# Memory effect in $YPO_4$:Ce,Nd – a model material

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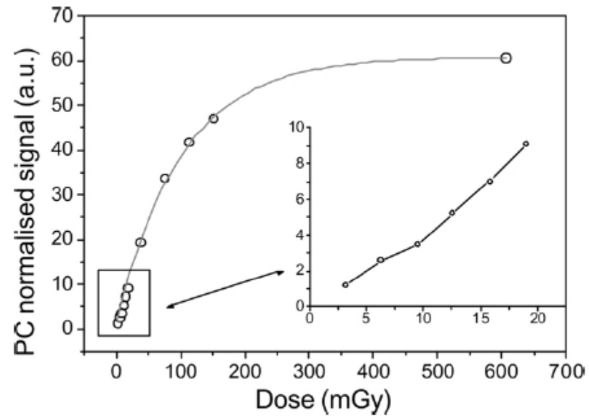
# Few examples

**Definition:**

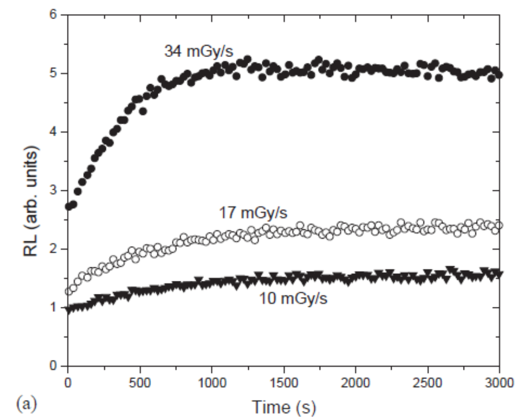
Radio-luminescence (RL) intensity increase with the accumulated dose. Also called: “bright burn”, RL sensitization

Diamond (photo-conductivity)



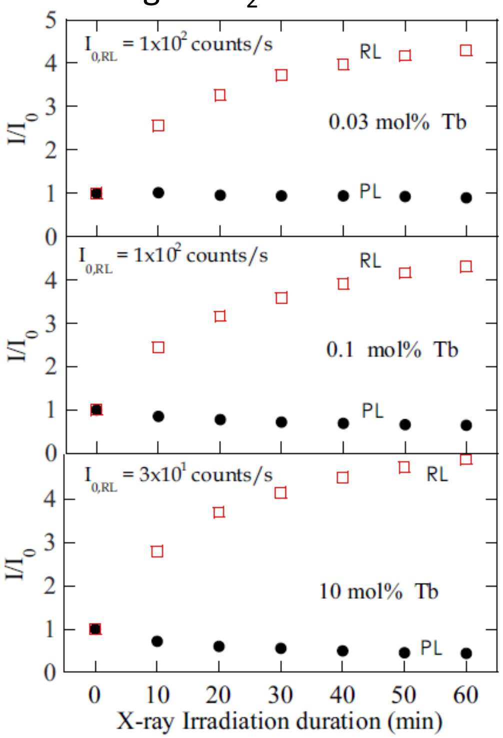

Manfredotti *et al.* Diam&Rel Mat, 13 (2004) 914

$Al_2O_3$:C



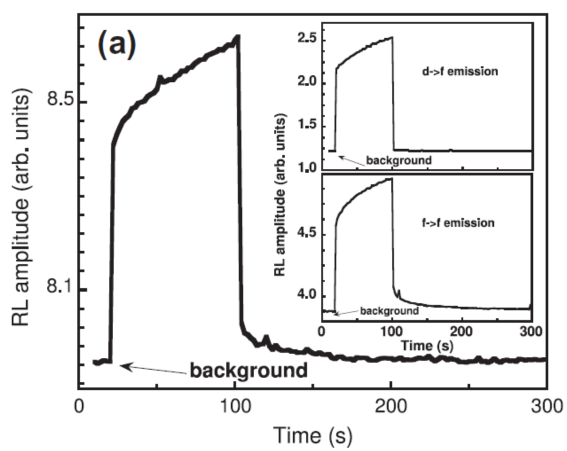

Polf *et al*. Rad Meas, 38 (2004) 227

Sol-gel $SiO_2$:Tb



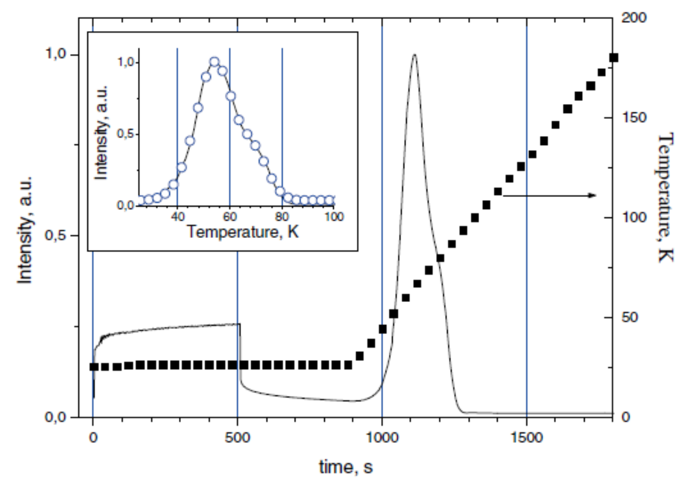

Fasoli *et al.* PSSc, 4 (2007) 1056

$Lu_2Si_2O_7$:Pr




Mihokova *et al.* Opt Mater, 34 (2012) 872

$ZnMoO_4$




Spassky *et al*. PSSa, 206 (2009) 1579

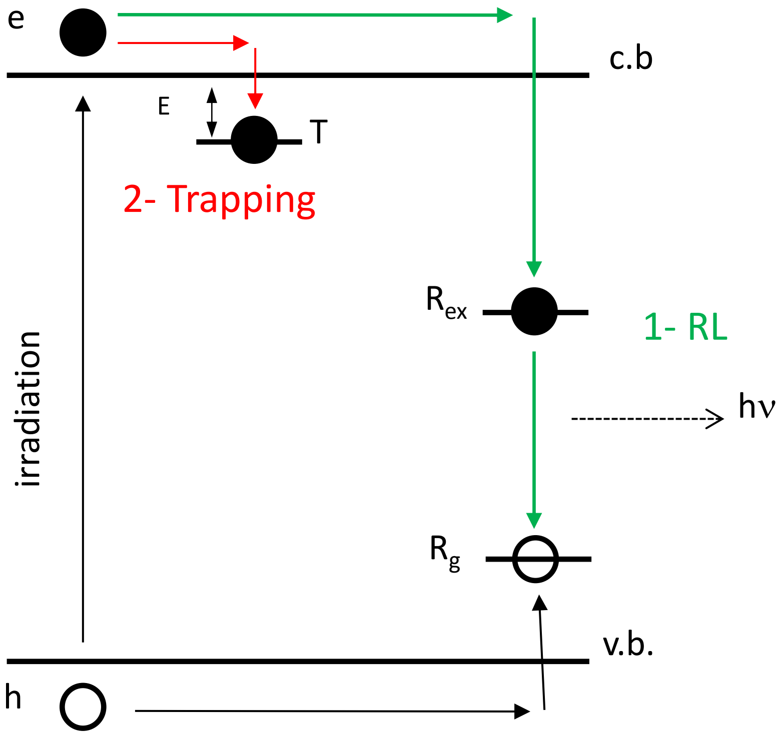
# Phenomenon interpretation

**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 …)



# Why $YPO_4$:Ce,Nd?

**'Standard' (LSO, YAG …) scintillators are complex systems:**

Many traps whose concentration is substantially unknown.

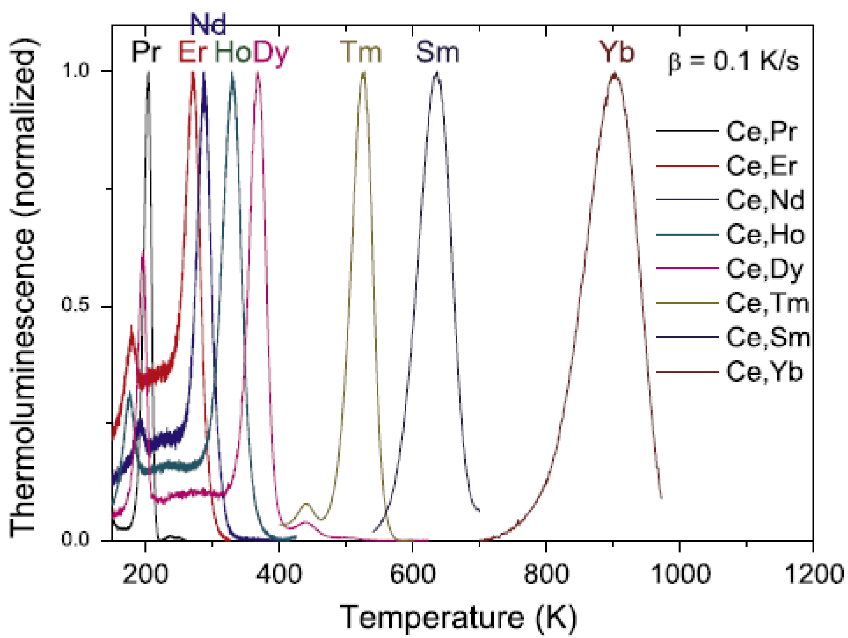
**$YPO_4$:Ce, Nd**

- Well characterized system
- Ce acts as recombination centre
- Nd behave as a electron trap

Ce and Nd concentrations can be chosen during synthesis, and can also be checked.

Bos *et al.* results suggest that the Nd-related glow peak is the dominant TSL feature.

$YPO_4$:Ce, RE glow curves




Bos *et al*; Rad Meas 46 (2011) 1410

# Samples and characterization

Single crystals grown by spontaneous nucleation from a PbO-$P_2O_5$ flux

- $YPO_4$: Ce 0.1%
- $YPO_4$: Ce 0.1%, Nd 0.01%, 0.1% and 0.5%

Characterization:

- Radio-luminescence (RT)
- High Temperature (293-590 K) Thermo-Luminescence (TSL)
- Low Temperature (10-320 K) TSL
- Sensitization

Experimental conditions:

HT-TSL: heating rate 1 K/s, irrad. at RT (293 K)
LT-TSL: heating rate 0.1 K/s irrad. at 10 K or 20 K
Sensitization: X-ray irradiation at 20 kV, 10 mA (~60 mGy/s) and 250 K ≤ T ≤ 310 K

# Sensitization measurements

- $YPO_4$:Ce 0.1%, Nd 0.5%:

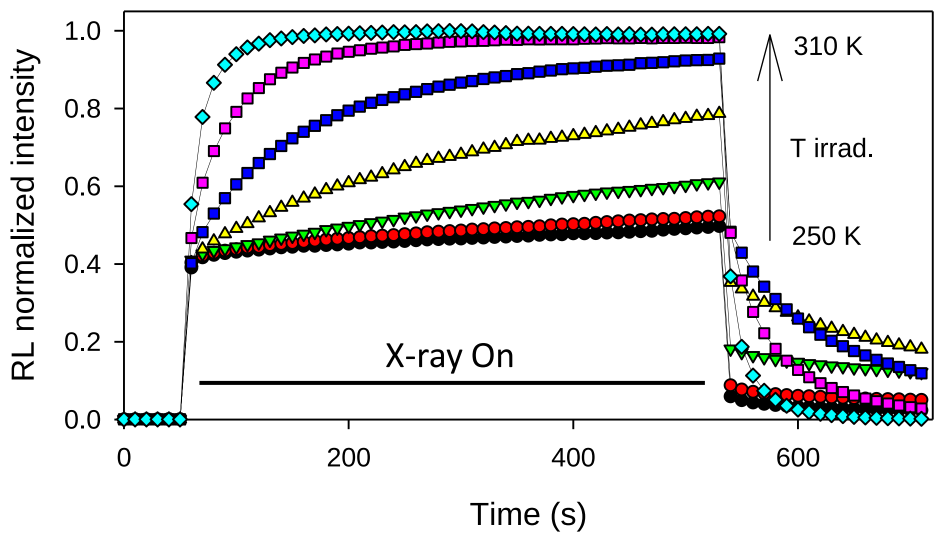
$Ce^{3+}$ RL intensity clearly increases with the irradiation time.
The intensity change is influenced by the temperature in both shape and overall magnitude.

- $YPO_4$:Ce 0.1%:

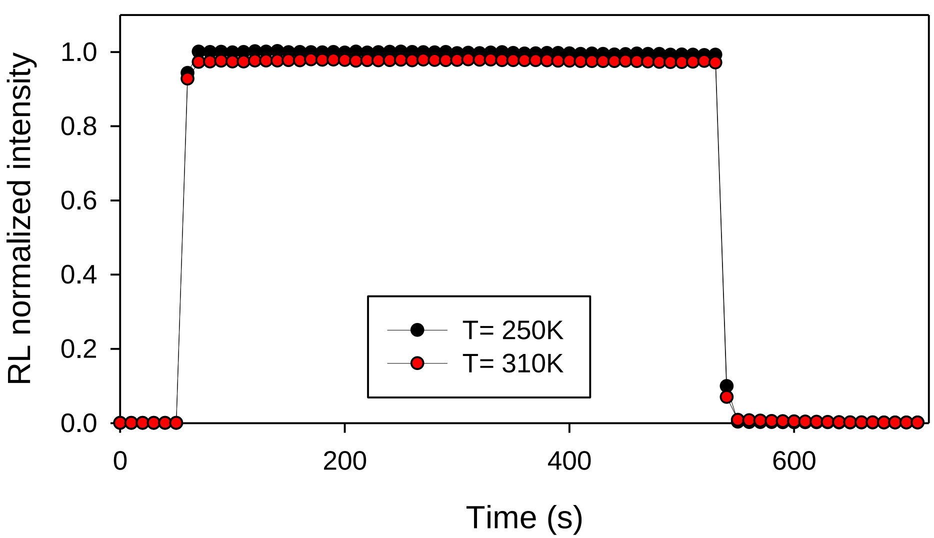
No RL intensity modifications with irradiation time or temperature.

Other Nd contents:
Same intensity change behaviour as in the case of Nd 0.5% but lower in magnitude, which increases by increasing the Nd concentration

$YPO_4$:Ce 0.1%, Nd 0.5%,
$Ce^{3+}$ emission (310-370nm)

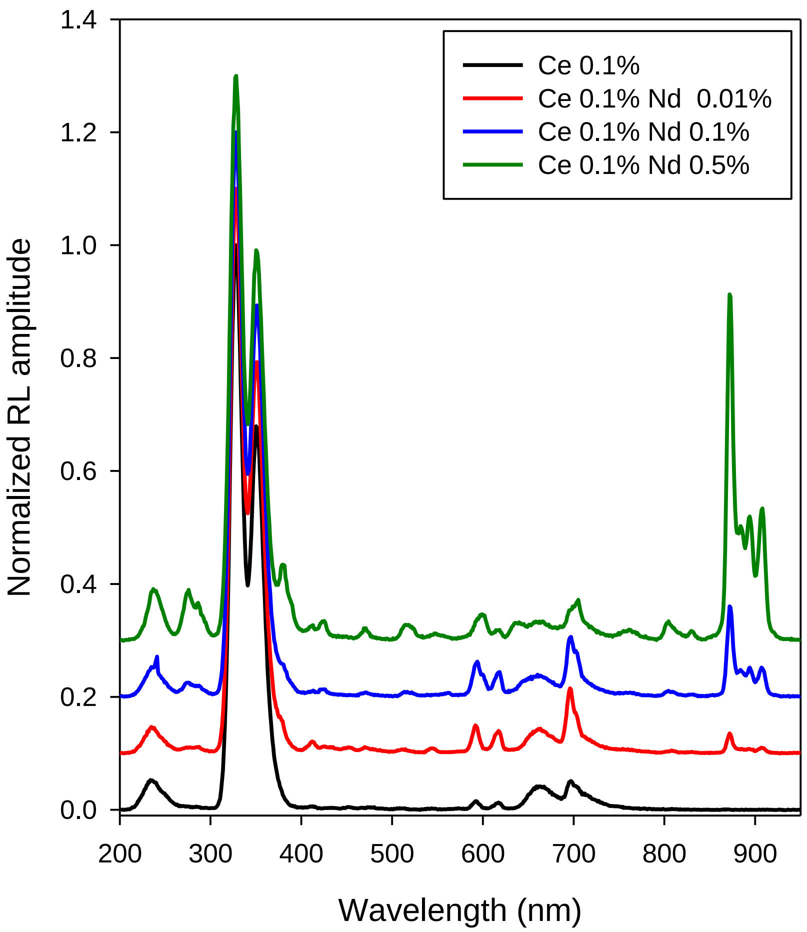



$YPO_4$:Ce 0.1%



# Radio-luminescence (RL)

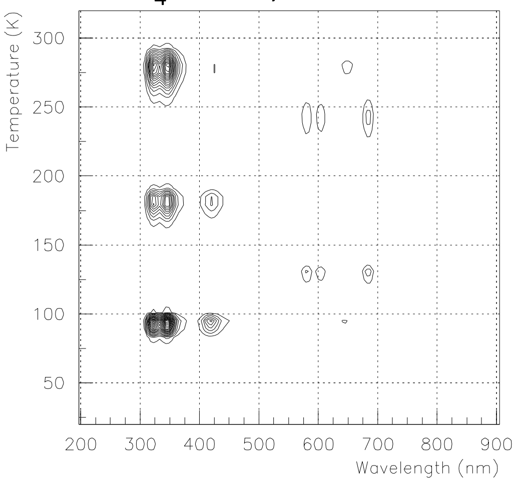
YPO$_4$:Ce, Nd RL spectra Vs Nd content




- Evident $Ce^{3+}$ 5d-4f radiative transitions (300-400 nm)
- $Nd^{3+}$ 4f-4f (850-920 nm) and 5d-4f (200-300 nm) ones increase with concentration
- Traces of $Eu^{3+}$ (peaks at about 590, 610 and 700 nm)

# Thermally stimulated luminescence

YPO$_4$:Ce 0.1, Nd 0.01%

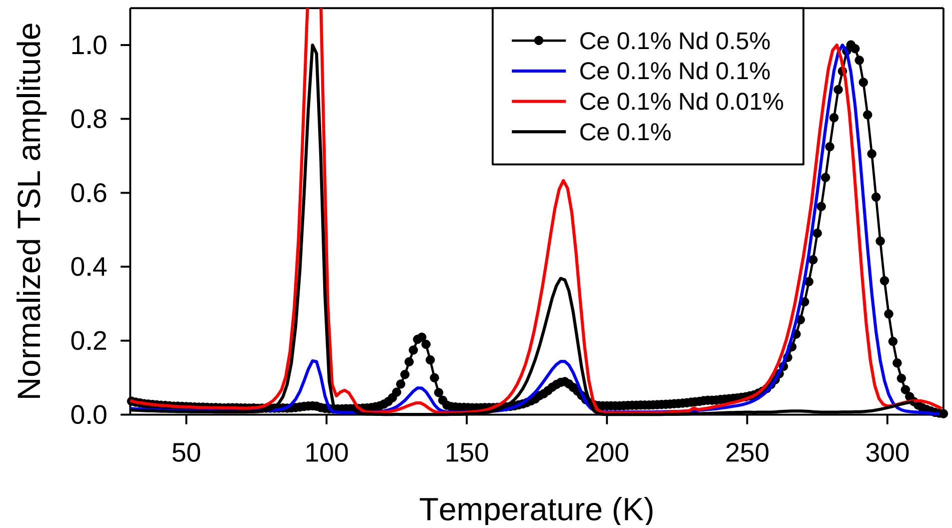



Nd-related glow peak at 280/300 K slightly shifts as the Nd content is increased. Nd trap E= 0.85 eV, s= $10^{13}$ $s^{-1}$

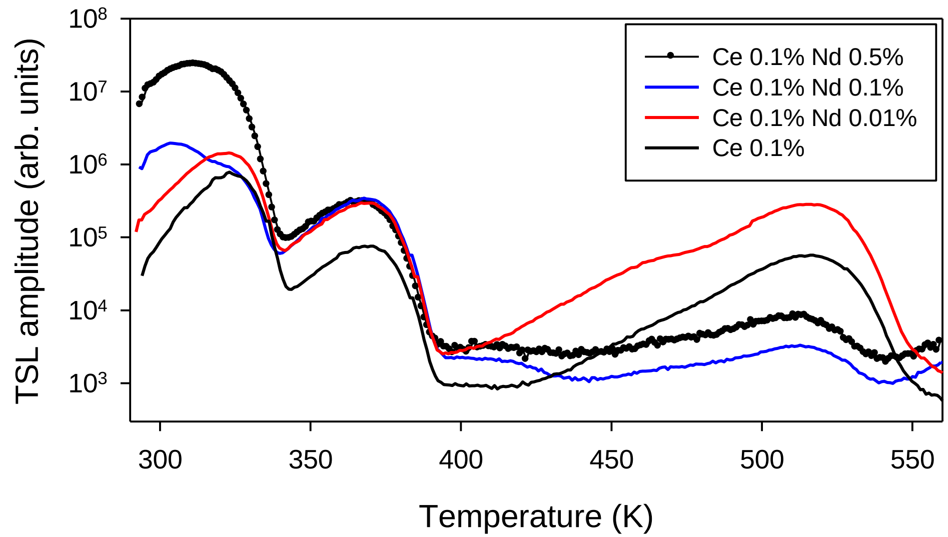
Low T meas.:
Electron traps at 90 and 183 K
Hole traps at 130 and 250 K

High T meas.:
Wavelength resolved meas. show only the $Ce^{3+}$ emission. Other 4/5 glow peaks are clearly visible

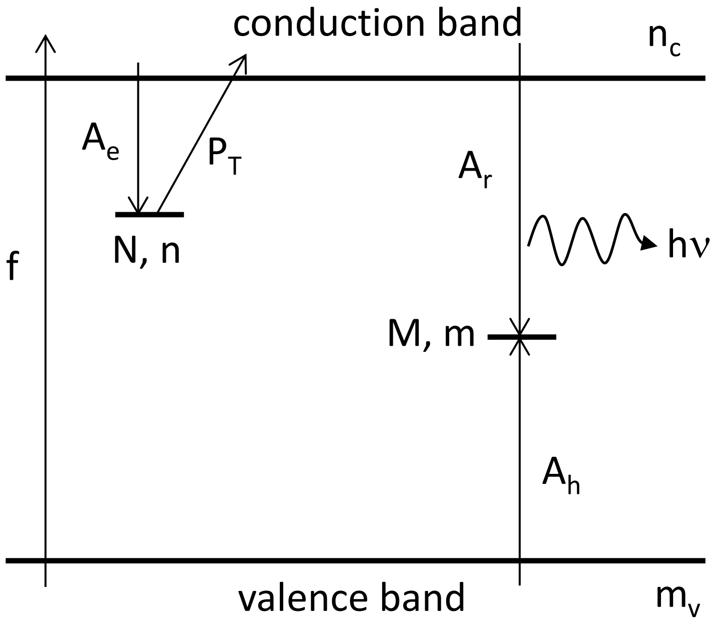
LT TSL glow curves, Ce emission (310-370nm)




HT TSL glow curves



# Memory effect: model




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

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

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

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

$$n_c + n = m_v + m$$

$$I_{RL} \propto n_cA_rm$$

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 ($cm^3\ s^{-1}$)

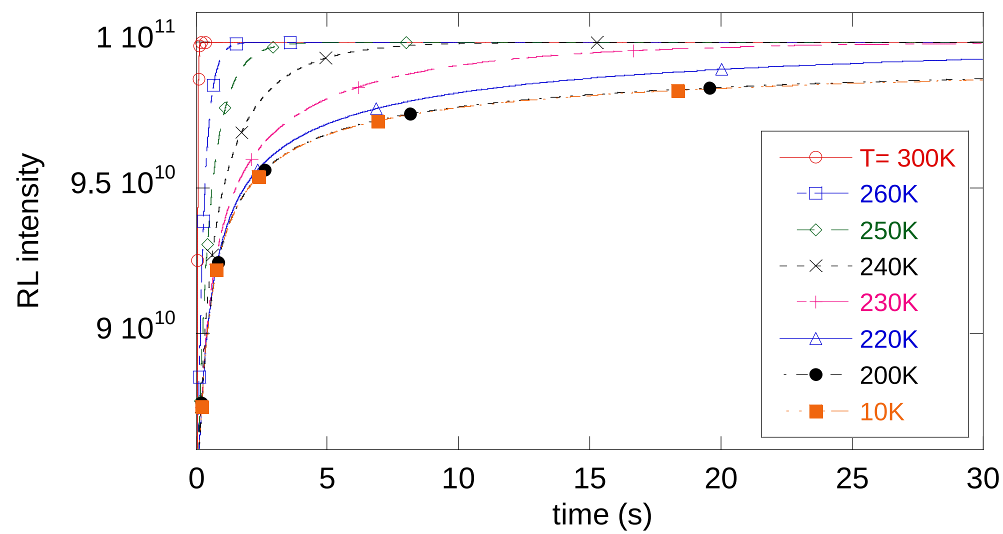
# Model simulations

Differential equation solution evaluated on test parameter values

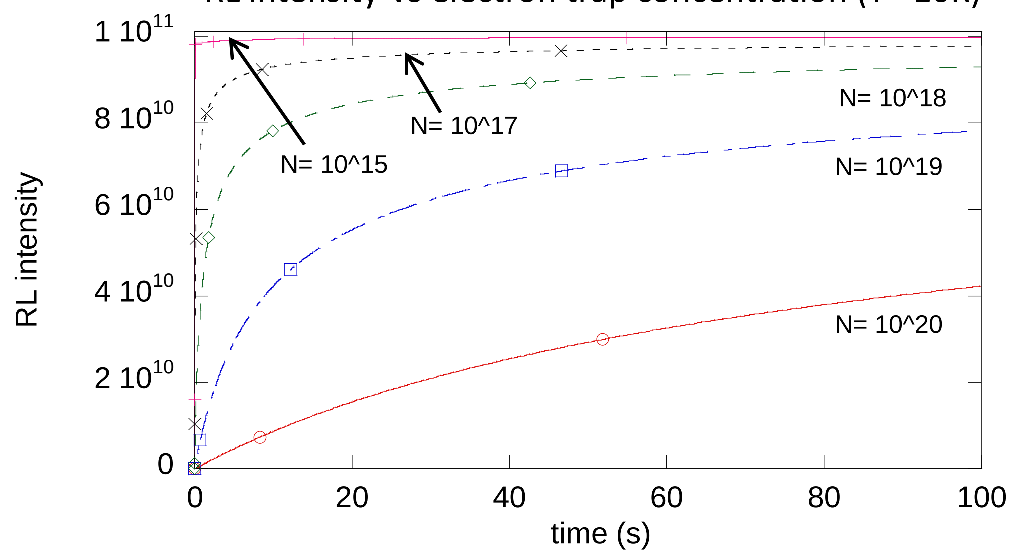
| Parameter | Value |
|---|---|
| f ($cm^{-3}s^{-1}$) | $10^{11}$ |
| M ($cm^{-3}$) | $10^{19}$ |
| $A_e$ ($cm^3s^{-1}$) | $10^{-15}$ |
| $A_r$ ($cm^3s^{-1}$) | $10^{-8}$ |
| $A_h$ ($cm^3s^{-1}$) | $10^{-7}$ |
| E (eV) | 0.6 |
| s ($s^{-1}$) | $10^{12}$ |

This model clearly predicts RL intensity increase which is dependent on the electron trap concentration and on the temperature.

RL intensity Vs irradiation temperature ($N=10^{16}$)



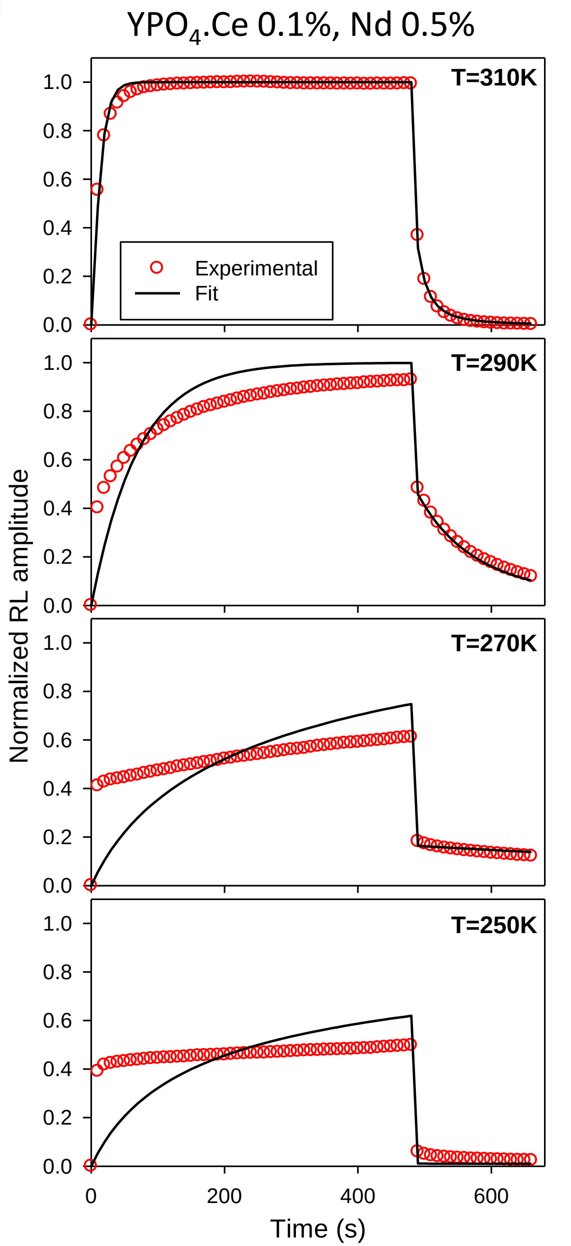

RL intensity Vs electron trap concentration (T= 10K)



# Model fit to experimental data

Transition coefficients ($A_e$, $A_h$ and $A_r$) are left free, the other parameters are kept fixed.

| Fixed parameters | |
|---|---|
| f ($cm^{-3}$) | $10^{13}$ |
| E (eV) | 0.85 |
| s ($s^{-1}$) | $10^{13}$ |
| N ($cm^{-3}$) | $5\ 10^{19}$ |
| M ($cm^{-3}$) | $1\ 10^{19}$ |




Good reconstruction of the experimental results only for the highest temperature.

The fit quality progressively worsens as the temperature is reduced.

Space for improvements:

- Hole recombination on trapped electrons
- Deeper filled traps
- Co-presence of other excitation routes for $Ce^{3+}/Nd^{3+}$ luminescence

# Conclusions

$YPO_4$:Ce,Nd appears to be a good model material for the study of the memory effect:

- the Nd-related electron trap give rise to a glow peak which is, at least for high concentrations, much more evident than those related to intrinsic defects.
- the RL intensity growth is well evident.

The model is not completely satisfactory:

- It clearly predicts trends in the RL intensity dependence on the accumulated dose, as well as irradiation conditions and sample related parameters.
- good reconstruction of experimental curves only for high temperatures.
- it can be improved (currently under way) by considering the presence of other (deeper) traps, holes recombination on trapped electrons, …

# Acknowledgements

This work has been supported by:

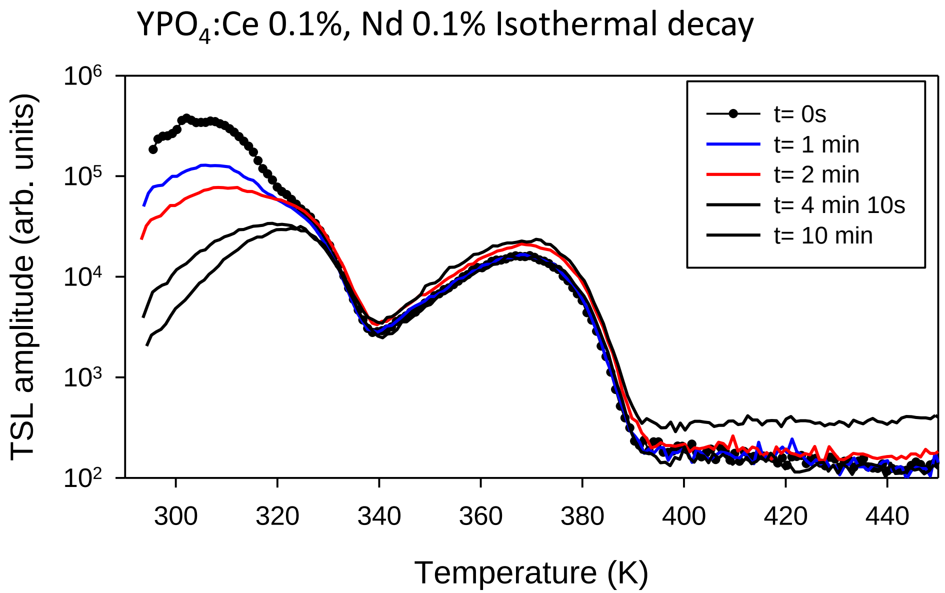
dgcis direction générale de la compétitivité de l'industrie et des services

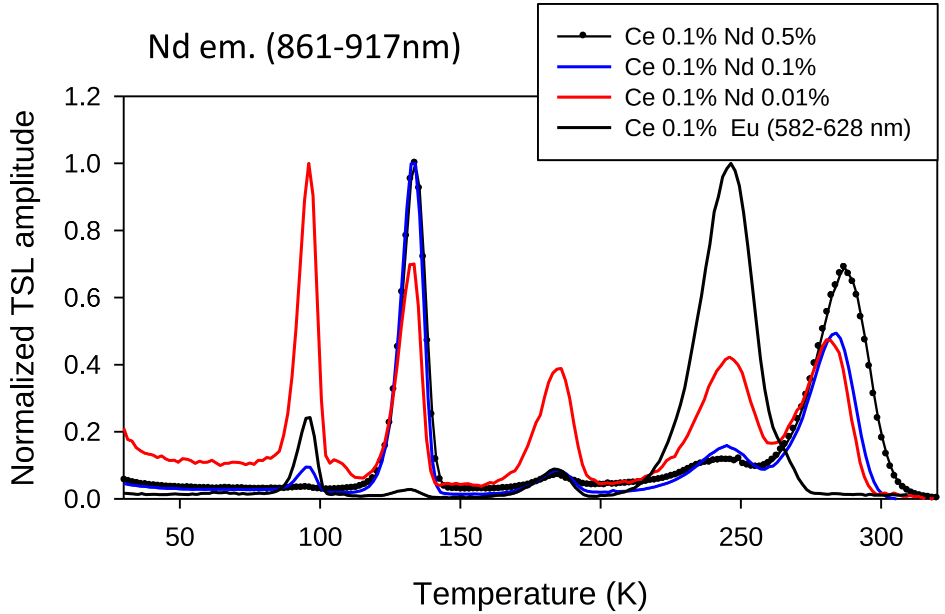
oséo

Pays Voironnais

# Thank you for your attention!

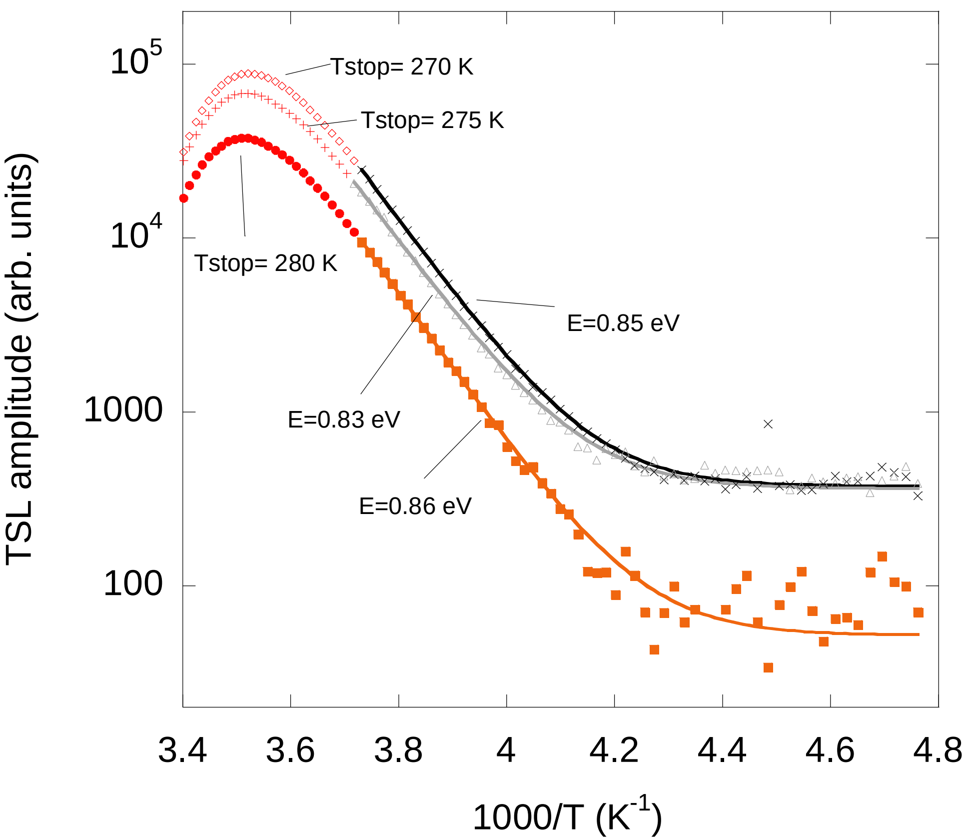
# Supplementary (1)



# Supplementary (2)

YPO$_4$:Ce 0.1%, Nd 0.1%
Nd-related trap PC and IR

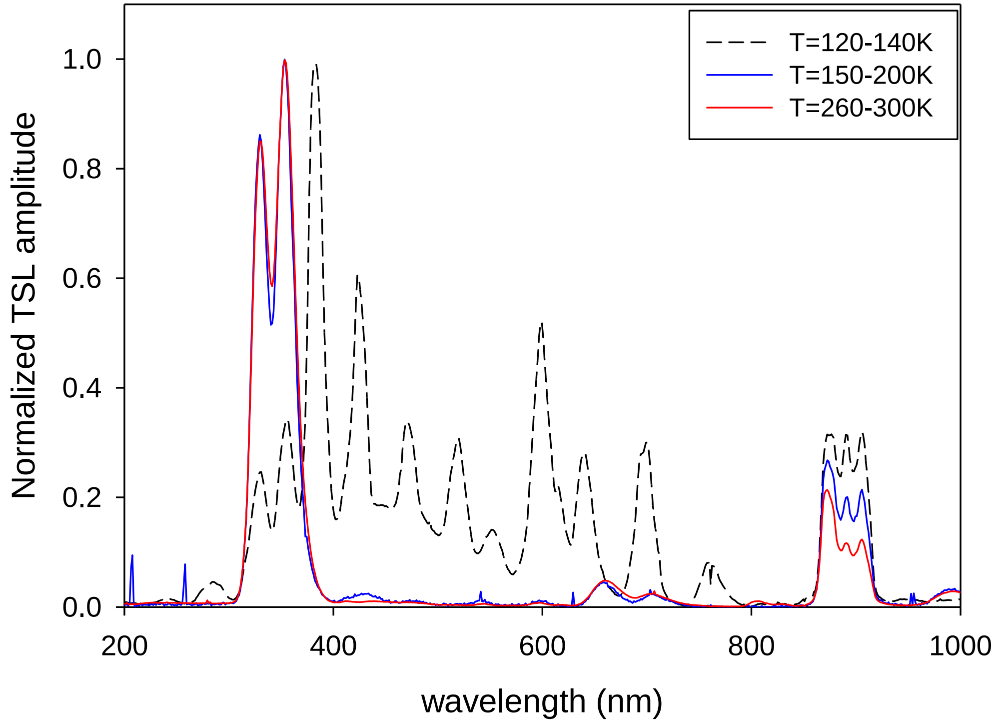



| Tmax (K) | E (eV) | s (1/s) | notes |
|---|---|---|---|
| 95.5 | 0.24 | 2E+11 | Low T meas. |
| 132.9 | 0.38 | 5E+12 | |
| 184.0 | 0.49 | 4E+11 | |
| 244.4 | 0.53 | 1E+09 | |
| **284.0** | **0.85** | **1E+13** | **[Nd]=0.1%** |
| 322.1 | 1.00 | 5E+14 | High T meas. |
| 369.6 | 1.06 | 2E+13 | |

# Supplementary (3)

TSL spectra clearly show different emission intensity ratio between $Ce^{3+}$ and $Nd^{3+}$ at the main glow peaks

LT TSL spectra




TSL, Ce emission (310-370nm)