

TSL studies for the engineering of optical materials

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RESEARCH GROUP: Inorganic materials for sensing and photonics

Composition

3 permanent staff members: N. Chiodini, A. Paleari, A. Vedda

3 post-doc, 1PhD student, 2 undergraduates

Main investigation fields:

1. Optical properties of rare earth ions in silica and silica based glass-ceramics with crystalline nano-phases, to obtain materials suitable to be used as scintillators in the detection of ionizing radiations and looking at the optical properties useful in photonics

2. Crystalline scintillators, such as tungstates, rare earth-doped perovskites, garnets and complex fluorides

3. Micro-and nano structured luminescent materials (SrHfO_3 , $\text{Lu}_4\text{Hf}_3\text{O}_{12}$, HfO_2)

Experimental facilities:

Synthesis laboratory

Inorganic chemistry laboratory for sol-gel preparations. Film deposition by spin-coating. Furnaces for densification processes, instrumentation for optical finishing.

Physical characterization laboratory:

optical absorption

photo- thermo- and radio-luminescence spectroscopy (10-800 K)

micro-Raman scattering

refractive index measurement

profilometry

complex impedance spectroscopy

FTIR absorption

ICP-Mass with laser ablation

XRF

Within collaborations:

SEM, TEM, XRD

The effect of Ga^{3+} doping
on the band structure
of $\text{Lu}_3\text{Ga}_x\text{Al}_{5-x}\text{O}_{12}$ garnets

Outline

- Experimental data

- UV-Vis Absorption spectra

- VUV Excitation spectra

- TSL (initial rise technique)



Band gap



C.B. and V.B.

- DFT calculations (VASP code) (Los Alamos)

$\text{Lu}_3\text{Ga}_x\text{Al}_{5-x}\text{O}_{12}$ Crystals

- $\text{Lu}_3\text{Ga}_x\text{Al}_{5-x}\text{O}_{12}$ (LuGAG) single crystals grown by micro pulling down (m-PD) technique at the University of Sendai (Japan)
- Crystals size: 6 x 4 x 1 mm³ approximately

LuGAG:Ce

Ce: 0.7 mol% (in the melt)

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

LuGAG:Eu

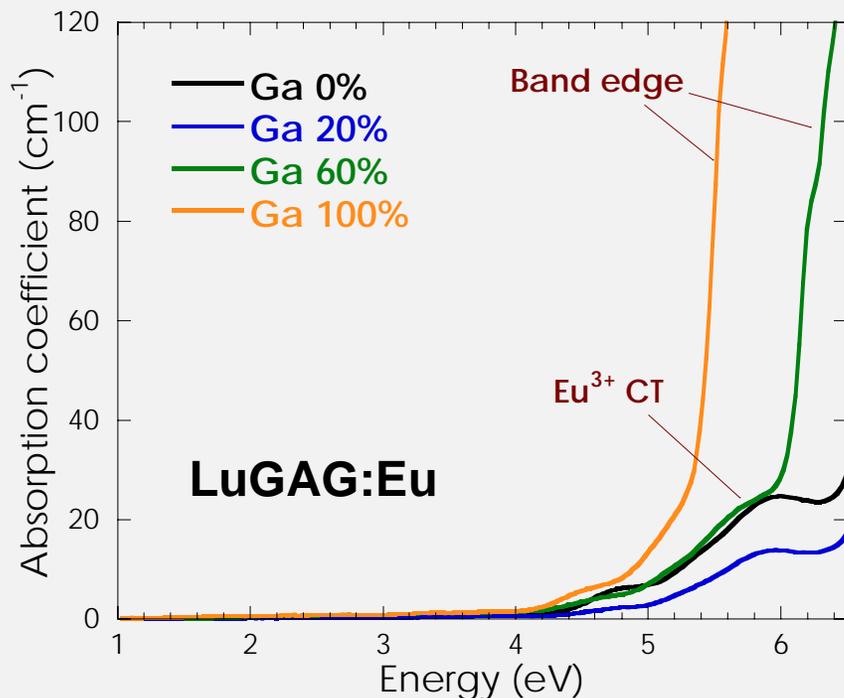
Eu: 0.1 mol% (in the melt)

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

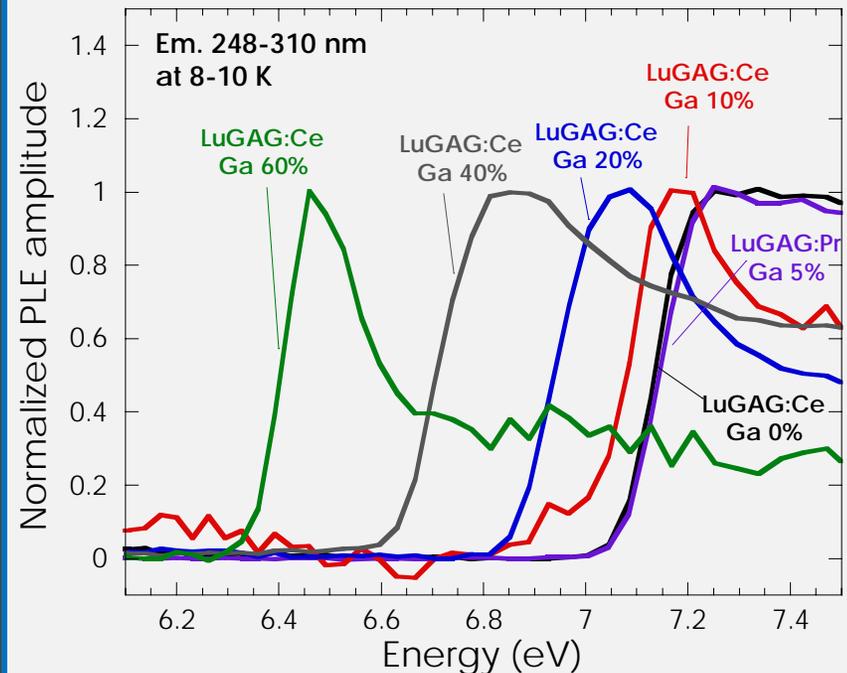
Band Gap shrinking

Ga substitution induces a band gap shrinking as evidence by a low energy shift of the absorption edge in UV-VIS absorption and inVUV-PLE measurements.

Abs spectra

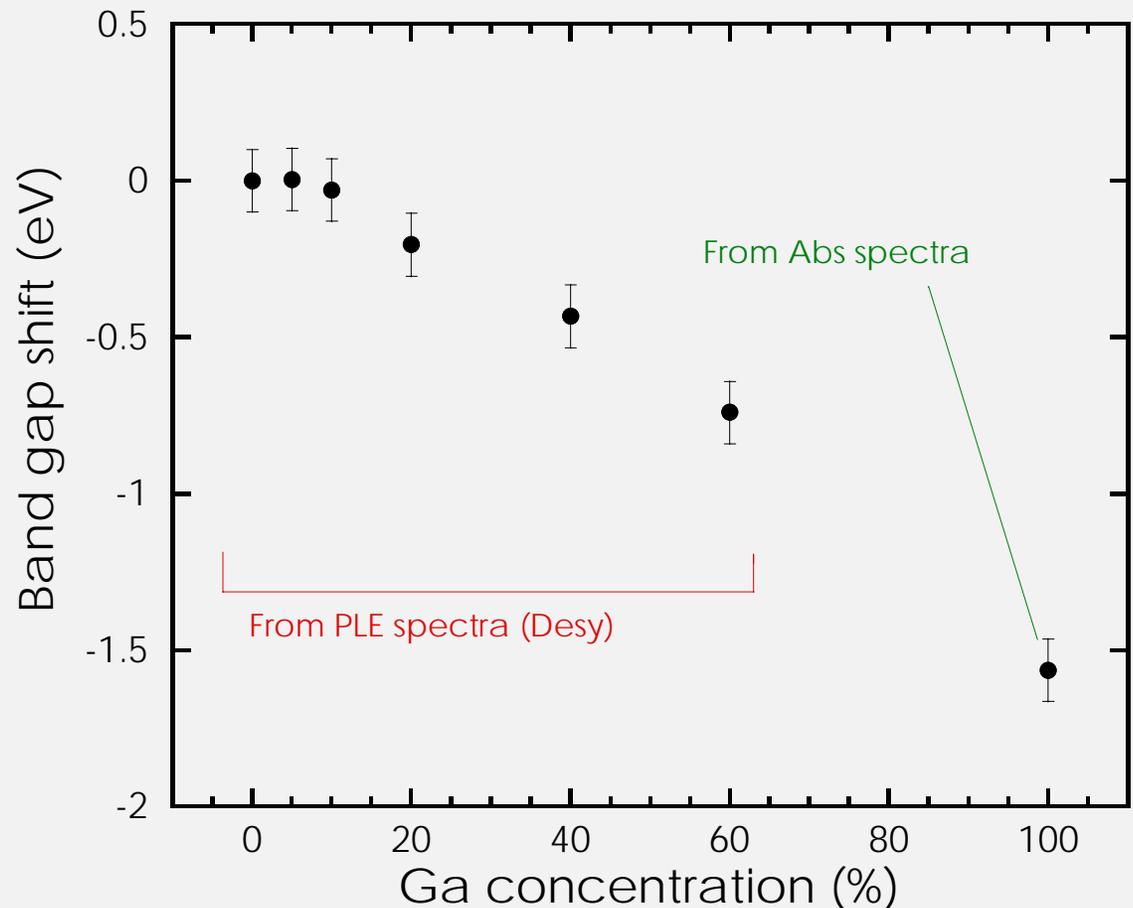


PLE (at DESY)

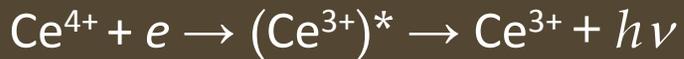
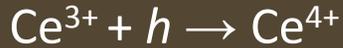


Band Gap shrinking

- The band gap reduction was evaluated by combining PLE and Abs data.
- In LuGG (with 100% of Ga) the band gap is 1.6 eV smaller than in LuAG with no Ga content

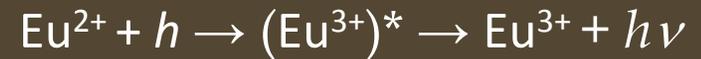


TSL mechanism (Ce, Eu)



↑
Released from an *e* trap

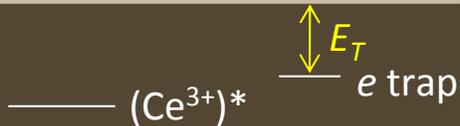
Irradiation



↑
Released from a *h* trap

Heating

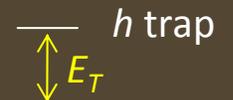
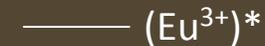
C.B.



V.B.

TSL (initial rise technique) allows the evaluation of the thermal activation energy E of the *e* traps (in Ce-doped LuGAG) and *h* traps (in Eu-doped LuGAG)

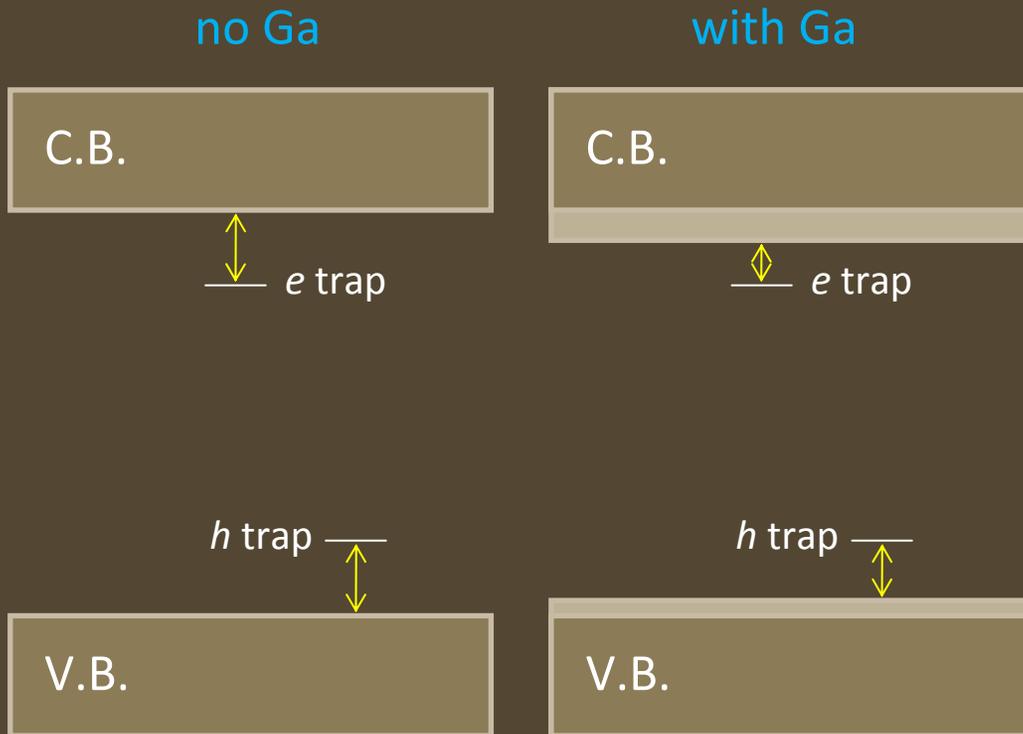
C.B.



V.B.

Working assumption

- We assume the e and h traps 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.



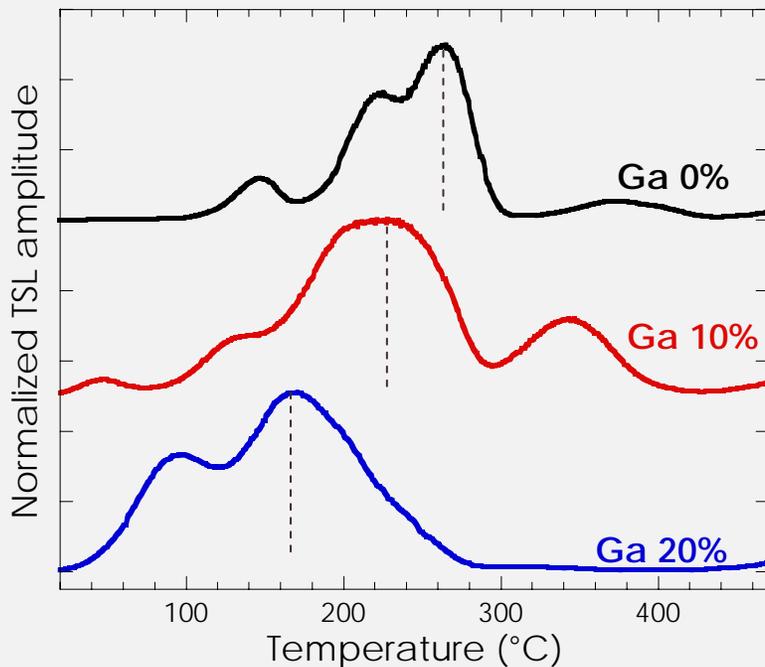
But let's not forget that:

- 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.

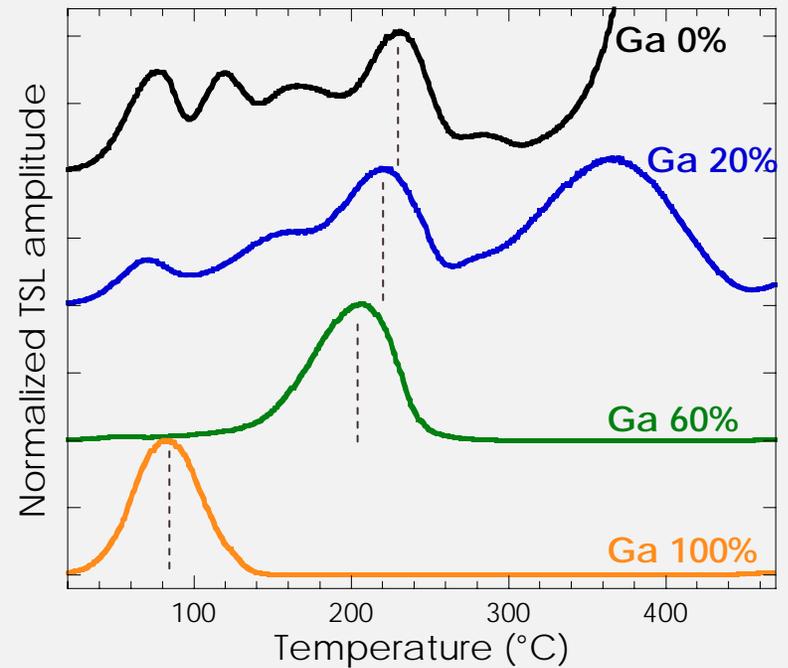
TSL glow curves

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

LuGAG:Ce



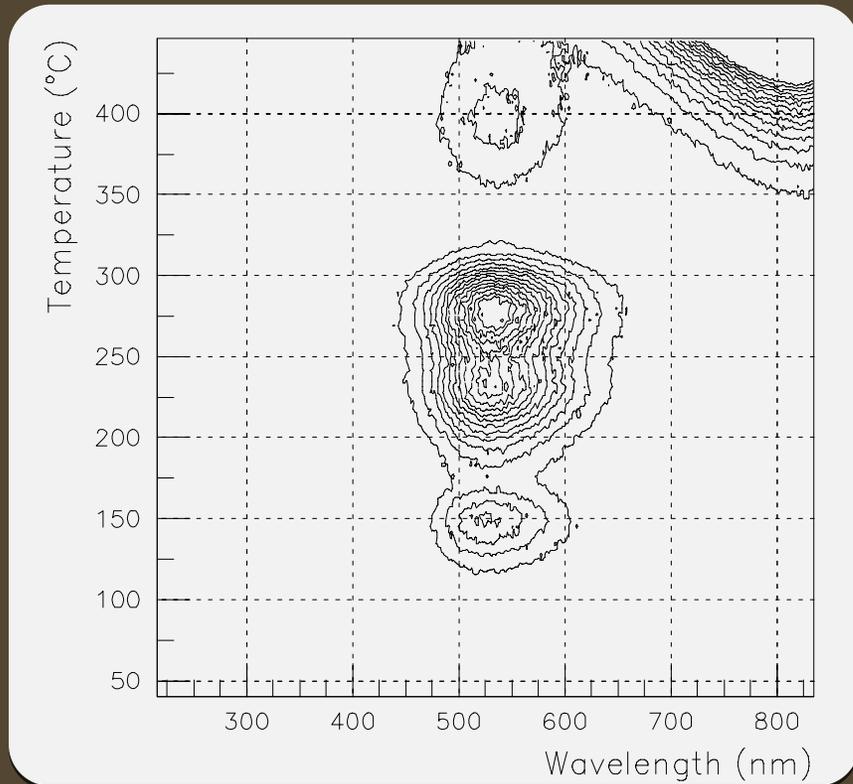
LuGAG:Eu



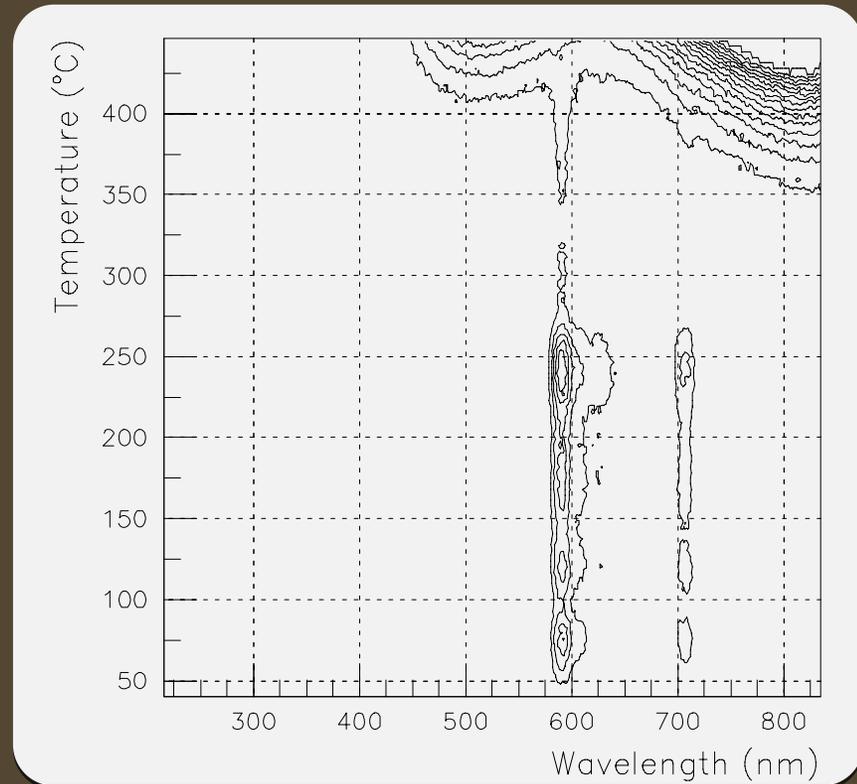
Wavelength resolved TSL

The dopant trivalent ion (Ce^{3+} , Eu^{3+}) is the recombination centre for all of the observed TSL peaks with the exception of the 450 °C peak in LuGAG:Eu.

LuGAG:Ce

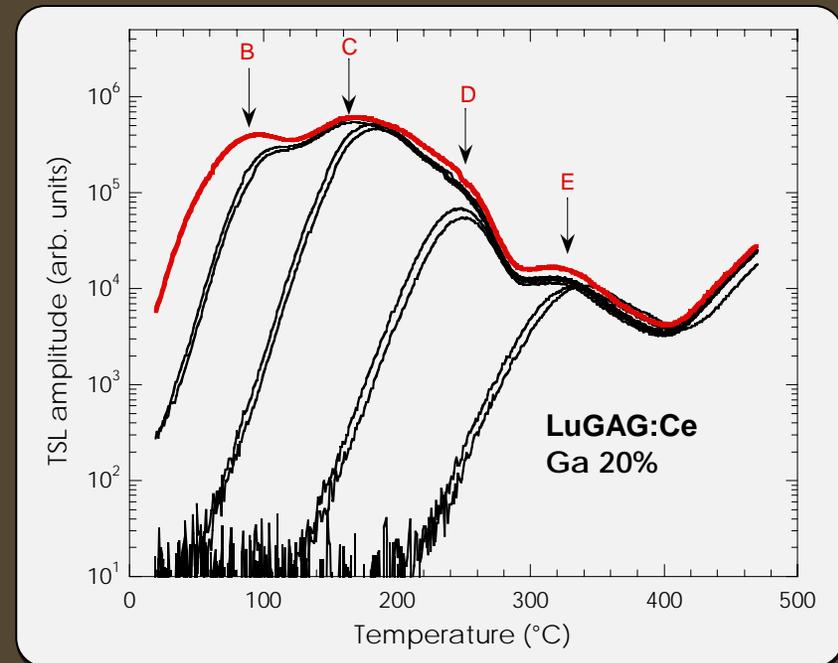
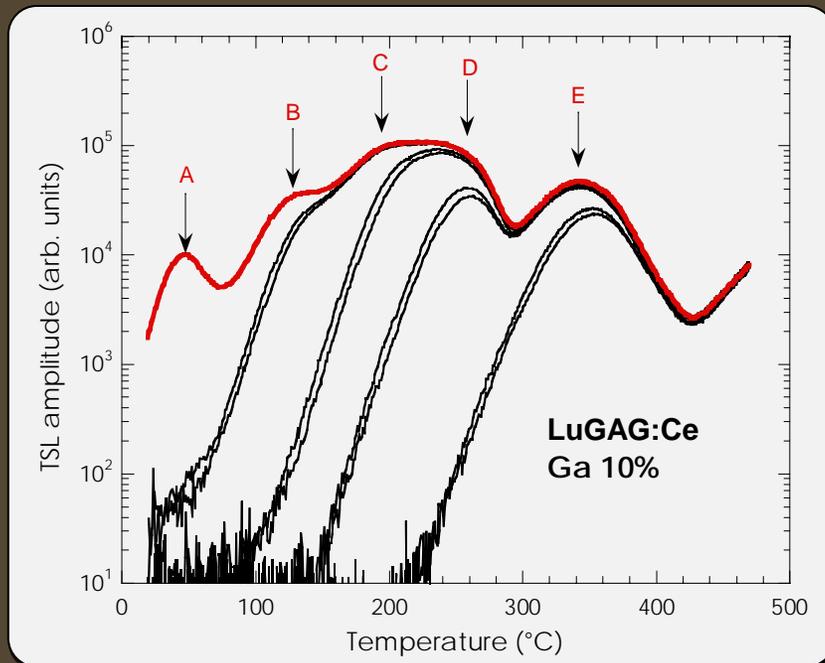
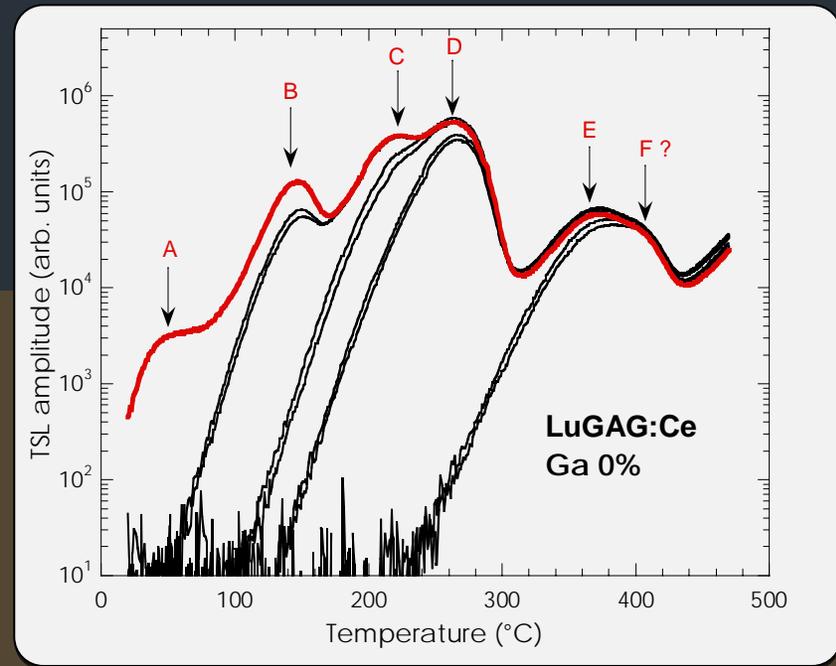


LuGAG:Eu



Initial rise technique

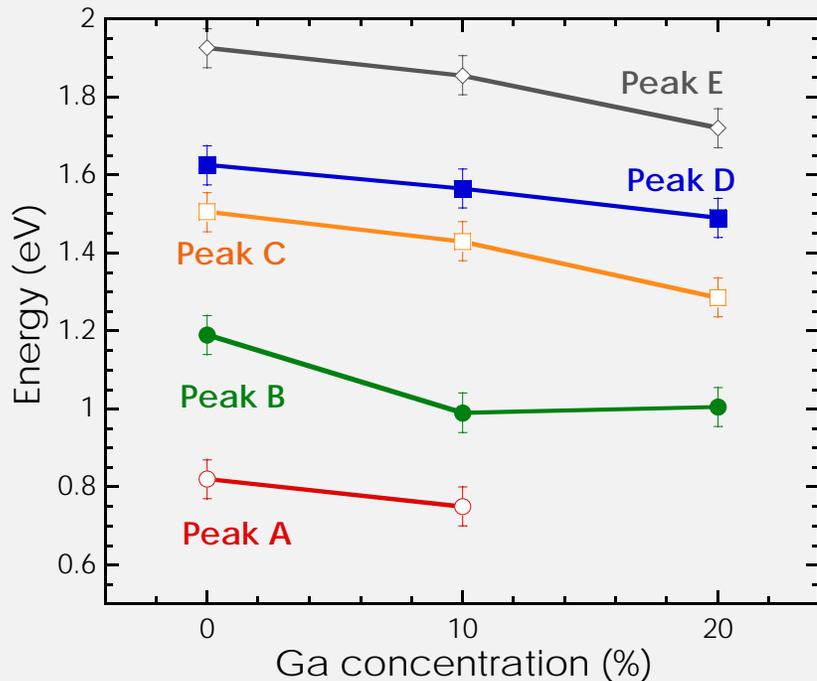
- Several TSL peaks can be identified in the glow curves.
- The thermal activation energies of the TSL peaks was evaluated by means of the initial rise technique



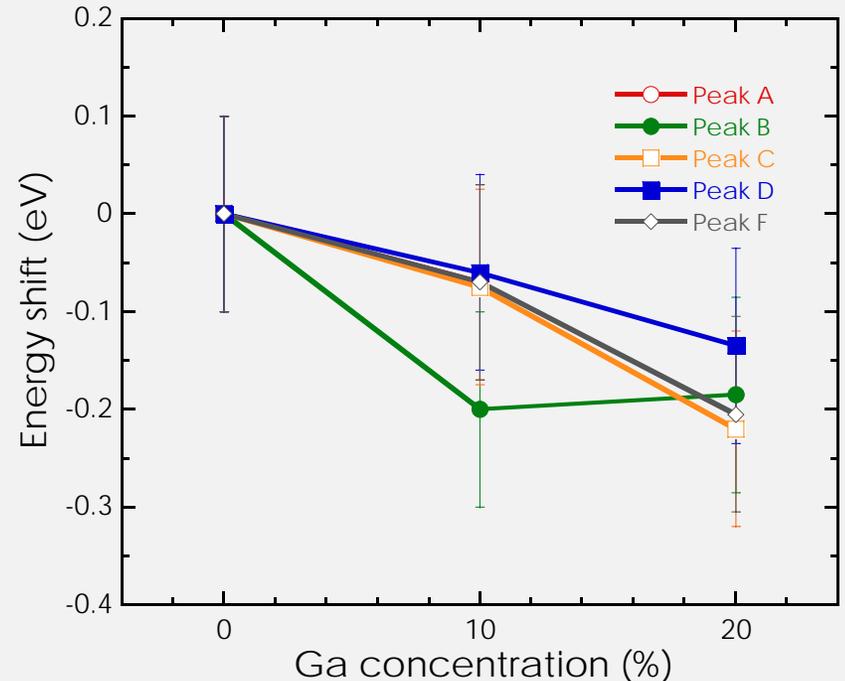
C.B. Shift - LuGAG:Ce

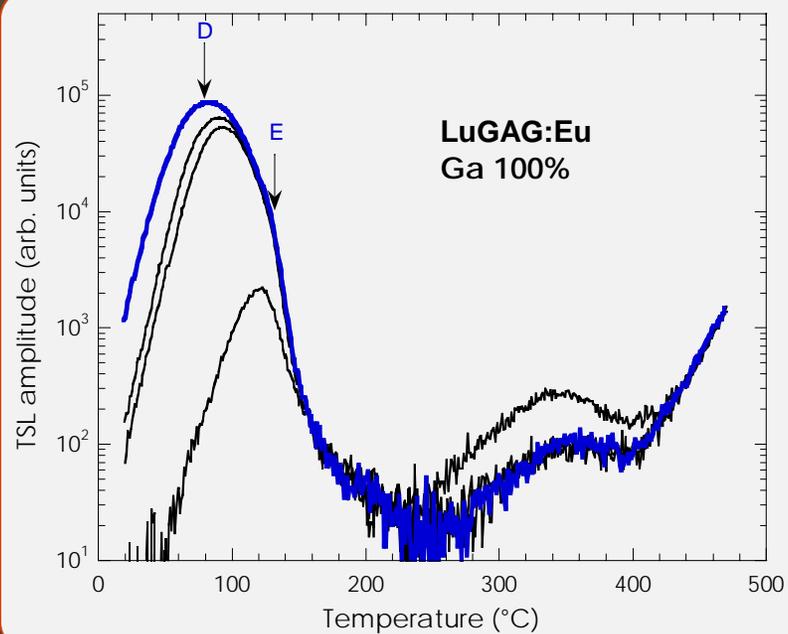
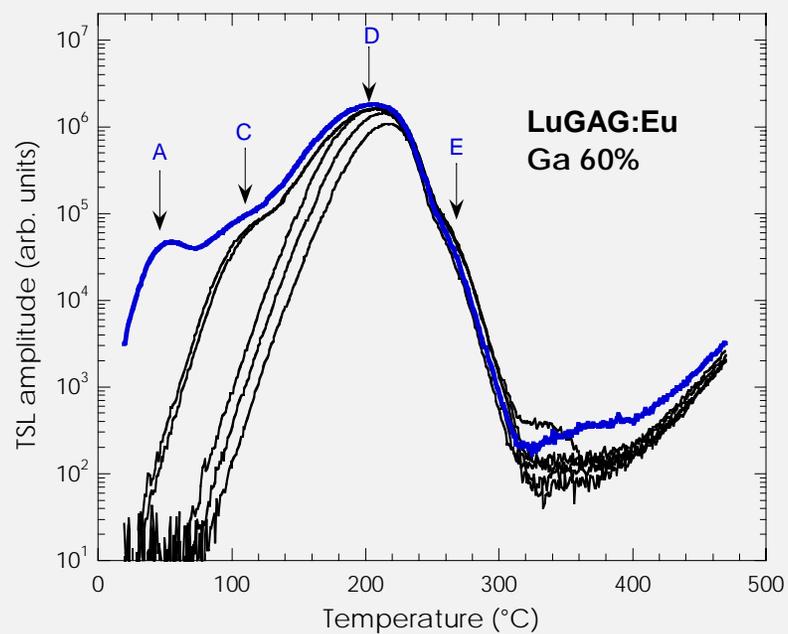
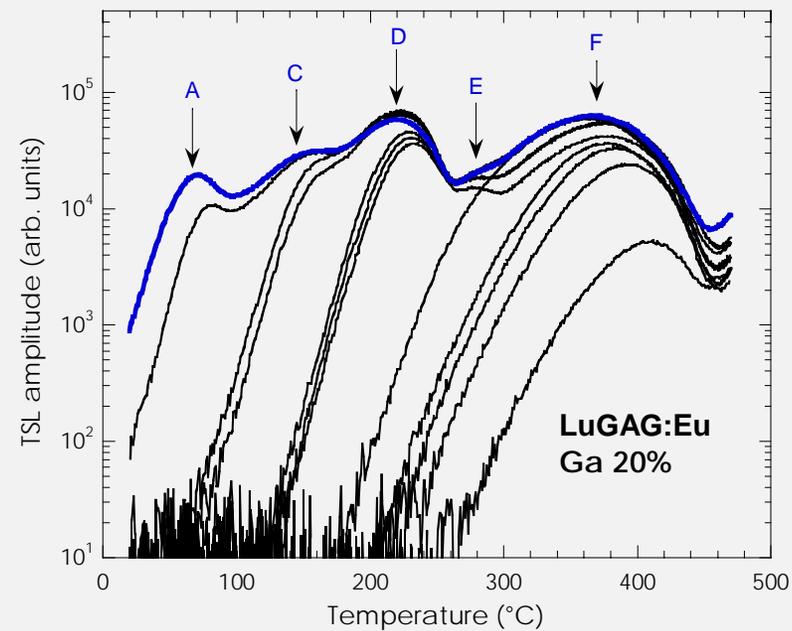
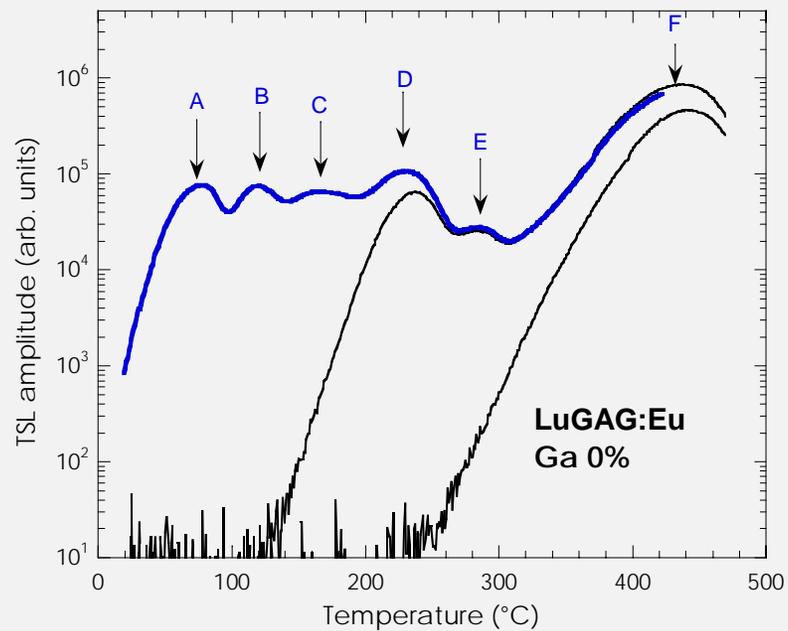
The thermal activation energy of all the TSL peaks shifts by approximately the same amount, suggesting that our assumption that the traps are fixed is a good approximation.

Thermal activation energy



Energy Shift

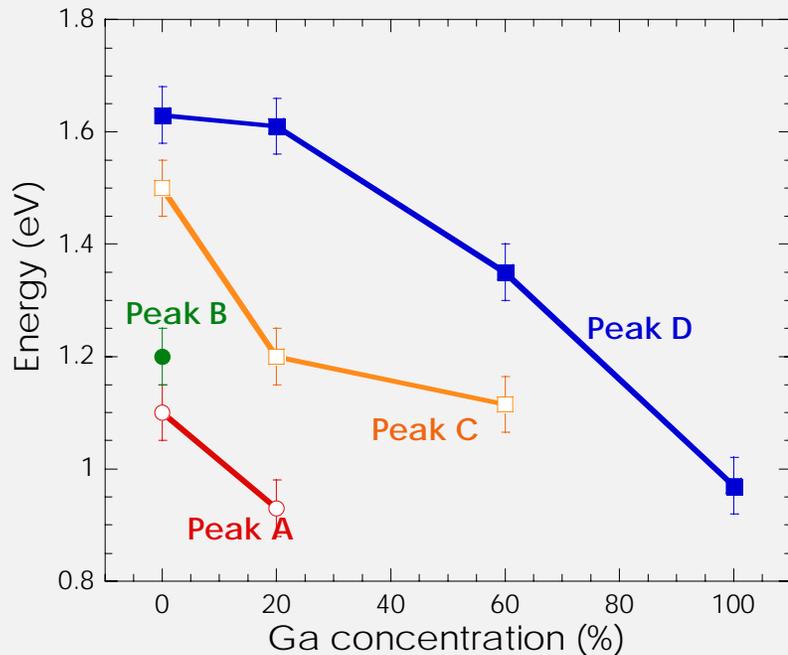




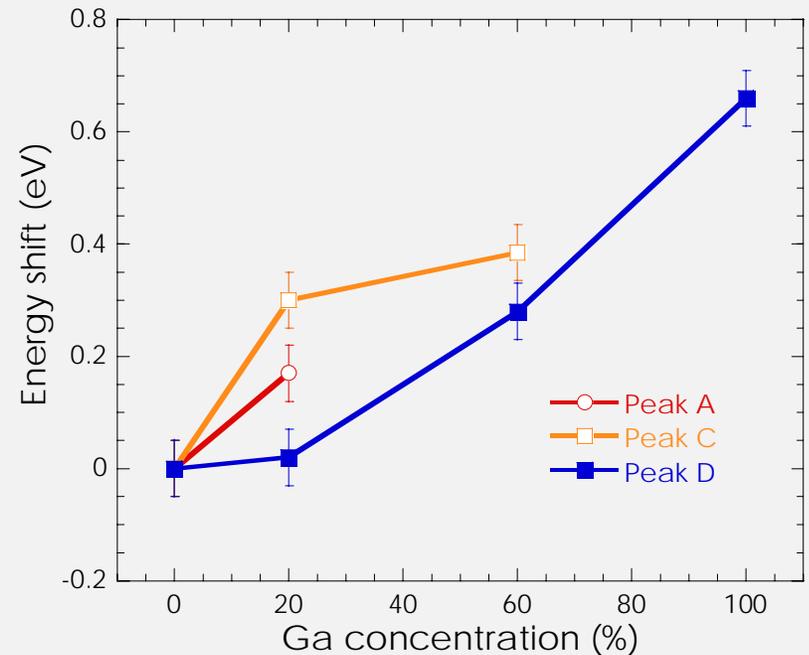
V.B. Shift - LuGAG:Eu

- The thermal activation energy shift of the h -traps looks slightly more dispersed.
- The trap related to the most intense TSL peak (D) shifts up to about 0.7 eV.

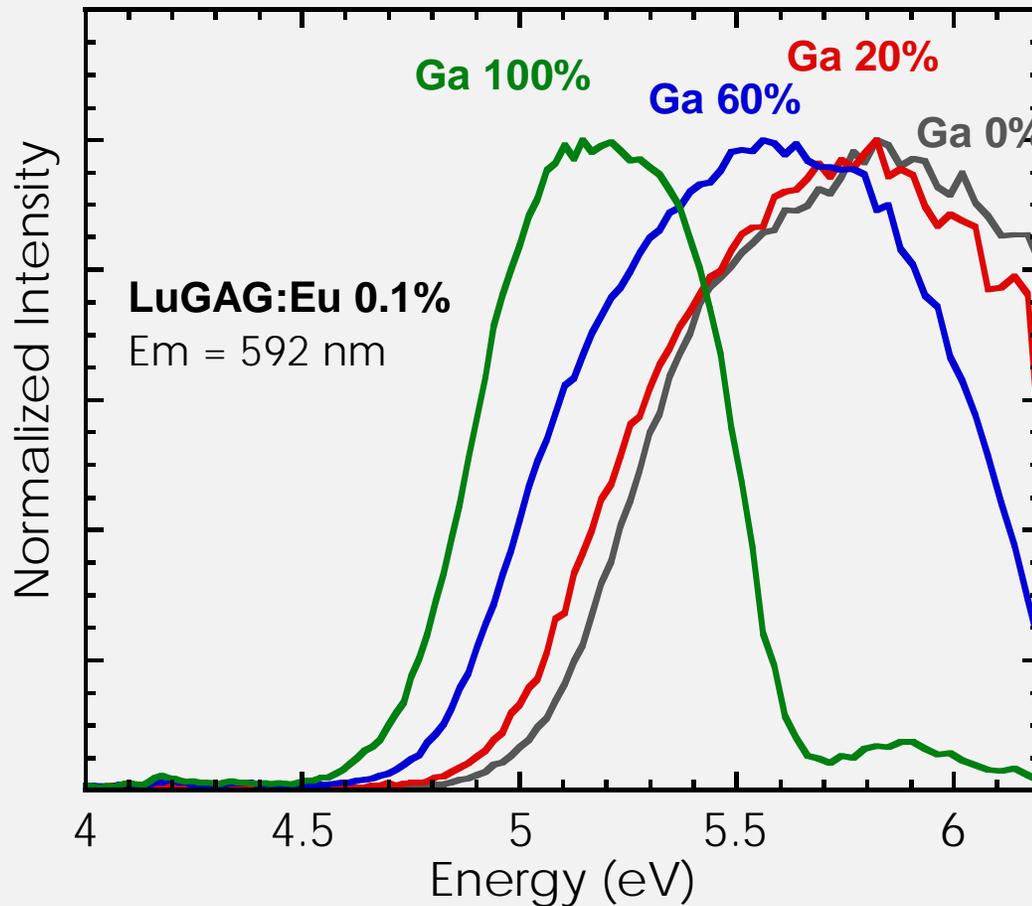
Thermal activation energy



Energy Shift

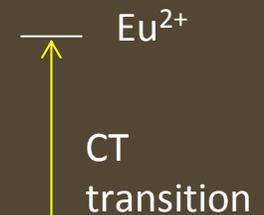


Charge transfer band (CT)



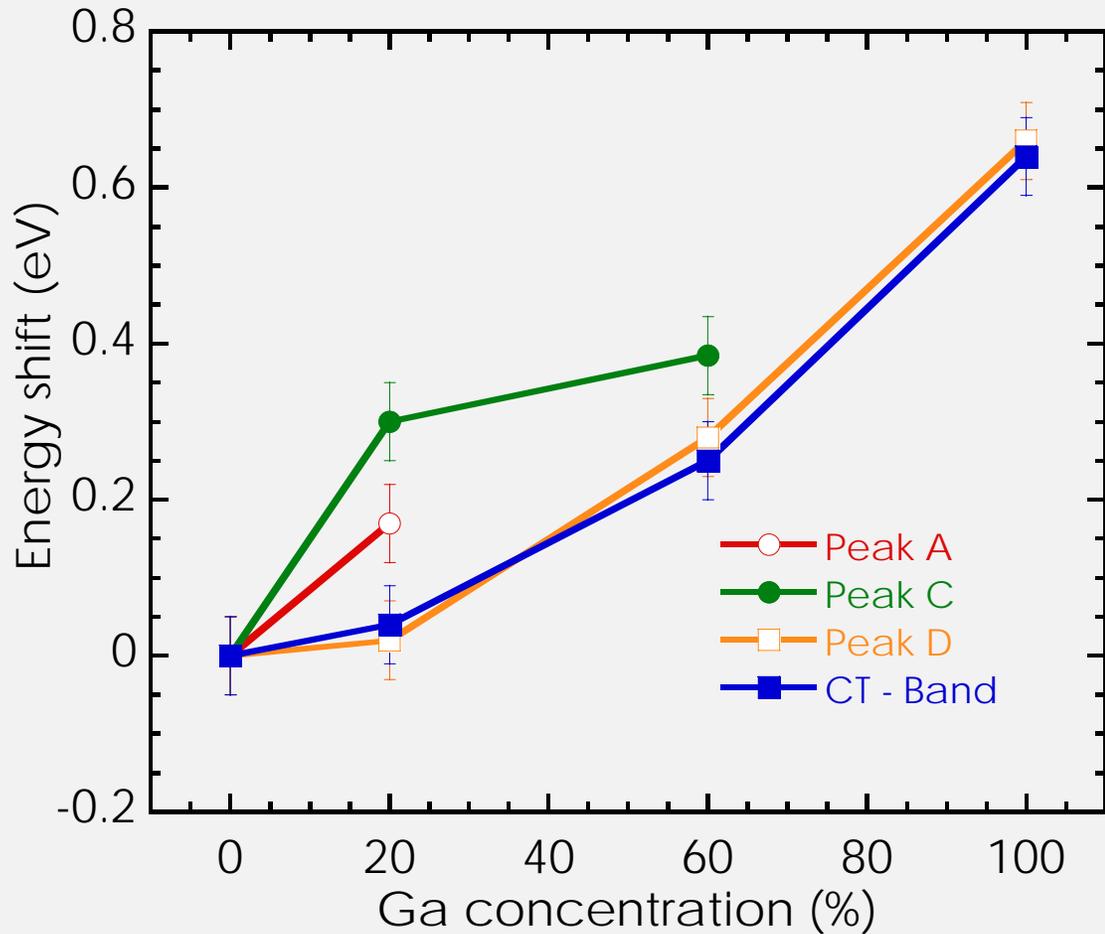
- The CT band allows the monitoring of the V.B. shift independent from TSL data.

C.B.



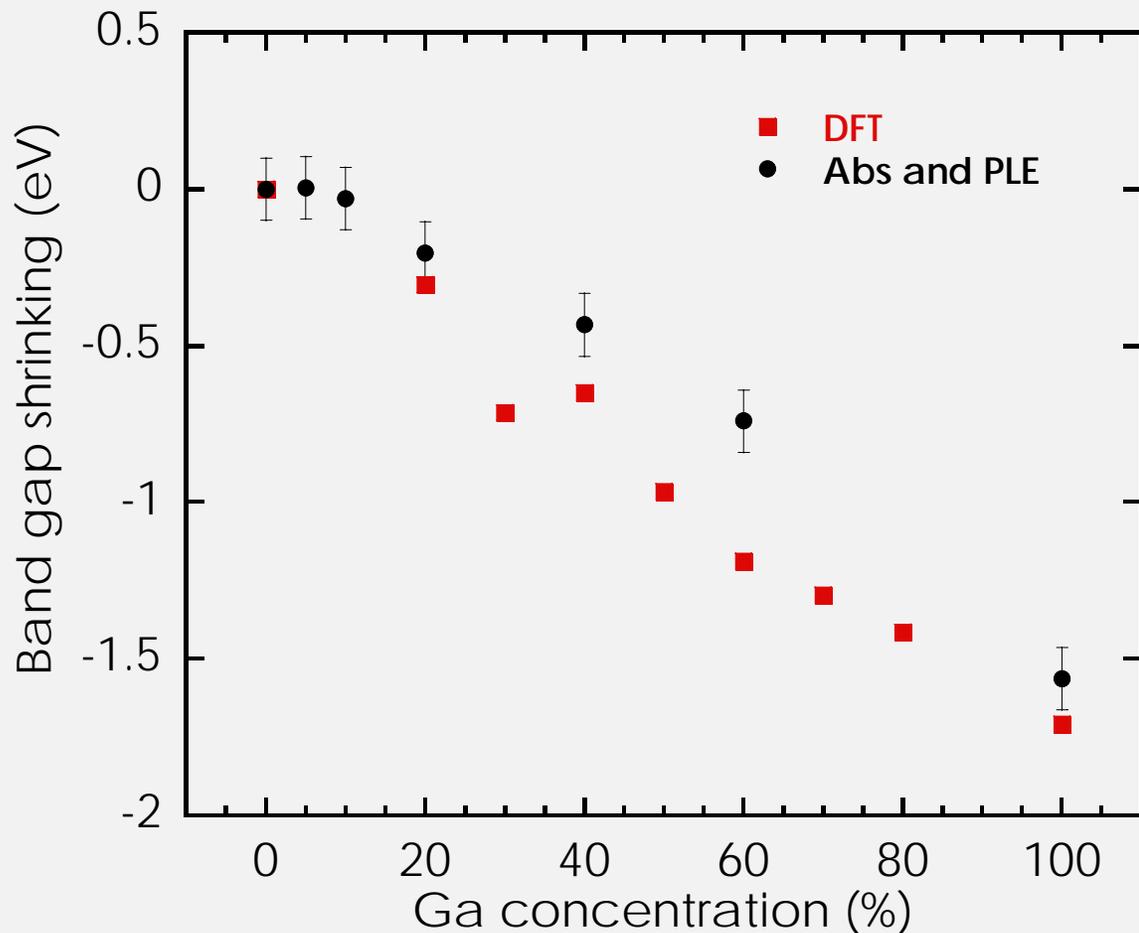
V.B.

CT band vs. TSL



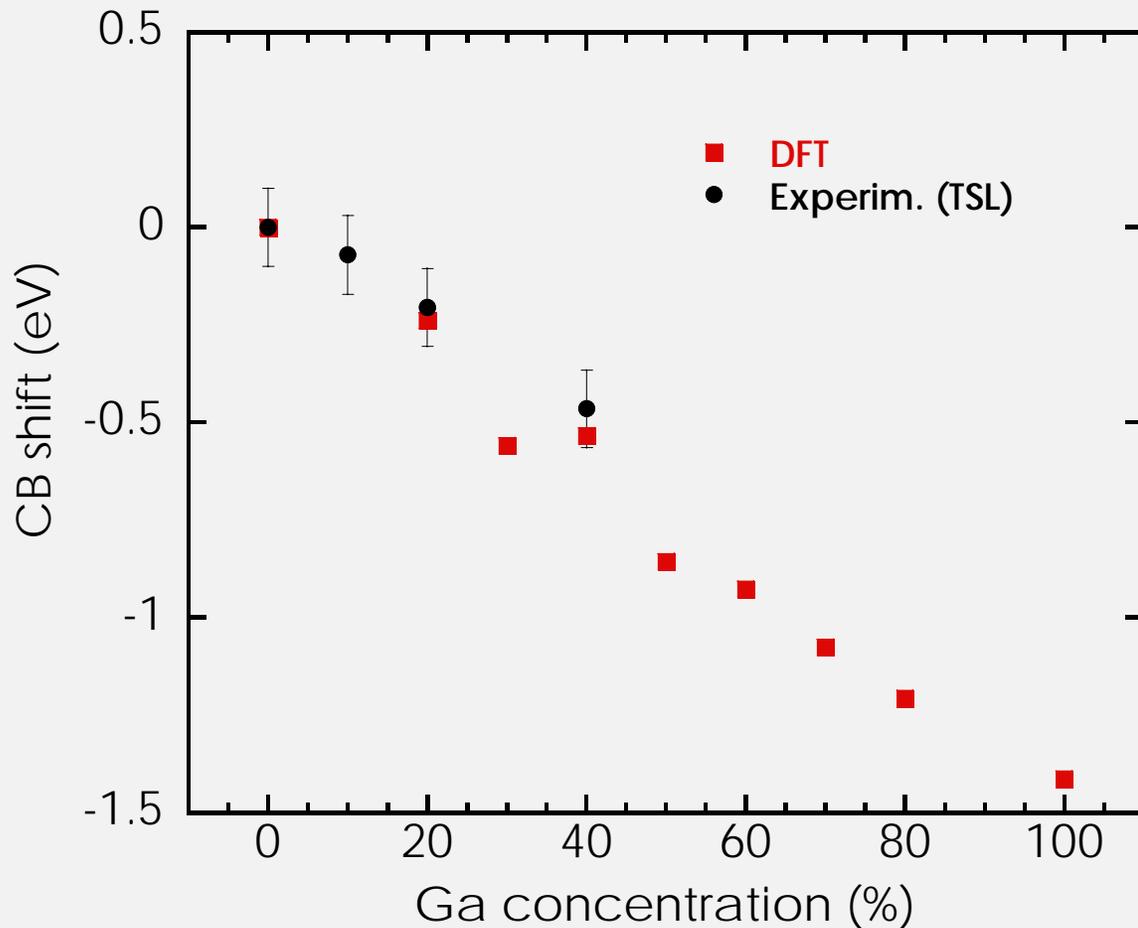
CT band shift is consistent with the V.B. shift evidenced by TSL data of peak D.

DFT vs Exper. - Band Gap



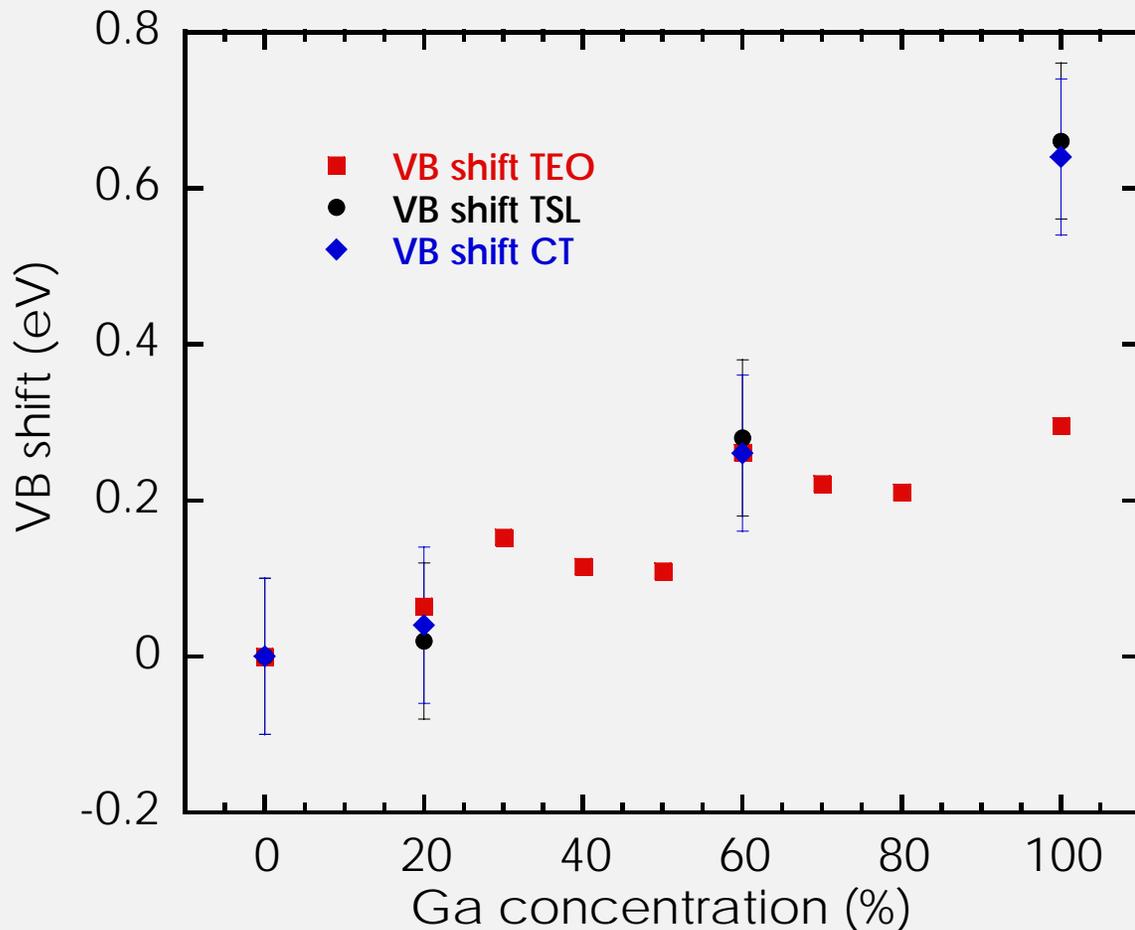
- DFT calculations, as expected, underestimate the band gap value (3.85 eV).
- The band gap shrinking is nevertheless reliable and in good agreement with the experimental data obtained from Absorption and photoluminescence excitation spectra.

CB shift DFT vs Experiment



- DFT calculations and TSL data are in agreement on the C.B. shift.

VB shift DFT vs Experiment



- DFT calculations and TSL data on the V.B. shift are slightly less consistent.
- DFT predicts a lower band shift than observed.

Conclusions

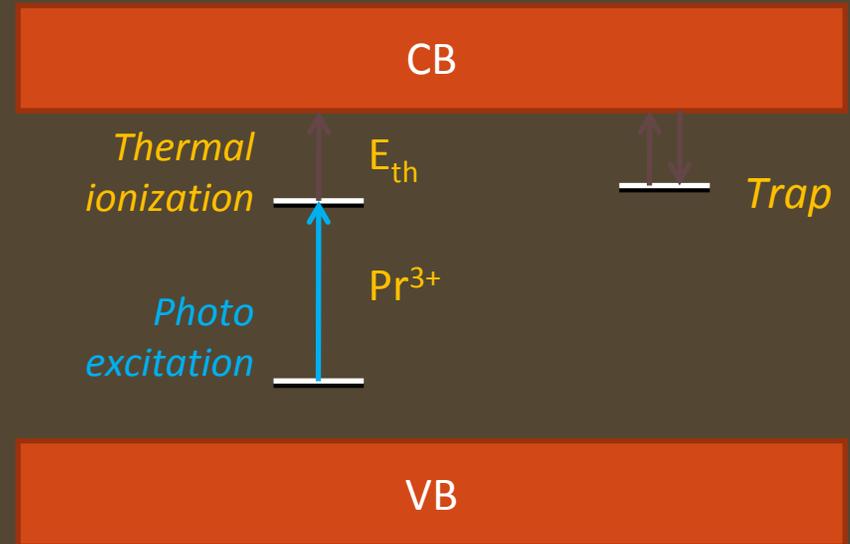
- Experimental data (Abs and PLE) evidence that Ga substitution in LuGAG induces a band gap shrinking of approximately 1.6 eV.
- TSL analyses (initial rise technique) show that the band gap shrinking is due to a shift of both the C.B. and V.B.
- Ab initio DFT calculations (VASP code) predict similar results showing a good quantitative agreement with the experimental data.

M. Fasoli, A. Vedda, M. Nikl, C. Jiang, B.P. Uberuaga, D.A. Andersson, K.J. McClellan, and C.R. Stanek, *“Band-gap engineering for removing shallow traps in rare-earth $\text{Lu}_3\text{Al}_5\text{O}_{12}$ garnet scintillators using Ga^{3+} doping”*, Phys. Rev. B 84, 081102(R) (2011).

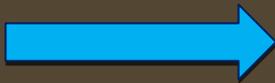
Evaluation of the lanthanide excited state thermal ionization barrier in luminescent materials

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.
- The thermal ionization energy barrier E_{th} can be evaluated by exploiting trapping states.



1. Thermally Stimulated Luminescence (**TSL**)
2. Delayed Recombination Temperature Dependence (**DRTD**)



Exploiting stable TSL peaks

- If we excite, at a given temperature, Pr^{3+} in the $4f-5d_1$ absorption band, the **fraction** of electrons thermally promoted to the CB is:



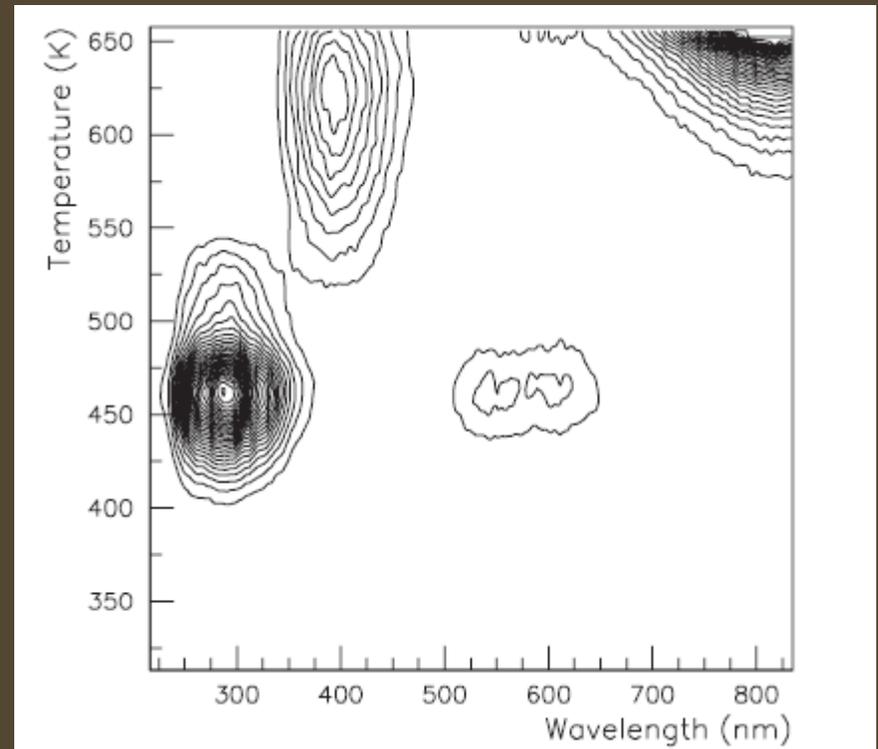
$$e^{-\frac{E_{th}}{k_b T}}$$

Excitation: 240 nm (5 nm b.p.)
Temperature range: 283-353 K

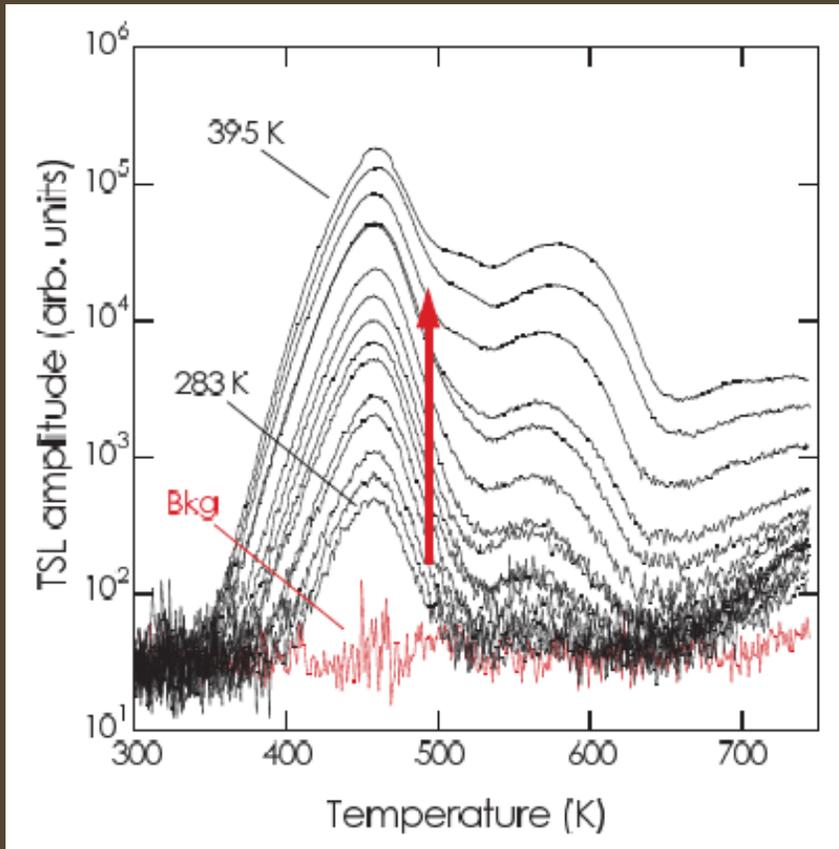
- The fraction of ionized electrons trapped in a **stable** defect can be evaluated from the **TSL glow curve**.
- By plotting the TSL peak intensity as a function of the illumination temperature the value of the thermal ionization barrier E_{th} can be evaluated.
- If no TSL peak is stable in a convenient temperature range we are forced to deal with unstable traps.



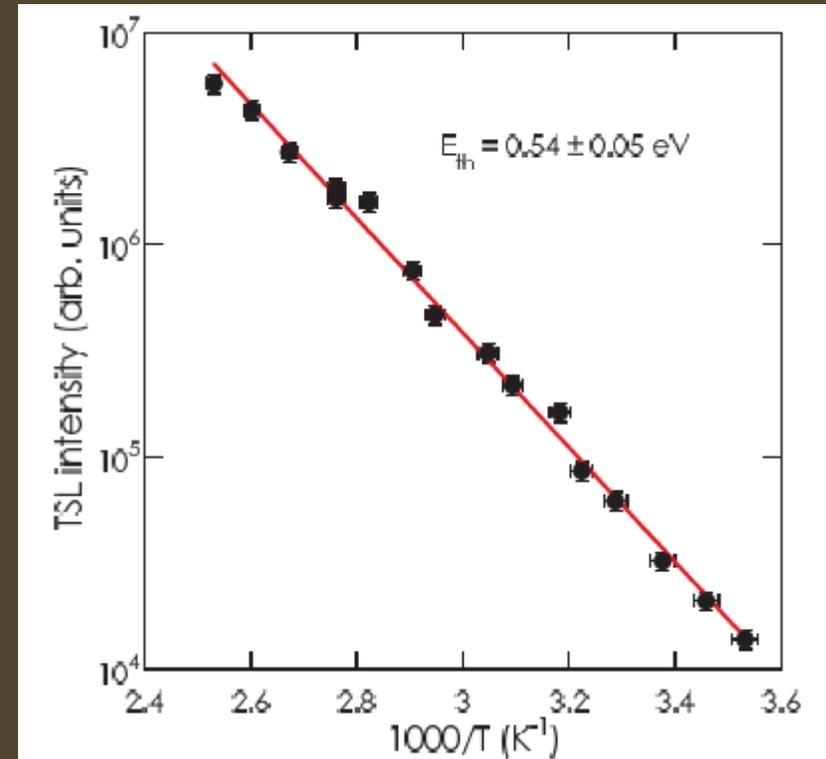
Delayed recombination



Results



TSL glow curves of LPS:0.5mol%Pr after light illumination (240 nm, $630 \mu\text{W}/\text{cm}^2$) at different temperatures. The arrow indicates temperature increasing.



Arrhenius plot of the integrals obtained from the glow curves of Fig. 1 from 430 and 490 K after subtracting the background signal.

Conclusions

The method can be applied also on powder materials and thin films.

It exploits the TSL glow curves to evaluate the fraction of electrons thermally ionized.

- Needs a stable TSL peak
- Fast and simple
- No correction required for the dependence of quantum efficiency of the recombination center upon temperature

M. Fasoli, A. Vedda, E. Mihokova, and M. Nikl, "*Optical methods for the evaluation of lanthanide excited state thermal ionization barrier in luminescent materials*", Phys. Rev. B 85, 085127 (2012).