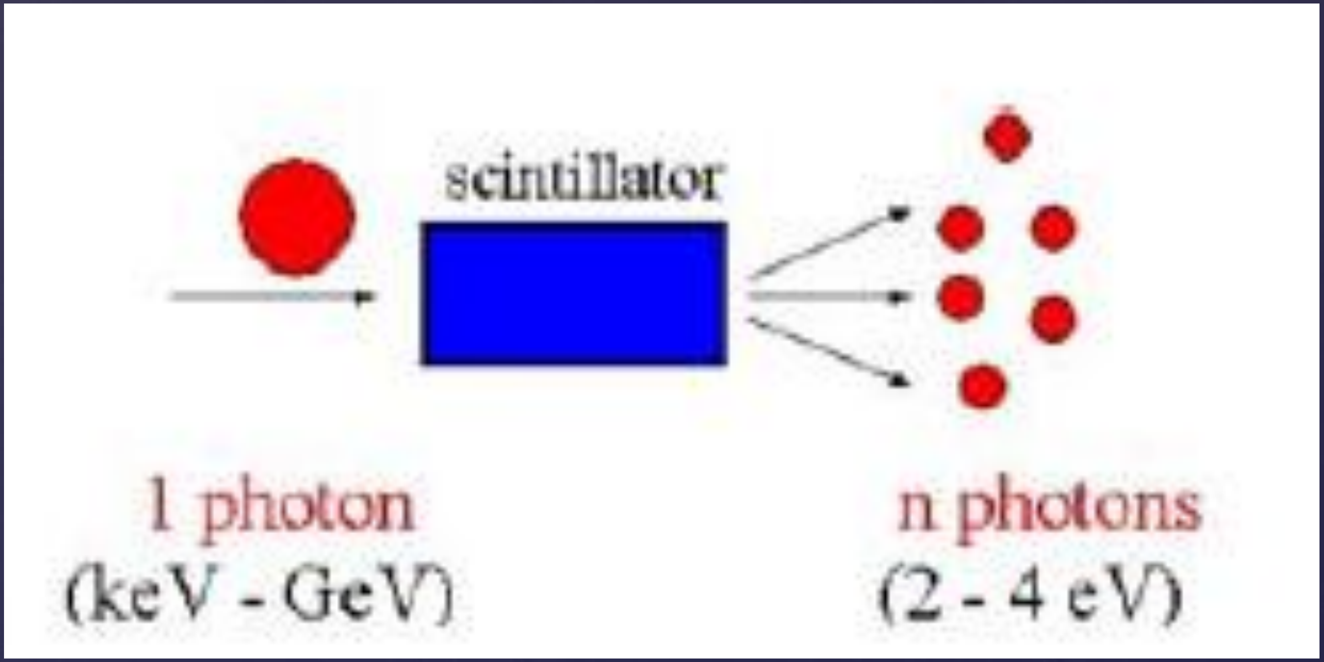

scintillator
1 photon
(keV - GeV)
n photons
(2 - 4 eV)

Scintillator requirements

TABLE 1.4
Scintillator Requirements in Various Applications[43]

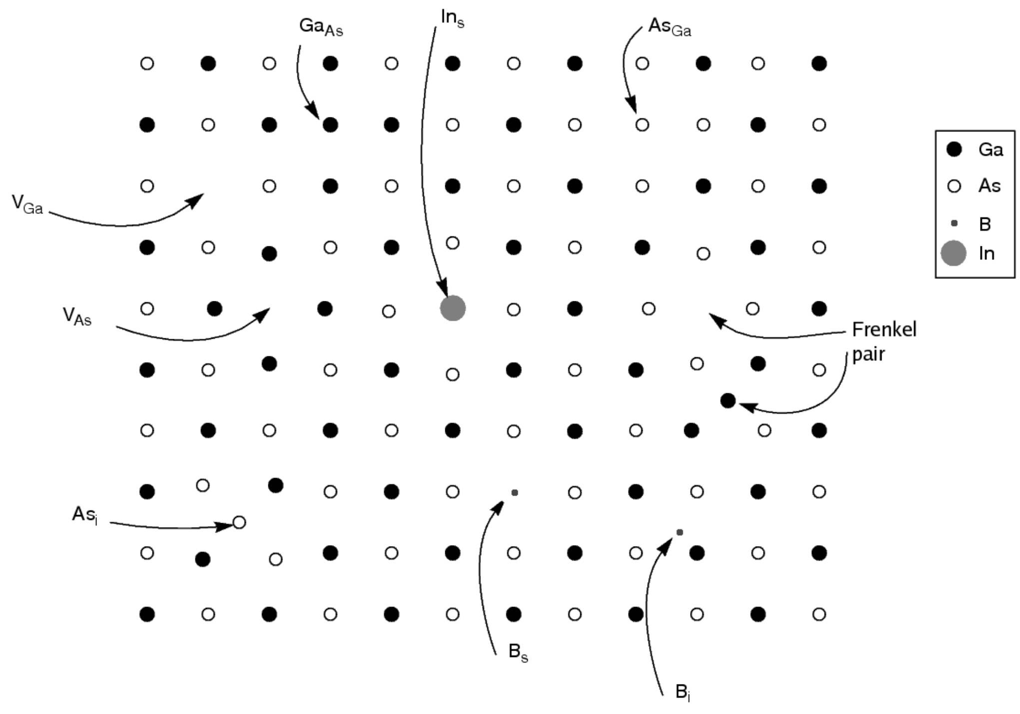
Application	L_R (ph/MeV)	τ_1 (ns)	Density (g/cm^3)	Z	λ_r (nm)	Rug.	Rad H (Mrad)
HEP	>200	≪20	High	High	>450	+	>10
IEP	High	Varies	High	High	>300	+/–	+/–
Nuclear physics	High	Varies	High	High	>300	–	–
Astrophysics	High	Less imp.	High	High/low	>450	+	–
PET	High	<1	High	High	>300	–	–
Gamma cameras	High	Less imp.	High	High	>300	+/–	–
Positron lifetime	High	<1	High	High	>180	–	–
Synch. rad. det.	High	10–100	High	High	>300	–	–
Industrial appl.	High	Varies	High	High	>300	+	–
Neutrons	High	10–100	Low	Li,B,Gd	>300	–	–
X-ray CT	High	No afterglow	>4	>50	>450	–	+
X-ray imaging	High	Less imp.	High	High	>450	+/–	+

Rodnyi

Defects in crystalline materials

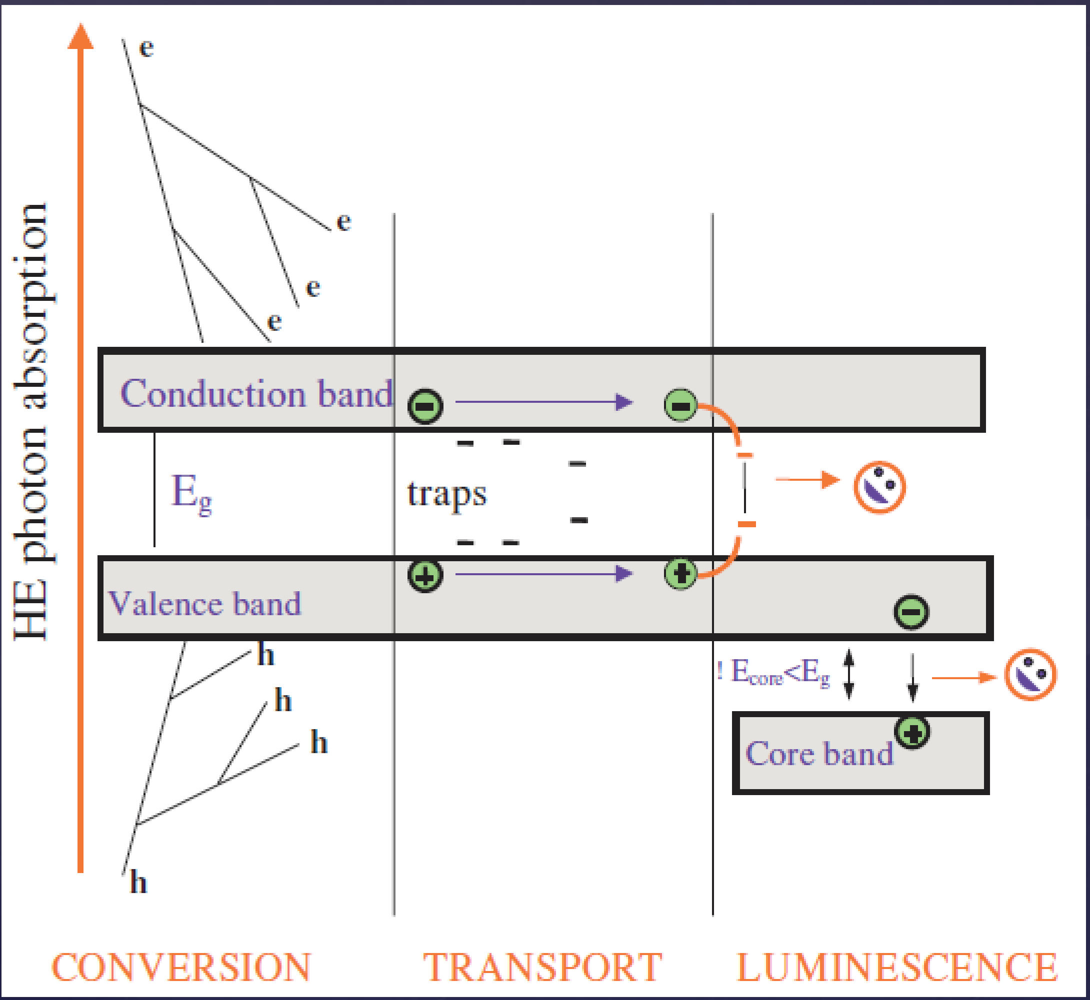
Any deviation from the perfect crystal structure can be considered a defect

- **Point defects**: (vacancies, interstitials, antisites, colour centres, polarons …), both intrinsic and extrinsic
- **Line defects**: dislocations …
- **Two dimensional defects**: interfaces, grain boundaries, twins, stacking faults …
- **Three dimensional defects**: precipitates, voids …



The next slides will be focused exclusively on point defects

Scintillation process



The luminescence is only the last of a complex series of events

Light Yield $Y = \frac{E_{ph}}{\beta E_g} S\ Q$

Transport stage is the least predictable process, depending on material quality, lattice imperfections, manufacturing technology.

Also the luminescence stage can be affected by parasitic phenomena

Factors contributing to defect formation/inclusion in crystals

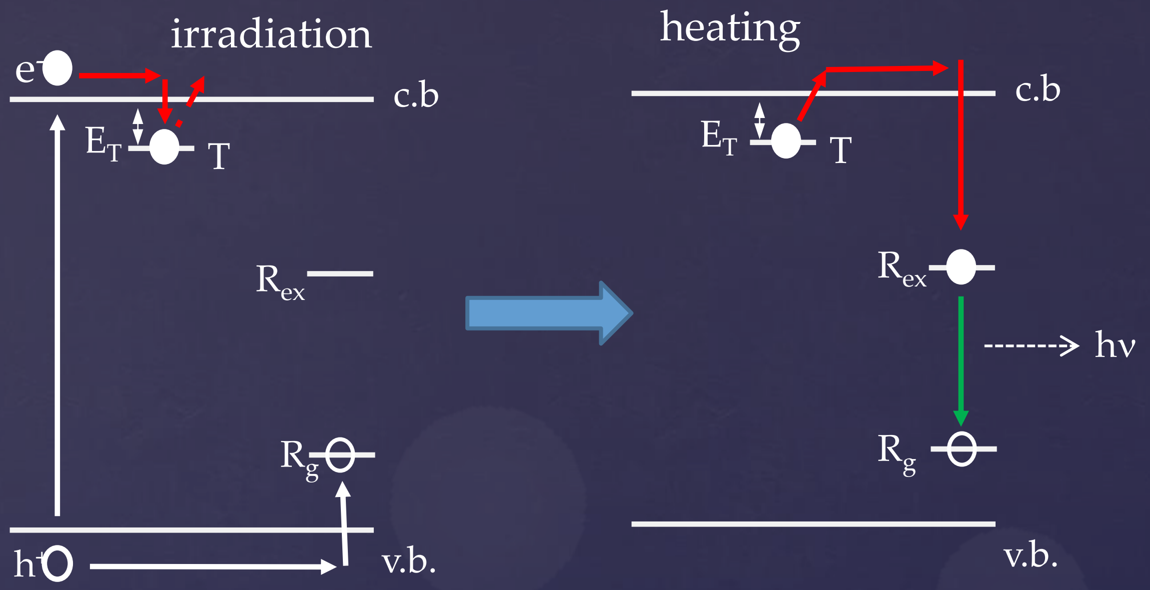
Raw material purity

Synthesis technology

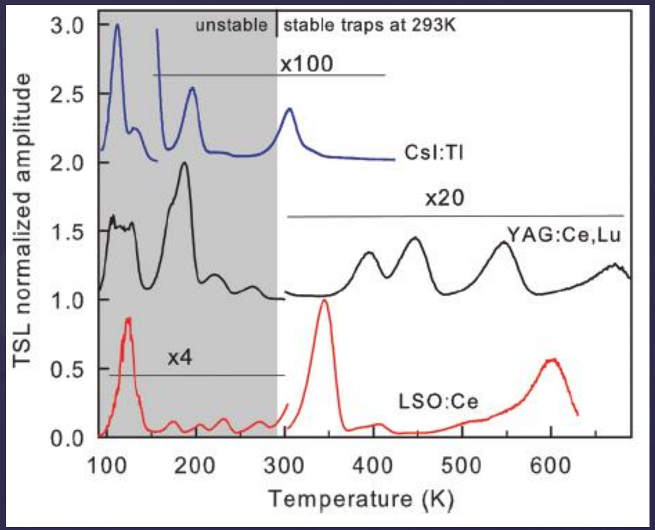
Ionizing radiation

Thermodynamics

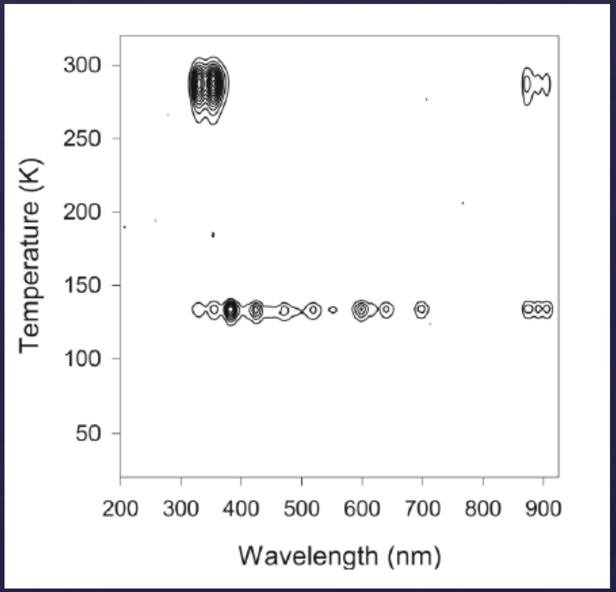
Defect characterization: TSL



Glow curves with PMT



Glow curves with spectral infos



Traps can be studied by heating at a constant rate the sample after irradiation. Probability of escape from the trap:

$$P = C \exp(-E_T/kT)$$

Strongly dependent on T, appearance of peaks.

Obtained info: E_T, τ, species of trap (in wavelength resolved mode)

Moretti PCCP 2016,
JPhysChemC 2014

Point defect role on scintillation

Point defects perturb the band structure of the materials resulting in the formation of localized levels inside the band gap

$$Y = \frac{E_{ph}}{\beta E_g} S\, Q$$

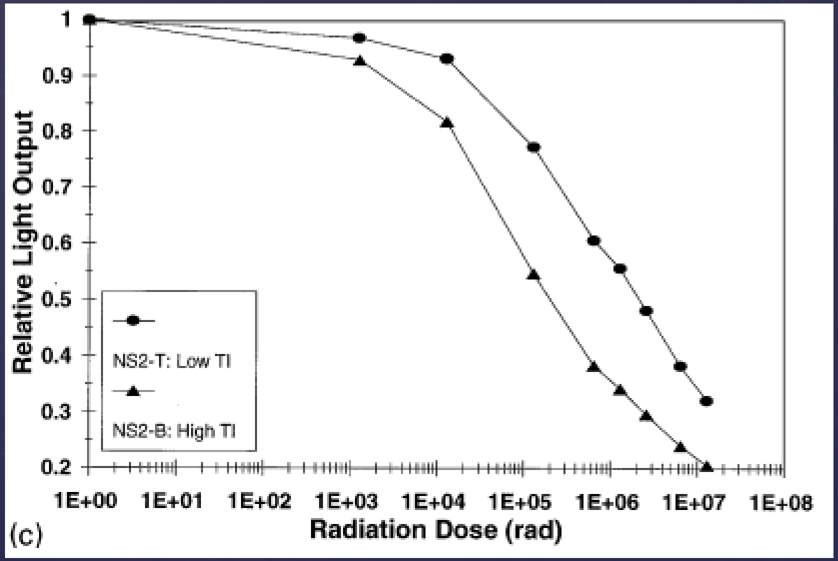
Role on S	Role on Q (broadly speaking)
Perturb the charge carrier recombination process on luminescence centres	Give rise to luminescence quenching phenomena or to scintillation light re-absorption

The two effects are not always well distinguishable!

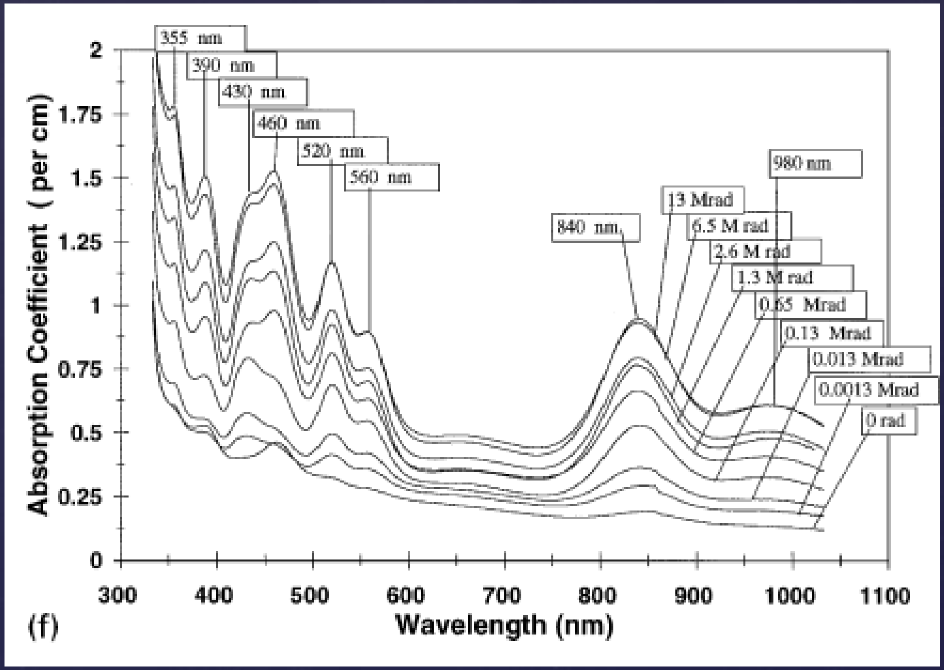
Point defect role on Q - reabsorption

- Usually not a big deal for good quality raw materials and optimized growth condition
- However, formation of new, or modification of already existing, defects can be induced by ionizing radiation in high doses.

CsI:Tl relative light yield



CsI:Tl optical absoption for different ^{60}Co γ-doses



Absorptions related to F_A centres, induced by irradiation

Chowdhury, NIMa 1999

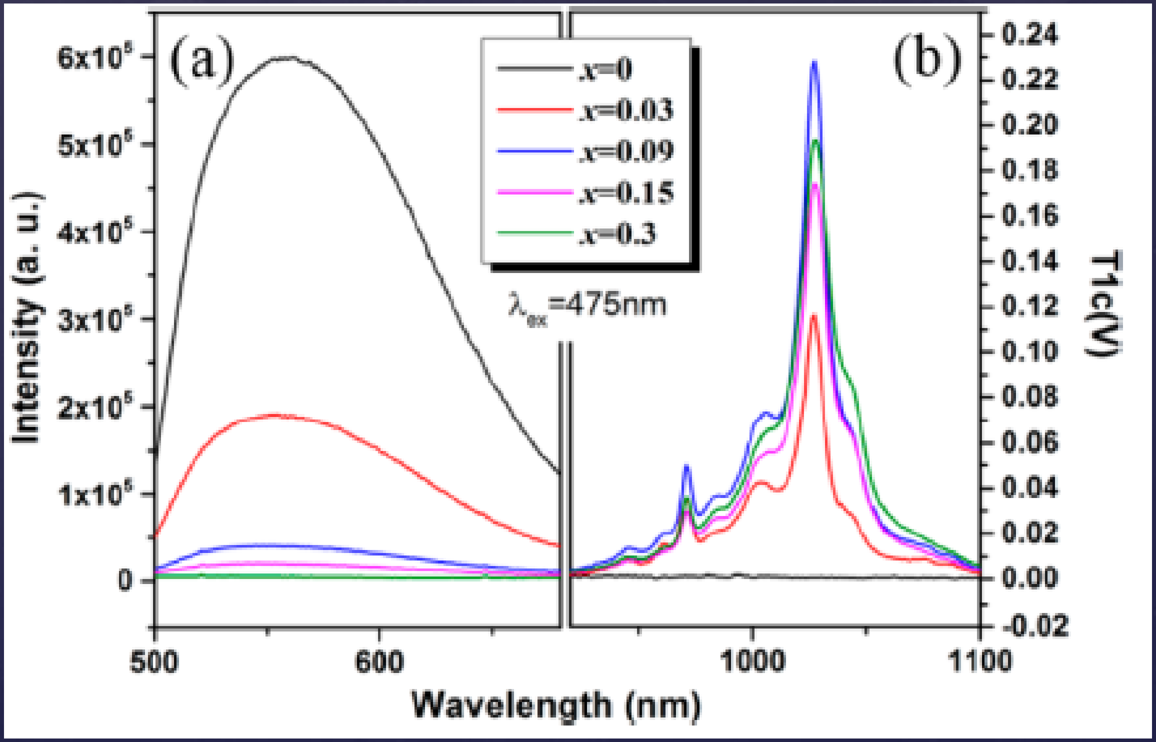
Point defect role on Q - quenching

Usually not a big deal for good quality raw materials

Require close spatial correlation between emitting and quenching centres → high concentration

$Ce^{3+*} + Yb^{3+} \rightarrow Ce^{4+} + Yb^{2+} \rightarrow Ce^{3+} + Yb^{3+(*)}$

GGAG:Ce, x Yb photoluminescence upon Yb content



Luo, Inorg Chem 2016
Barandiaran, PCCP 2015

Point defect role on S

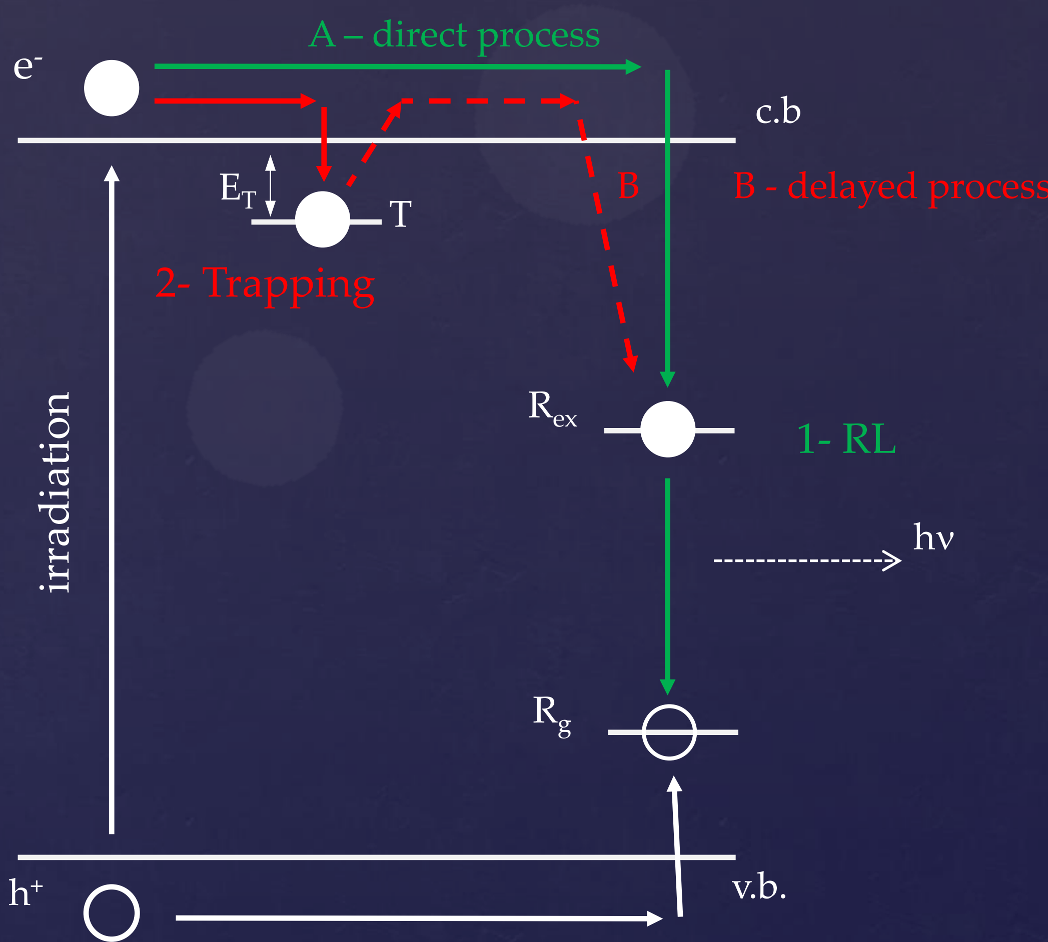
Competition between charge carrier trapping on defect sites and recombination on luminescent centres

Time spent by the charges on the defects strongly depends on trap thermal depth (E_T)

$$\tau = C' \exp\left(E_T/_{kT}\right)$$

According to E_T value (from 10^{-2} to 10^{0} eV), huge range of τ can be measured (<μs, > kyear).

Valid also for hole trapping states



Point defect role on S

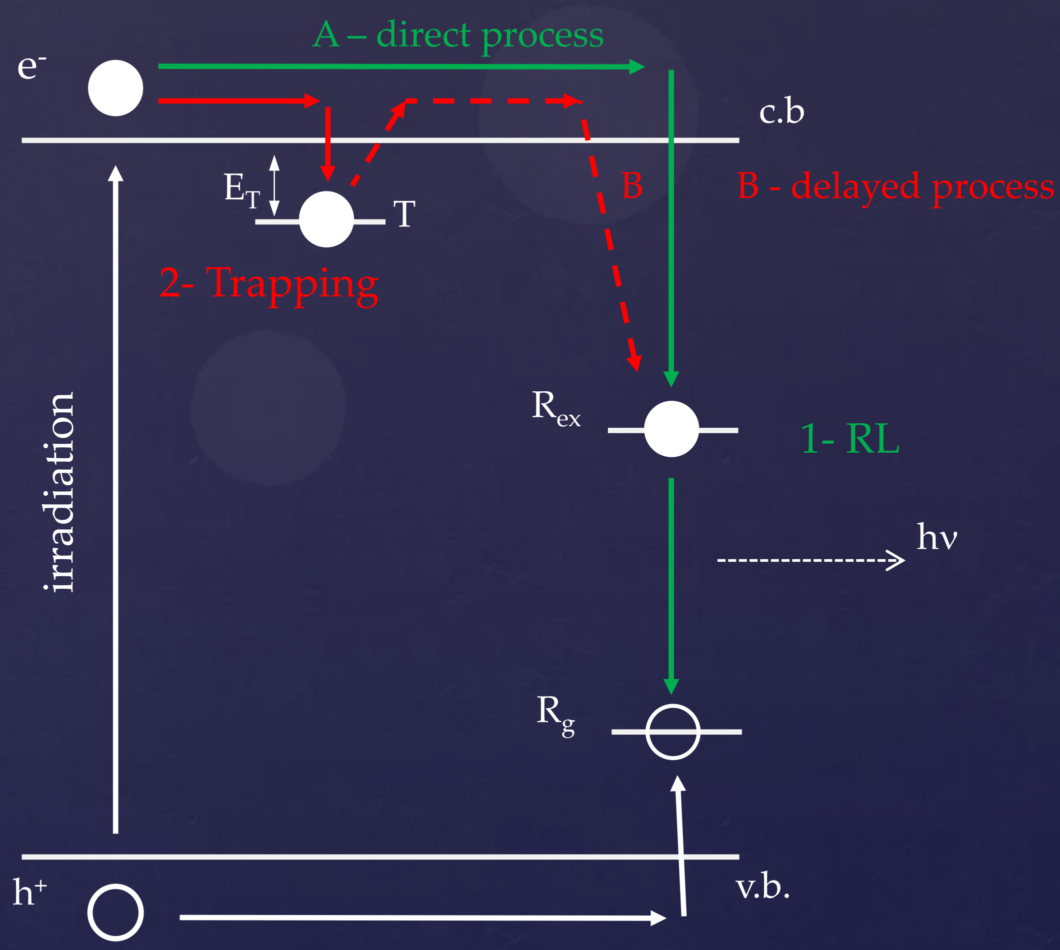
Competition between charge carrier trapping on defect sites and recombination on luminescent centres

Due to charge carrier trapping by defect the scintillation decay cannot be a single exponential

If at room temperature τ is of the order of:

- µs – ms: slow scintillation decay tails
- min., hours: afterglow
- even longer: permanent trapping

Charge carrier slow migration toward recombination centres is also the cause of rise time in scintillation time profile

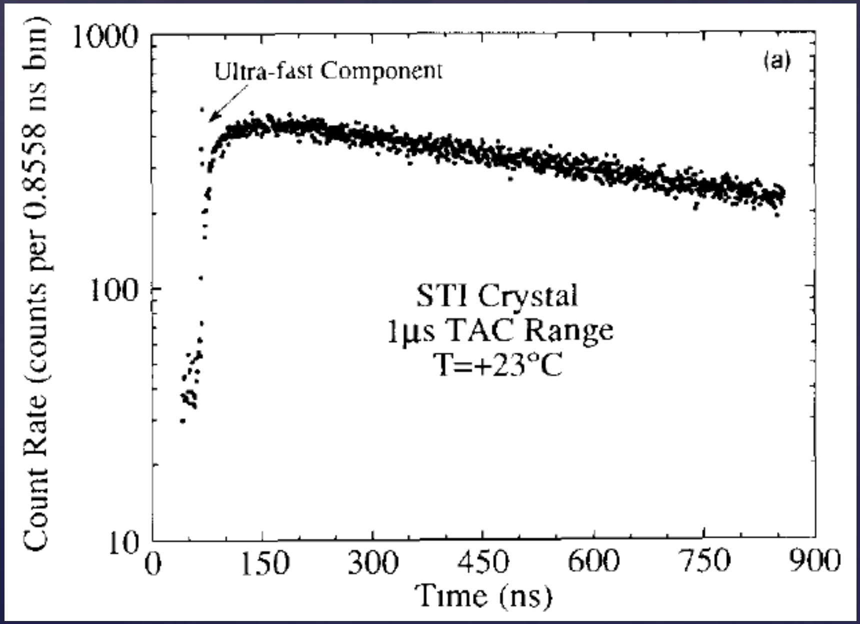


(self-)trapping and rise time: CsI:Tl

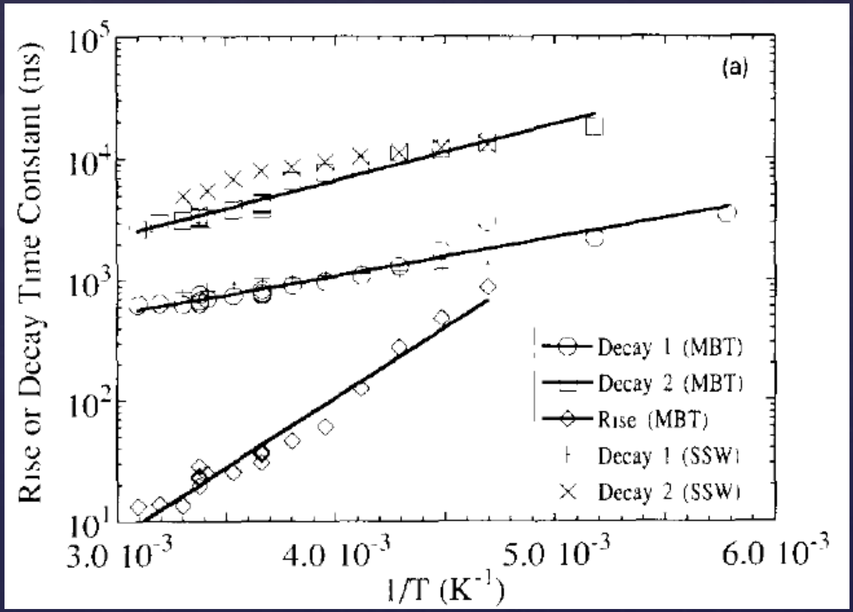
Rise time due to self trapped hole (STH , V_k) migration/thermal decomposition dependent on:

- temperature
- Tl content

CsI:Tl scintillation decay curve



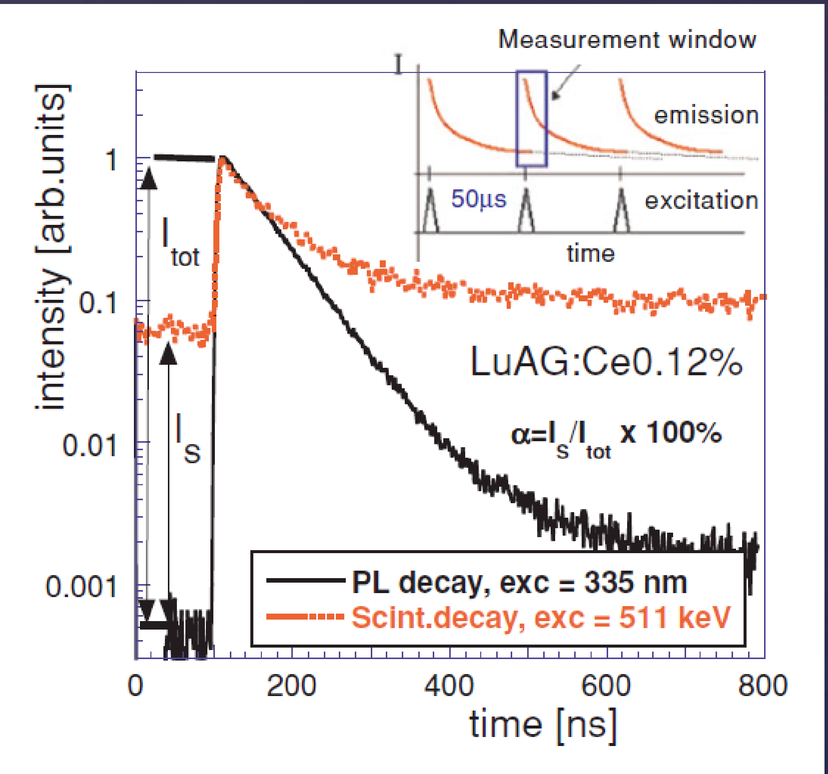
CsI:Tl, rise and decay temperature dependence

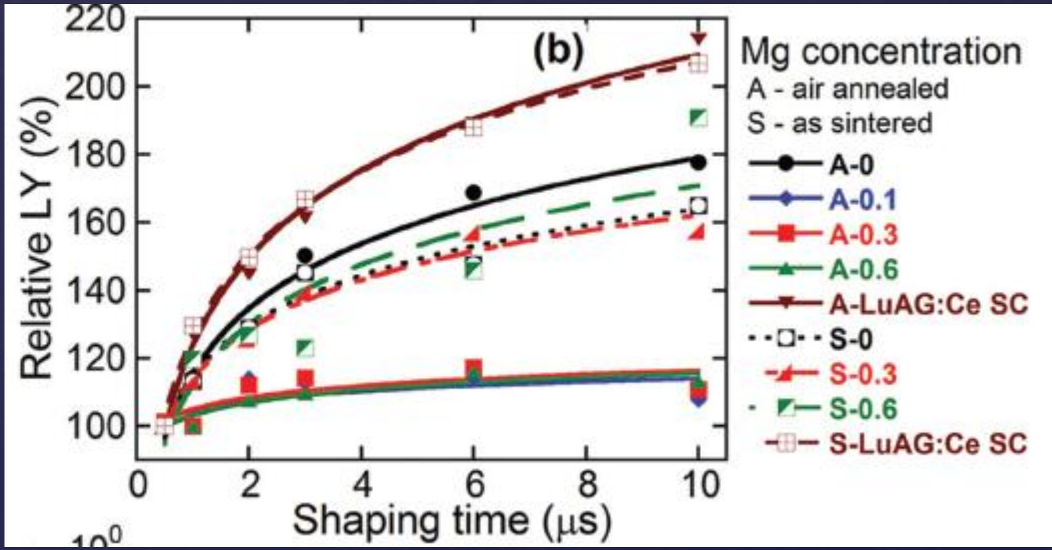


Valentine NIMa 1993

Scintillation slow decays

Scintillation decay profile is not single exponential, the scintillation tails often represent a relevant fraction of the total amount of emitted light.

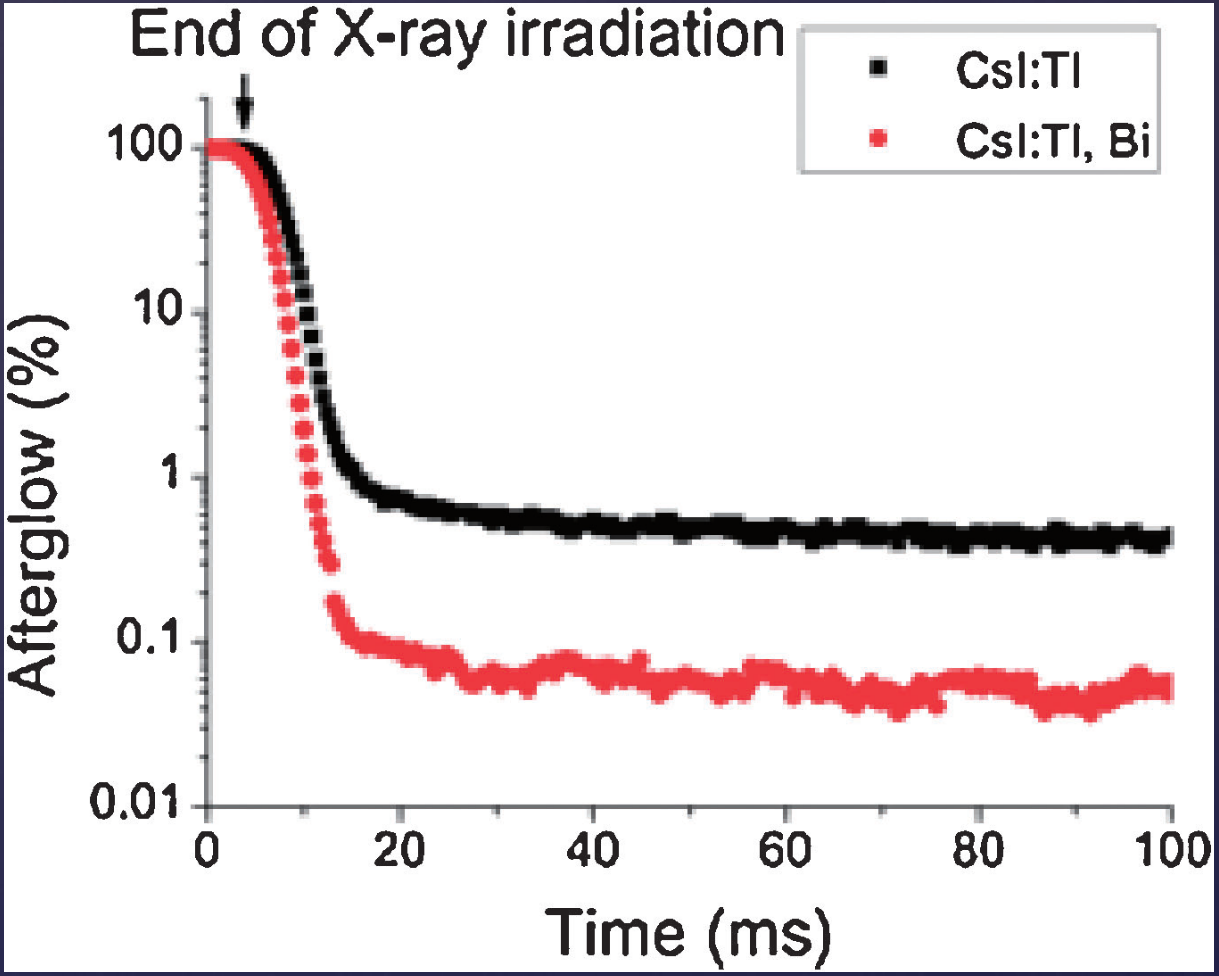




Nikl MatSciTech 2006

Liu AdvOptMater 2016

On a longer timescale



Totsuka APEX 2012

Persistent luminescence

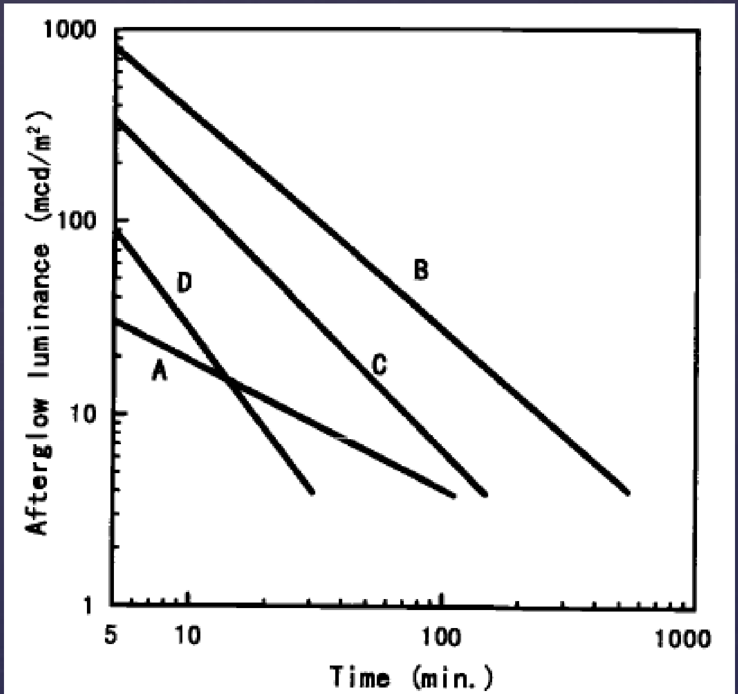
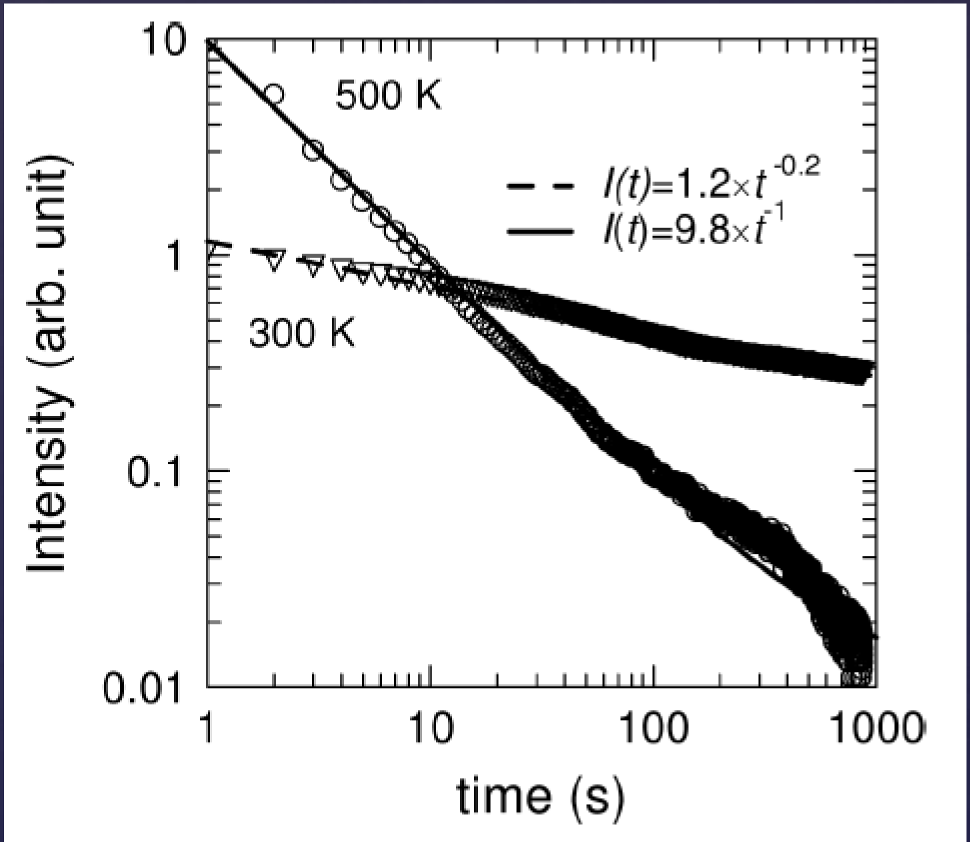


Fig. 2. Phosphorescence characteristics measured at 22°C after 10 min exposure to 200 lx of D_{65} light (the standard light with the color temperature of 6504 K). A: $SrAl_2O_4:Eu^{2+}$, B: $SrAl_2O_4:Eu^{2+}$, Dy^{3+}; C: $SrAl_2O_4:Eu^{2+},Nd^{3+}$; D: commercially used ZnS:Cu,Co.

LSO:Ce



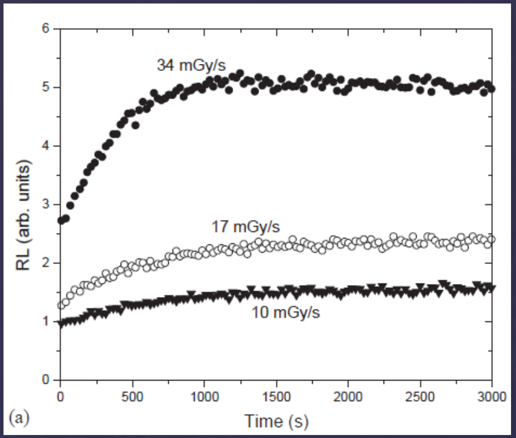
Matsusawa J ElettroCemSoc 1996

Yamaga OptMaterExpress 2012

Luminescence sensitization (aka bright burn, hysteresis)

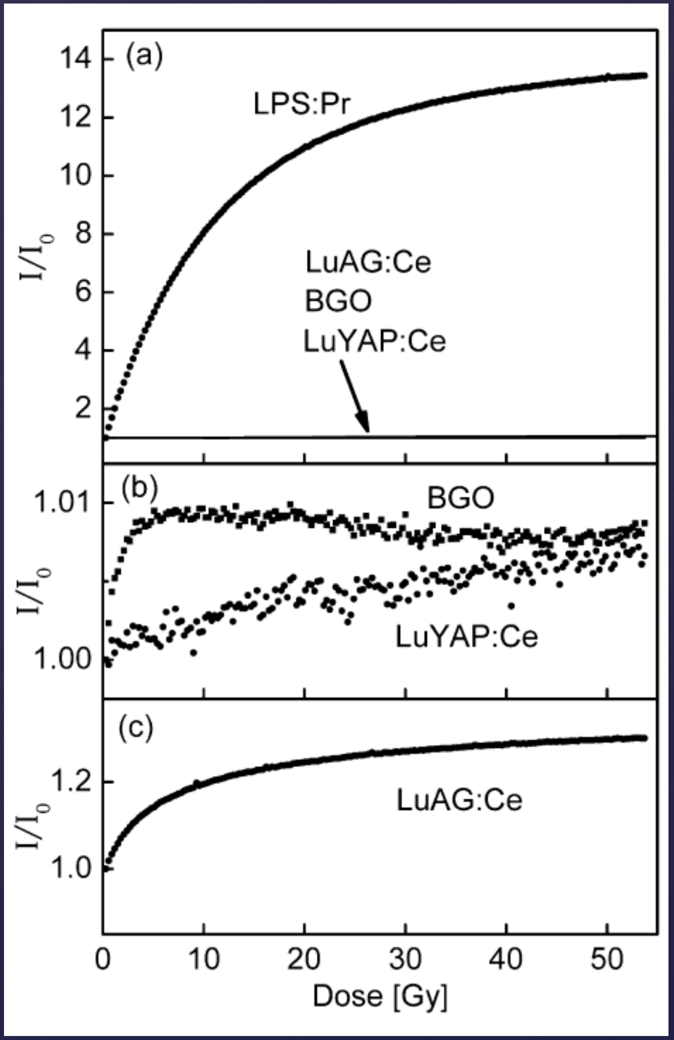
Definition:
Radio-luminescence (RL) intensity increase with the accumulated dose.

Al_2O_3:C



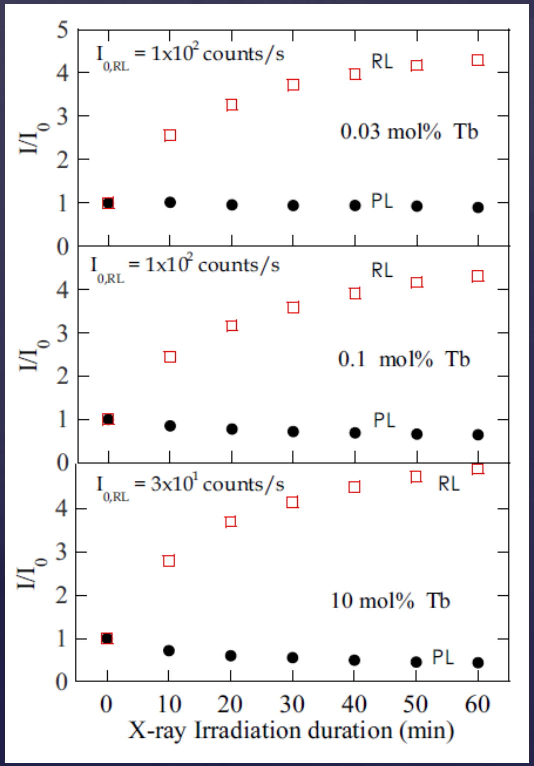
Polf Rad Meas 2004

… and various other



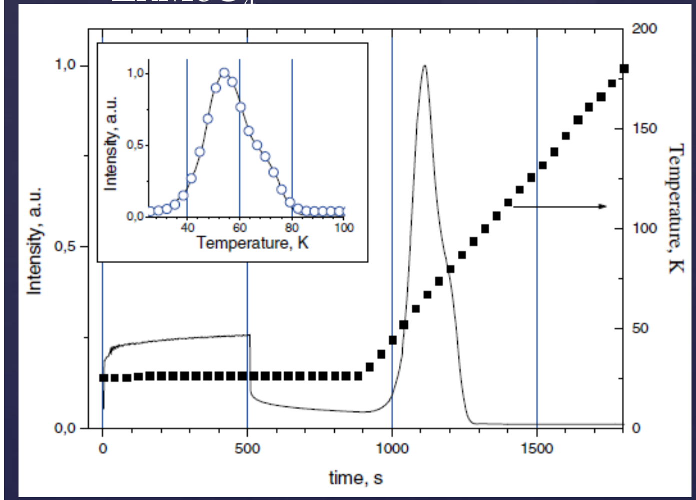
Dell'Orto J Phys Chem C 2013

Sol-gel SiO_2:Tb



Fasoli PSSc, 2007

$ZnMoO_4$



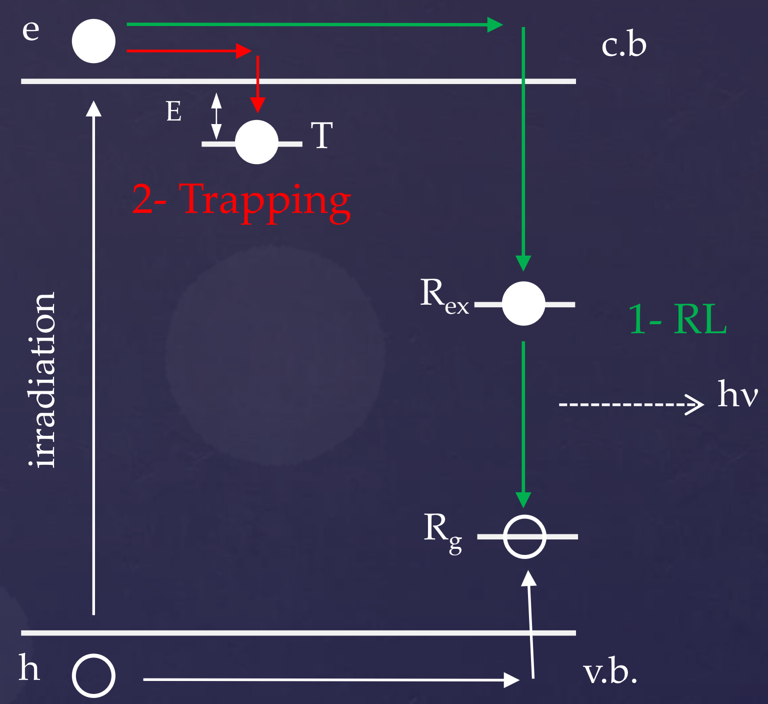
Spassky 2009

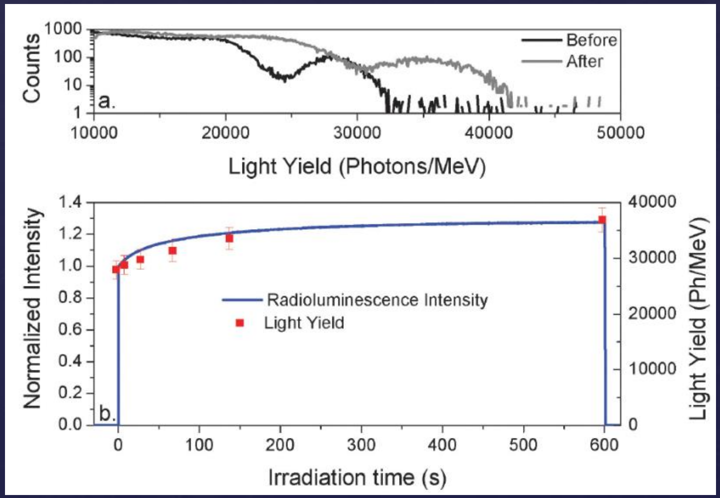
Phenomenon interpretation

Cause:
Progressive filling of traps present in the scintillator during irradiation

Increase of the radiative recombination probability of free carriers due to reduced competition between emission centres (1) and traps in carrier capture (2)

Memory effect may represent a problem in those applications which rely on consistent RL intensity as a function of the dose rate (e.g. CT, digital radiography, real time RL dosimetry …). It can also affect LY



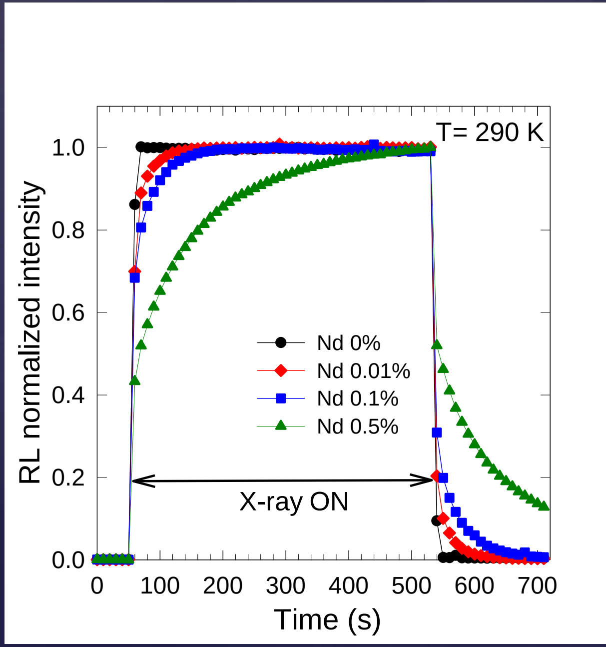


Patton PCCP 2016

A model material: YPO_4:Ce,Nd

'Standard' (LSO, YAG …) scintillators are complex systems:
Many traps whose concentration is substantially unknown.

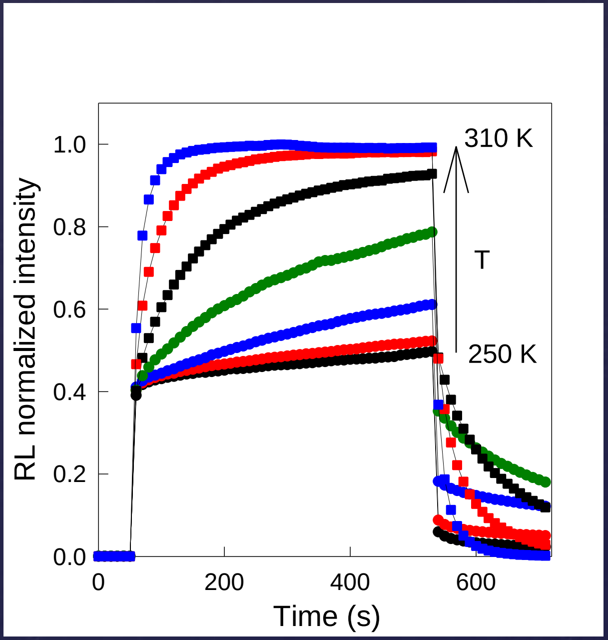
RL sensitization VS Nd content at 290 K
Ce^{3+} emission (310-370nm)



Radioluminescence (RL) as a function of irradiation time is characterized by an evident sensitization which strongly depends on the Nd content.

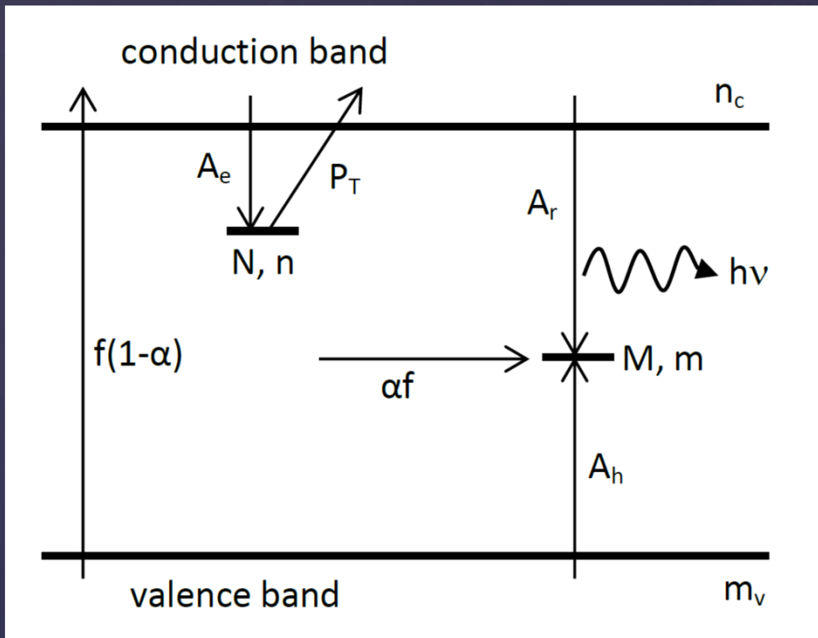
The RL sensitization is evidently affected by the measurement temperature, and thus by the Nd related trap stability.

RL sensitization VS T, Nd 0.5 mol%
Ce^{3+} emission (310-370nm)



Moretti JPhysChemC 2014

Mathematical modelling



$$\frac{dn_c}{dt} = f(1-\alpha) - n_c(N-n)A_e + ns\exp\left(-\frac{E}{kT}\right) - n_cA_rm$$

$$\frac{dn}{dt} = n_c(N-n)A_e - ns\exp\left(-\frac{E}{kT}\right)$$

$$\frac{dm_v}{dt} = f - m_v(M-m)A_h$$

$$\frac{dm}{dt} = m_v(M-m)A_h - n_cA_rm$$

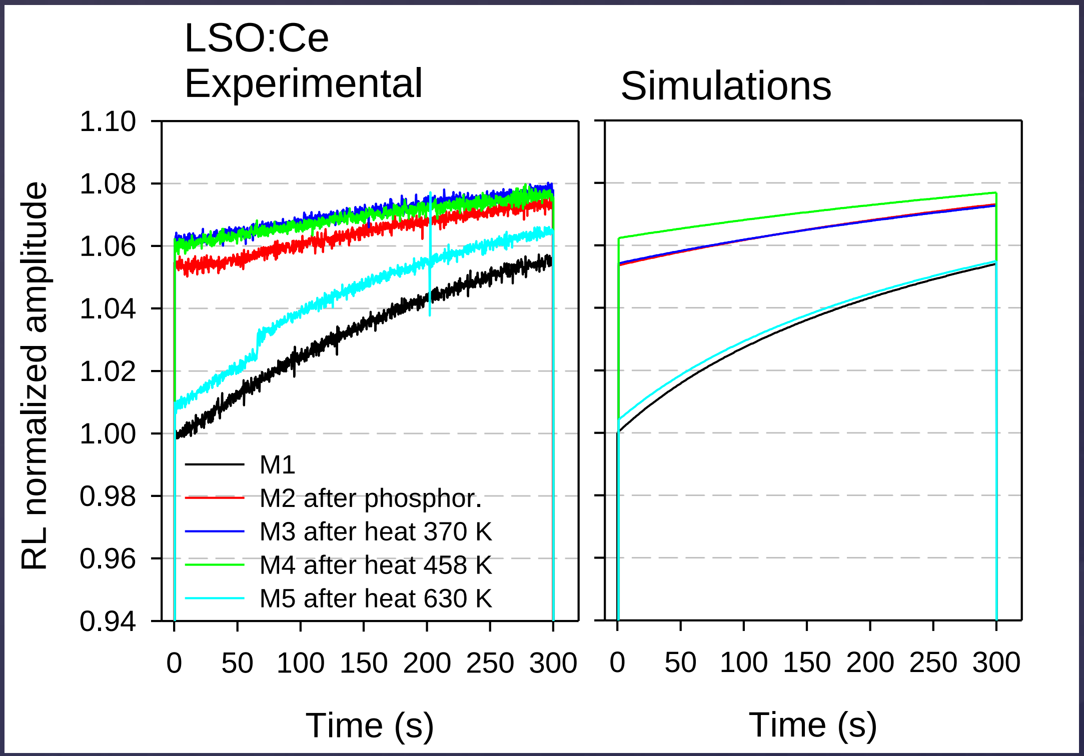
$$n_c + n = m_v + m$$

$$I_{RL} \propto n_cA_rm + \alpha f$$

Where:
n, n_c : electron concentration (cm^{-3}) on traps and in the conduction band, respectively
m, m_v : hole concentration (cm^{-3}) on traps and in the valence band
M, N : hole and electron traps concentration (cm^{-3})
f : electron/hole pair creation rate ($cm^{-3}\,s^{-1}$)
A_e, A_r and A_h : transition coefficients ($cm^3\,s^{-1}$)
α : direct recombination coefficient

* Moretti *et al.* J Phys Chem C 118 (2014) 9670

Testing the model

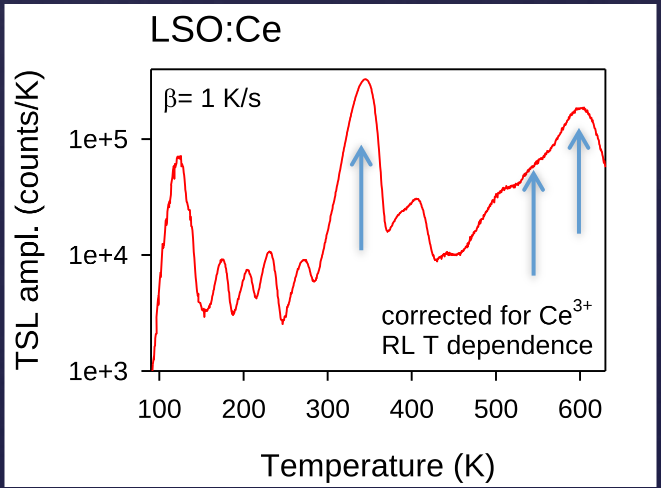


Experimental results (T = 290 K):

- Clear slow increase during all irradiations
- Complex intensity dependence upon different partial cleaning T (T_{pc})
- Higher T traps?

Simulation results:

- Rather good general shape reconstruction with at least 3 stable traps
- RL intensity upon T_{pc} not always in good agreement with experimental results
- No improvements by considering unstable traps



Measurement scheme:
T_{irrad} = 290 K, t_{irrad}= 300 s
T_{pc} = 370, 458, 630 K

Moretti PCCP 2016,

Luminescence sensitization

Complex phenomenon dependent on:

Irradiation dose and dose rate

Measurement and storage temperature

Trap concentrations and energies

Irradiation history

Dealing with defects

Several strategies are currently used in reducing the role of traps:

Post-growth annealing in suitable atmospheres

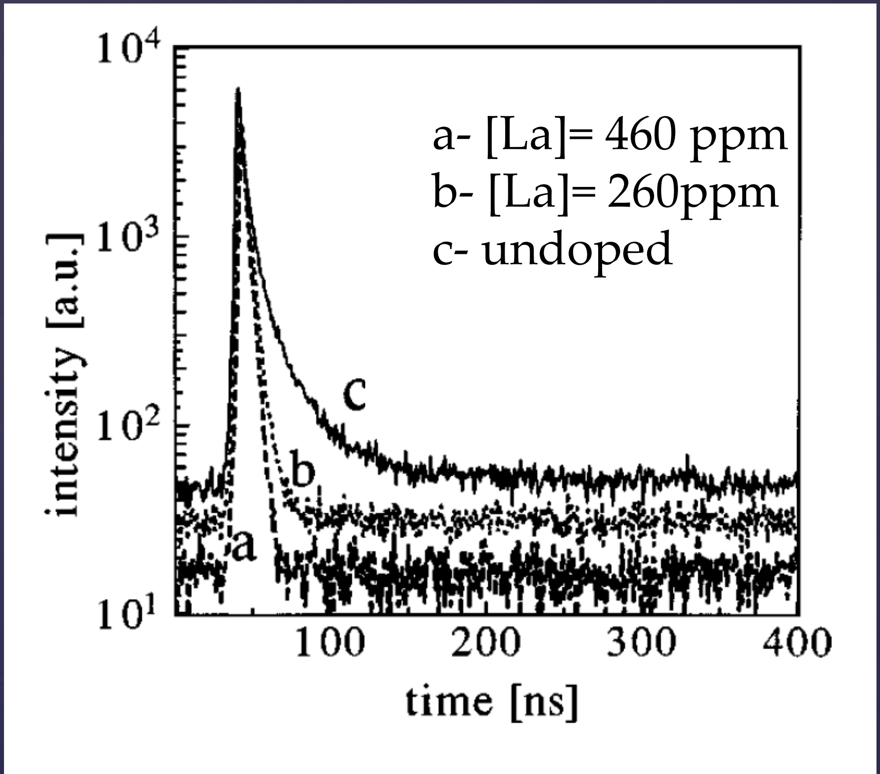
Trap compensation/inactivation with alio-valent ions

Band gap engineering

Recombination process tailoring

Defect engineering

(Co-)doping: $PbWO_4$:La

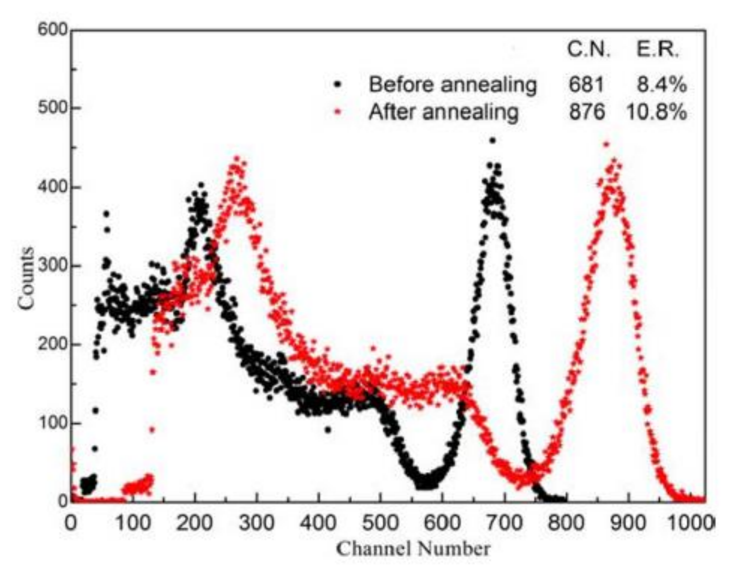


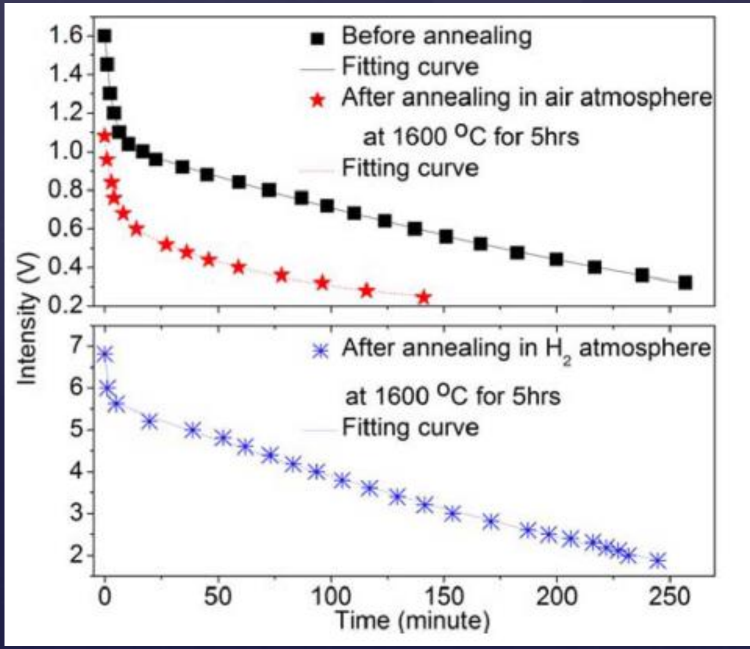
La^{3+} doping in $PbWO_4$ compensate for Pb vacancies and related defects. However, La^{3+} also is the cause of non-radiative recombination centres resulting in lower LY

The same strategy works also for CsI:Tl (Sm, Eu, or Bi) with a really evident reduction in the afterglow. The mechanism is however not really clear

Nikl APL 1997

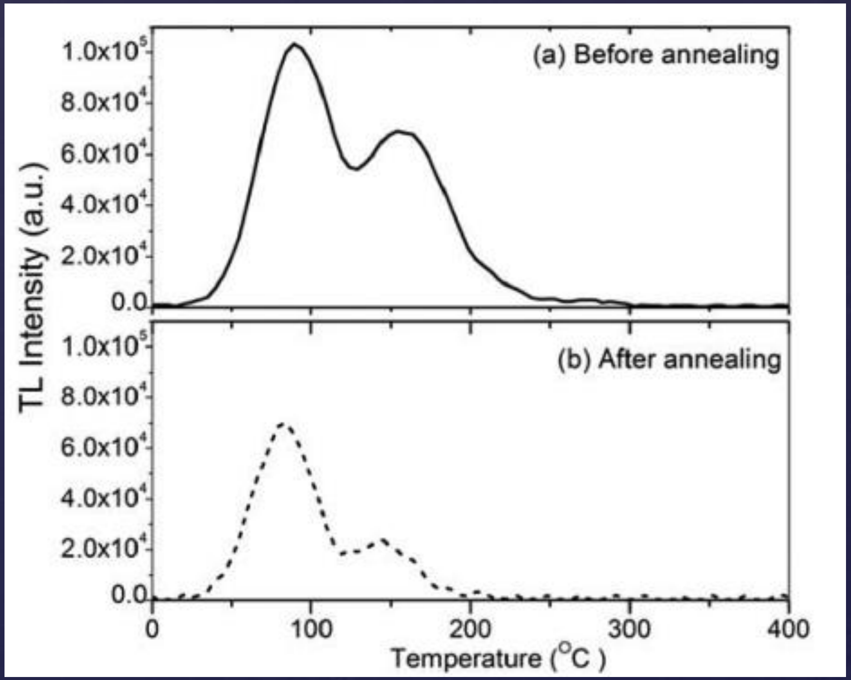
Annealing in suitable atmosphere: LSO:Ce





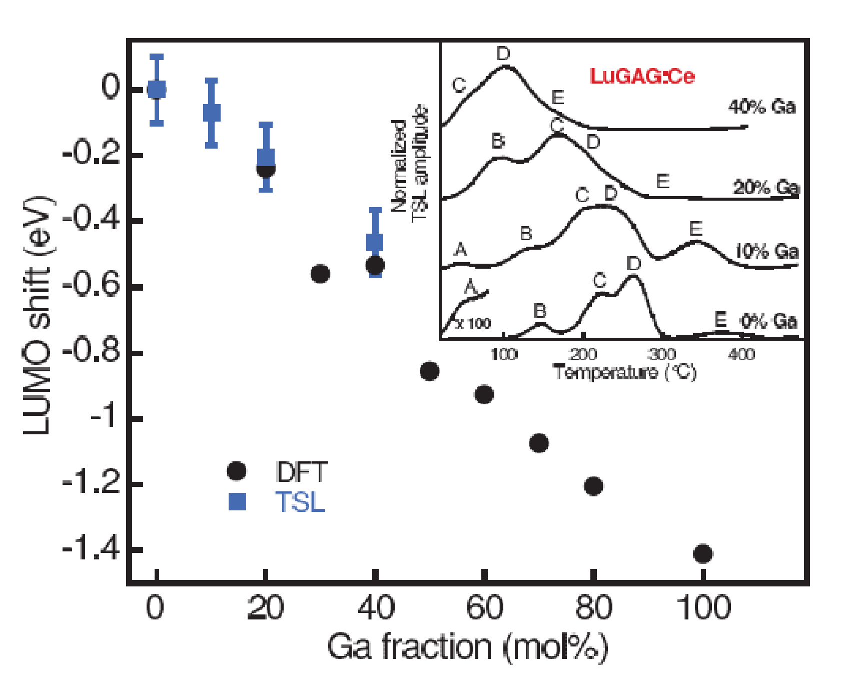
Annealing in air at 1400°C, reduces the importance of TSL, increases light yield.

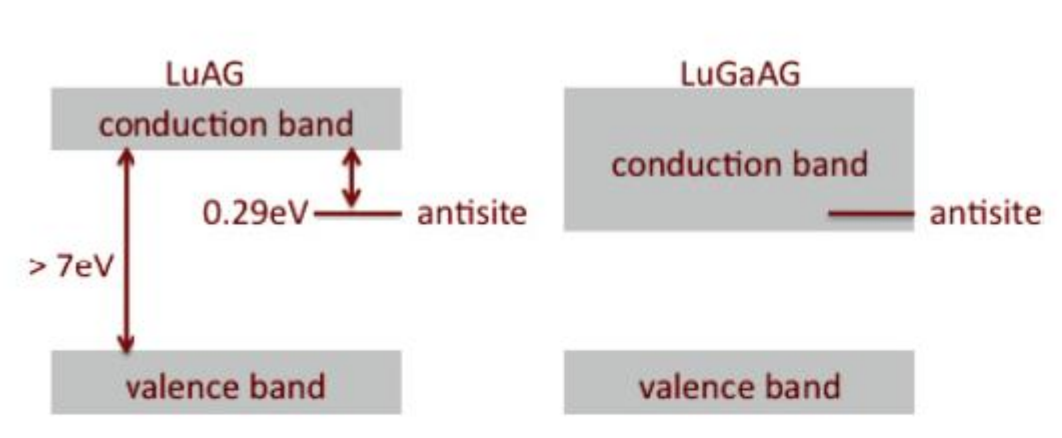
To note: also formation of Ce^{4+}



Ding IEEETNS 2010

Band gap/composition engineering

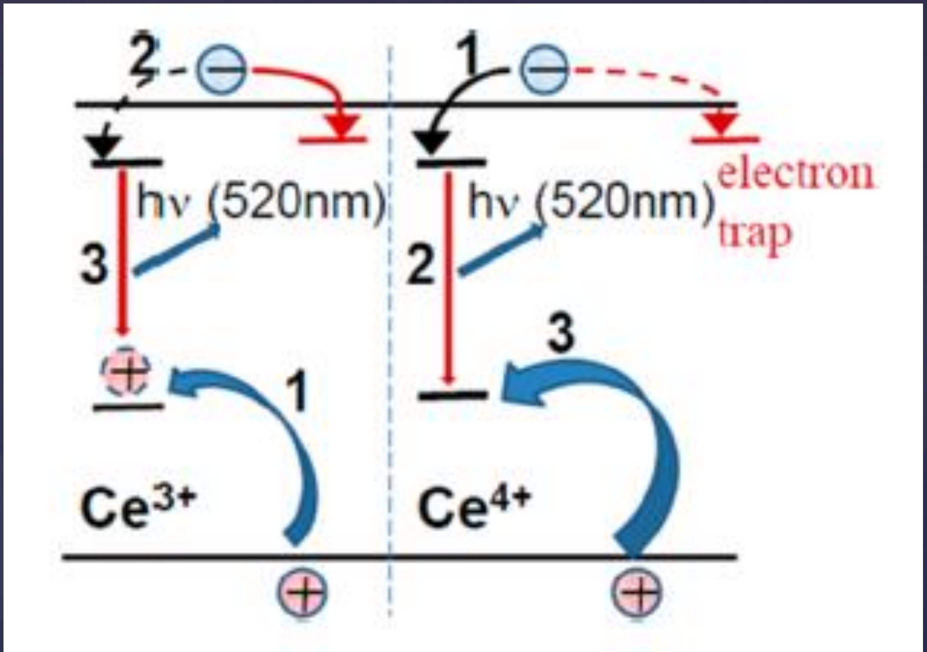




Reduction of band gap by alloying LuAG:Ce + LuGaG:Ce
Traps tend to be less stable at room temperature, higher probability of thermal ionization of Ce^{3+}.
Subject of vast research activity in the last few years

Fasoli PRB 2011

Recombination process engineering

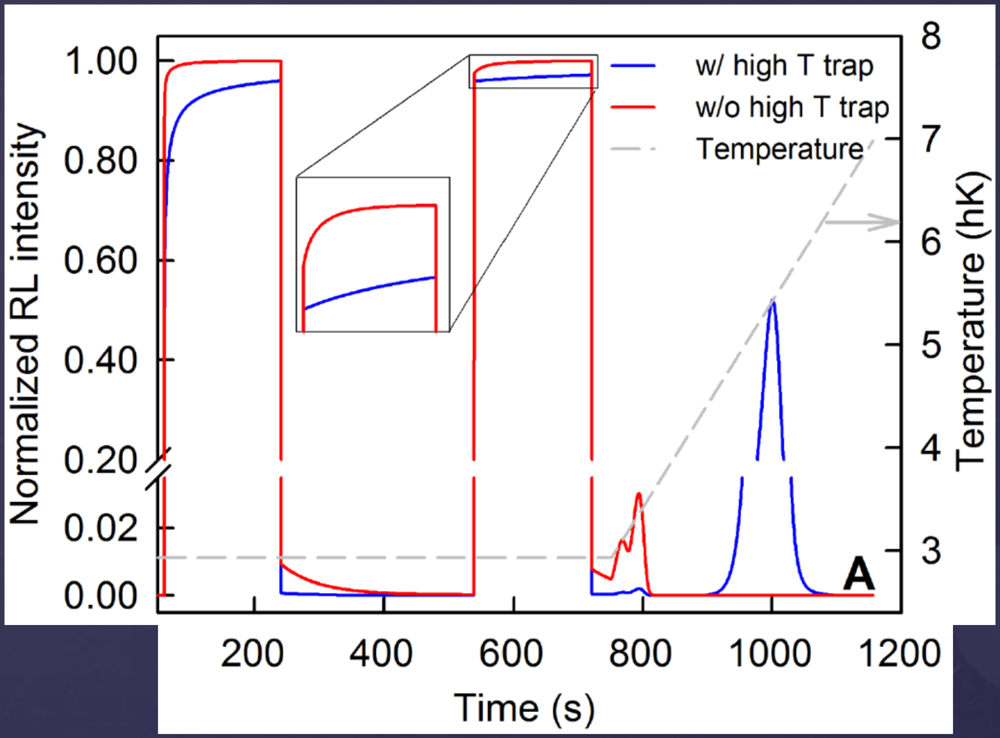


Mg or Ca codoping in Ce doped LSO and garnets favours the formation of Ce^{4+}

Ce^{4+} can promptly capture an electron in the conduction band disfavouring the electron trapping at defect sites

Blahuta IEEETNS 2013
Nikl CrystGrowthDes 2014
Moretti Jlumin 2012

Defect engineering



Based on CsI:Tl simulation results

Effect of an additional theoretical very stable and high concentration trap:

- More evident sensitization during the first irradiation, but
- Lower afterglow
- Less evident x-ray induced sensitization during the second irradiation
- Lower TSL contribution of the two shallow traps
- But lower RL intensity

Simulation results suggest a positive effect of high stability and concentration trap in the reduction of memory effects

New approach: make the sample selectively worse from a defect point of view by co-doping with suitable ions

Moretti PCCP 2016,

Conclusions

The presence of defects in scintillators is the cause of:

Loss of transparency of the material
Luminescence centre quenching
Delayed recombination phenomena
Luminescence hysteresis – memory effects

The defect effect on the scintillation process is very complex and it results in a non-trivial relation among light output, trap characteristics (energy, concentration, numerosity), sample irradiation hystory, and measurement temperature.

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