Influence of defects and traps in the scintillation process

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Outline

- Trapping processes during ionizing irradiation
- De-trapping and e-h recombinations
- Thermoluminescence (TSL)
- Wavelength resolved TSL measurements
- TSL vs RL spectra
- Examples of uncommon applications: amorphization, phase transitions
- TSL equations
- Data analysis: initial rise, variable heating rate method, curve fitting
- Role of traps in scintillation
- Prediction of RT trap lifetimes
- Slow tails in scintillation decay, afterglow, permanent trapping
- Examples: Lead tungstate, perovskites, crystalline silicates
Scintillation: **Physical processes**

- **High Energy photon absorption**
- **Conduction Band**
  - **Traps**
  - **Luminescent Centre**
- **Valence Band**
  - **Photon (VIS-UV)**

**Conversion**
**Transport**
**Luminescence**
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 $\tau$ can be measured (of even less than 1 $\mu$s up to thousands years)
TSL-TSC process – simple scheme (electron traps)

Conduction band

Valence band

Heating

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)
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.
Different kinds of recombination paths

1. Classical recombination through conduction band

2. Thermally assisted tunneling (trap-centre recombination)
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
An example: low T Thermally Stimulated Luminescence (TSL) of PbWO$_4$

3D TSL measurement after x-ray irradiation at 10 K

After temperature integration

TSL emission spectra

After wavelength integration

RT decay times in the micro-milli second time scale

TSL glow curves
Comparison between TSL and radio-luminescence (RL) spectra

One would expect that they are the same... but the nature of traps as well as specific trap-centre spatial correlations makes them often different.

Case of Lu$_2$SiO$_5$ :RE

Significant differences between RL and TSL:

RL spectra are governed by the emissions of principal dopant ions.

TSL spectra display mainly emissions from RE which capture holes during irradiation (Ce$^{3+}$,Tb$^{3+}$—Ce$^{4+}$,Tb$^{4+}$) even if they are present as trace impurities.

Evidence of the electronic nature of traps.
Spatial correlation between Gd$^{3+}$ and traps in silica

The difference between RL (where both Ce$^{3+}$ and Gd$^{3+}$ emissions are observed) and TSL spectra (featuring only Gd$^{3+}$ emission line) is due to the spatial correlation between Gd$^{3+}$ and oxygen-related electron traps.
TSL glow curves are sensitive to material amorphization.

The amorphous structure of a material often induces broadening of TSL glow peaks due to the presence of continuous distributions of trap levels.

Crystalline quartz

Amorphous silica
TSL glow curves can also be sensitive to phase transitions

Example of Ammonium Bromide (NH₄Br)

- 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

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

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

First order recombination: no retrapping

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

General order recombination: non negligible probability of retrapping
Data analysis: partial cleaning and initial rise method

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

\[ I = c \cdot \exp(-E/k_B T) \]

\[ E_1 = 1.05 \text{ eV} \quad \tau_{RT} \approx 5.5 \text{ h} \]

\[ E_2 = 1.60 \text{ eV} \quad \tau_{RT} \approx 10^6 \text{ y} \]

\[ E_3 = 1.92 \text{ eV} \quad \tau_{RT} \approx 10^{11} \text{ y} \]
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,

\[
\frac{\beta E}{kT^2_m} = s \exp \left( -\frac{E}{kT_m} \right)
\]

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

From:

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

Plotting \( \ln T_m^2/\beta \) vs \( 1/T_m \)

\[ E = 0.92 \text{ eV} \]
\[ s = 3 \times 10^{10} \text{ s}^{-1} \]

Slope = \( E/k \)

Intercept = \( \ln (E/sk) \)

Possibility to extend to general order kinetics

Need of good separation between different peaks
Glow Curve Fit

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

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.
Role of traps in scintillation

If the RT decay time $\tau$ is of the order of micro- or milli- seconds

Slow tails in the scintillation decay

Longer $\tau$ (minutes, hours)

Afterglow

Very long $\tau$ (days, years)

Permanent trapping

Traps can be studied by heating at a constant rate after irradiation (slow scintillation tails correspond to TSL peaks at cryogenic temperatures, while afterglow and permanent trapping are related to peaks above RT)

The determination of trap parameters by some method of analysis allows the evaluation of the order of magnitude of the RT lifetime $\tau$ (higher precision is commonly prevented by several error sources and by the temperature dependence of the frequency factor, which is hardly predictable)
The investigation of the role of traps in scintillation involves the following steps:

- Evidence of slow scintillation tails or afterglow

- Need to understand the nature of responsible defects

- Study of defects by an independent technique giving information about thermal stability of defects and their radiative recombination properties (TSL)

- Correlation of TSL data with other techniques which allow structural information about traps (e.g. EPR)

- Tuning of material synthesis to reduce the investigated defects
Role of traps in scintillation time decay
Comparison between silicates, garnets, and perovskites

The presence of fewer shallow traps in silicates with respect to other scintillators (very low TSL intensity below RT) is in agreement with the absence of slower components in the scintillation decay.
Example of lead tungstate (PbWO$_4$ – PWO)

Doping with La$^{3+}$ reduces slow components in the scintillation decay, as well as TSL glow peaks at cryogenic temperatures

La$^{3+}$ favours the reduction of intrinsic lattice defects

Present only in Mo-doped samples

Intrinsic RT scintillation decay time

Suppressed by trivalent ion doping
Effect of different ion dopings in very slow decay components in PWO

Scintillation decays of a) undoped PWO and b) PWO(2750Mo,500Nb,50Y) at RT.

TSL glow curves of differently doped PWO samples

Alpha coefficient: normalized difference between the signal level before the excitation pulse and the true background (It measures the level of very slow components)

Good correlation between alpha coefficients of differently doped samples and TSL integral intensities below RT
YAIO$_3$ undoped crystals

Several emission centres for each glow peak

Recombinations involving valence/conduction bands
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.
Doping of YAlO$_3$ with Yb$^{3+}$, Eu$^{3+}$, and Tm$^{3+}$

Trapping of electrons during irradiation

Hole traps are similar to those observed in undoped crystals. Rare earth ions compete with oxygen vacancies in electron trapping (becoming temporarily Yb$^{2+}$, Eu$^{2+}$, Tm$^{2+}$) and act as recombination centres in the TSL process.
Detrapping and recombination: Case of YAlO$_3$:Yb

Due to their long RT decay times, traps responsible for the TSL peaks above 100 K (mostly O-centres) cause slow tails in the scintillation time decay.
Doping with Ce$^{3+}$, Pr$^{3+}$, and Tb$^{3+}$

Trapping of holes during irradiation – a TSL pattern different from that occurring with Yb$^{3+}$, Eu$^{3+}$, Tm$^{3+}$ doping is expected

Tunneling emission

Evidence of one or two dominant TSL peaks, similar to those observed in the cases of undoped, Yb, Eu, and Tm doped crystals

TSL spectral emissions of rare-earth ions trapping holes
RE-doped YAP
TSL spectra Example: 190 K peak

Emissions from electron and hole trapping RE ions observed in the same TSL peaks.
In RE-doped YAP, traps and recombination centres do not act like separate entities, but rather as parts of **defect complexes** in which carriers can be transferred from intrinsic levels (O\(^{-}\) centres and oxygen vacancies) to the rare earth ion levels.

The observation of a nearly temperature independent TSL emission suggests that tunnelling driven recombination processes occur in addition to the temperature driven recombination, supporting the existence of such complexes with **close spatial correlation between traps and centres**.

Due to the formation of defect complexes, the kind of recombination centre (capturing holes or electrons, e.g. Ce or Yb) is not always a proof of the nature (electron- or hole-kind) of a trap.

The comparison of the TSL patterns of **crystals doped with a variety of rare earth ions** proved to be essential in order to highlight this phenomenology, which nevertheless could be more common in TSL experiments than expected.
Consequences of trap levels RT decay times on scintillation efficiency

As the glow curve peak occurs at a much higher temperature in the case of Pr doping, the RT lifetime of its main trap is about one order of magnitude larger with respect to that of Ce-doped YAP.

This can be one of the reasons why delayed radiative recombination processes in YAP:Pr are more pronounced and its photoelectron yield is lower with respect to that of YAP:Ce in spite of its higher steady state RL efficiency.
Lu$_2$SiO$_5$:Ce and Lu$_{1.96}$Y$_{0.04}$SiO$_5$:Ce — identification of the nature of traps thanks to their localized recombination mechanism

Recombination mechanism:

Ce$^{4+}$ + e (freed from the electron trap) → Ce$^{3+*}$ (excited state) → 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
No dependence of maximum temperatures from dose 

\[ n(r) \sim \exp(-\phi r) \]

In the case of a thermally assisted tunneling process

Where “s” is the frequency factor and “r” is the distance between the trap and the recombination centre

Exponential dependence of the frequency factors from Lu1(Ce)-Oxygen distances

Oxygen vacancies act as electron traps responsible for TSL peaks
Conclusions

TSL is a powerful technique for the study of luminescent materials; especially when performed in wavelength resolved mode, it can really provide a deep insight in the trapping-recombination processes occurring in a scintillator.

Several types of recombination mechanisms between traps and luminescent centres exist. Their comprehension needs very often the possibility to vary sample parameters like kind of doping, dopant concentration, synthesis and annealing conditions, and to probe their influence on TSL features. Anyway, in some cases only qualitative descriptions of the recombination processes remain possible.

Data analyses are delicate; the handling of trap parameters needs a clear consciousness of the error sources linked to experimental data and numerical methods. This is important especially if a comparison with similar parameters obtained by other techniques has to be performed. Such consciousness of the limits of the technique doesn't lower, but increases its potential allowing to handle data in a critical and therefore constructive way.
References


