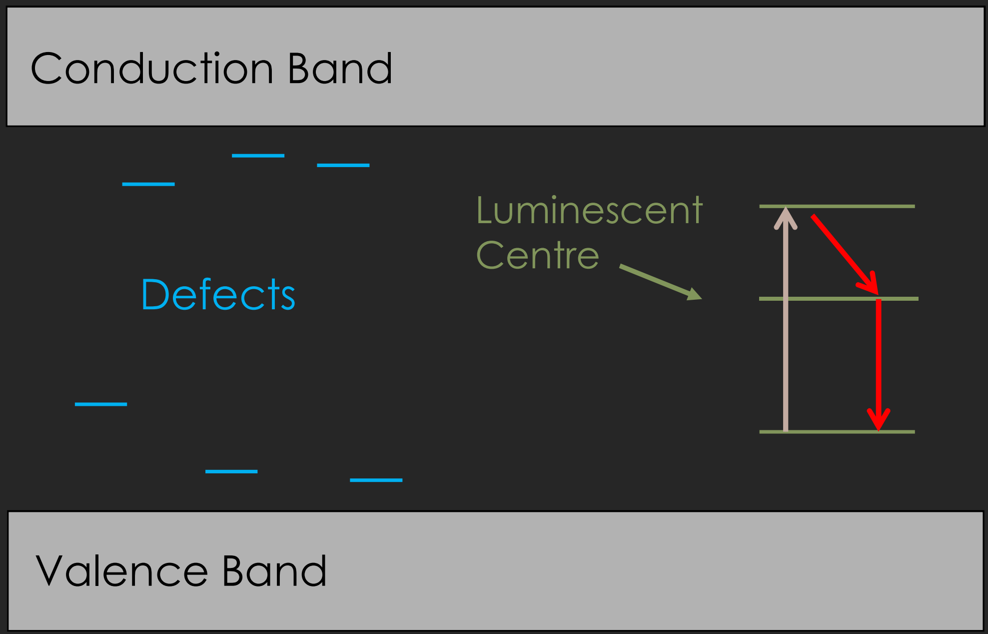
Exploiting defects for luminescent materials investigation

Mauro Fasoli

University of Milano-Bicocca

Laser vs. scintillation mechanism

Critical defects are application dependent



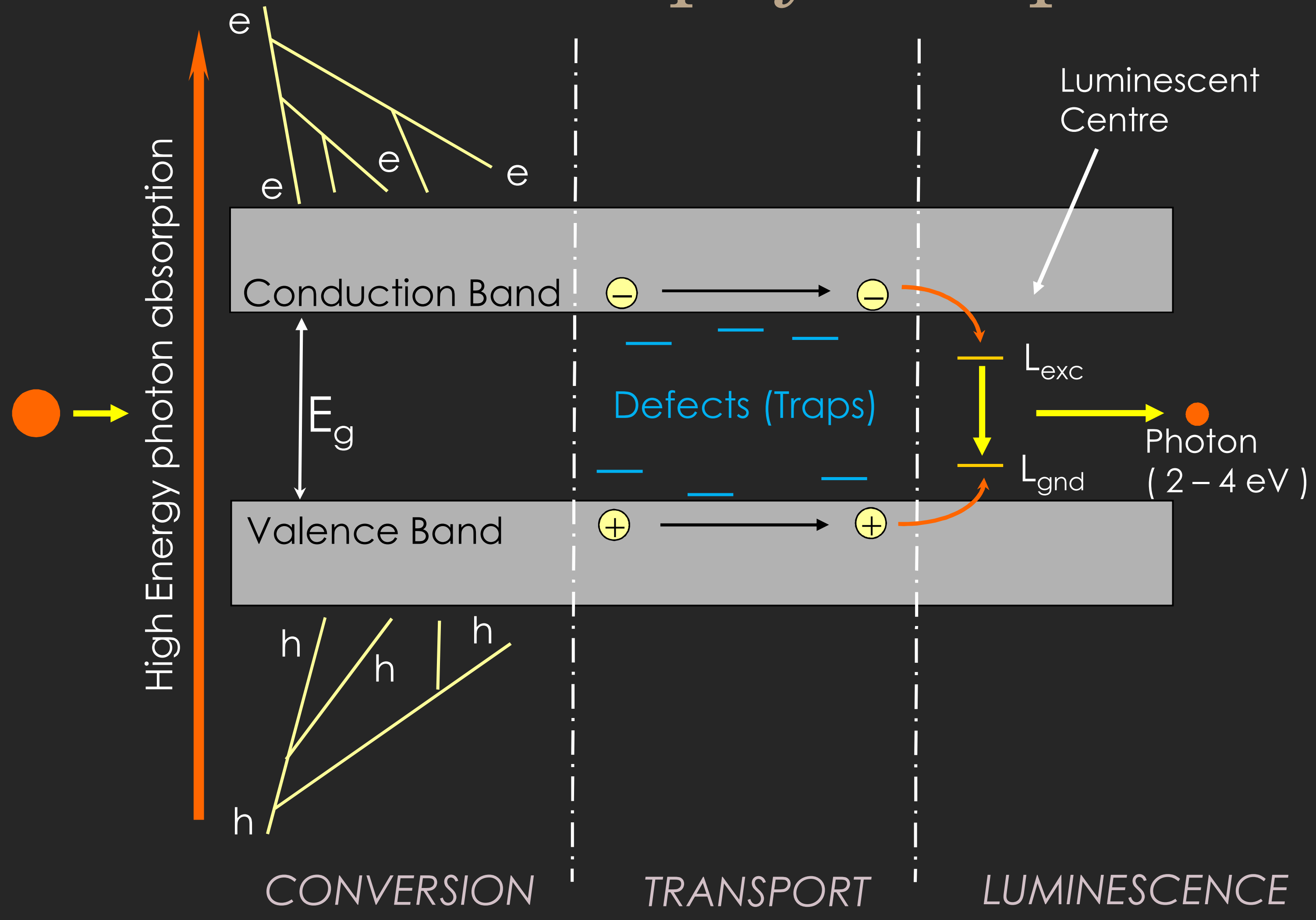
Lasers

The lasering process does not involve the delocalized bands.

Critical defects:

- colour centres
- non radiative recombination paths
- scattering centres

Scintillators: physical process



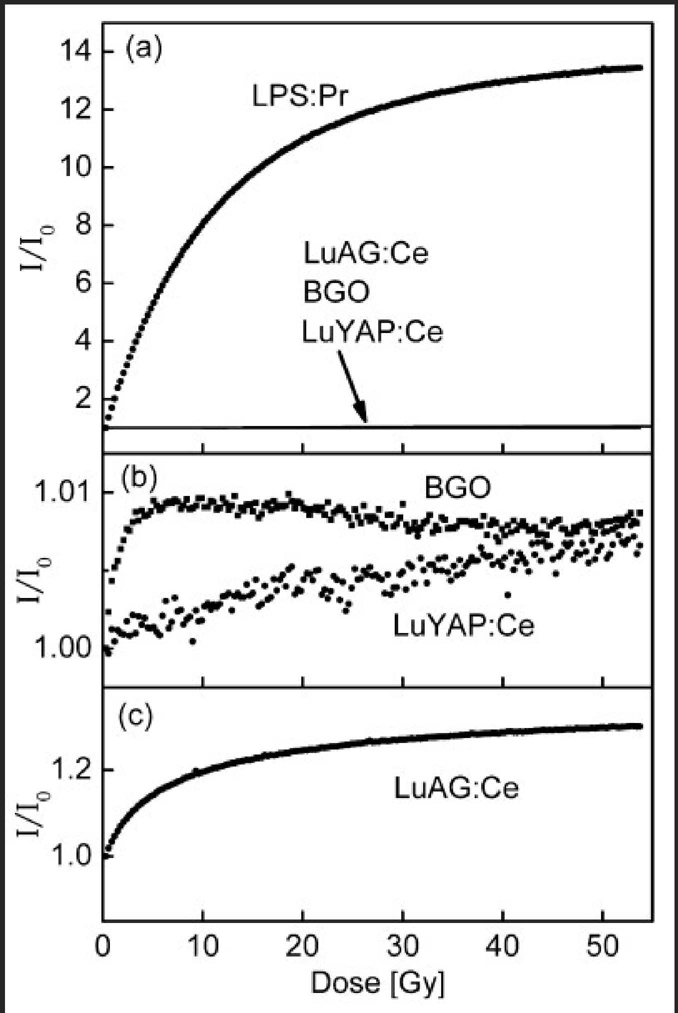
Scintillators

Defects can also act as charge traps during the transport stage

Critical defects:

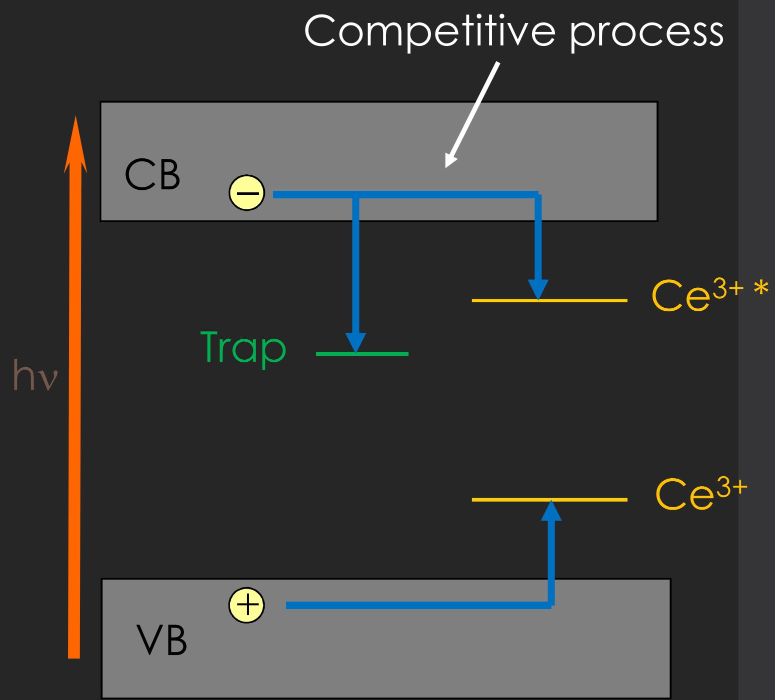
- colour centres
- non radiative recombination paths
- scattering centres
- traps

Deep traps in scintillators



Effects on luminescence properties:

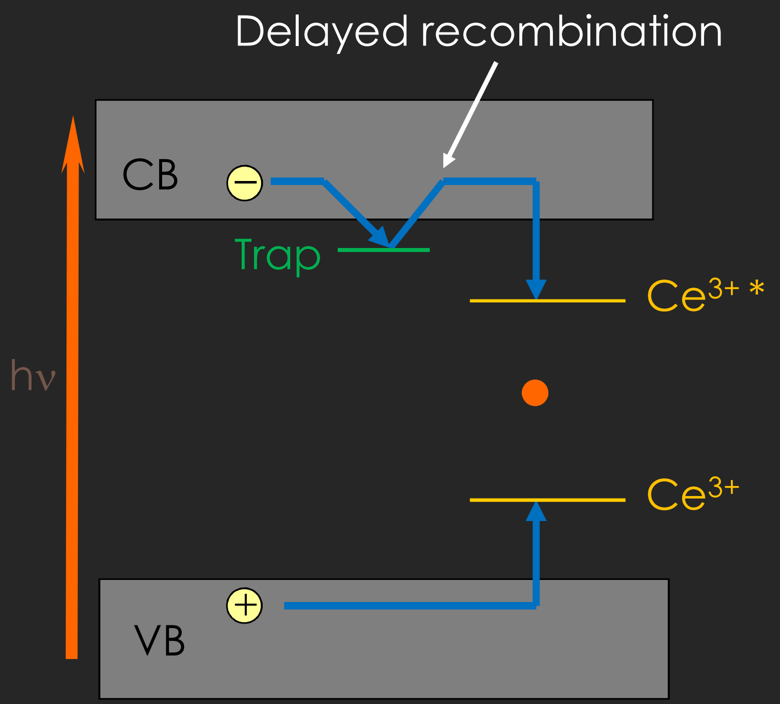
- Reduced light yield
- Bright burn



Room temperature RL efficiency of several crystals versus irradiation dose. Data are normalized to the respective initial value.

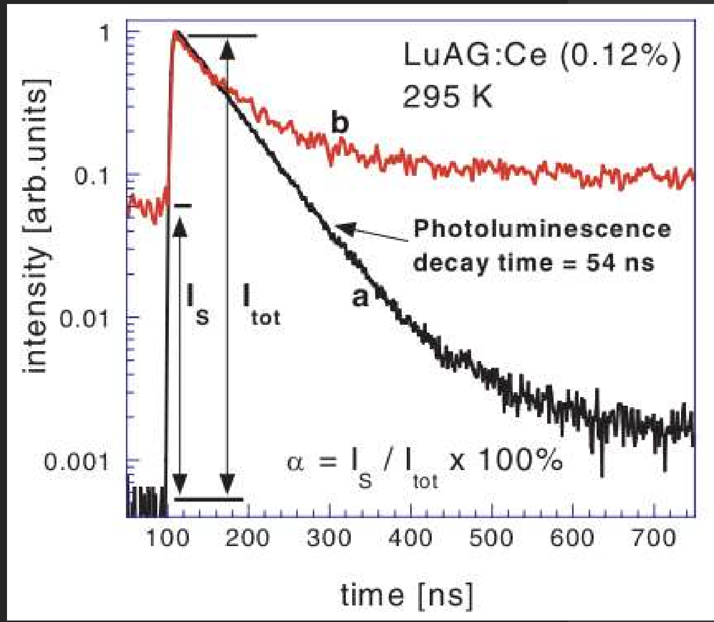
E. Dell'Orto et. al., J. Phys. Chem. C (2013), 117, 20201

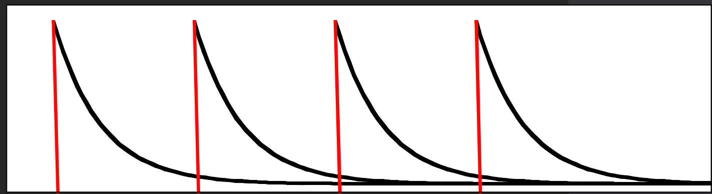
Shallow traps in scintillators



Effects on luminescence properties:

- Slow decay component
- Afterglow

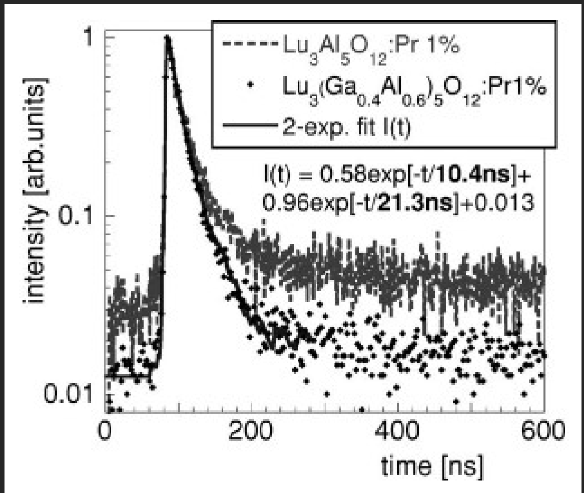


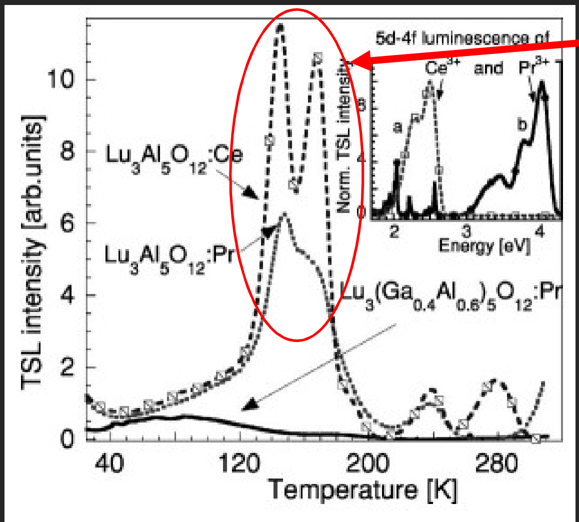


phys. stat. sol. (b) **242**, No. 14, R119–R121 (2005) / **DOI** 10.1002/pssb.200541225

phys. stat. sol. (a) **202**, No. 2 (2005) / www.pss-a.com

Shallow traps "removal"



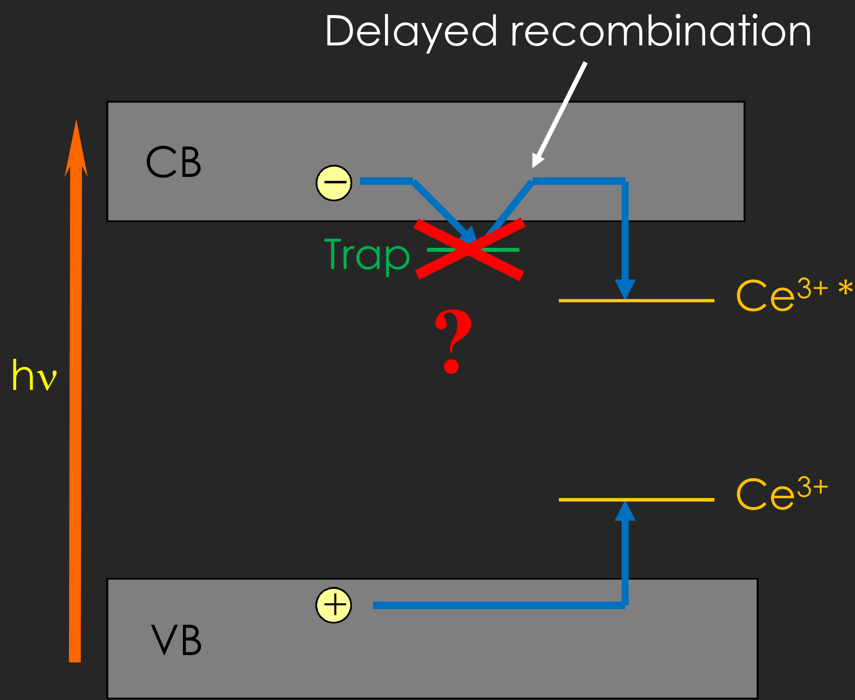


$Lu_3Al_5O_{12}$

↑

Ga

Antisite
E = 0.29 eV

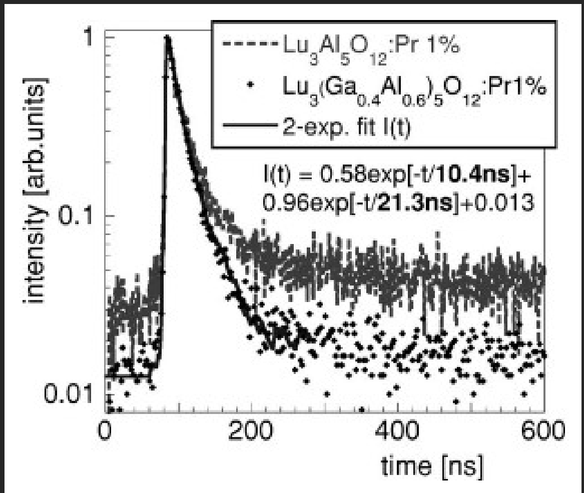


- **Substitution** of **Al** with **Ga** ions (40%) was shown to **remove** both the **slow** scintillaton **component** and the **antisite TSL peaks**.

Why ?

APPLIED PHYSICS LETTERS **88**, 141916 (2006)

Shallow traps "removal"



$Lu_3Al_5O_{12}$

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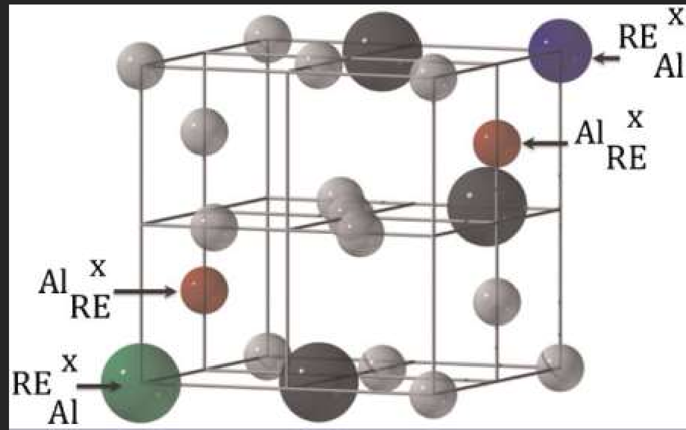
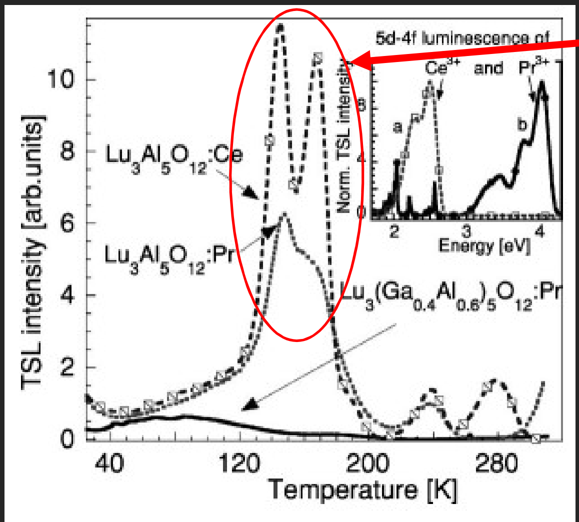


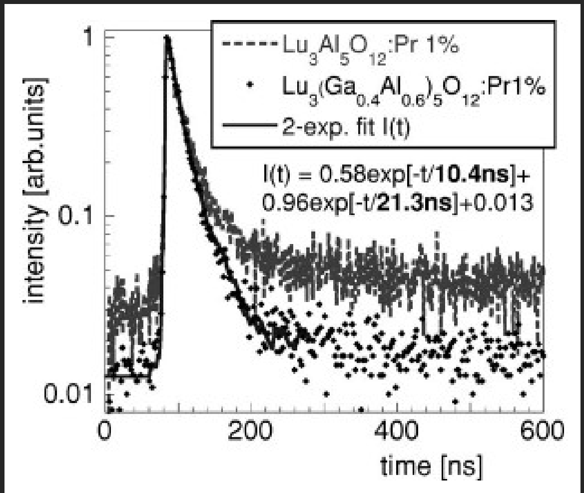


Antisite
E = 0.29 eV

Atomistic simulations showed that the addition of Ga to $RE_3Al_5O_{12}$ garnets generally lowers the cation antisite defect formation energy, thus suggesting that **Ga additions** should lead to a **higher concentration** of **antisite defects**

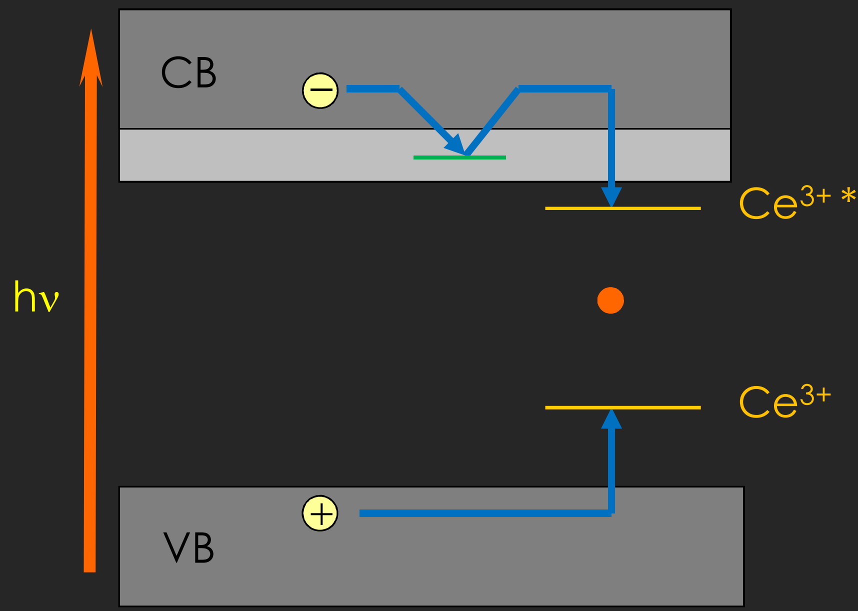
C.R. Stanek et al.
Phys. Status Solidi B **250**, No. 2, 244–248 (2013)

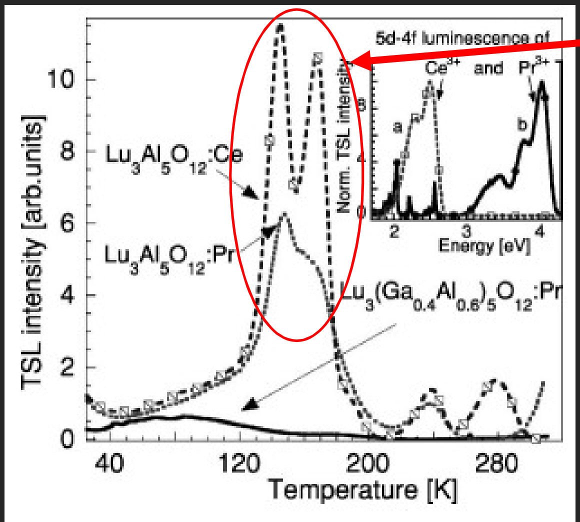
Shallow traps "removal"



$Lu_3Al_5O_{12}$

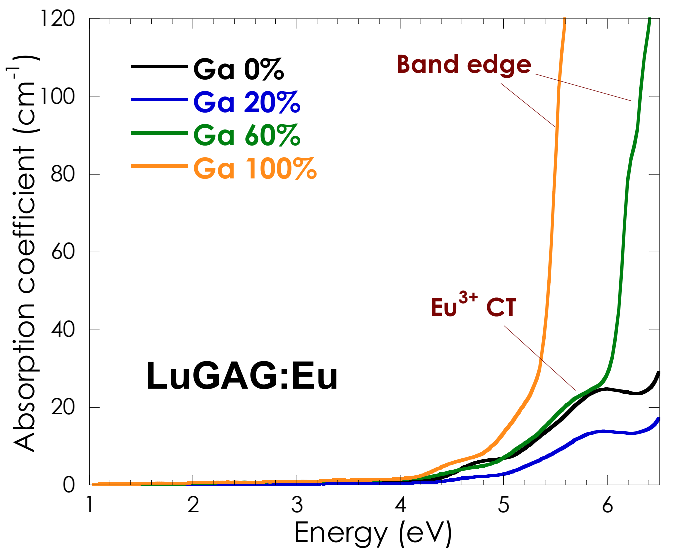
Ga

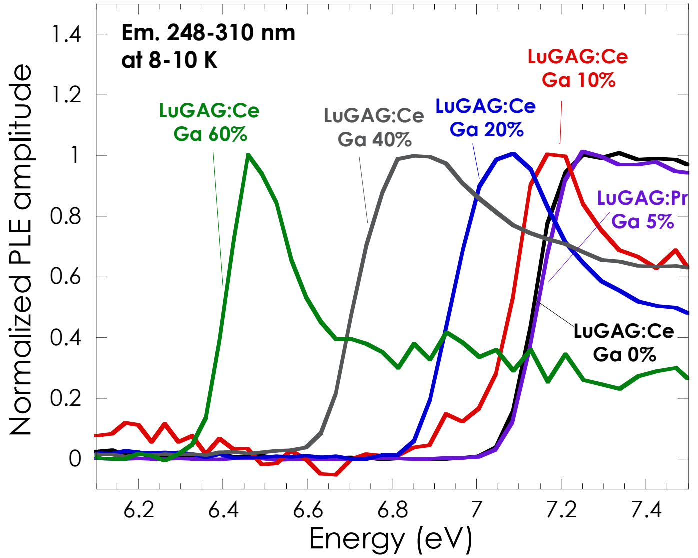




Antisite
E = 0.29 eV

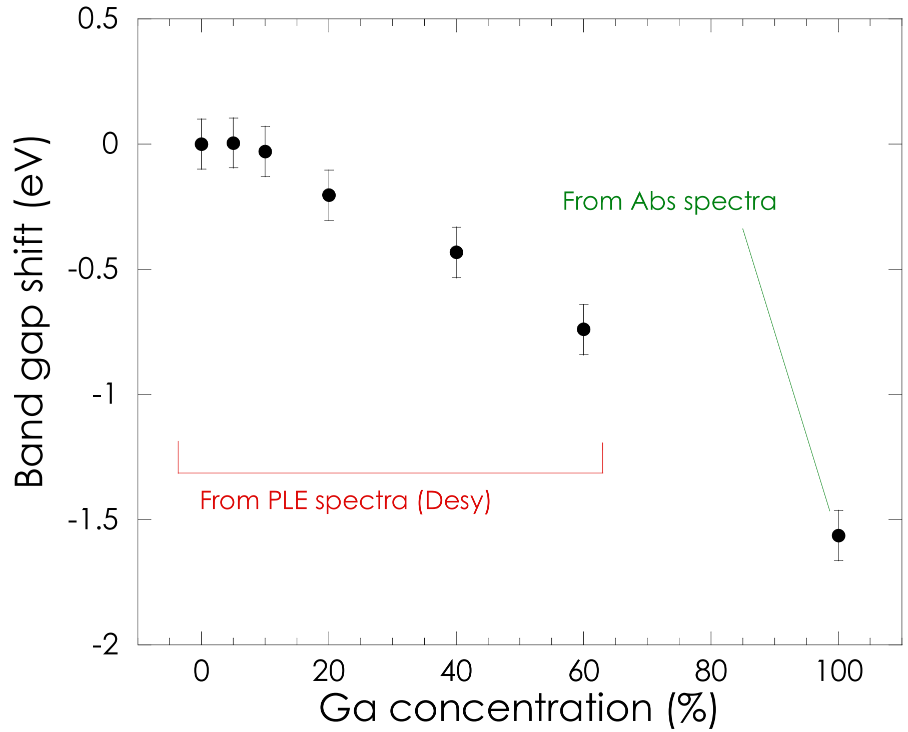
Is the removal of the delayed recombination due to a CB shift ?



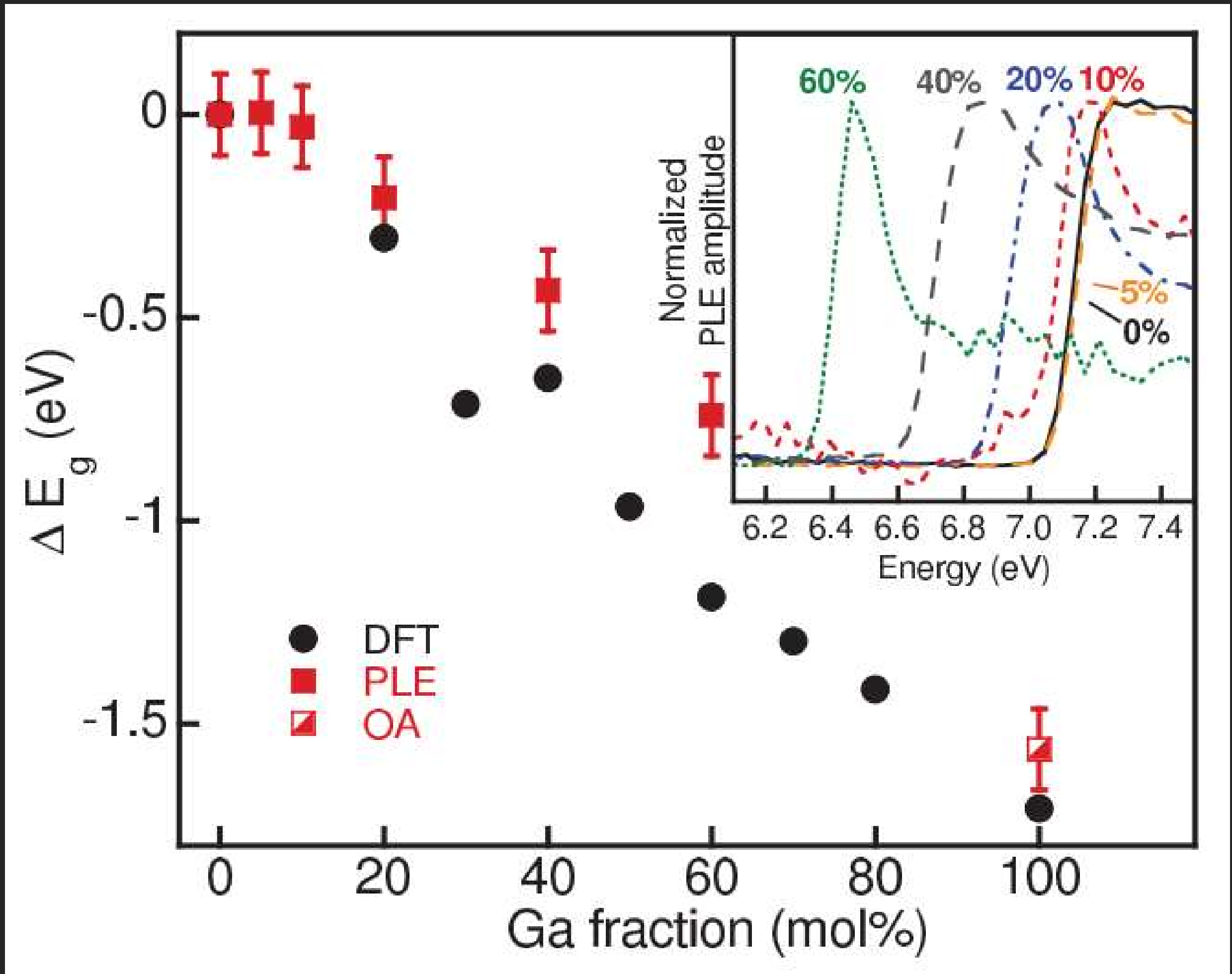


Band Gap shrinking

- Ga substitution induces a band gap shrinking evidenced by a low energy shift of the absorption edge in UV-VIS OA and in VUV-PLE.



DFT vs Exper. - Band Gap



DFT Calculations (C. Stanek - Los Alamos)

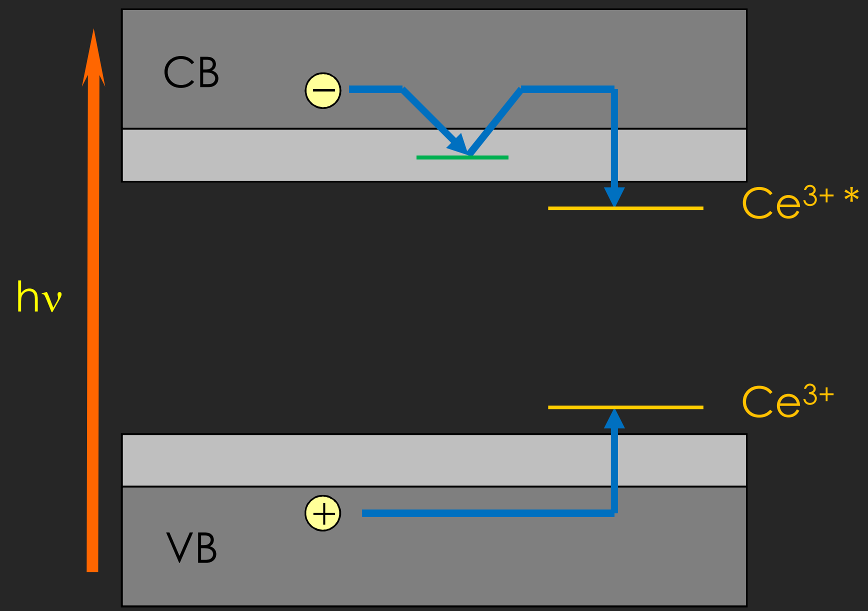
- VASP (Vienna Ab Initio Simulation Package). PAW PBE potentials.
- DFT calculations, as expected, underestimate the band gap value (3.85 eV).
- The band gap shrinking is nevertheless reliable and in good agreement with the experimental data obtained from absorption and photoluminescence excitation spectra.

Band gap shrinking

Is the band gap shrinking evidenced by **OA** due to:

- Shift of the CB?
- Shift of the VB?
- Both?

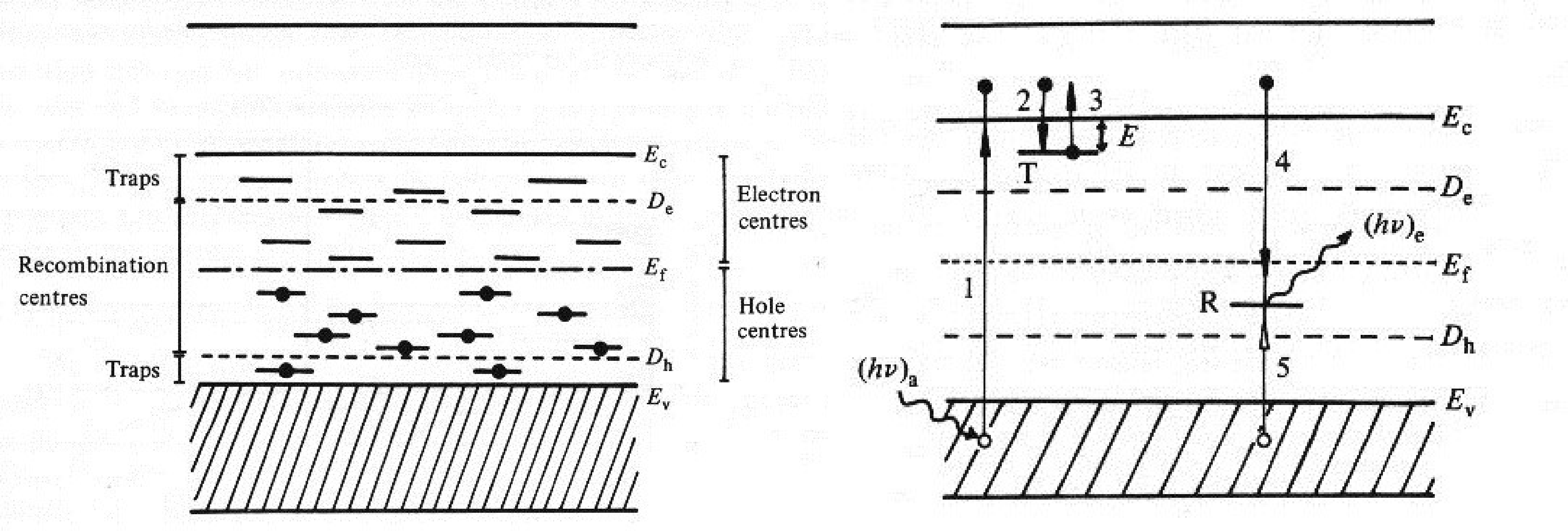
We need a different technique



Outline

- Thermoluminescence mechanism
- Delocalized bands shift
- Localization of the excited levels of a luminescence centre

Traps and recombination centres

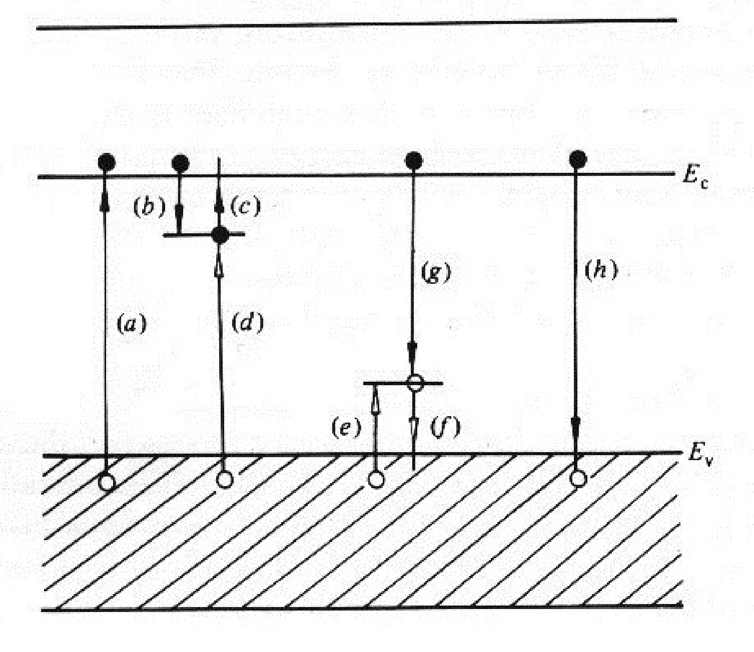


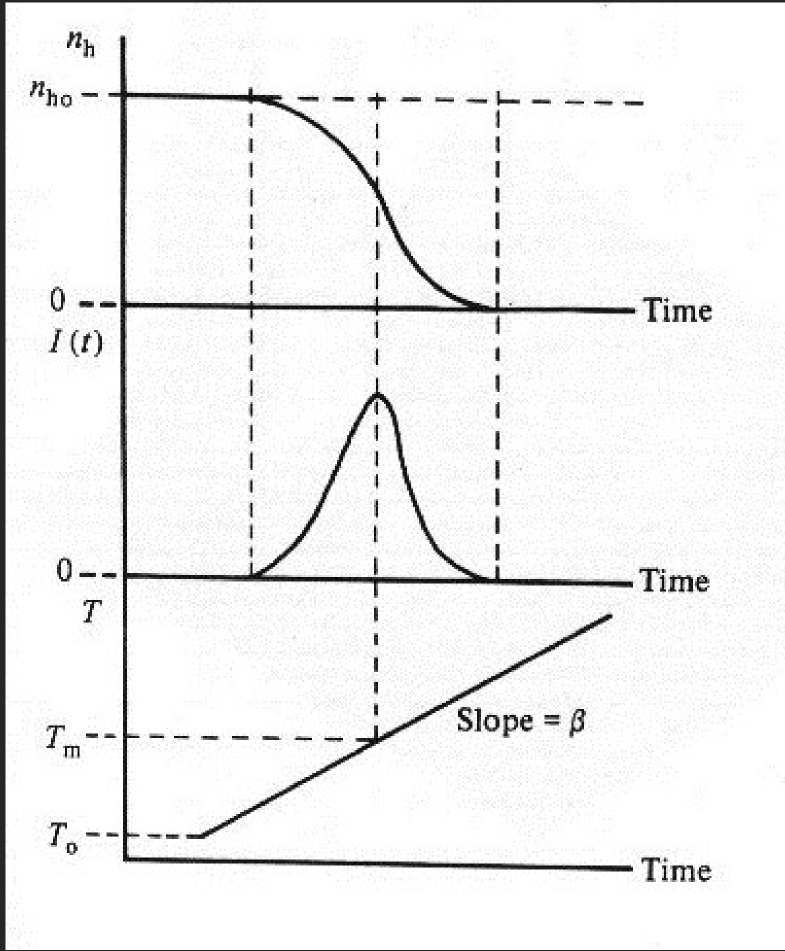
Detrapping probability

$$p = \tau^{-1} = s \exp(-E/kT).$$

McKeever S.

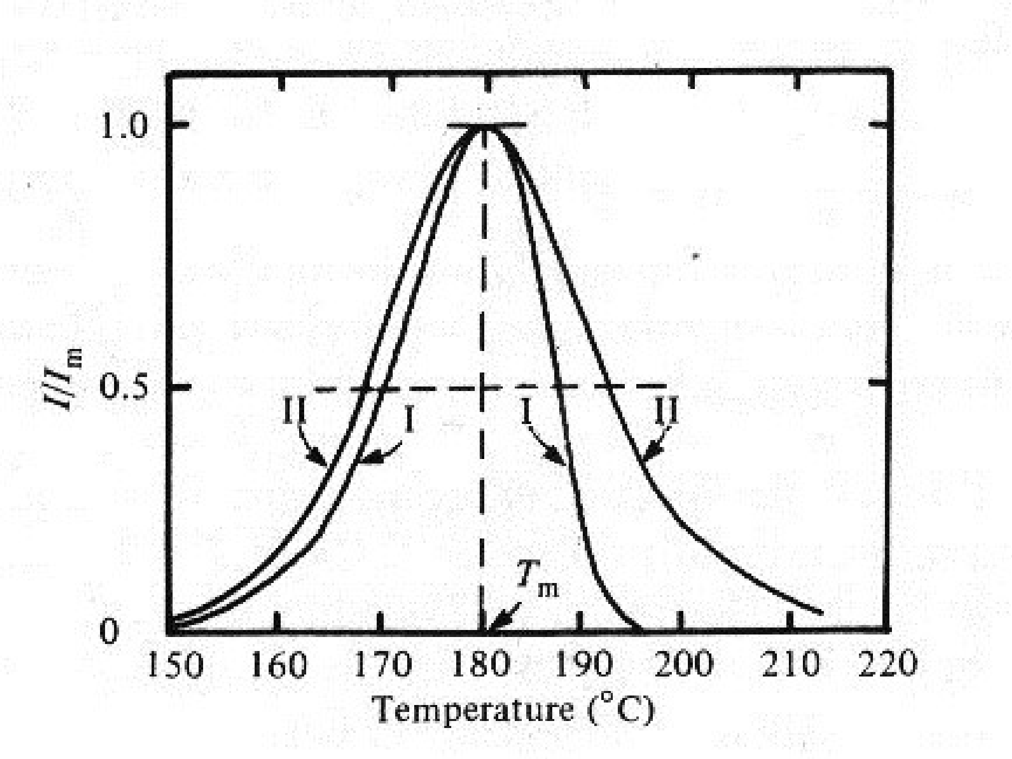
Thermally Stimulated Luminescence





- Irradiation
- Heating at a constant rate
- Light detection vs. temperature (glow curve)

TSL Kinetics Orders



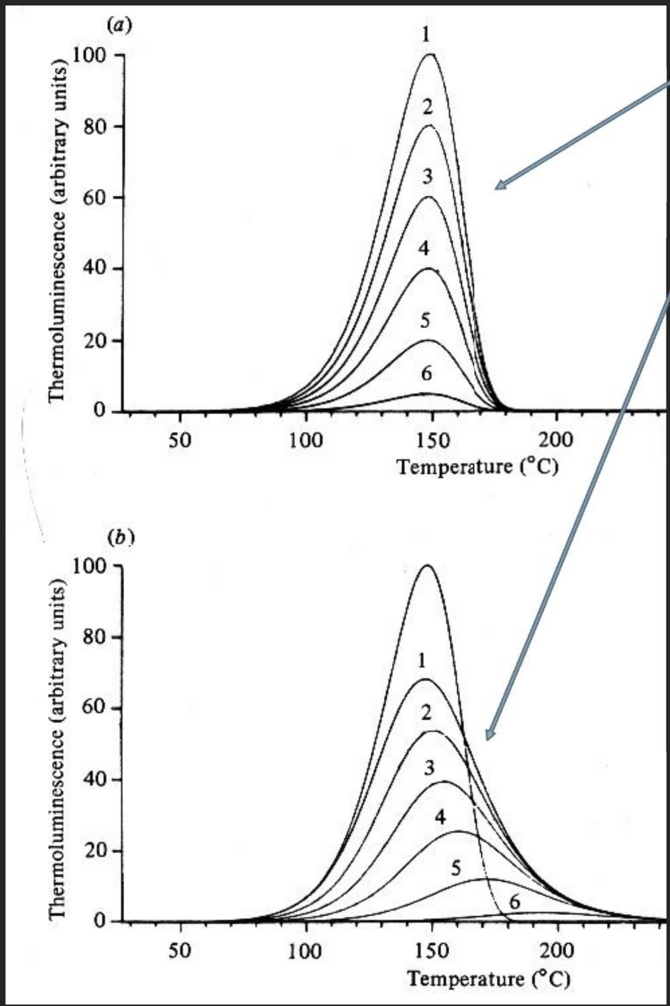
I Order kinetics

$$I(T) = n_0 s \exp(-E/kT) \exp\left[-(s/\beta)\int_{T_0}^{T} \exp(-E/kT)\mathrm{d}T\right],$$

II Order kinetics

$$I(T) = n_0^2 s' \exp(-E/kT) / \left[1 + (n_0 s'/\beta)\int_{T_0}^{T} \exp(-E/kT)\mathrm{d}T\right]^2$$

Initial rise technique



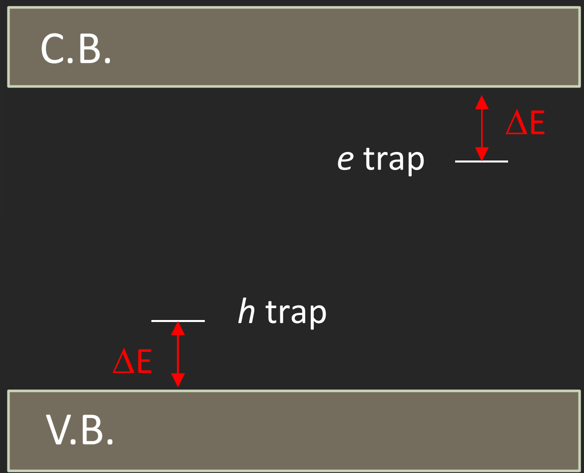
I Order kinetics

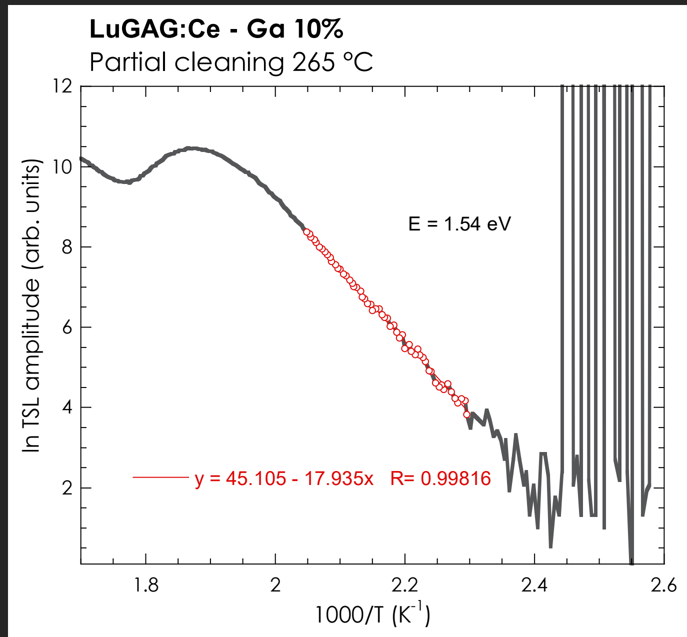
$$I(T) = n_0 s \exp(-E/kT) \exp\left[-(s/\beta)\int_{T_0}^{T} \exp(-E/kT)\,dT\right],$$

II Order kinetics

$$I(T) = n_0^2 s' \exp(-E/kT) \Big/ \left[1 + (n_0 s'/\beta)\int_{T_0}^{T} \exp(-E/kT)\,dT\right]^2$$

Allows the evaluation of the trap thermal depth regardless of the kinetics order





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Band gap shrinking

Is the band gap shrinking evidenced by **OA** due to:

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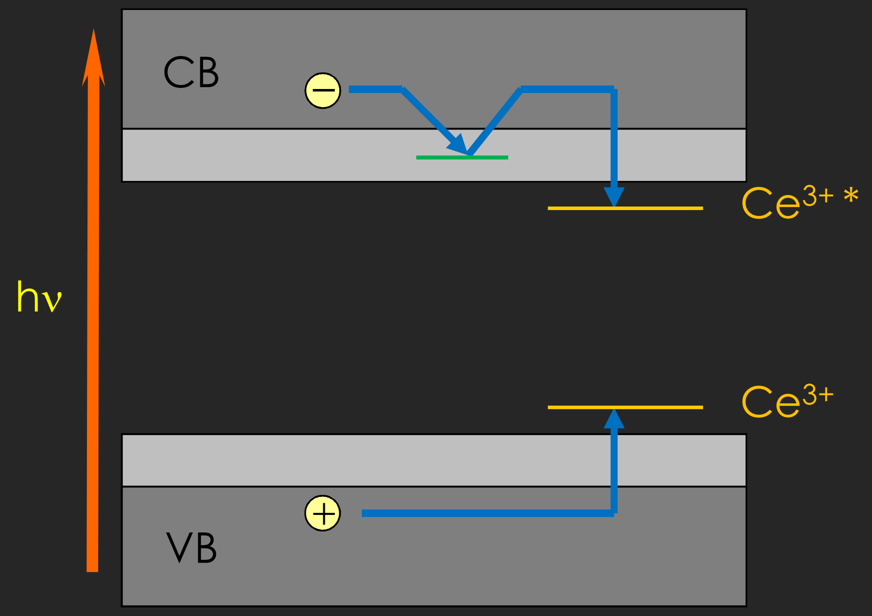
We need a different technique

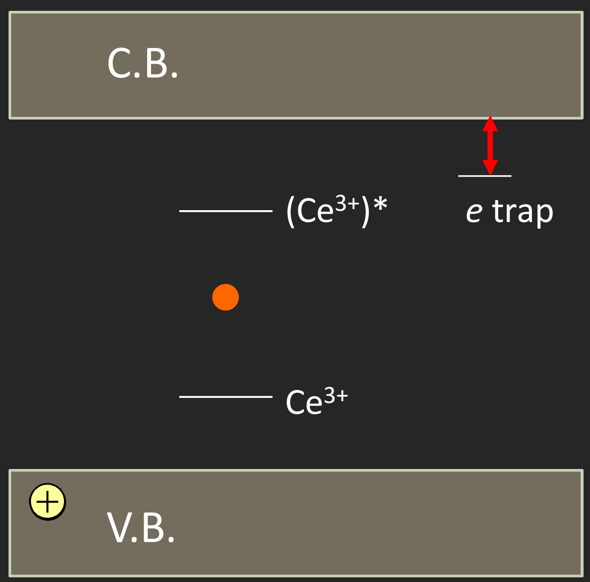


Thermoluminescence mechanism (Ce, Eu)

$Ce^{3+} + h \longrightarrow Ce^{4+}$	Irradiation	$Eu^{3+} + e \longrightarrow Eu^{2+}$
$Ce^{4+} + e \longrightarrow (Ce^{3+})^* \longrightarrow Ce^{3+} + h\nu$	Heating	$Eu^{4+} + h \longrightarrow (Eu^{3+})^* \longrightarrow Eu^{3+} + h\nu$

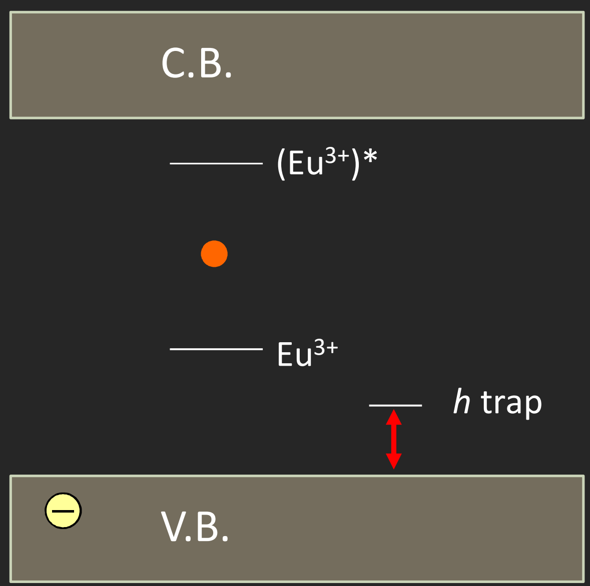
Released from an *e* trap

Released from a *h* trap



TSL and traps type

- Ce^{3+} emission is observed whenever an electron is released form a trap.
- Eu^{3+} emission is observed whenever a hole is released form a trap.



$Lu_3Ga_xAl_{5-x}O_{12}$ Samples

- $Lu_3Ga_xAl_{5-x}O_{12}$ (LuGAG) single crystals grown by micro pulling down (m-PD) technique at the University of Tokyo (Japan)
- Crystals size: 6 x 4 x 1 mm^3 approximately

LuGAG:Ce

Ce: 0.7 mol% (in the melt)

Ga: 0%, 10%, 20% and 40%

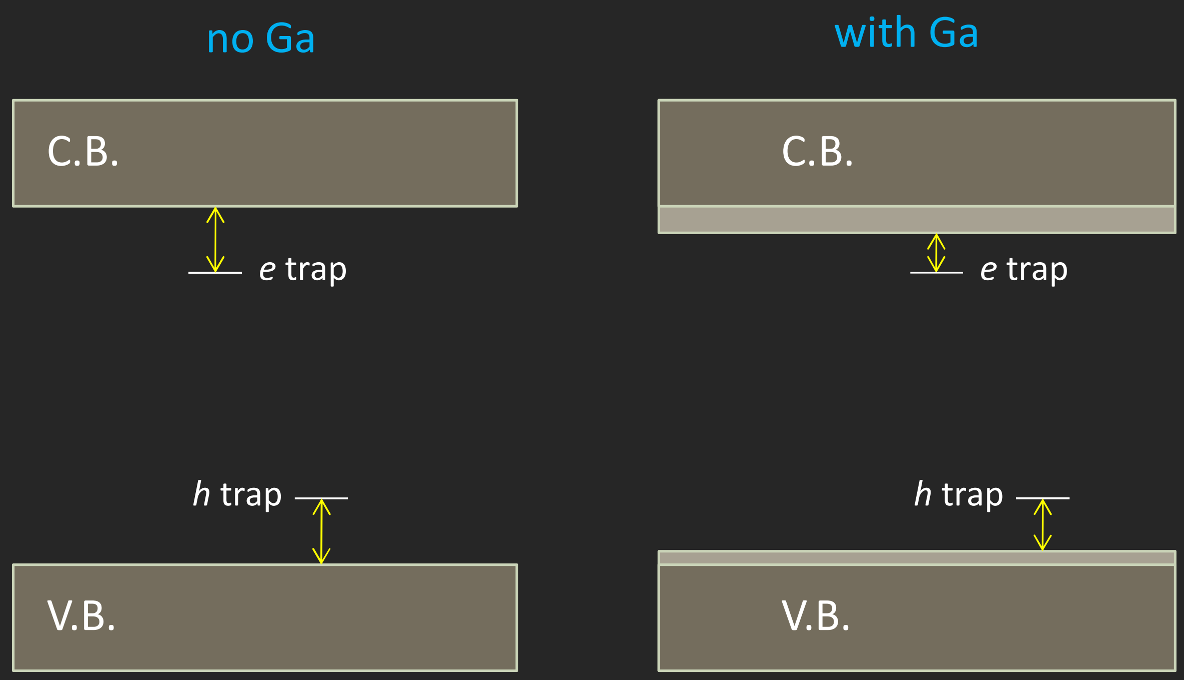
LuGAG:Eu

Ce: 0.1 mol% (in the melt)

Ga: 0%, 20%, 60% and 100%

Working assumption

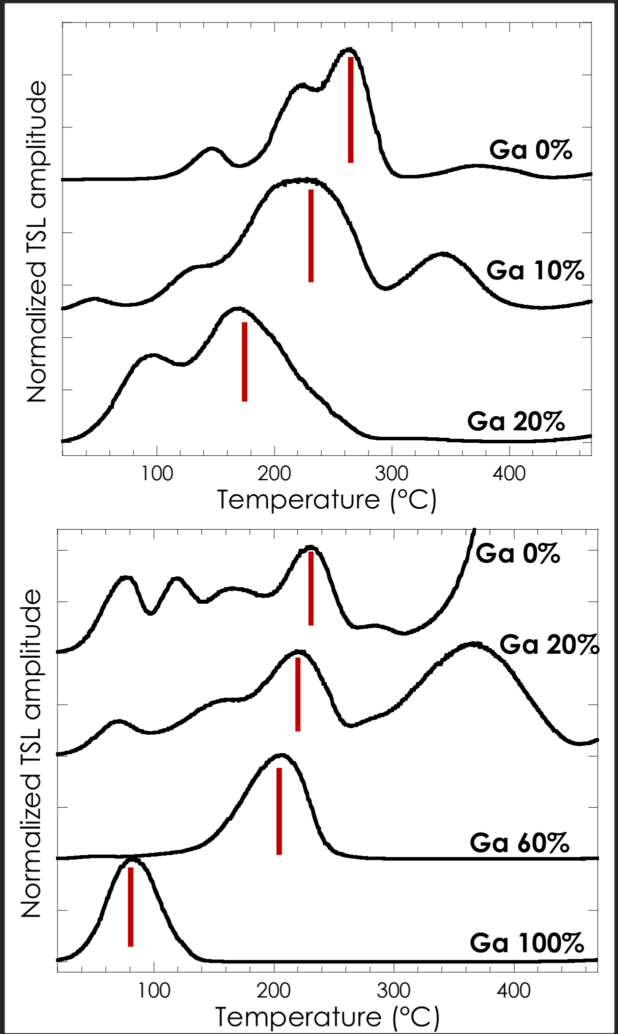
- We assume the e and h traps energy levels as fixed.
- A change in the TSL thermal activation energy of an e trap (h trap) can thus be an approximate evaluation of the C.B. (V.B.) shift.



But let's not forget that:

- The C.B. and V.B. are not flat.
- The thermal activation energy is not directly comparable with the optical transition energy.
- The traps themselves could be affected by Ga substitution.

TSL glow curves



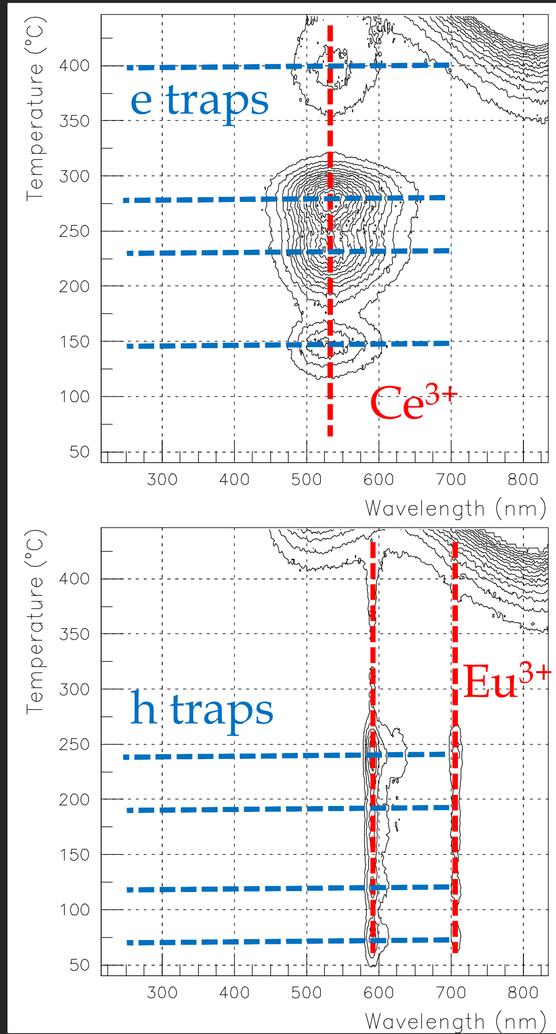
LuGAG:Ce

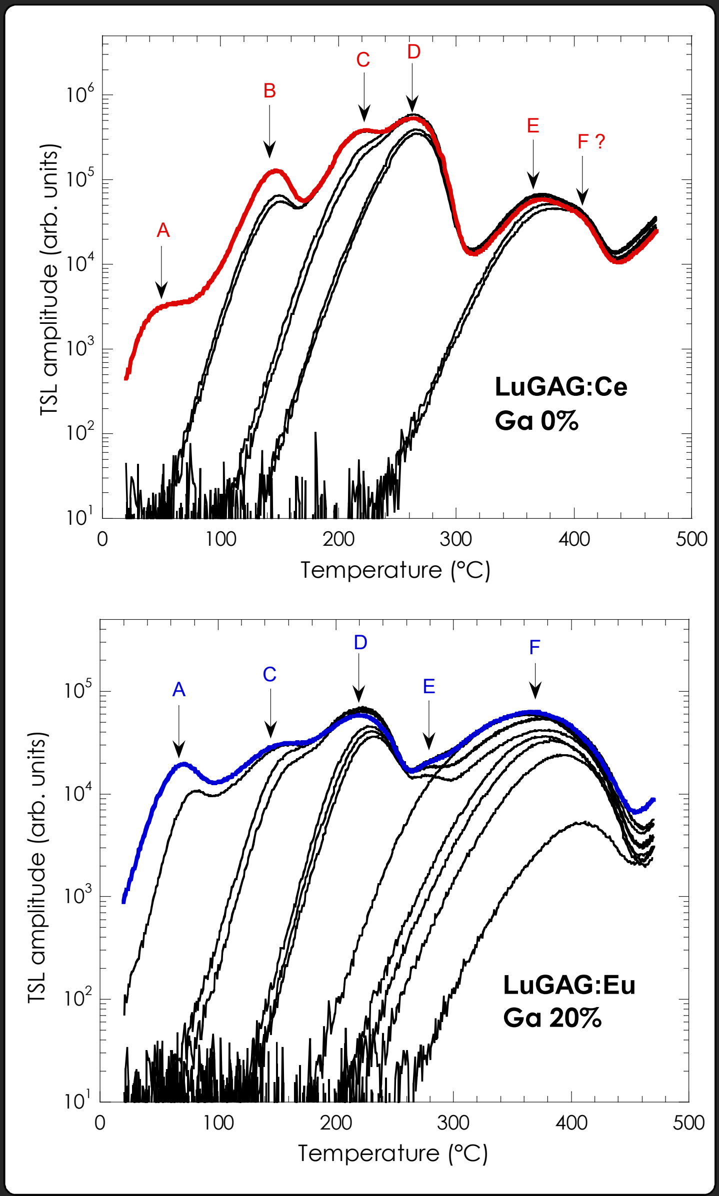
(CB shift)

As expected, Ga substitution induces a low temperature shift of the TSL peaks in both Ce- and Eu-doped LuGAG samples.

LuGAG:Eu

(VB shift)



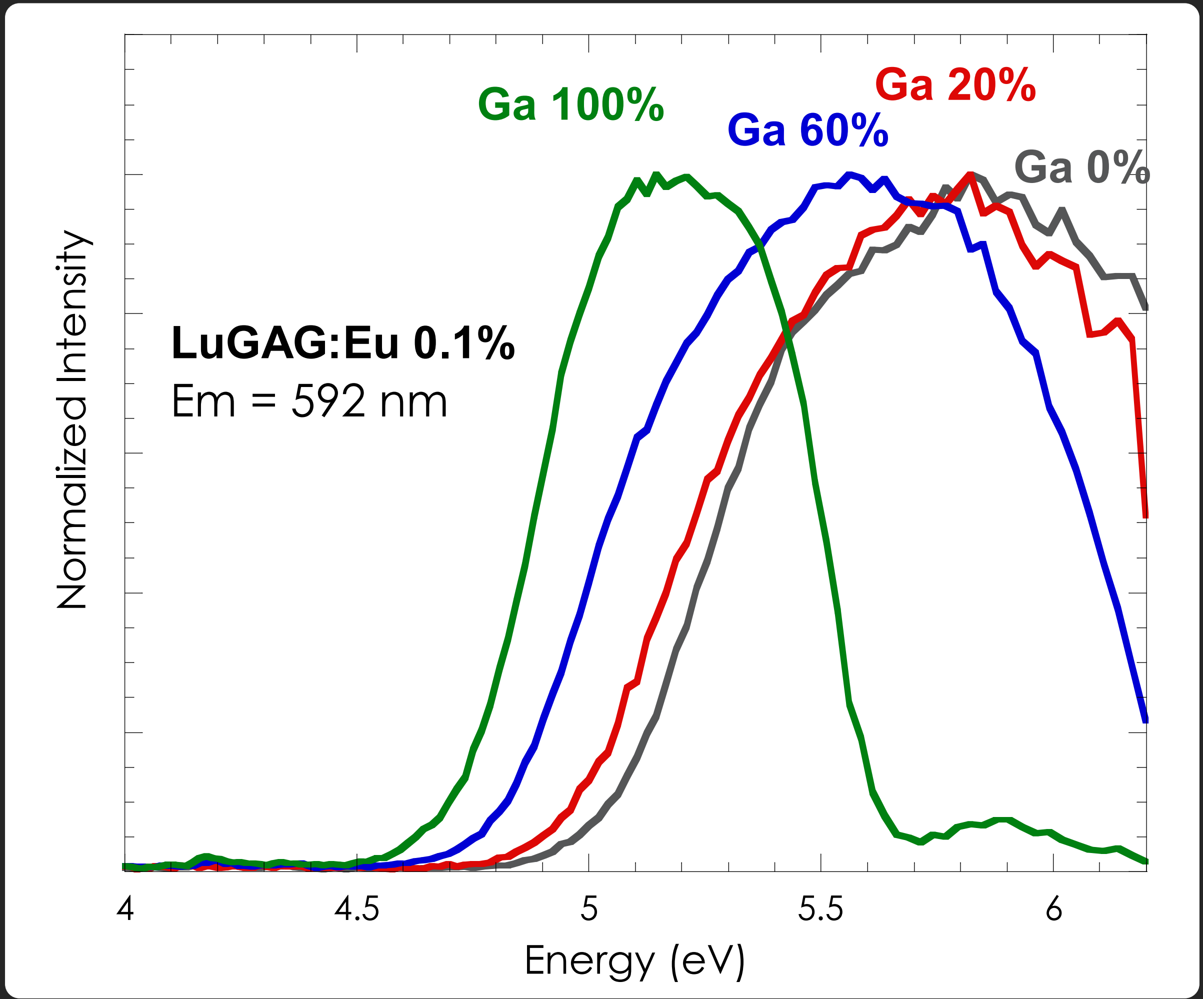


Initial rise technique

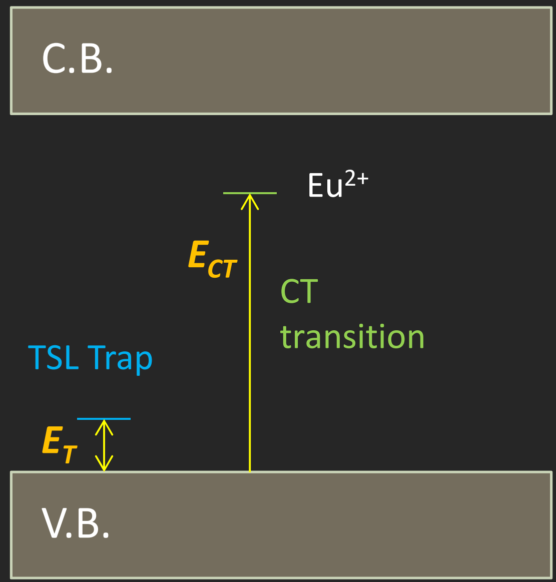
- Several TSL peaks can be identified in the glow curves.
- The thermal activation energies of the TSL peaks ws evaluated by means of the initial rise technique

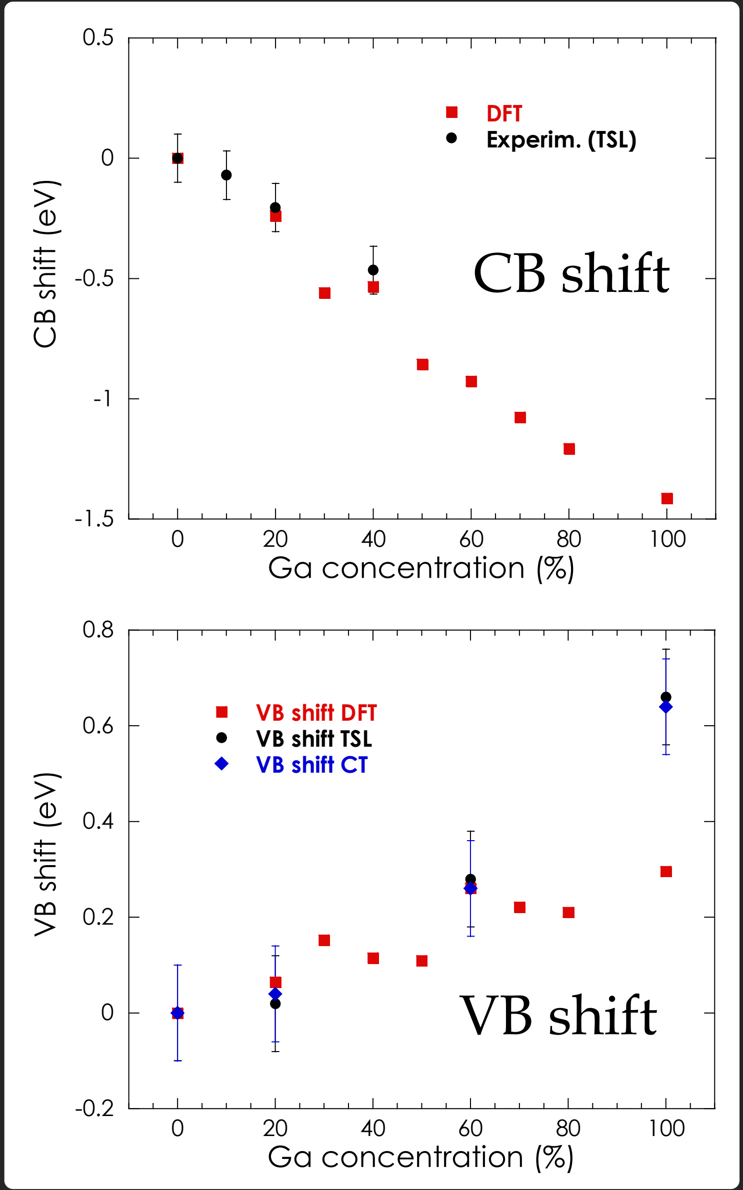
$Lu_3(Ga_xAl_{1-x})_5O_{12}$

Charge transfer band (CT)



- The CT band allows the monitoring of the V.B. shift independently from TSL data.



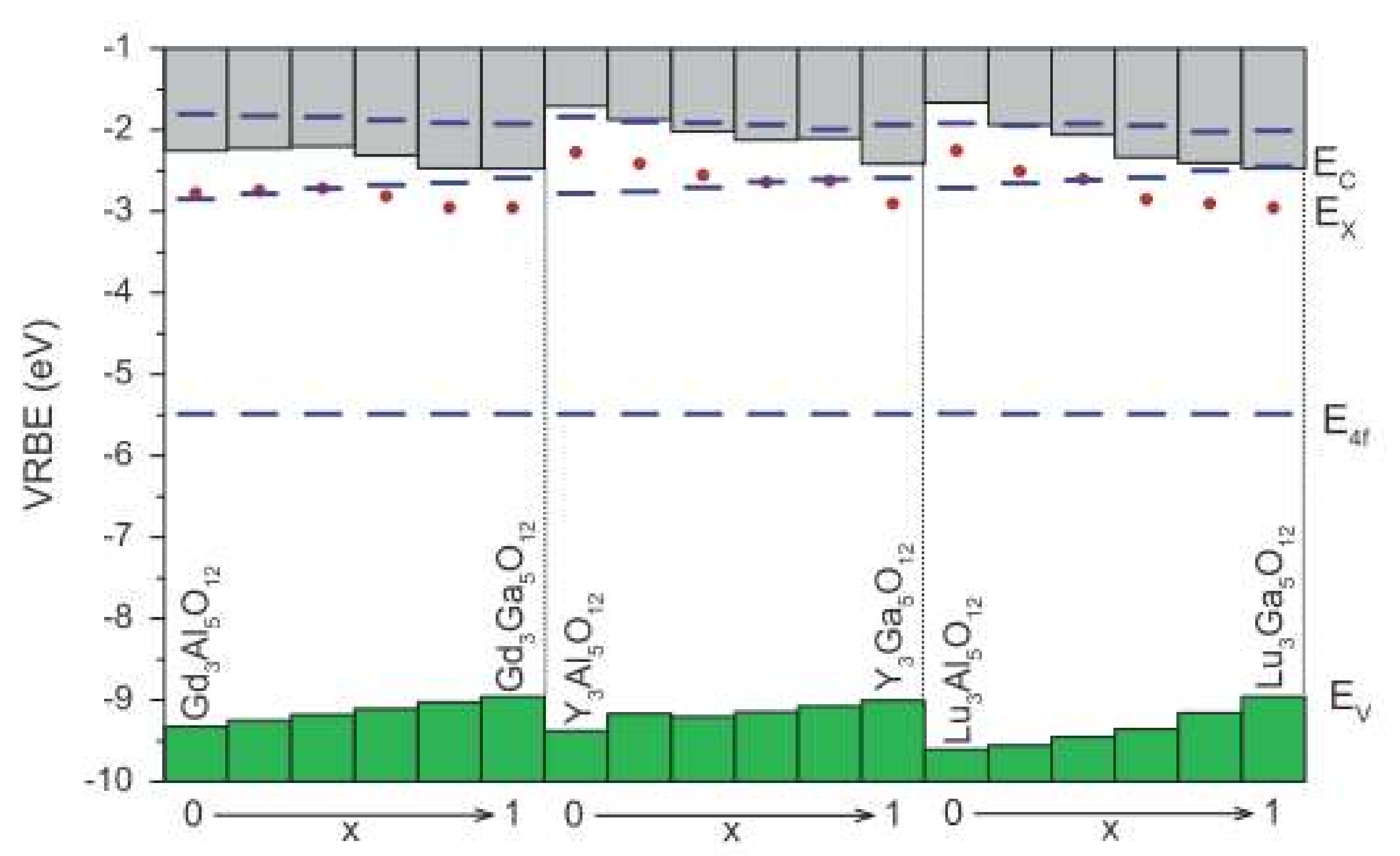


DFT vs Experiment

- DFT calculations and TSL data are in good agreement on both the C.B. and V.B. shift.
- A significant discrepancy is observed for the V.B. shift of the 100% Ga sample
- Ce doped LuGAG with a higher Ga content would be useful in order to extend the available experimental data.

Fasoli et al. Phys. Rev. B, ***84,*** *081102(R)* ***(2011)***

Cerium energy levels in garnets



P. Dorenbos,
J. Lumin.
134 (2012) 310

Outline

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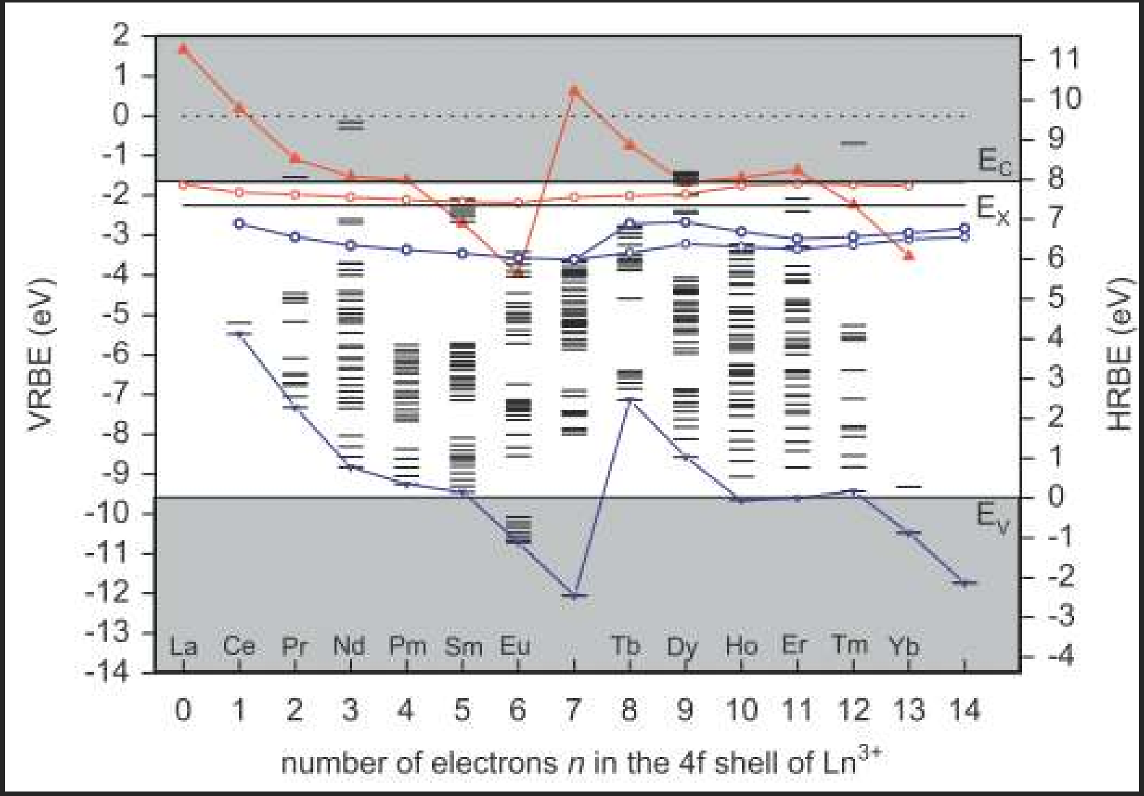
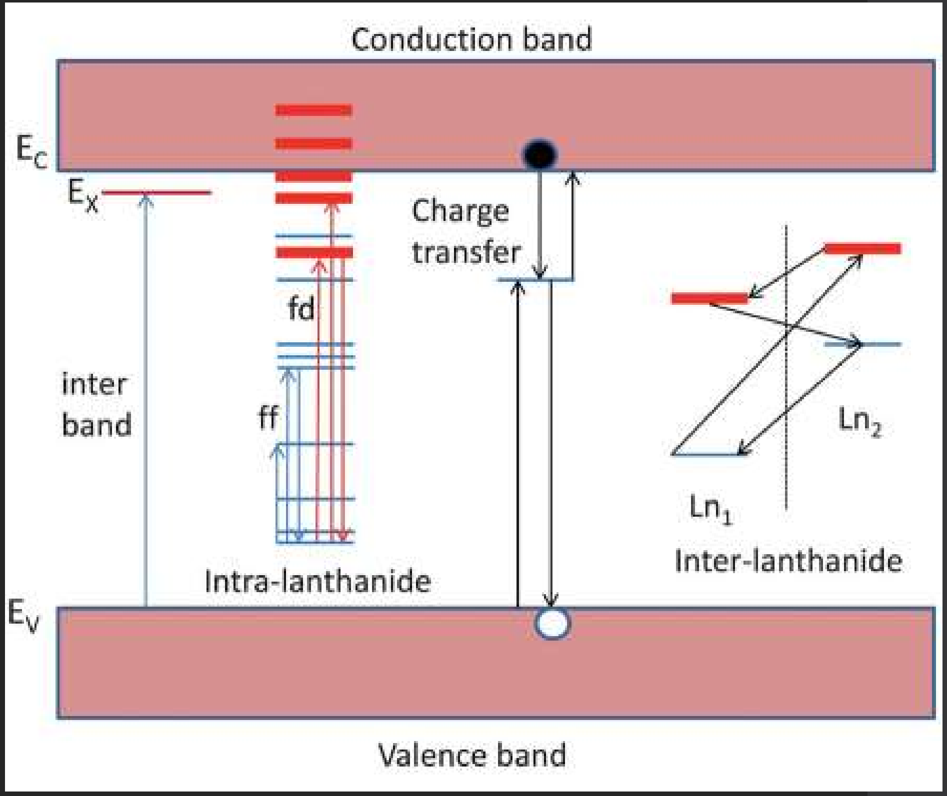
- Delocalized bands shift
- Localization of the excited levels of a luminescence centre

Rare earths energy levels

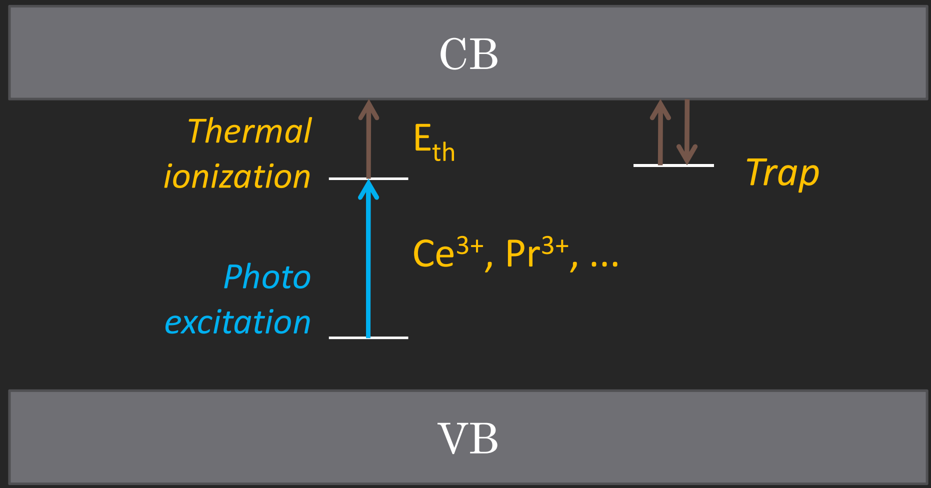




P. Dorenbos, J. Mater. Chem. **22**, 42 (2012) 22344

Thermal ionization of the luminescent center

- When the excited level of the luminescence center is close enough to the conduction band, thermal ionization can occur.
- Under photo excitation of the luminescence center the electron can escape from the excited level to the conduction band and, possibly, get trapped in localized defects.
- In bulk materials the thermal ionization energy barrier E_{th} can be evaluated by means of photoconductivity measurements.
- A different method is required for powder samples and thin films.



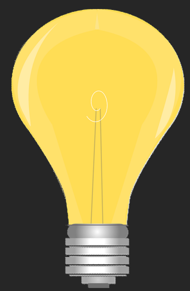
Thermally Stimulated Luminescence **TSL**

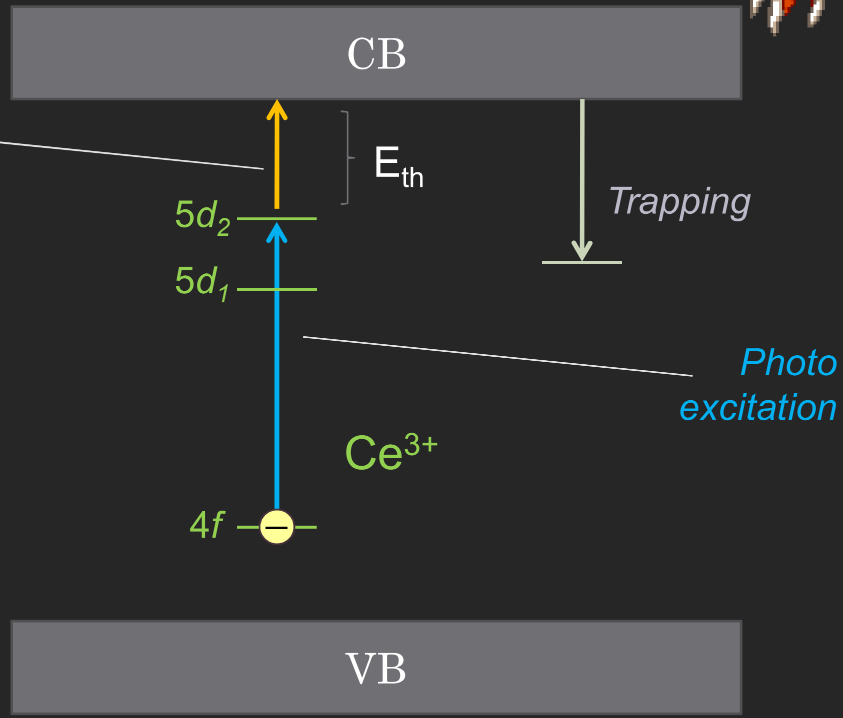
Ionization energy evaluation

- If we excite, at a given temperature, Ce^{3+} in a 4f-5d absorption band, the fraction of electrons thermally promoted to the CB is:

$$e^{-\frac{E_{th}}{k_b T}}$$

- The fraction of ionized electrons trapped in a stable defect can be evaluated from the TSL glow curve.



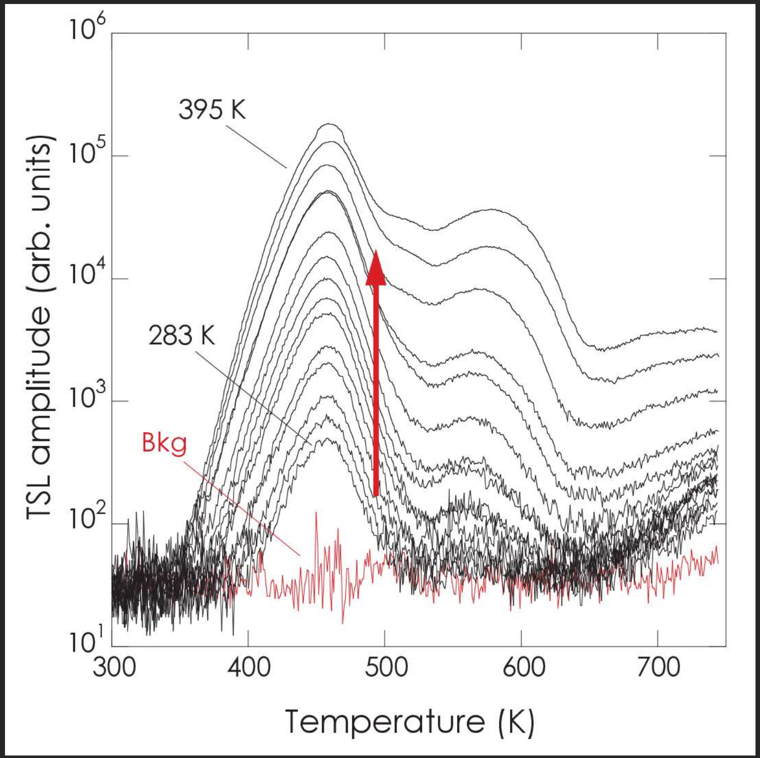


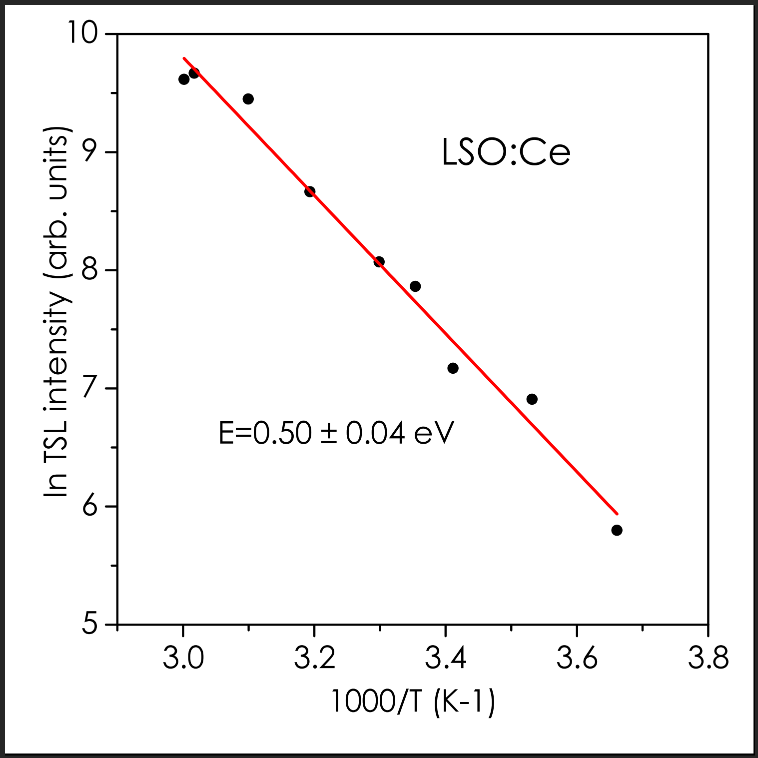
Plotting the **TSL peak intensity** as a function of the **illumination temperature** in an Arrhenius plot the value of the thermal ionization barrier E_{th} can be evaluated.

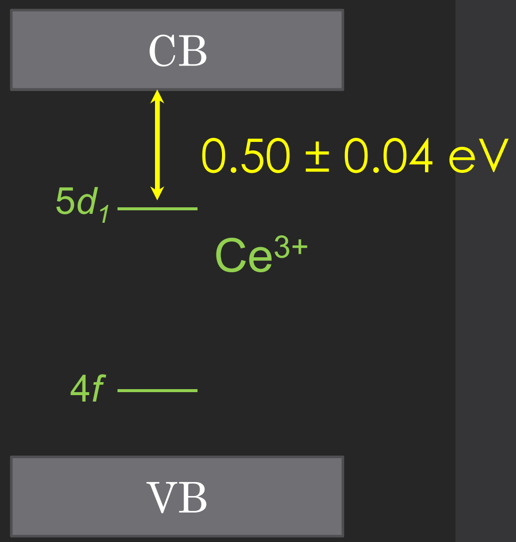
Fasoli et al. Phys. Rev. B, ***85,*** *085127* ***(2012)***

Ionization energy evaluation: Example

The energy separation between the CB and the $5d_1$ level was found to be 0.50 ± 0.04 eV, consistent with the value 0.45 ± 0.02 eV obtained by *van der Kolk et al., APL **83**, 9,1740 (2003)* from photoconductivity data.







Samples

- $Lu_3Ga_xAl_{5-x}O_{12}$ (LuGAG) single crystals grown by micro pulling down (**μ-PD**) technique at **Tohoku University(Japan)** by A. Yoshikawa and H. Ogino
- Crystals size: 6 x 4 x 1 mm^3 approximately

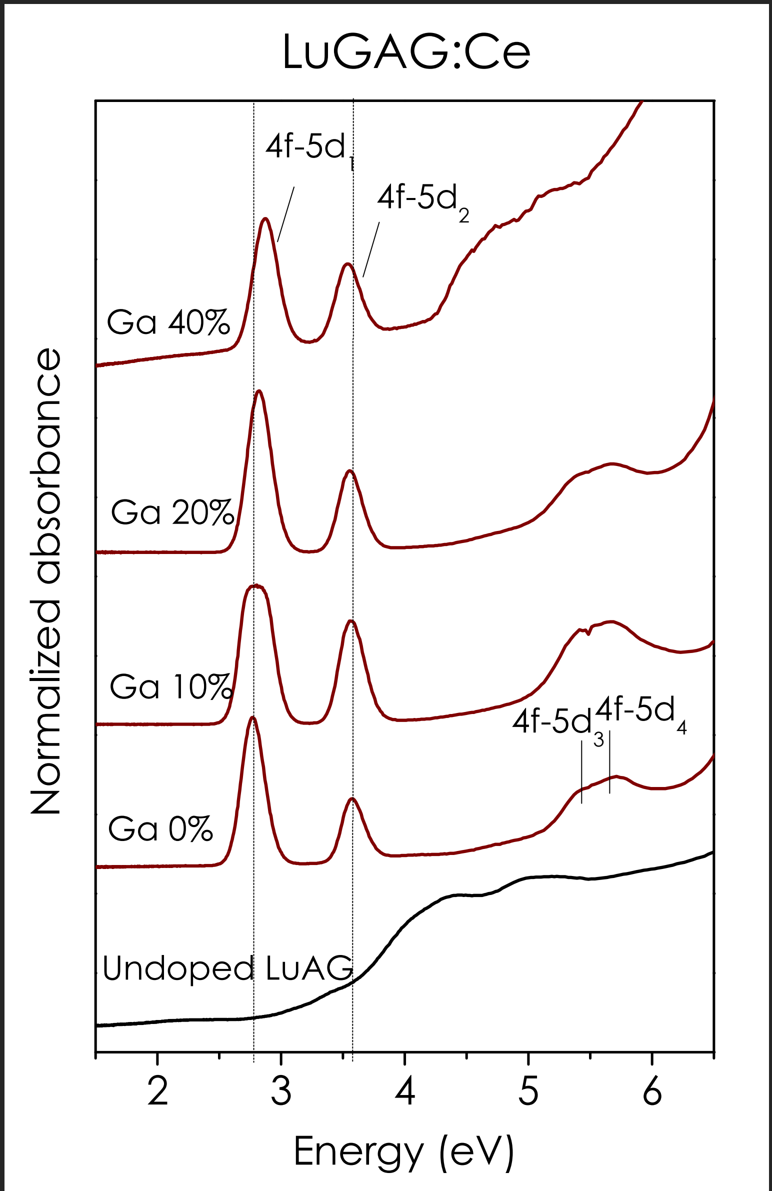
LuGAG:Ce

Ce: 0.7 mol% (in the melt)

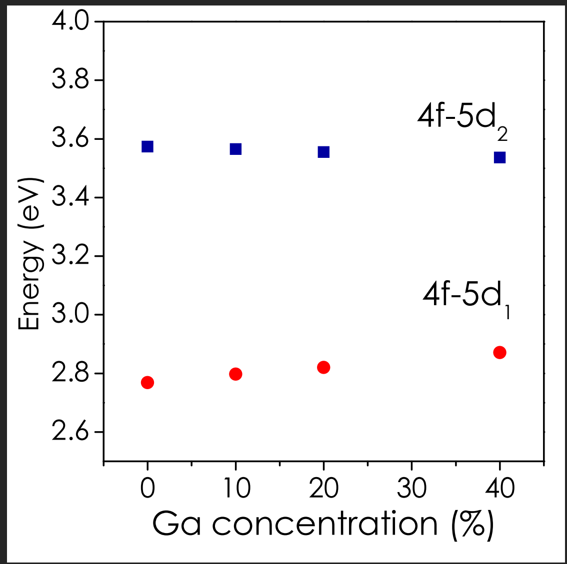
Ga: 0%, 10%, 20% and 40%

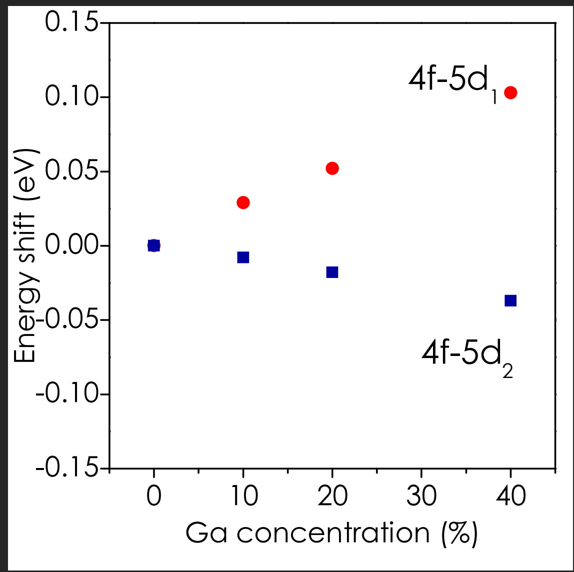
Experimental setup

- Excitation light was obtained from a Xenon lamp coupled to a double monochromator Gemini, Jobin-Yvon (FWHM 2 nm).
- The sample was mounted on a Peltier cell and its temperature was controlled by a Cooltronic TC2812 Peltier controller.
- TSL glow curves were collected with a 2 °C/s heating rate.



Optical absorption: energy shift





A progressive shift of 4f-5d Ce transitions was evidenced by optical absorption measurements.

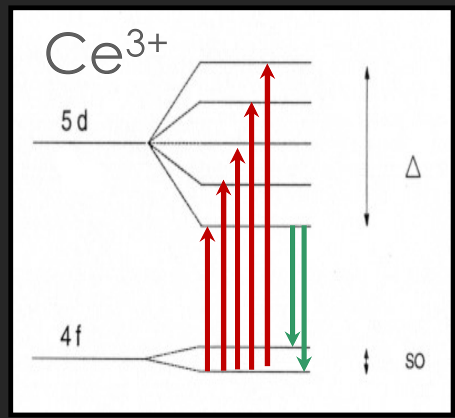
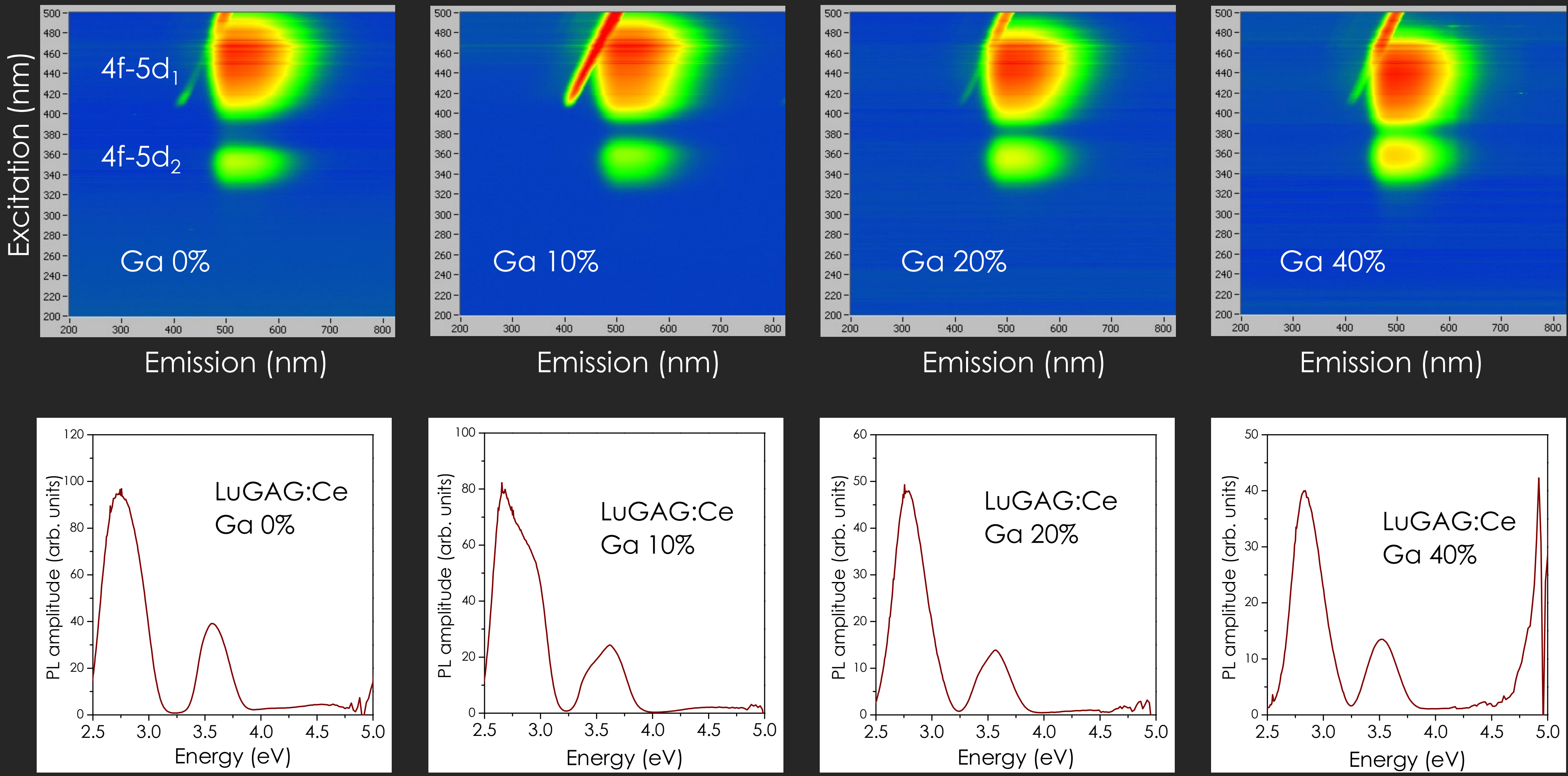


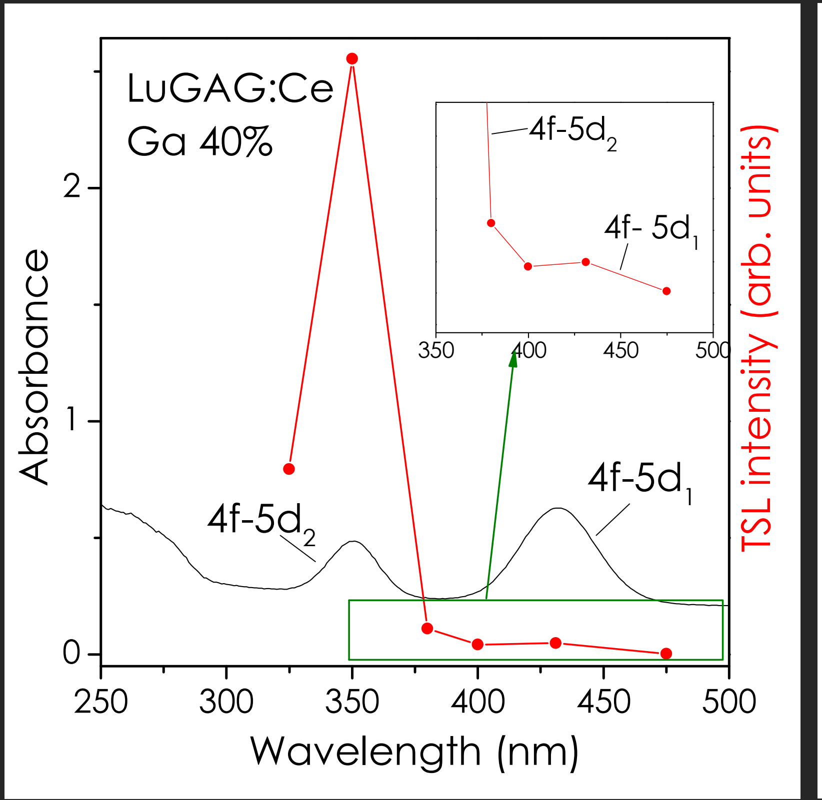
Photo-luminescence: LuGAG:Ce

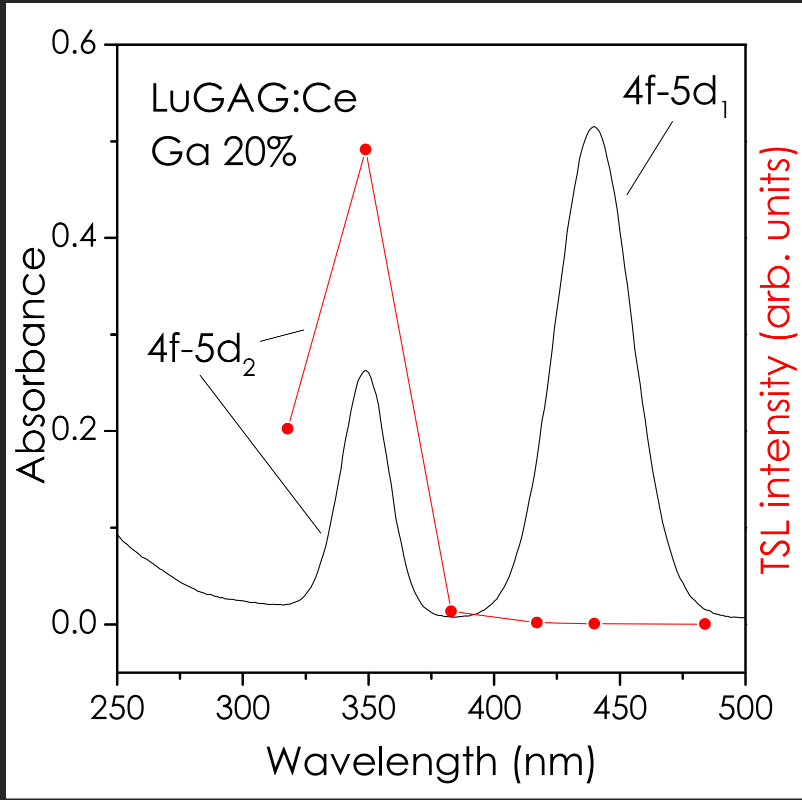


PL/PLE

PLE

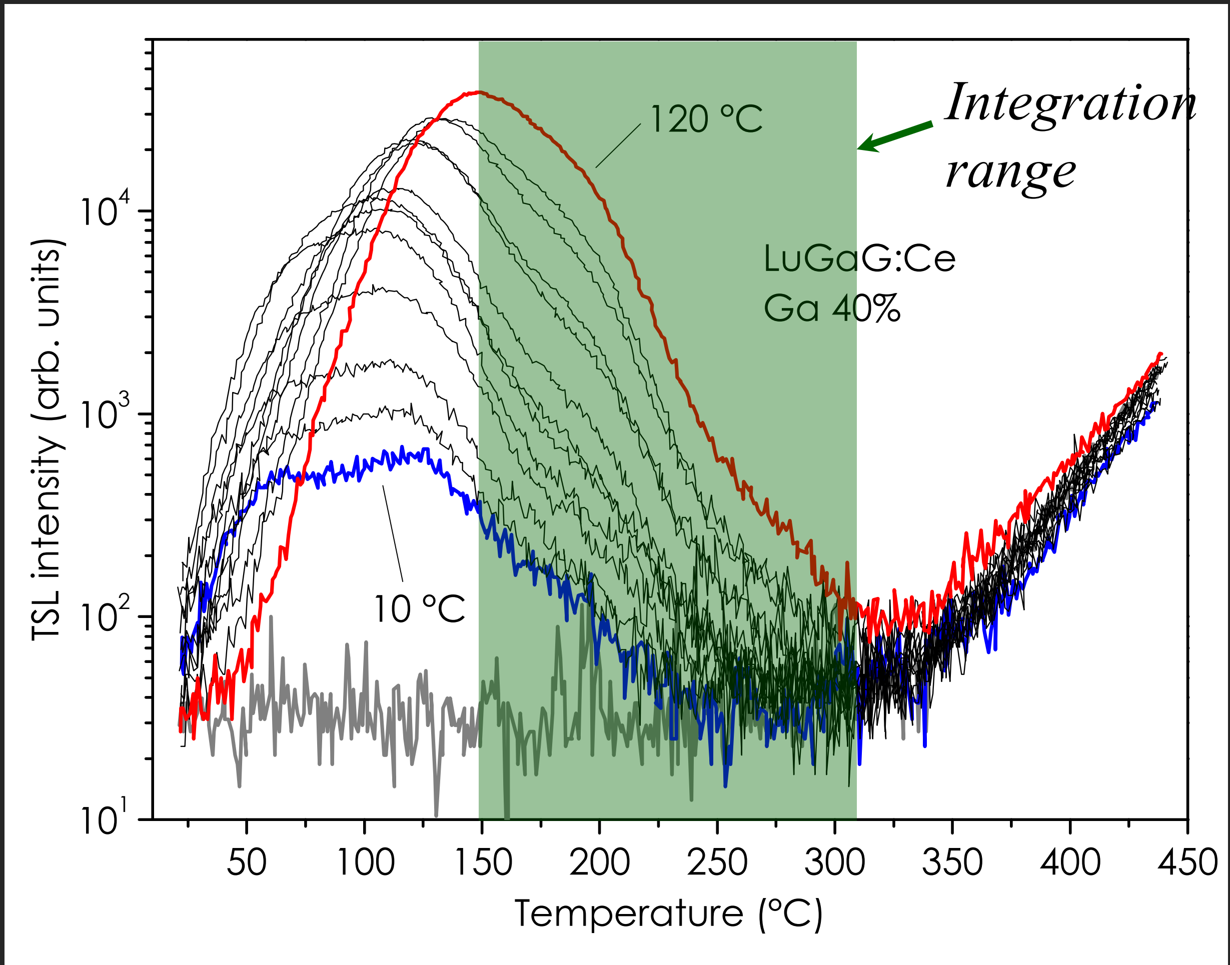
TSL excitation spectrum
(TSL intensity vs. excitation wavelength)

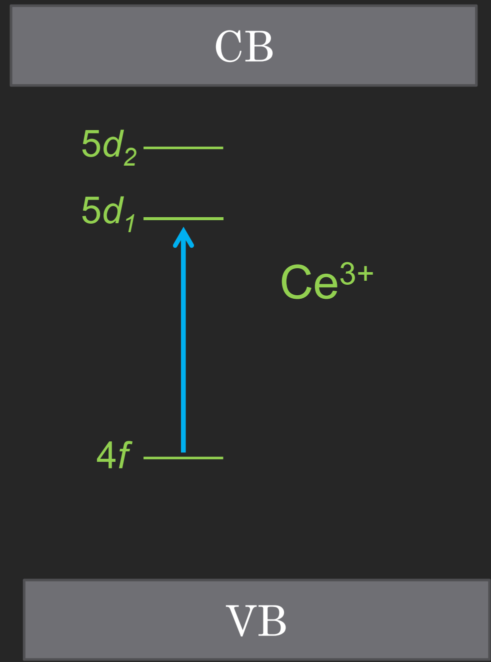




- It is extremely important to first verify the TSL excitation spectrum in order to check the ionization path of the trapped electrons.
- In LuGAG:Ce (Ga 20%), for example, exciting with 440 nm light the trapped electrons are nevertheless ionized via the 5d$_2$ Ce level.

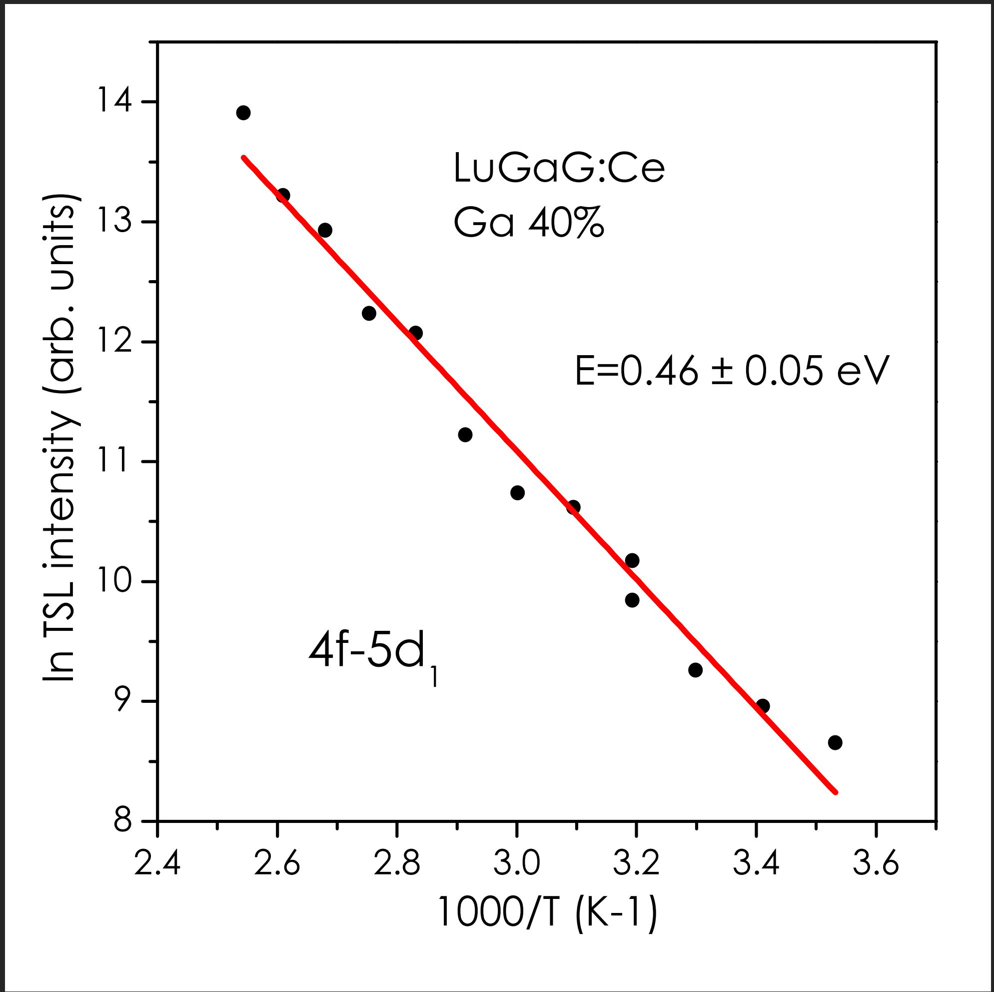
Glow curves: LuGAG:Ce Ga 40% (4f-5d$_1$)

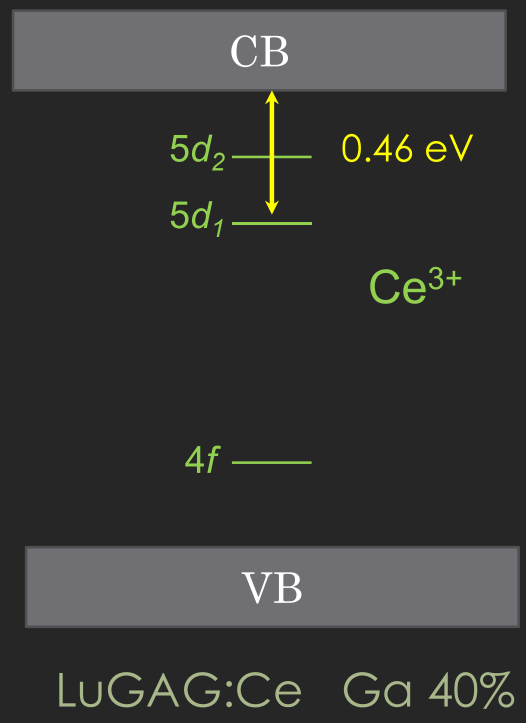




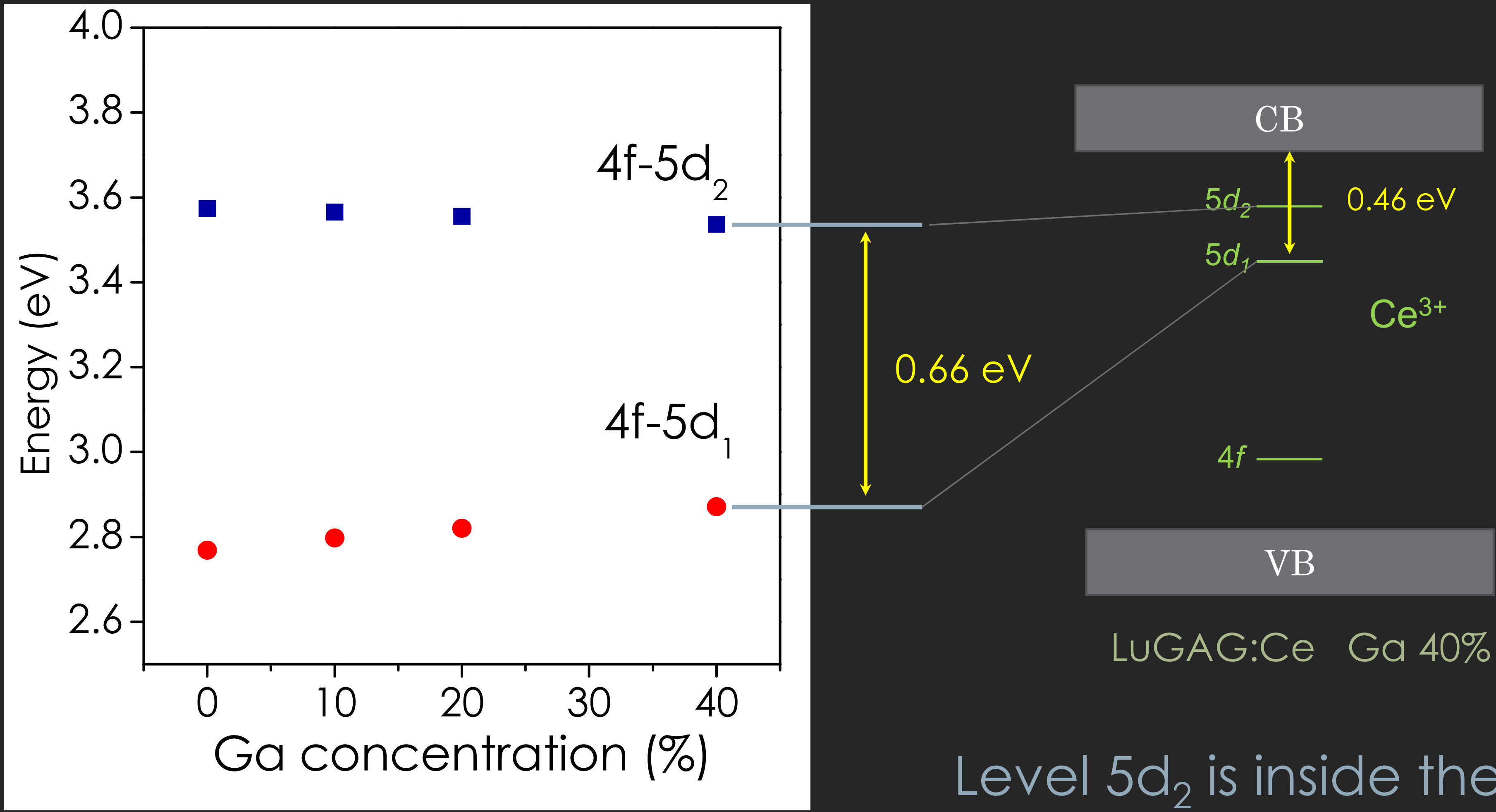
LuGAG:Ce Ga 40%

Arrhenius plot: LuGAG:Ce Ga 40% (4f-5d_1)



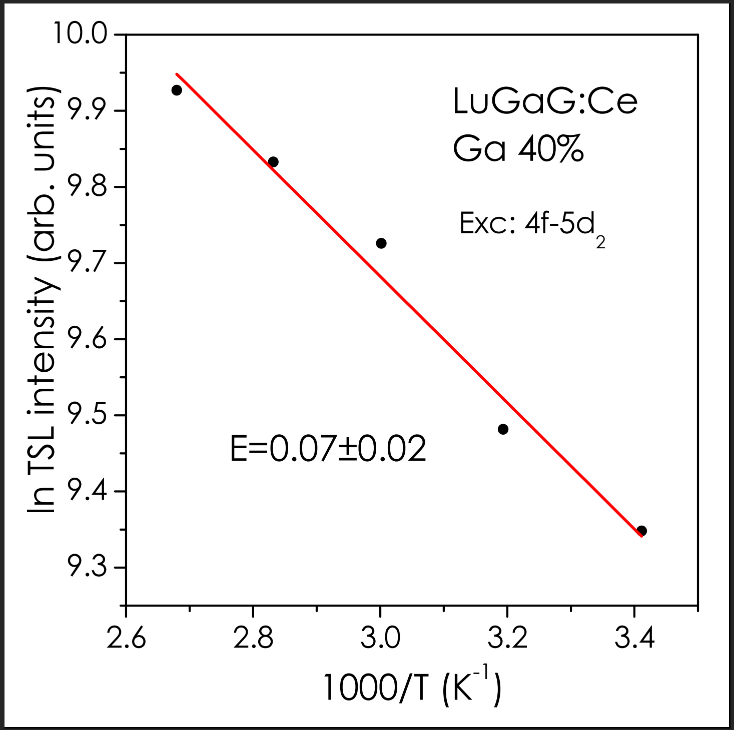


Arrhenius plot: LuGAG:Ce Ga 40% (4f-5d$_1$)

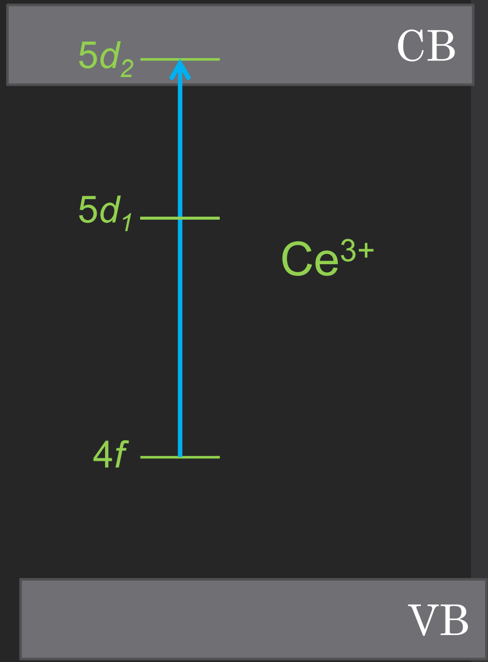


Level 5d$_2$ is inside the CB

Ionization energy: LuGAG:Ce Ga 40% (4f-5d$_2$)

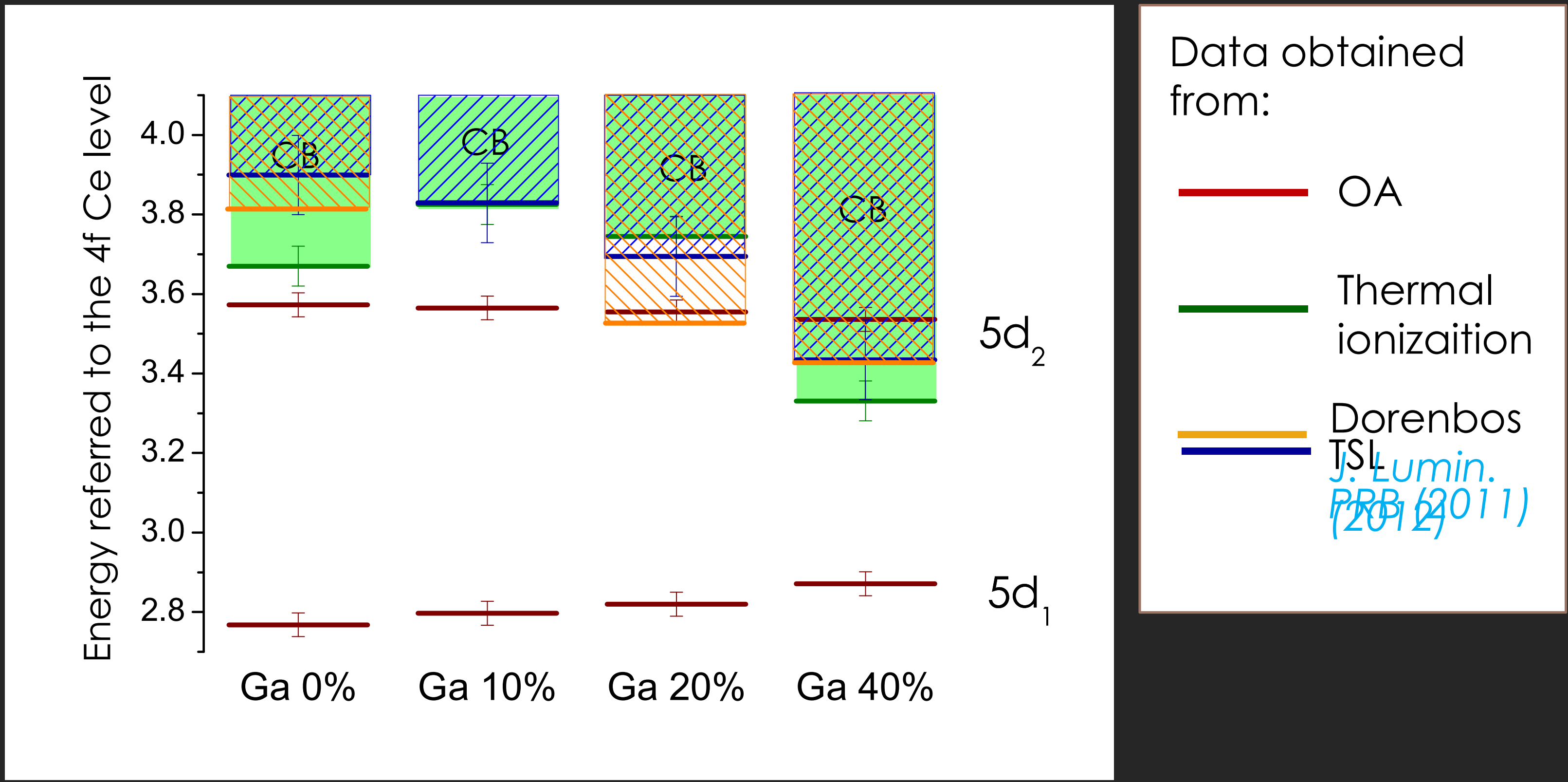


- **Despite** the 5d$_2$ Ce level in LuGAG:Ce Ga 40% lies **within th CB**, an **ionizaiton treshold** of about **0.07 eV** was evidenced.
- A similar energy (0.08 eV) was obtained by *van der Kolk et al.* for the 5d$_2$ Ce level in LSO:Ce and ascribed to the formation and subsequent dissociation of a Ce-bound exciton.
- Most of the vibrational lines in LuGAG Raman spectrum are in the 400-800 cm^{-1} range (0.05-0.1 eV).



LuGAG:Ce Ga 40%

Ce 5d level scheme in $Lu_3(Ga_xAl_{1-x})_5O_{12}$



Conclusions

- The presence of defects can be exploited to obtain useful informations on the optical properties of luminescent materials
- Unconventional use of the TSL technique allowed to:
  - selectively evaluate delocalized band shift
  - localize the excited levels of a luminescence centre in the band gap