

Characterization of defects in scintillators

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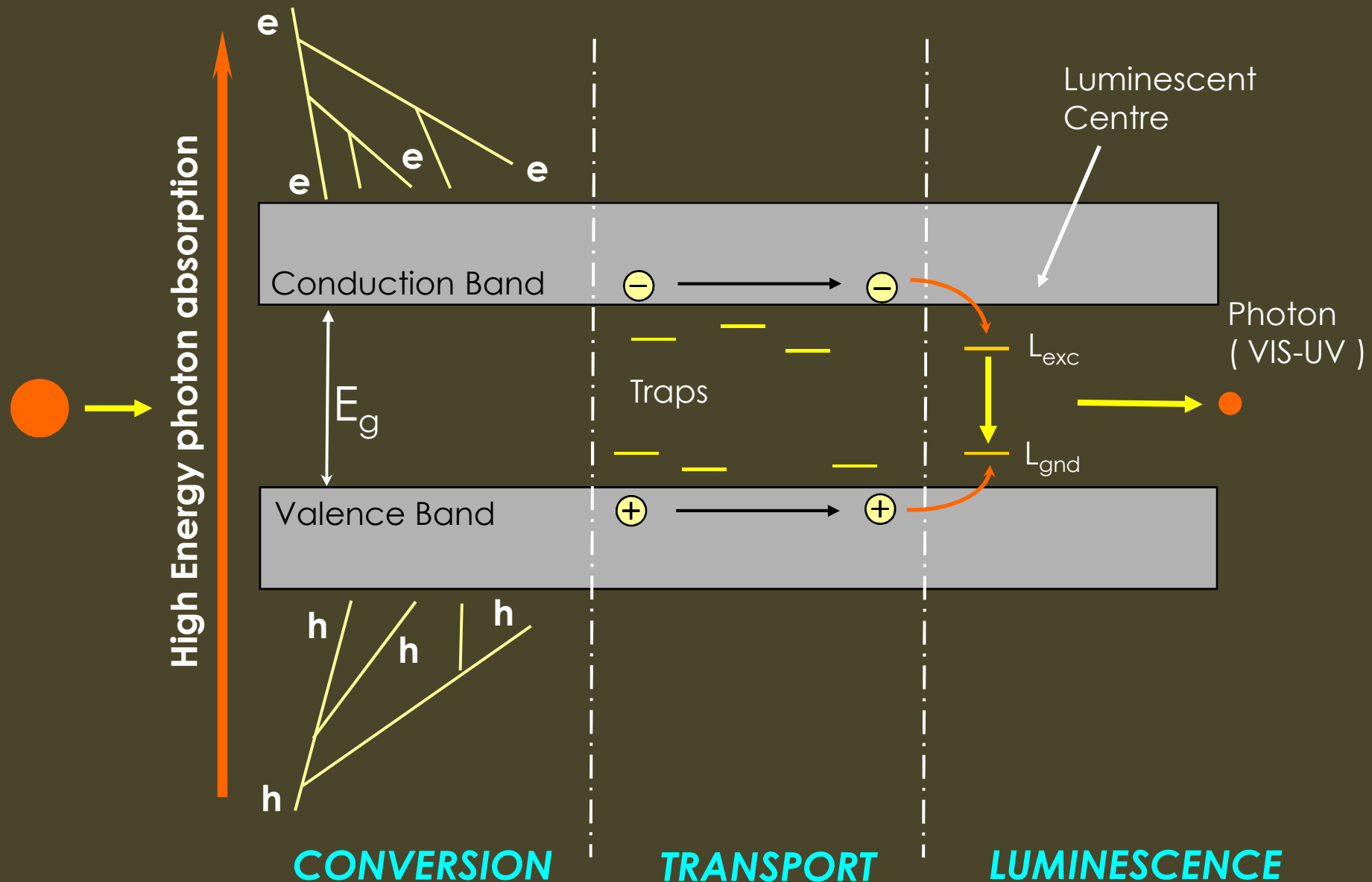
ASCIMAT Summer School, September 13, 2016



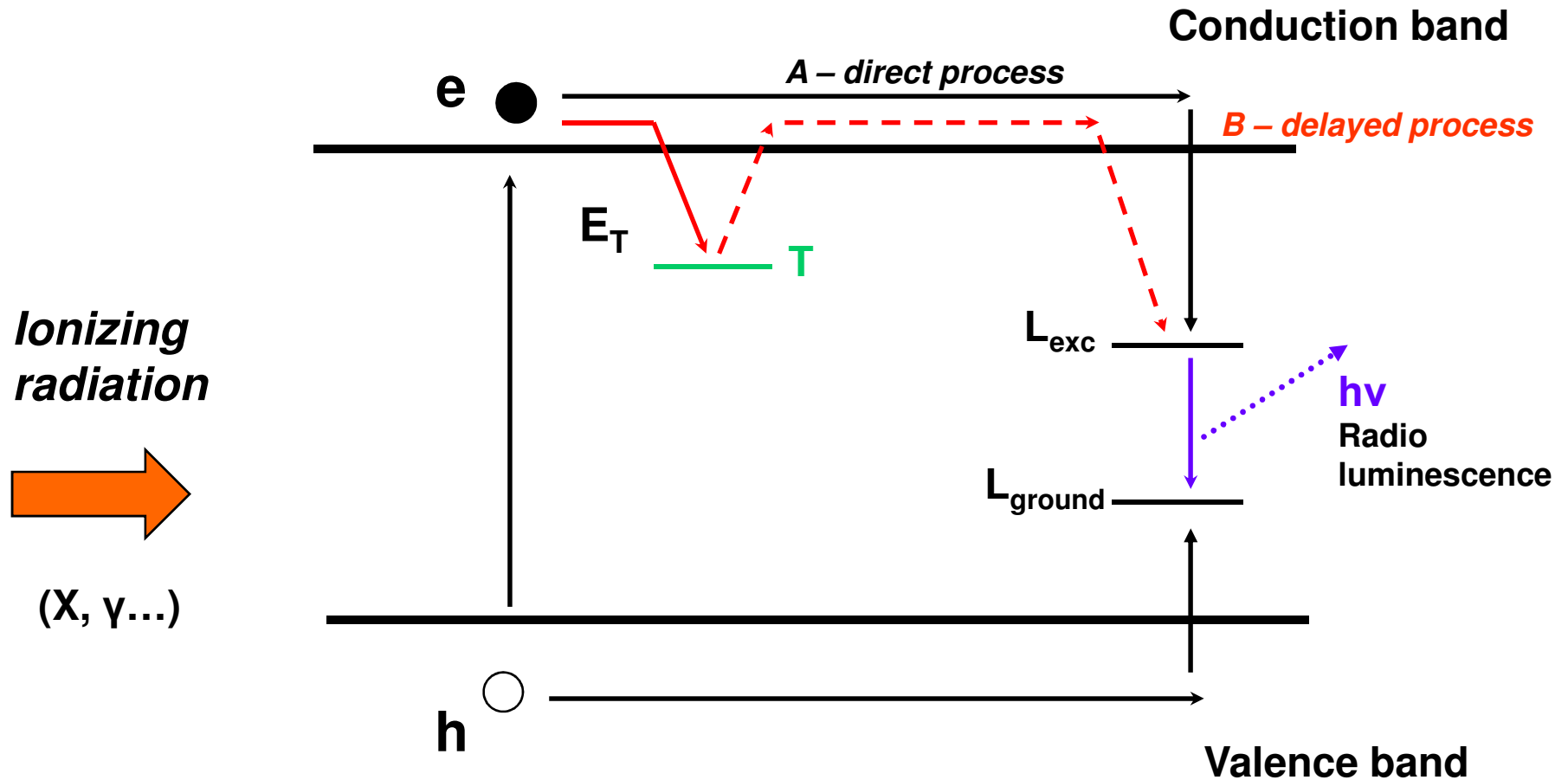
Outline

- Trapping processes during ionizing irradiation
- De-trapping and e-h recombinations
- Thermoluminescence (TSL)
- Wavelength resolved TSL measurements
- TSL equations
- Data analysis: initial rise, curve fitting
- Prediction of RT trap lifetimes
- Examples: silicates and garnets

Scintillation: *Physical processes*



TRAPPING-DETRAPPING PROCESSES: case of electron traps



Mean time spent in the trap = $\tau = C \exp(E_T/kT)$

According to the E_T value (typically from 10^{-2} up to 10^0 eV) a very wide range of τ can be measured (of even less than $1 \mu s$ up to thousands years)

Detrapping of carriers at
constant temperature

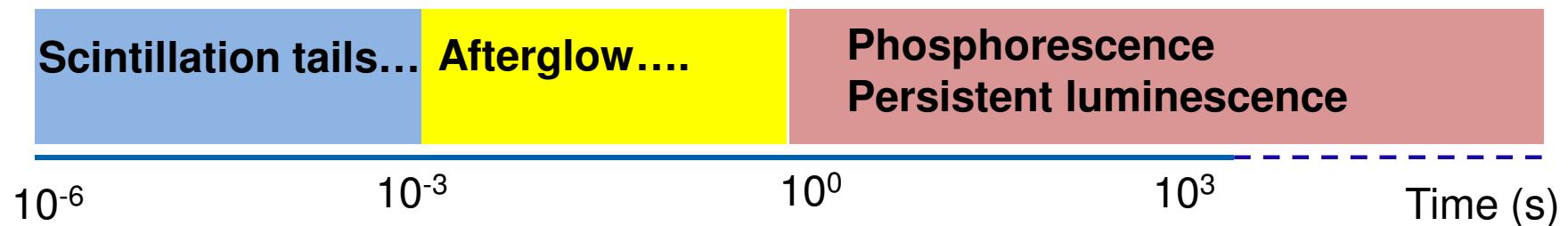
Scintillation slow tails, Afterglow, Phosphorescence, or Persistent Luminescence – several names to indicate the same class of phenomena: the emission of light following carrier detrapping from defects at constant temperature

Scintillation tails: typically μs – ms time scale **scintillator community**

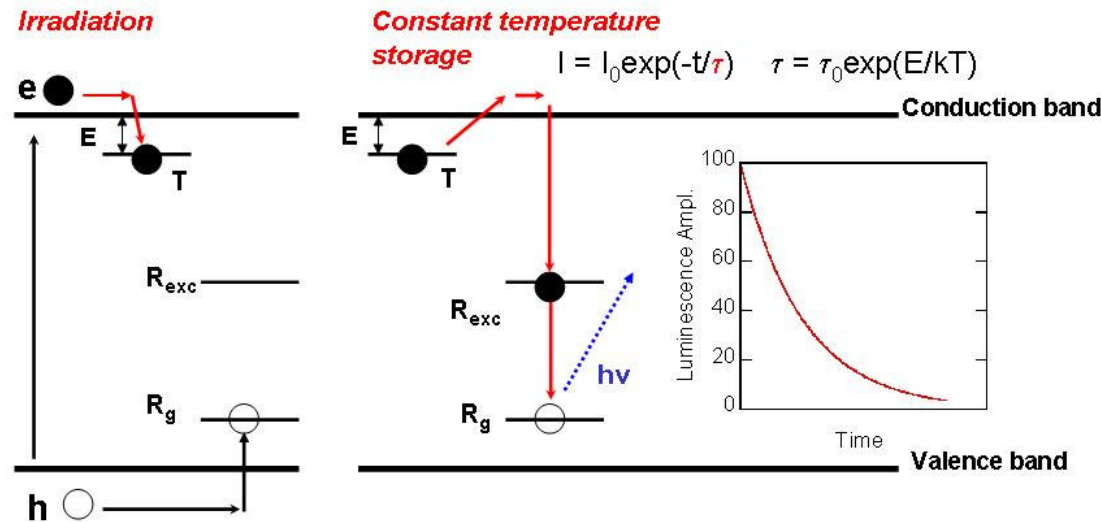
Afterglow: ms - s time scale **scintillator community**

Phosphorescence: s – min – hours - **Radiation dosimetry or spectroscopists communities**

Persistent luminescence: s – min – hours - **Persistent phosphors or spectroscopists communities**



Thermal detrapping process through conduction band



Detrapping probability

$$P_T = \nu \times \exp(-E_T / kT) = \frac{1}{\tau_T}$$

τ_T = phosphorescence decay time

$$N_T(t) = N_0 \exp(-P_T t)$$

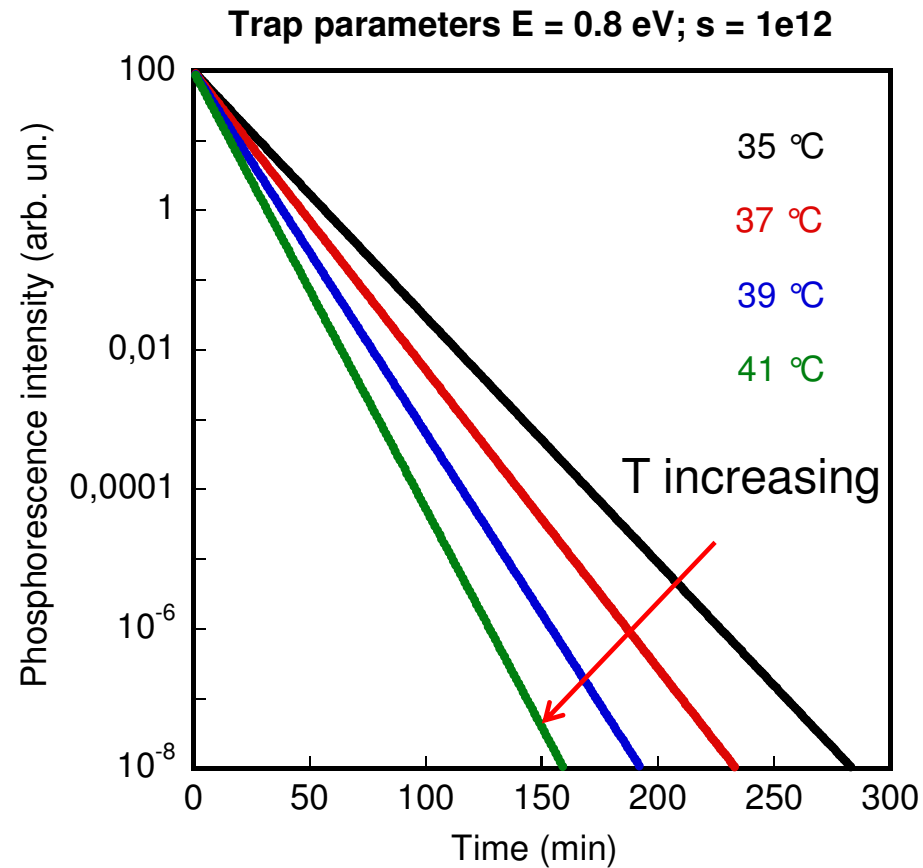
Considering only capture of electrons at luminescent centers and fast radiative decay from their excited state:

$$I(t) \div \frac{dN_e}{dt} \div \frac{dN_T}{dt} = C \cdot A_R N_0 \exp(-P_T t) = I_0 \exp(-t / \tau_T)$$

With N_T = number of electrons in the trap; N_0 is the number of traps initially filled by irradiation; $I(t)$ is the phosphorescence amplitude.

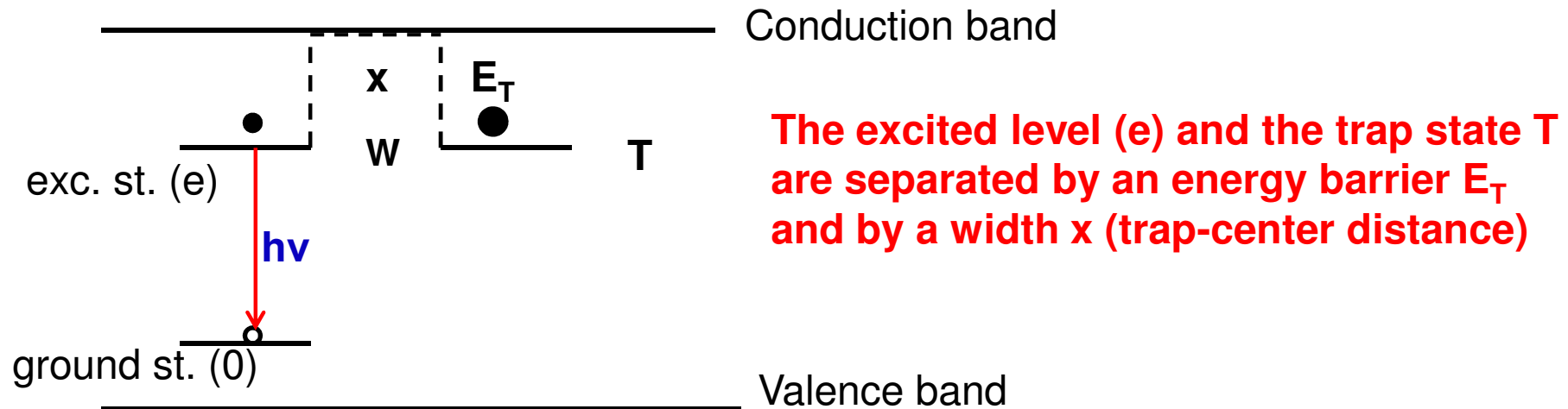
Exponential decay - faster by temperature increasing

$$I(t) \div \frac{dN_T}{dt} = C \cdot A_R N_0 \exp(-P_T t) = I_0 \exp(-t / \tau_T)$$



Strong temperature dependence of the signal in case of thermally activated traps

Phosphorescence due to athermal tunneling between a trap and a luminescent center



The filling (e.g. by x-rays) of the trap state causes also simultaneous population of the excited state of the luminescent center thanks to a tunneling probability of barrier penetration

The populations of the two states are linked by tunneling probability which, for a rectangular barrier, is

$$W = \frac{|A_e|^2}{|A_T|^2} = \exp(-kx) \quad k = \frac{4\pi\sqrt{2mE_T}}{h}$$

A_T and A_e are the amplitudes of electrons wave functions in the trap and in the excited level of the center respectively.

$N(t) = N_e(t) + N_T(t)$ are all excited electrons

$$N_e(t) = W \cdot N(t), N_T(t) = (1 - W) \cdot N(t), W < 1$$

We can write the usual decay law $\frac{dN(t)}{dt} = \frac{dN_e(t)}{dt} = -A_R N_e(t) = -A_R W N(t)$

and for the phosphorescence intensity we obtain:

$$I \div \frac{dN}{dt} = C \times A_R \times N_0 \exp(-A_R W t)$$

The decay time of phosphorescence is therefore: $\tau = \frac{1}{A_R W}$

Exponential decay, temperature independent, but strongly dependent on barrier configuration. The radiative decay time can be increased by several orders of magnitude.

If there is a continuous distribution of trap-center distances (a usual situation), all phosphorescence contributions from pairs at different distances must be summed (remember that $W=W(x)$). It can be demonstrated that in this case, after an initial transient time, the decay follows a $1/t$ law. P. Avouris and T. N. Morgan, J. Chem. Phys. 74, 4347 (1981)

$$I(t) = \frac{1}{C + t}$$

Spatial correlation between defects and luminescent centers

✓ It can occur due to the need of local charge compensation, or for the presence of slight lattice distortions induced by a different ionic radius of the luminescent species with respect to lattice constituents.

✓ How to evidence it? (TSL, afterglow)

✓ Which is its influence on scintillation properties? (Strong competition in free carrier capture?)

Several definitions, sometimes used as synonyms, but presenting slight physical differences

Trap-center recombinations, or localized transitions, or:

✓ **Recombination within a defect cluster** – the electron and the hole are trapped within the same complex defect. Low probability of alternative recombination paths through the conduction or valence bands.

✓ **Tunneling recombination (a-thermal or thermally assisted)** – trap and luminescent center are thought as closely lying but distinct defects, with states at similar energy levels in the band gap. Alternative and competitive recombination paths through the conduction or valence bands are also possible.

✓ **Anomalous fading** (in retrospective dosimetry and geochronology) – fading of a TSL peak independent from temperature.

Common characteristics in TSL: first order kinetics of the peaks, presence of only one recombination center. Absence of thermally stimulated currents.

Recombination within defect clusters

PHYSICAL REVIEW B

VOLUME 57, NUMBER 1

1 JANUARY 1998-I

Low-temperature thermoluminescence spectra of rare-earth-doped lanthanum fluoride

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JOURNAL OF APPLIED PHYSICS

VOLUME 88, NUMBER 11

1 DECEMBER 2000

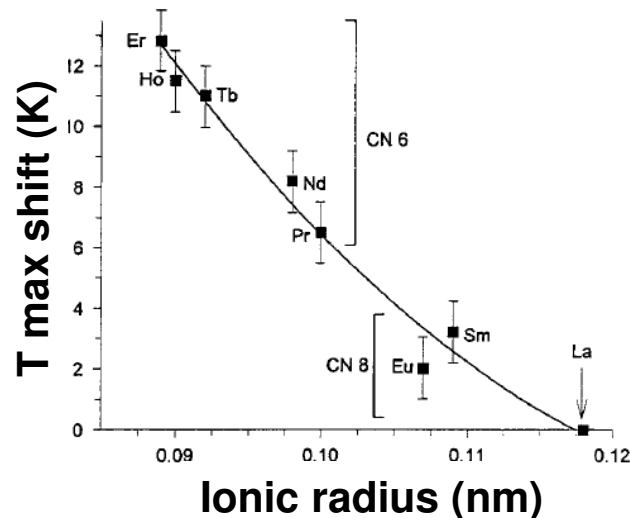
Patterns of glow peak movement in rare earth doped lanthanum fluoride

B. Yang

School of Engineering and Information Technology, Pevensey Building, University of Sussex, Brighton BN1 9QH, United Kingdom, and Department of Physics, Beijing Normal University, Beijing 100875, China

P. D. Townsend^{a)}

School of Engineering and Information Technology, Pevensey Building, University of Sussex, Brighton BN1 9QH, United Kingdom



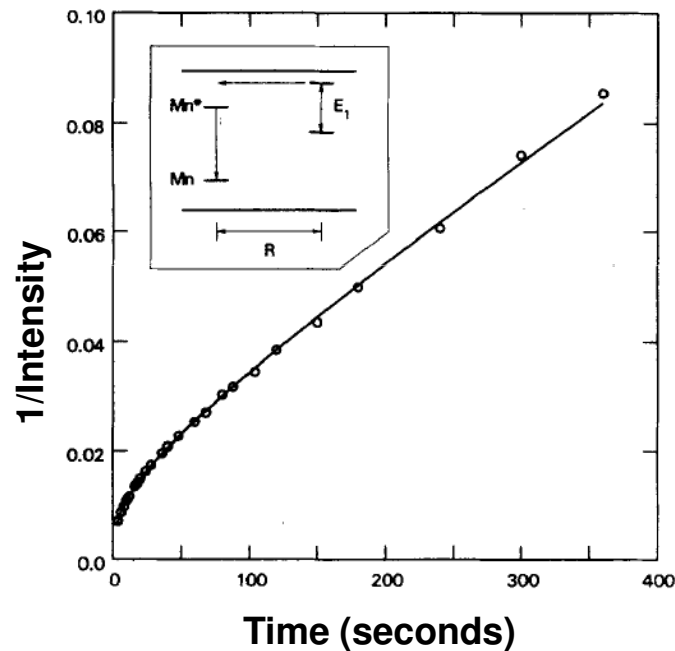
Shifts of the glow peak temperature with different RE ions dopings are a sign of the presence of defect clusters containing both the trap and the recombination center (the RE)

Tunneling recombination

A tunneling model for the decay of luminescence in inorganic phosphors: The case of $\text{Zn}_2\text{SiO}_4\text{:Mn}$

Phaedon Avouris and T. N. Morgan

J. Chem. Phys. **74**(8), 15 Apr. 1981



The t^{-1} decay law of the afterglow indicates a-thermal radiative recombinations between carriers in traps and in luminescent centers

phys. stat. sol. (a) **35**, 315 (1976)

Subject classification: 20.3; 10.2; 22.8.1

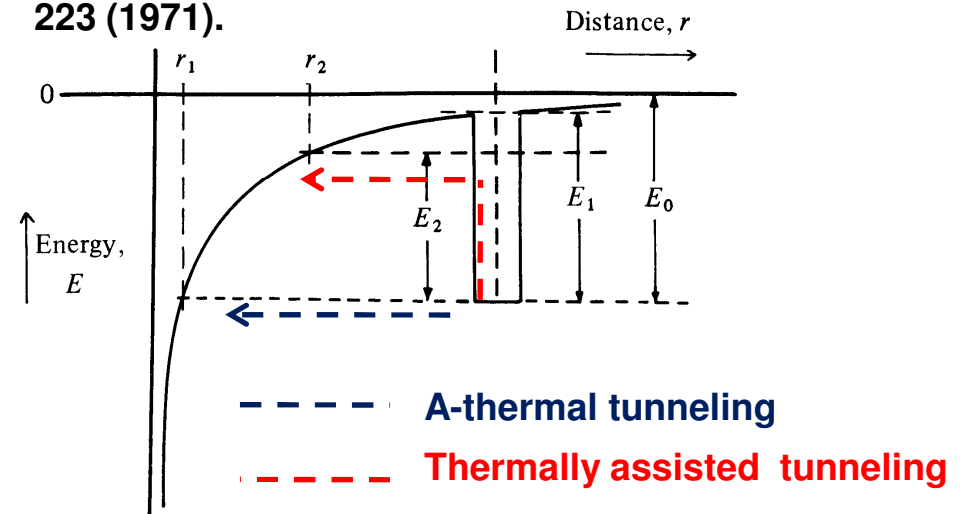
Laboratoire de Luminescence II ¹⁾ (a) ²⁾
and Laboratoire de Minéralogie-Cristallographie ¹⁾ (b) ³⁾,
Université P. et M. Curie, Paris

Tunneling Processes in Afterglow of Calcite

By

R. VISOCEKAS (a), T. CEVA (a), C. MARTI (a), F. LEFAUCHEUX (b),
and M. C. ROBERT (b)

In S.W.S. Mc Keever,
"Thermoluminescence of Solids". Adapted
from A.I. Mikhailov, Dokl. Phys. Chem. **197**,
223 (1971).



Anomalous fading

IOP PUBLISHING

J. Phys. D: Appl. Phys. **41** (2008) 225502 (15pp)

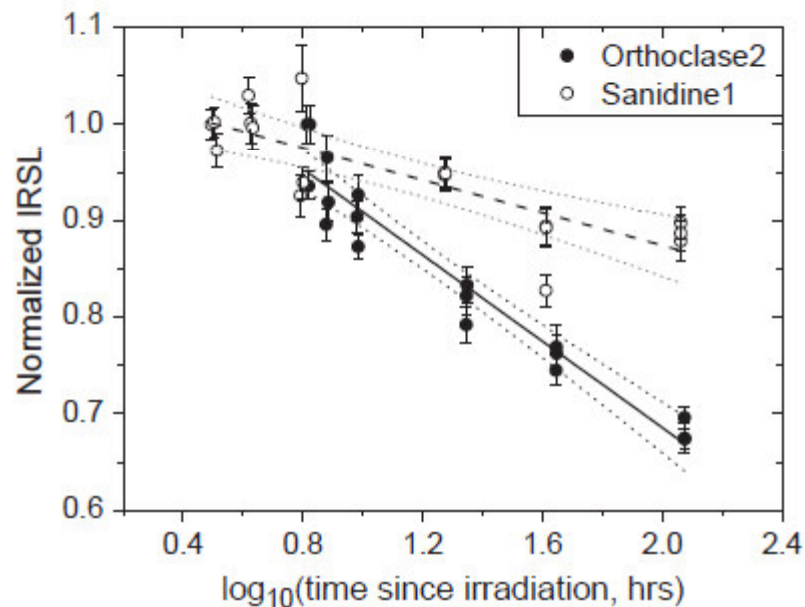
JOURNAL OF PHYSICS D: APPLIED PHYSICS

doi:10.1088/0022-3727/41/22/225502

Investigations of the dose-dependent anomalous fading rate of feldspar from sediments

Bo Li¹ and Sheng-Hua Li

Department of Earth Sciences, The University of Hong Kong, Pokfulam Road, Hong Kong, People's Republic of China



Journal of Luminescence **143** (2013) 704–709

Dependence of (anomalous) fading of infra-red stimulated luminescence on trap occupancy in feldspars

P. Morthekai^{a,*}, Mayank Jain^a, Grzegorz Gach^b, Dennis R. Elema^a, Henrik Prip^a

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^b AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Krakow, Poland

The occurrence of anomalous fading of traps in feldspars affects their use in optically stimulated luminescence (OSL) for retrospective dosimetry and Quaternary geochronology.

An application for which tunneling is foreseen: long persistent phosphors

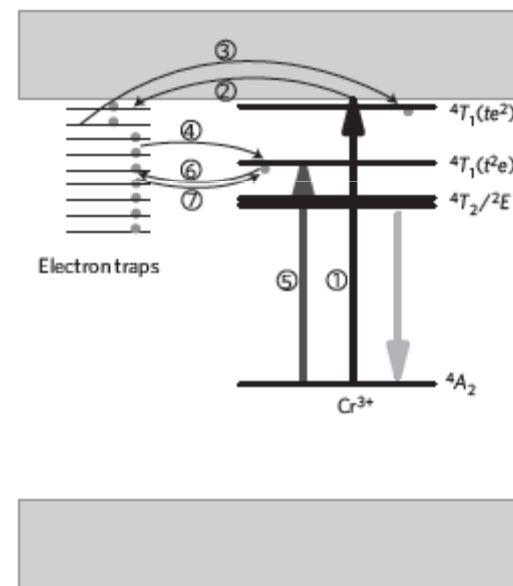
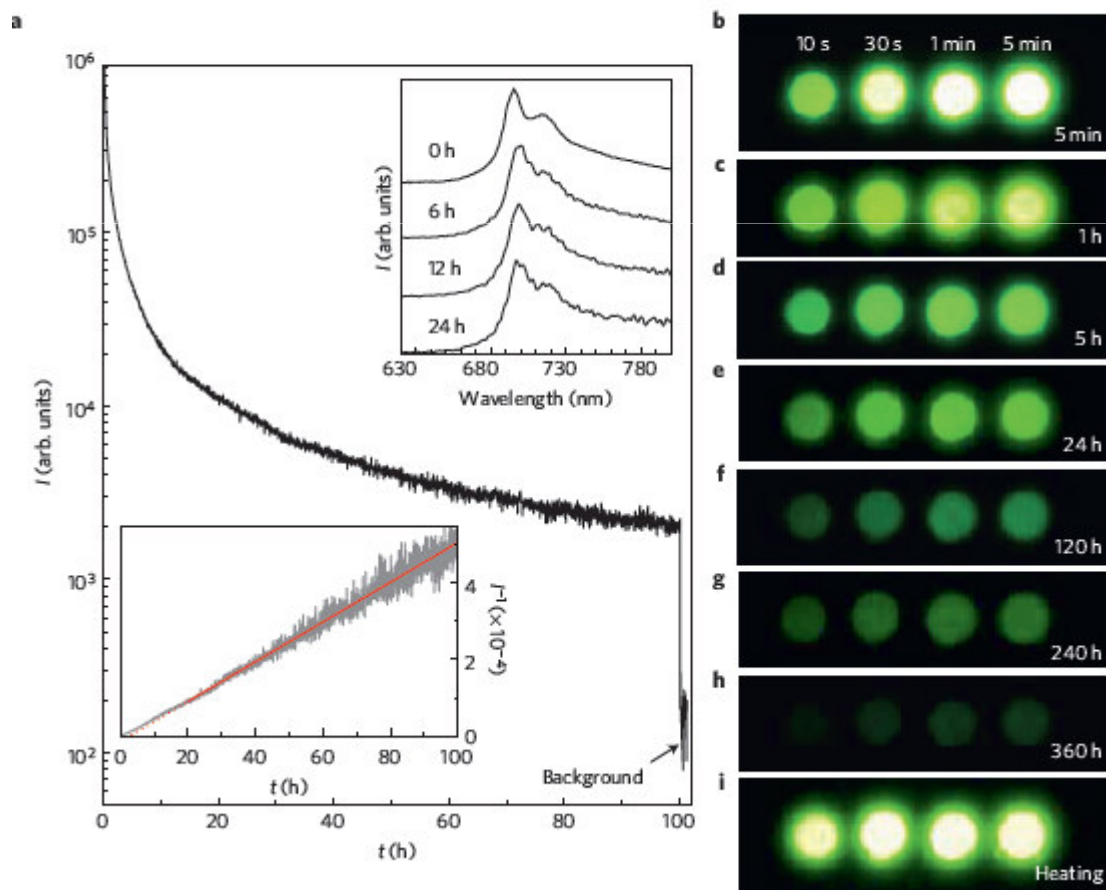
ARTICLES

PUBLISHED ONLINE: 20 NOVEMBER 2011 | DOI: 10.1038/NMAT3173

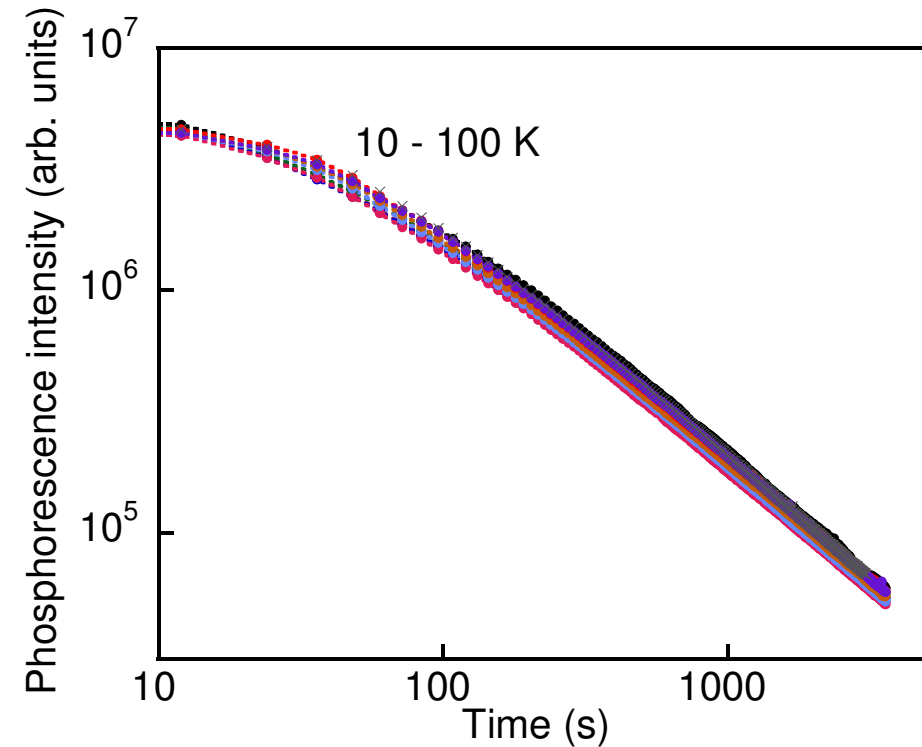
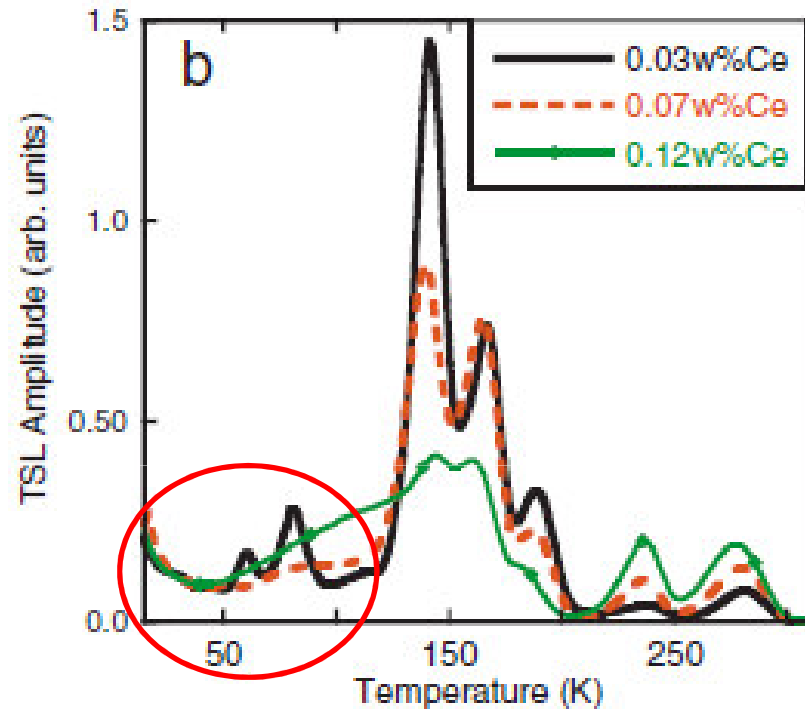
nature
materials

Sunlight-activated long-persistent luminescence in the near-infrared from Cr^{3+} -doped zinc gallogermanates

Zhengwei Pan^{1,2*}, Yi-Ying Lu¹ and Feng Liu^{1,2}

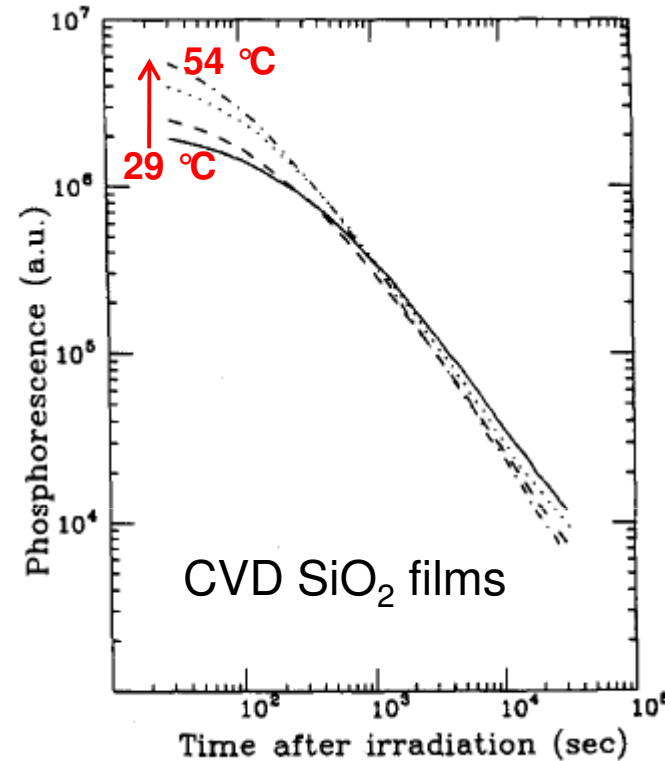
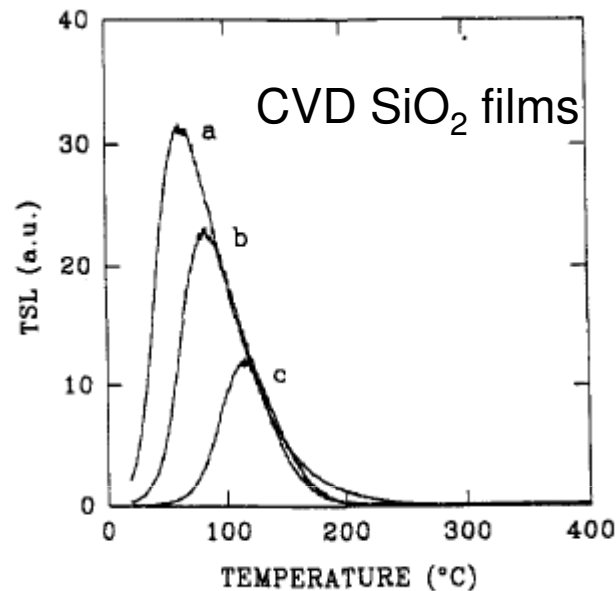


Case of LuAG:Ce – Athermal tunneling



Athermal decay of phosphorescence signal

Disordered materials: phosphorescence decay due to a continuous distribution of trap levels (energies)



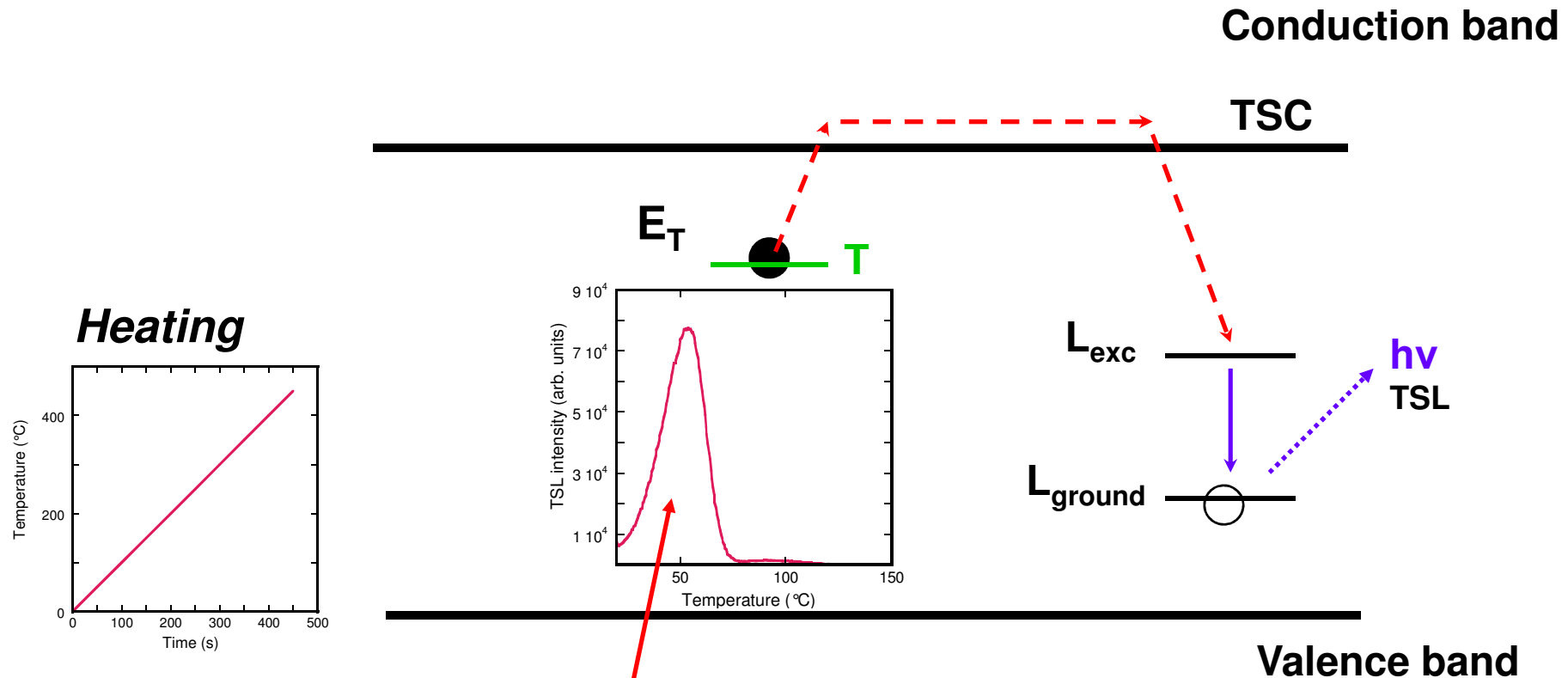
Solid State Comm. 91, 751 (1994)

A t^{-1} decay is observed if the signal originates from carrier detrapping from a continuous distribution of traps related to inhomogeneous broadening (the superposition of many close exponential components gives rise to the t^{-1} decay). It is *nearly* temperature independent (temperature dependence is limited to the initial part of the decay)

Investigation of traps by thermal
stimulation

Thermally stimulated luminescence

TRAP INVESTIGATION TSL-TSC process — (electron traps)



TSL signal measured by a **photomultiplier**, no information about the recombination centre

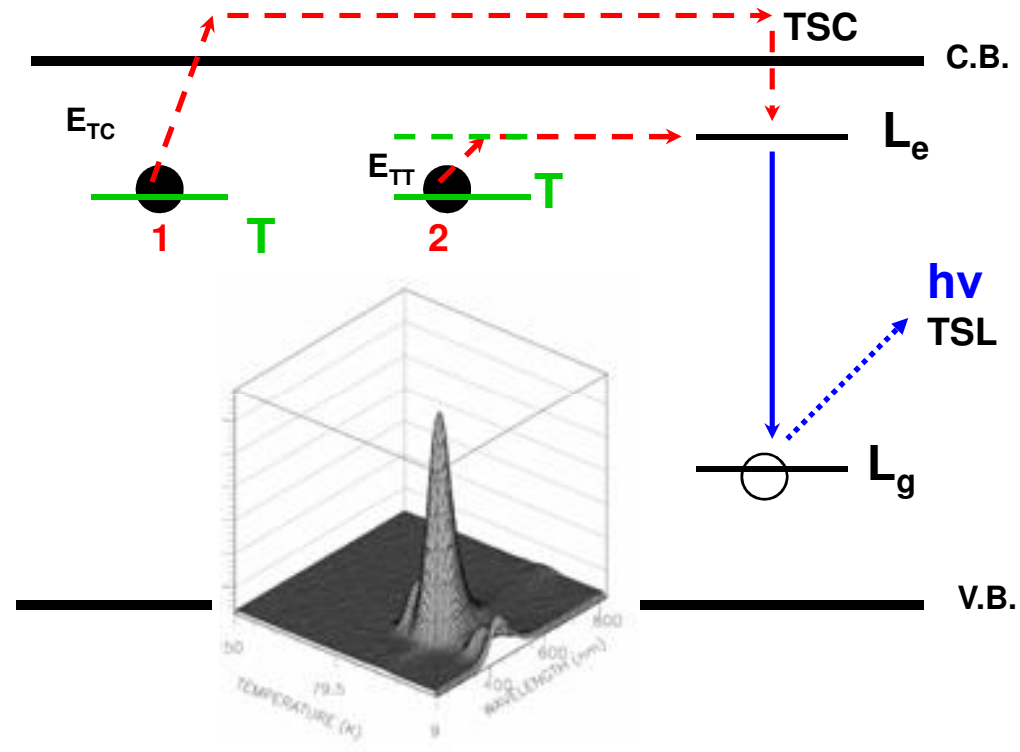
Probability of escape from trap: $P = K \exp(-E_T/kT)$

P increases very strongly with temperature

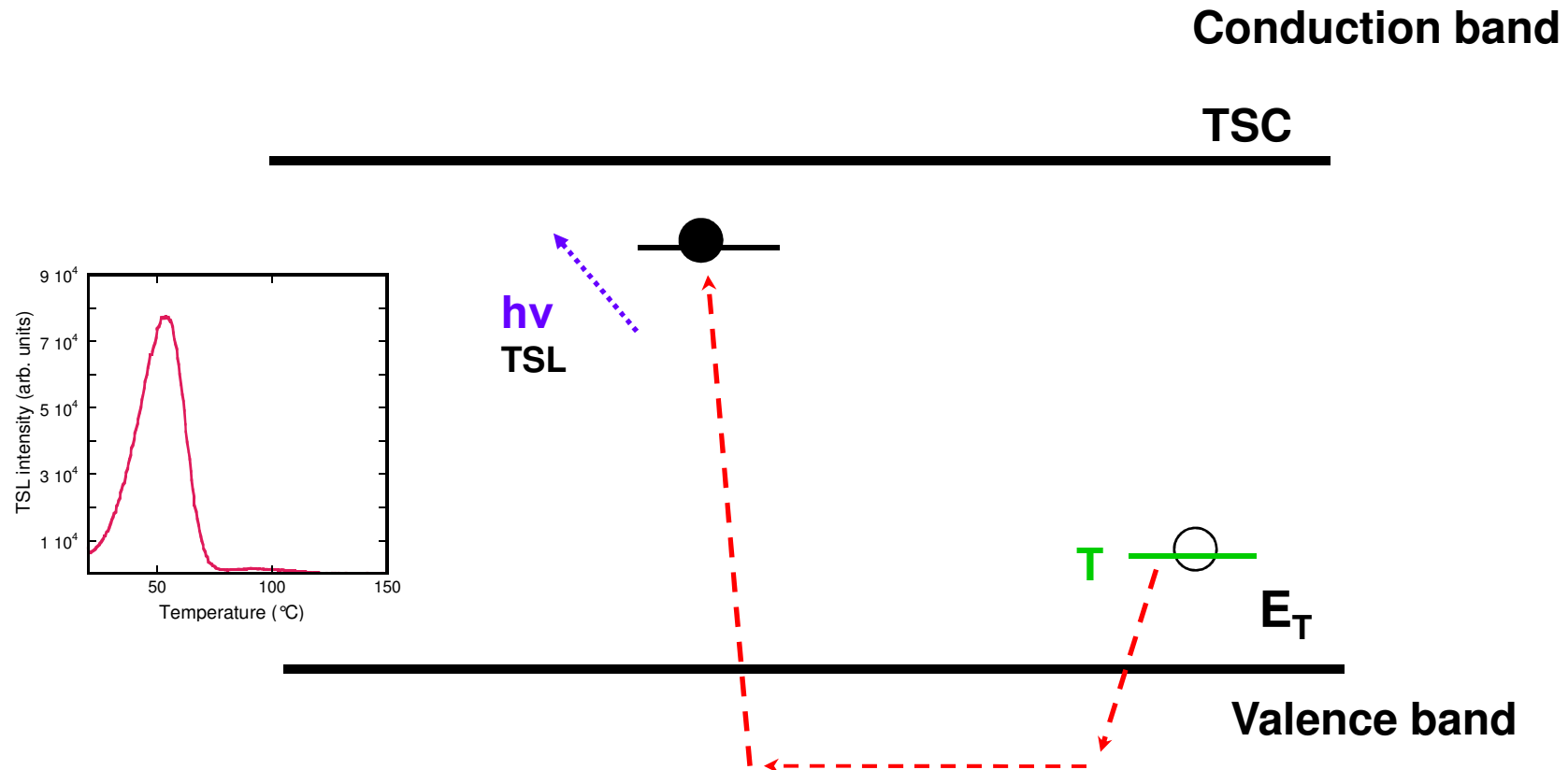
A **luminescence peak** appears (thermally stimulated luminescence)

Thermoluminescence - Different kinds of recombination paths

1. Classical recombination through conduction band
2. Thermally assisted tunneling (trap-centre recombination)



Case of hole traps



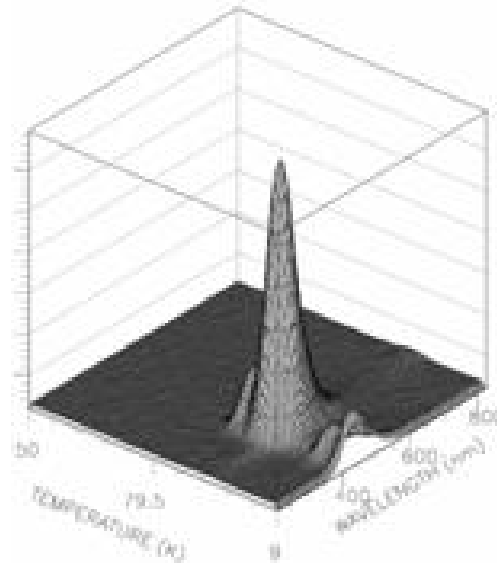
It is not possible to determine from a simple glow curve whether electron or holes are detrapped during heating

In a TSL process, the name “**trap**” is attributed to the defect from which carriers are freed by heating

The name “**recombination centre**” is attributed to the defect in which carriers are stably trapped, and in which carriers of opposite sign recombine radiatively

The same defects can act as traps or recombination centres in different temperature intervals

Wavelength resolved TSL measurements



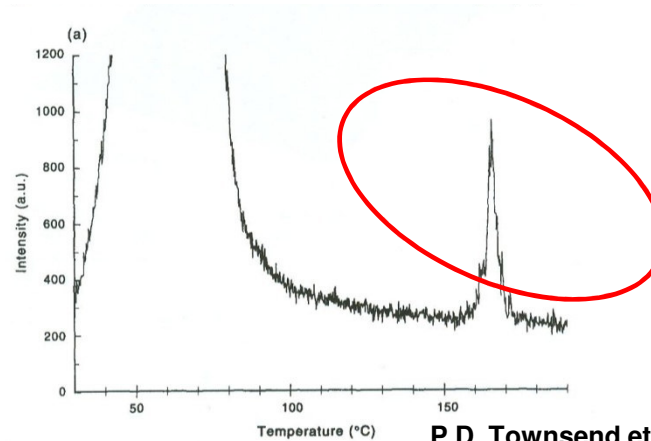
A wavelength resolved TSL measurement consists in a collection of emission spectra measured at constant temperature intervals (for example 1 K). Usually spectra are measured by a CCD.

Study of both traps and recombination centers

link to photo-, radio- luminescence, and scintillation

TSL glow curves can also be sensitive to phase transitions

Example of Ammonium Bromide (NH_4Br)



P.D. Townsend et al., Rad. Meas. 27, 31 (1997)

- ❖ Modifications of trap depths
- ❖ Increased effects in case of localized trap-centre recombinations
- ❖ Possibility to monitor temperature lags between heater and sample, which are a common error source in TSL measurements

DATA ANALYSIS

Evaluation of trap depth (E), frequency factor (s), and of room temperature trap lifetime (τ)

$$\tau = (1/s) \exp(E_T/kT)$$

To predict the role of a trap in the scintillation process

TSL equations

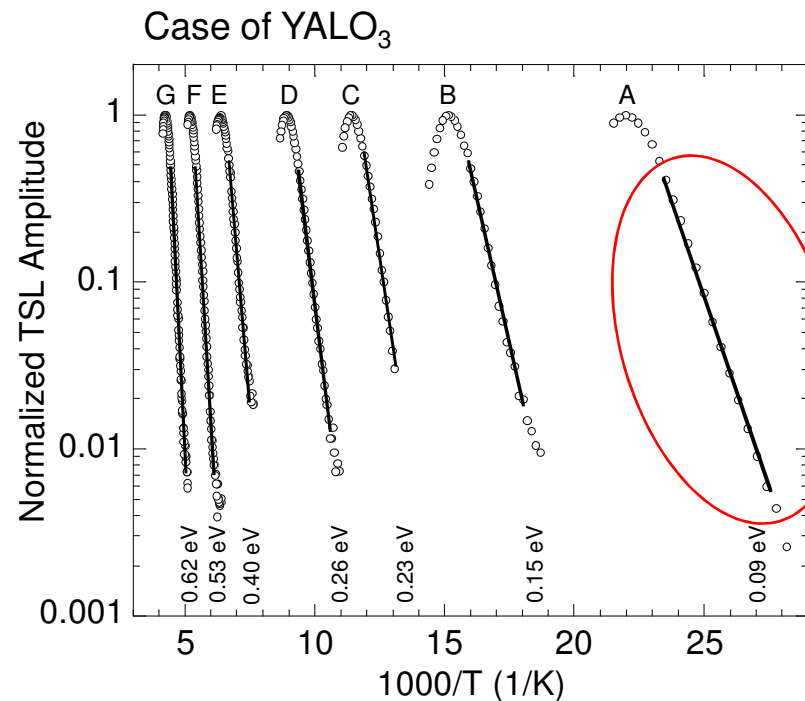
$$I(T) = sn_0 \exp(-E_T / kT) \exp \left[-\frac{s}{\beta} \int_{T_0}^T \exp(-E_T / kT') dT' \right]$$

First order recombination: no retrapping

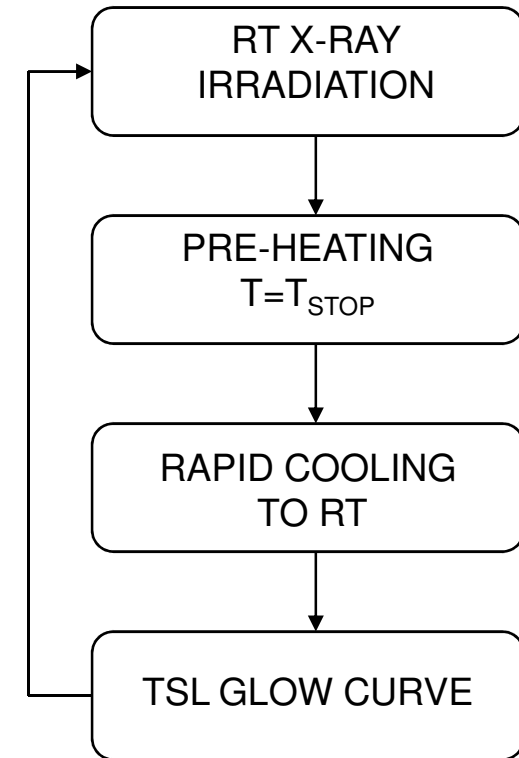
$$I(T) = s''n_0 \exp(-E_T / kT) / \left\{ 1 + [(b-1)s''/\beta] \times \int_{T_0}^T \exp(-E_T / kT') dT' \right\}^{b/(b-1)}$$

General order recombination: non negligible probability of retrapping

Data analysis: partial cleaning and **initial rise method**



$$I(T) = n_o s \exp\left(\frac{-E}{kT}\right)$$

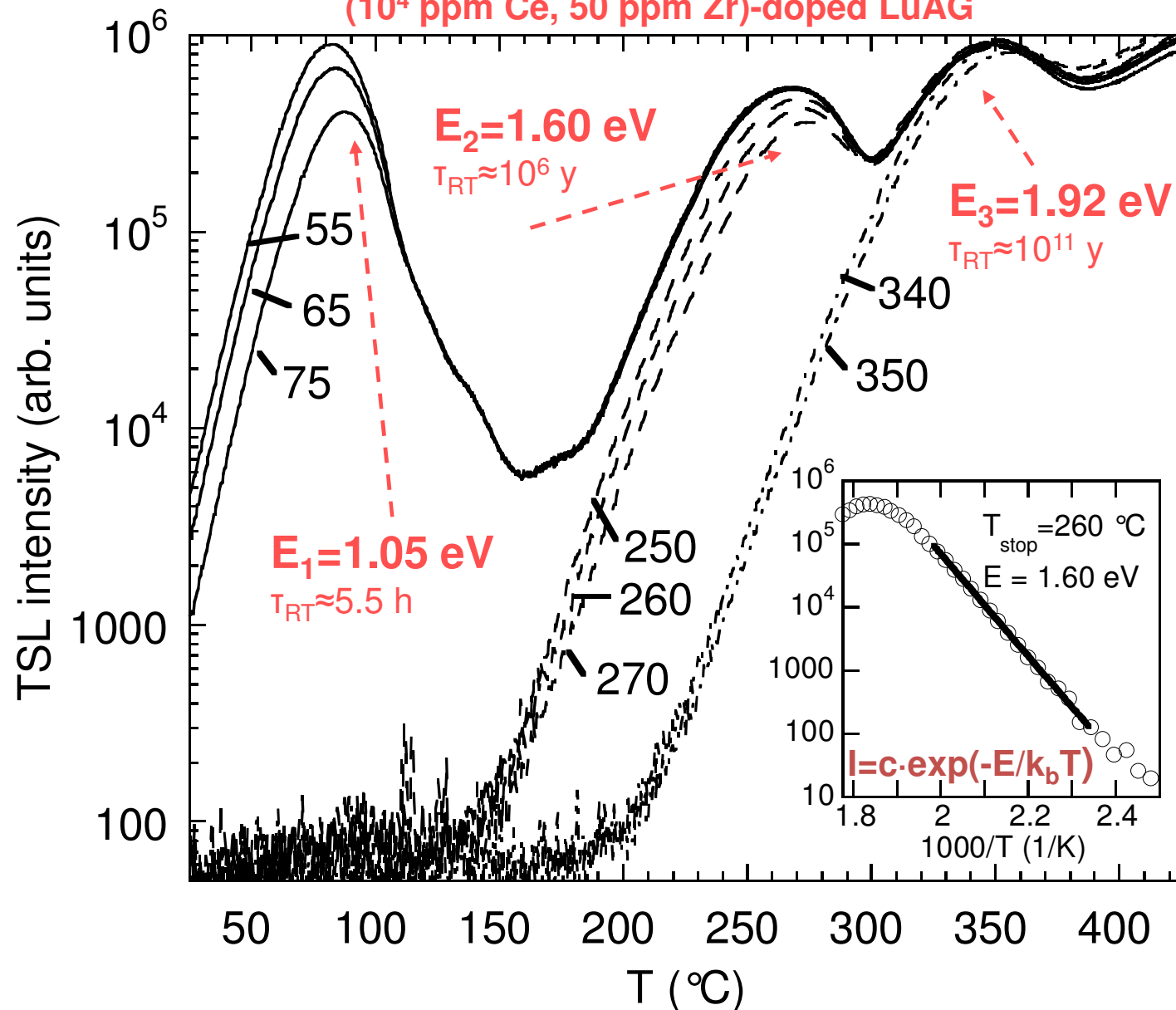


This procedure allows to evaluate the trap depth independently upon the kinetic order

EVALUATION OF TRAP DEPTHS

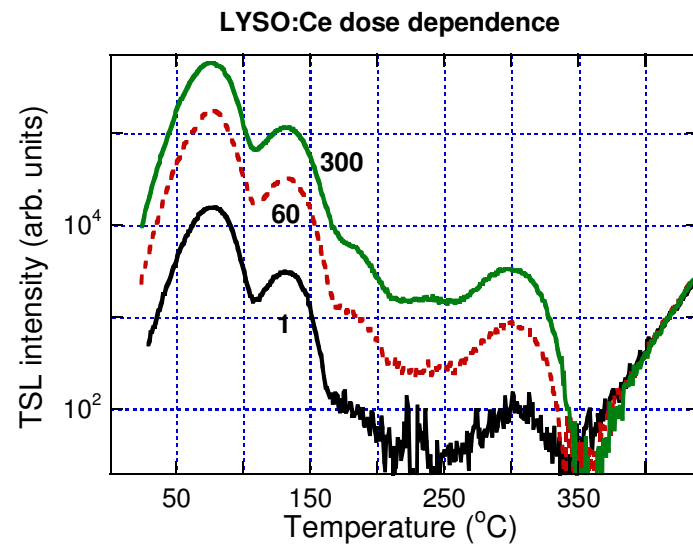
partial cleaning of glow curves and initial rise

(10^4 ppm Ce, 50 ppm Zr)-doped LuAG



Evaluation of the frequency factor (s). Simple case of first order kinetics

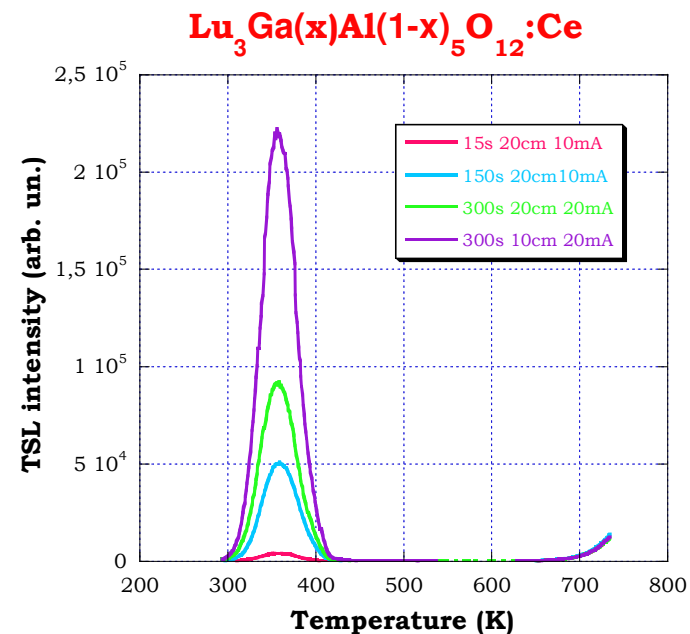
The presence of first order kinetics can be tested by verifying if TSL peak maxima do not vary with increasing dose. In this case,



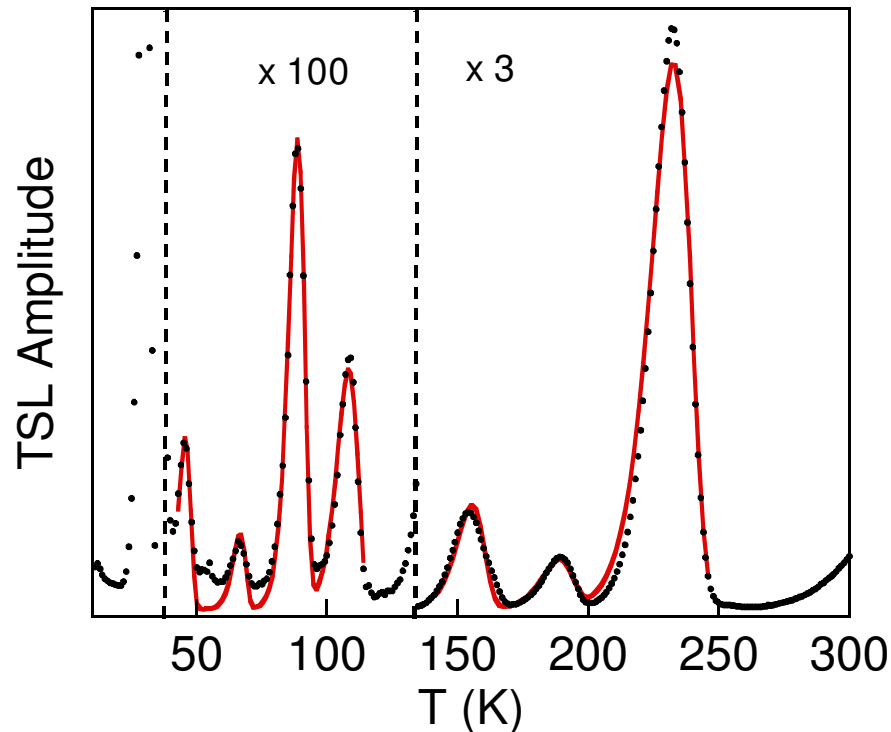
If E is already known, s can be evaluated (often only its order of magnitude due to several error sources)



$$\frac{\beta E}{kT_m^2} = s \exp\left(\frac{-E}{kT_m}\right)$$



Glow Curve Fit



TSL glow curve of YAP:0.1%Eu (full circles). The continuous red line represents the numerical fit of the glow curve in the framework of first order kinetics.

Made in the framework of first or general order kinetics

Difficult: E , s , and b (order of kinetic) are implicit parameters

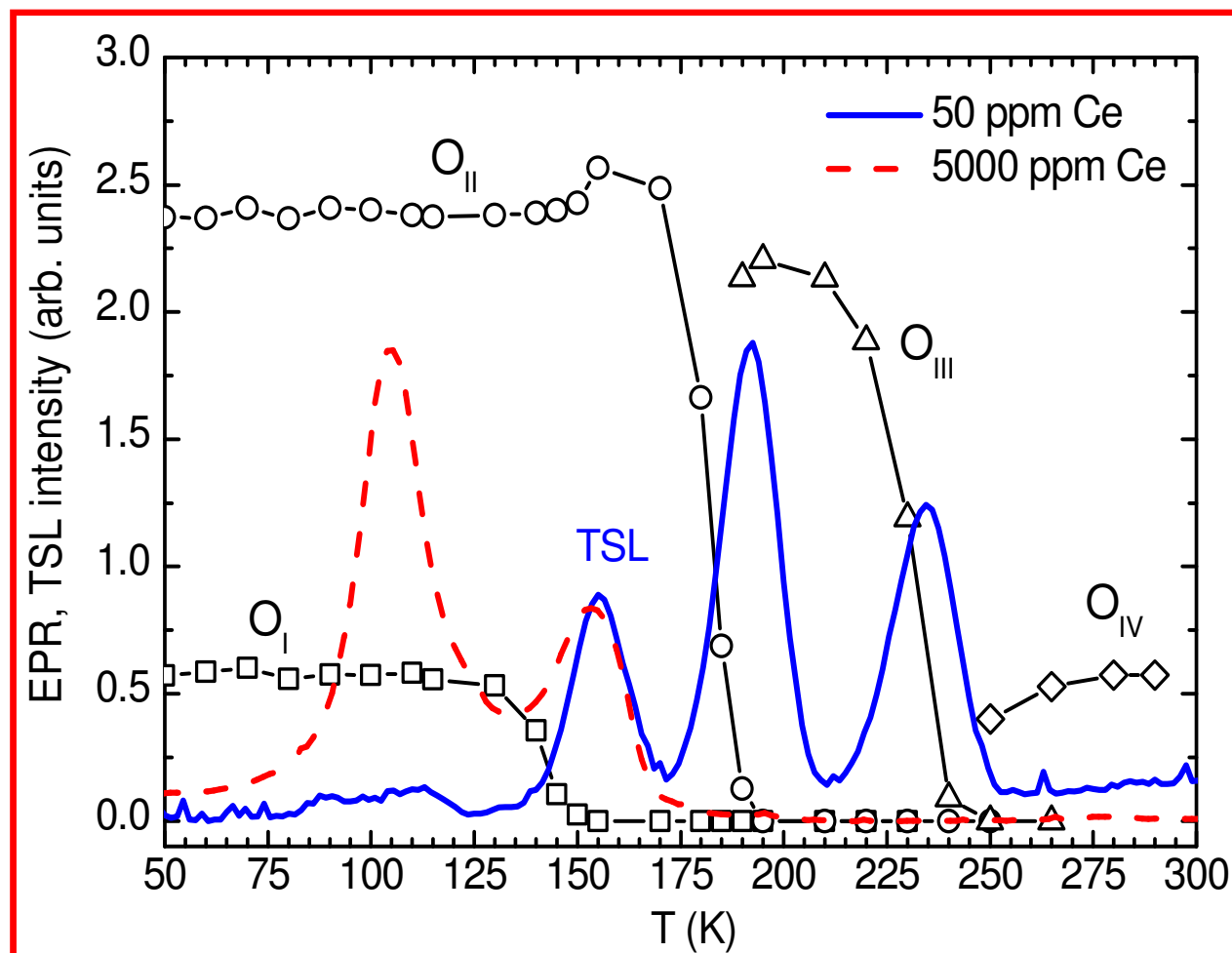
If several overlapping peaks are present, the number of parameters can be very high

Need of preliminary information by other methods

A few examples

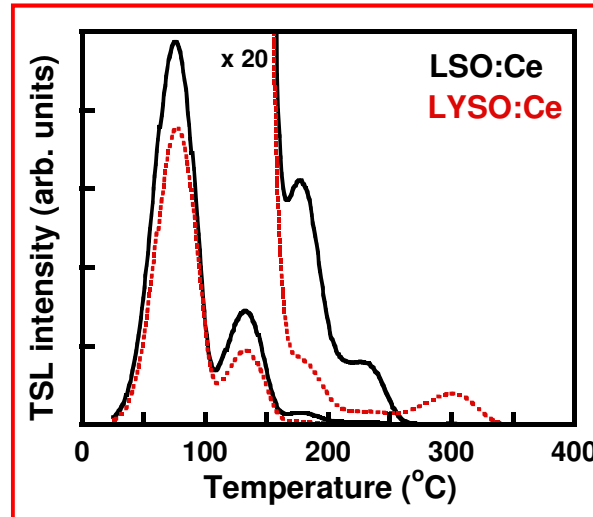
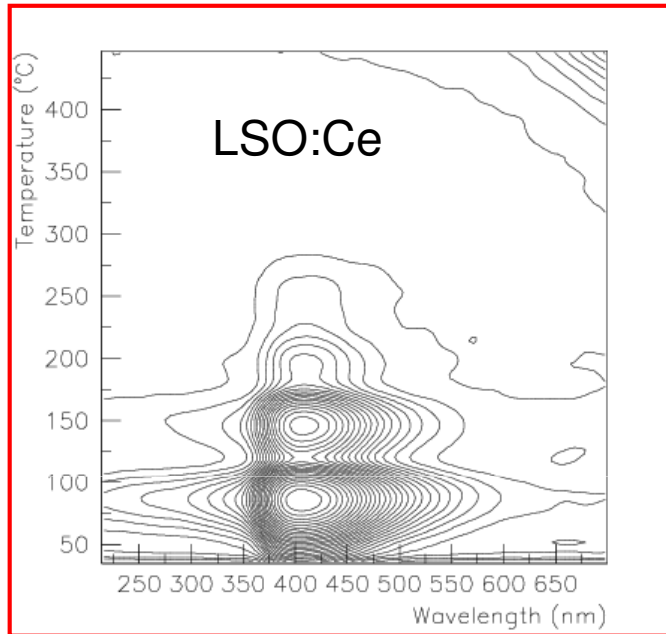
Structure of traps - example of YAlO_3

Correlation with EPR signals



The TSL peaks at 154 K, 190 K, and 232 K are due to the de-trapping of holes from O^- centres followed by recombination with electrons stored in oxygen vacancies – Phys. Rev. B 80, 045113 2009

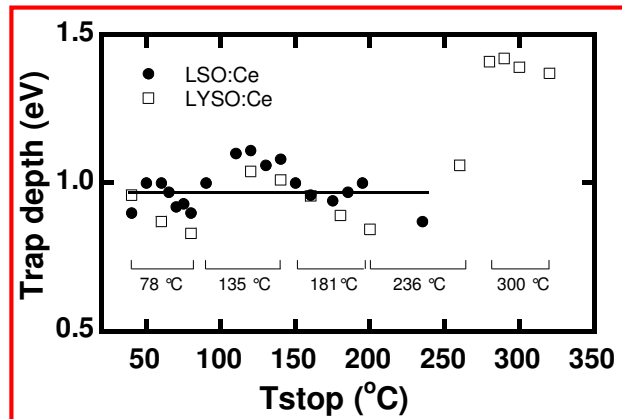
Lu₂SiO₅:Ce and Lu_{1.96}Y_{0.04}SiO₅:Ce – identification of the nature of traps thanks to their tunneling recombination mechanism



Recombination mechanism:

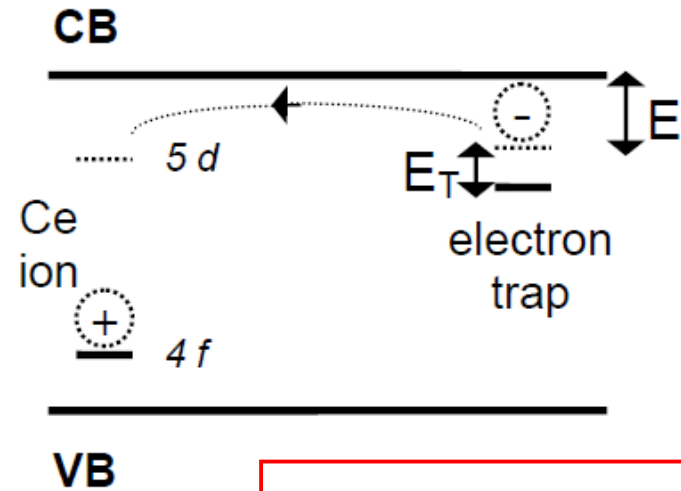
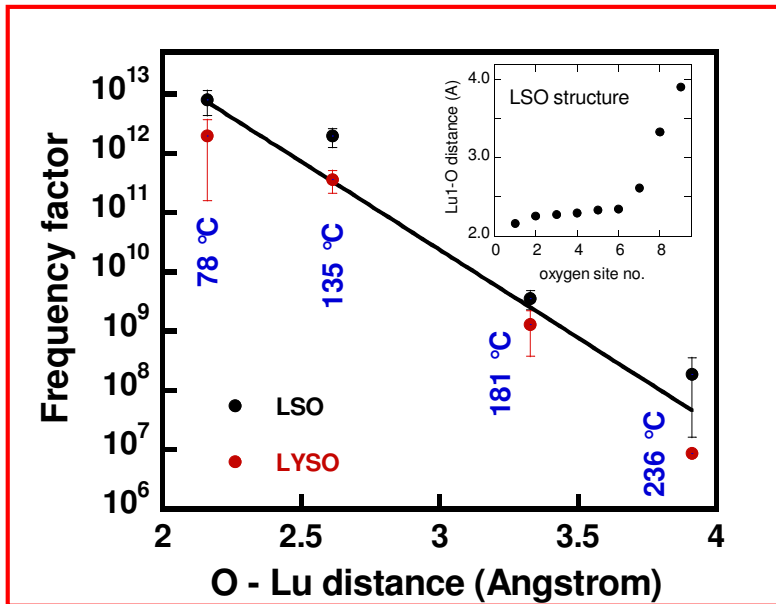
$\text{Ce}^{4+} + e$ (freed from the electron trap) $\rightarrow \text{Ce}^{3+*}$ (excited state) $\rightarrow \text{Ce}^{3+} + h\nu$ (TSL emitted light)

Evidence of the electronic nature of TSL traps



Constant trap depth for all glow peaks except the 300 °C one. Their different maximum temperatures are due to different frequency factors “s”

$$\frac{\beta E_T}{kT_m^2} = s \exp\left(\frac{-E_T}{kT_m}\right)$$



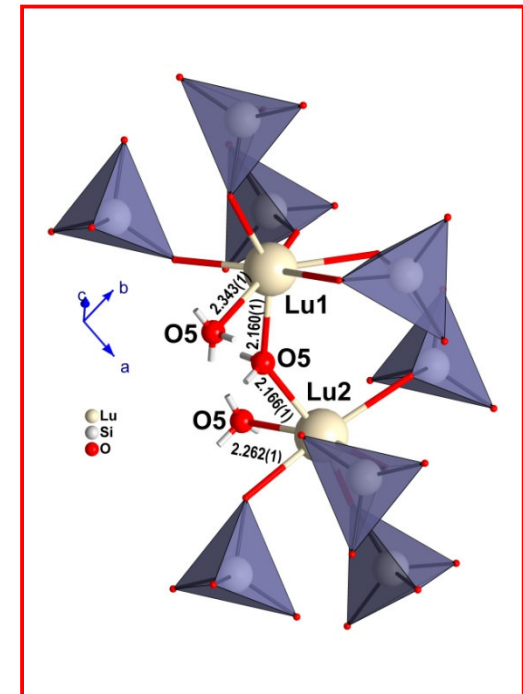
In the case of a thermally assisted tunneling process the frequency factor “s” depends upon the tunneling probability W:

$$s \propto W \cong \exp(-kx) \quad k = \frac{4\pi\sqrt{2mE}}{h}$$

Where “x” is the distance between the trap and the recombination centre, while E is the tunneling barrier

Exponential dependence of the frequency factors from Lu1(Ce)-Oxygen distances. Oxygen vacancies at different discrete distances from Ce act as electron traps responsible for TSL peaks.

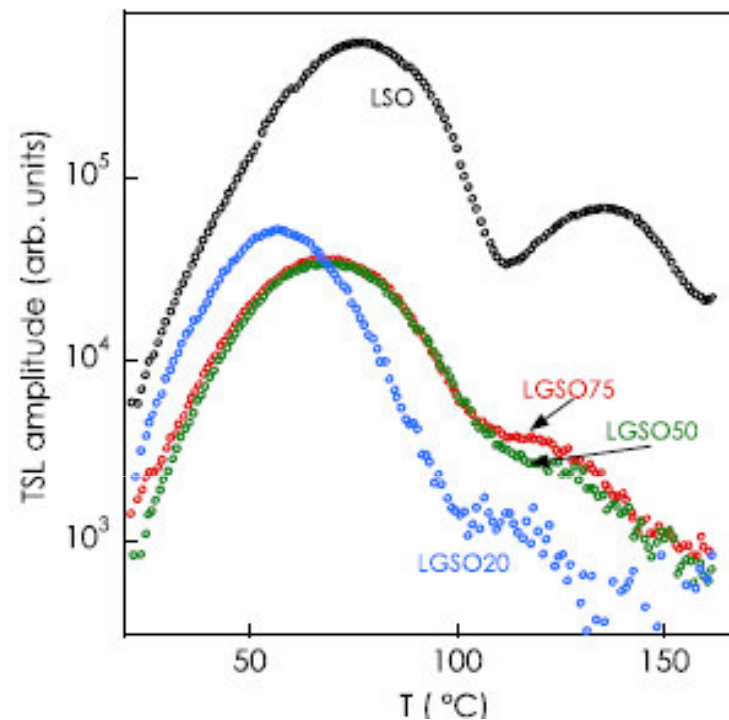
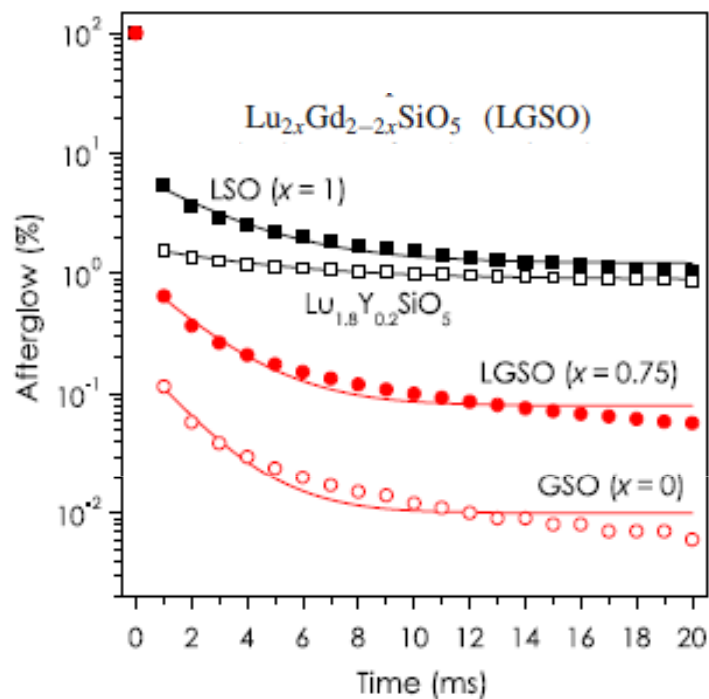
A. Vedda et al., PRB 78, 195123 (2008).



A similar phenomenology was observed in LuYAP:Ce (A. Vedda et al., PRB 61, 8081 (2000)).

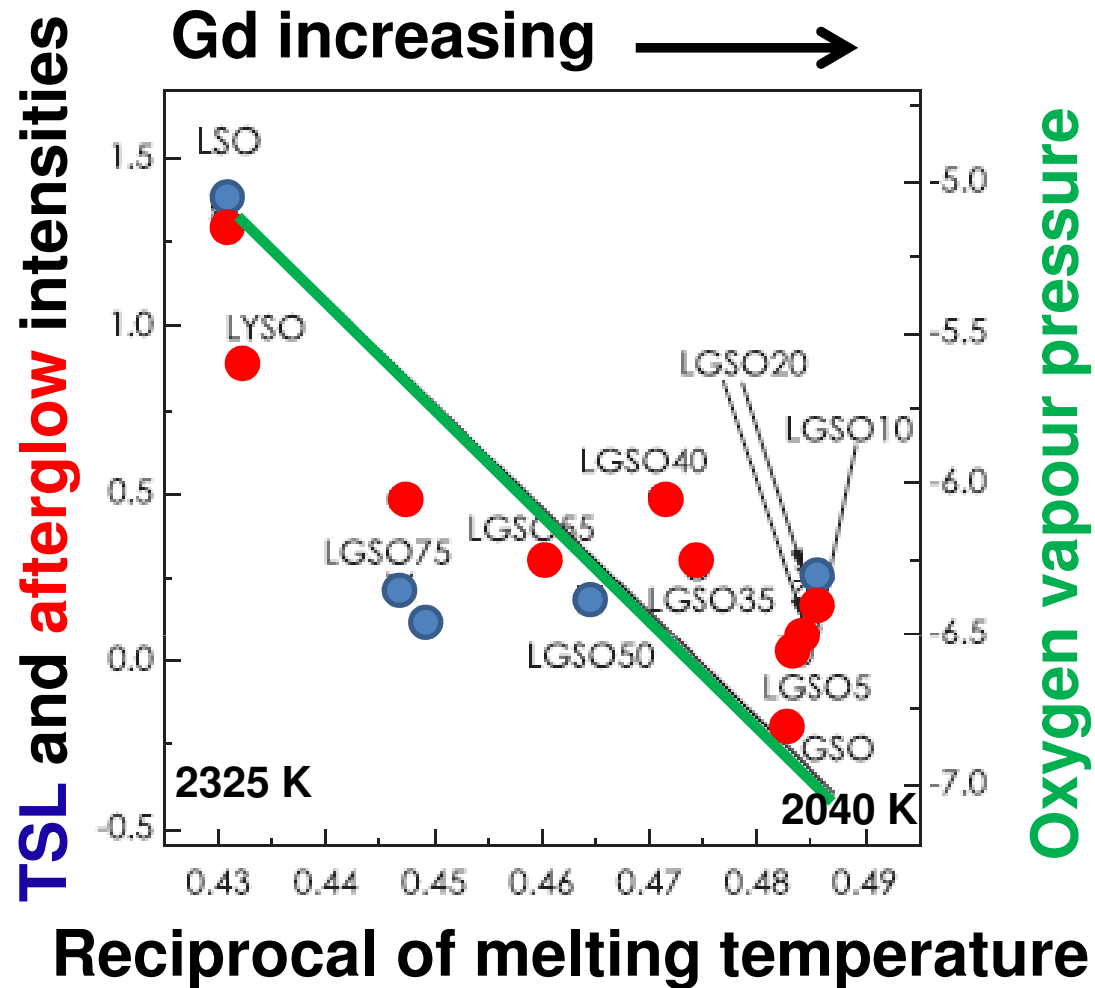
Afterglow and Thermoluminescence

$\text{Lu}_{2x}\text{Gd}_{2-2x}\text{SiO}_5:\text{Ce}$



Both afterglow and TSL intensities decrease **by increasing Gd (or Y) concentration in the host**, while keeping the same crystalline structure

Traps (oxygen vacancies) concentration decrease



Gd incorporation reduces **the melting temperature**
Defect concentration is reduced by melting temperature decrease (Gd increase)

Crystal Composition and Afterglow in Mixed Silicates: The Role of Melting Temperature

O. Sidletskiy,¹ A. Vedda,^{2,*} M. Fasoli,² S. Neicheva,¹ and A. Gekht¹

TABLE II. Parameters of Ce-doped LGSO, LYSO, and LSO in comparison with the literature data on main scintillators in x-ray CT [29,30].

Scintillator	Density (g/cm ³)	Relative light output (%)	Emission maximum (nm)	Primary decay (μs)	Afterglow (% at 3 ms)	Signal-to-noise ratio
CdWO ₄	7.9	100	530	2, 15	0.1	1000
CsI:Tl	4.51	330	550	1	>0.3	330
(Y, Gd) ₂ O ₃ :Eu	5.9	152	610	1000	5	20
Gd ₂ O ₂ S: Pr, Ce	7.34	180	520	2.4	0.1	1000
Gd ₂ O ₂ S: Tb(Ce)	7.34	180	550	600	0.7	140
Gd ₃ Ga ₅ O ₁₂ : Cr, Ce	7.09	138	730	150	0.1	1000
Lu_{0.4}Gd_{1.6}SiO₅: Ce	6.55	52	420	0.05	0.05	2000
LYSO:Ce	7.1	50	420	0.04	1.3	77
(reference)						
LSO:Ce (reference)	7.4	35	420	0.04	2.9	34

Good timing properties of mixed silicates

CONCLUSIONS

- ❖ Point defects in scintillators are the cause of several detrimental effects: they are responsible for slow scintillation tails, afterglow, low light yield, radiation damage.
- ❖ It is necessary to control them and to adopt material preparation strategies in order to reduce their concentration, or to make them inactive.
- ❖ Thermally Stimulated Luminescence is a powerful tool for the control of point defects especially when coupled to other techniques (EPR, scintillation)
- ❖ On the other hand, point defects can positively be exploited for the investigation of some material properties, like the thermal ionization energy of rare-earth ions excited levels.