European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

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New Sensing Technologies for Air Quality Monitoring

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PHOTOLUMINESCENCE BASED GAS SENSING WITH RARE-EARTH DOPED NANOSCALE OXIDES

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Luminescence based *versus* conductometric gas sensing

- **Different transducing mechanisms** in the same material (e.g. metal oxide)

- **Technical point of view**
  - more components required - LED+PD
  - non-contact method

- **Different stability issues** (e.g. there are no contact problems for luminescence)

Why rare-earths?

Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm

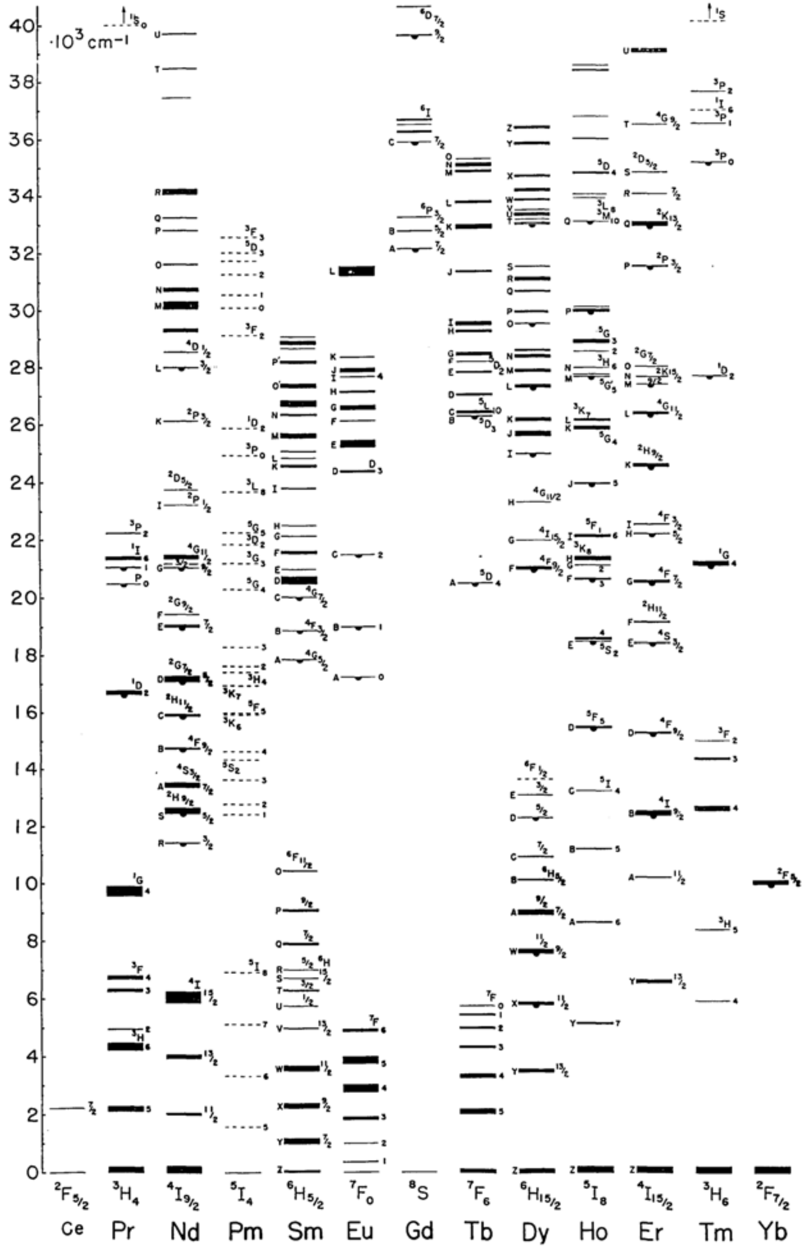
Good emission properties

=

•strong optical signal at room (or higher) temperature

•sharp PL lines – signal can be filtered

•long PL lifetime – easy lifetime detection



G. H. Dieke, H. M. Crosswhite, "The Spectra of the Doubly and Triply Ionized Rare Earths," Appl. Opt. **2,** 675-686 (1963);

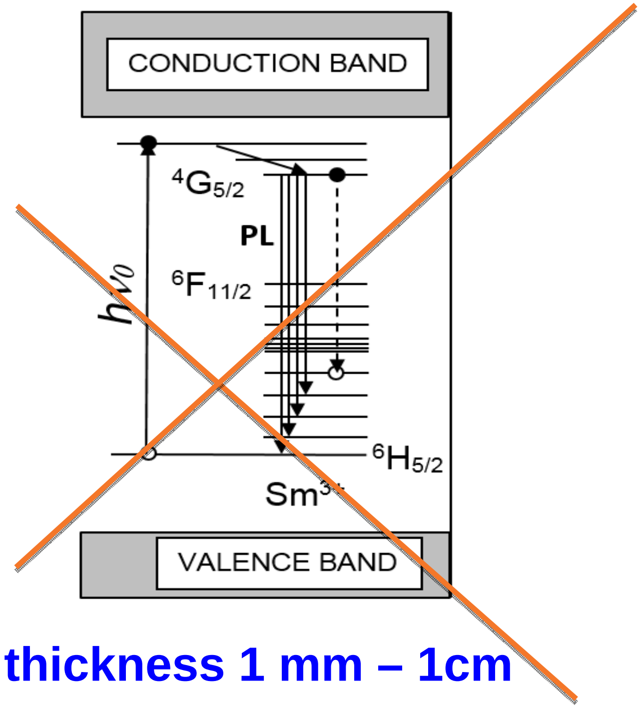
Problems

1. Optical absorption coefficients are extremely small

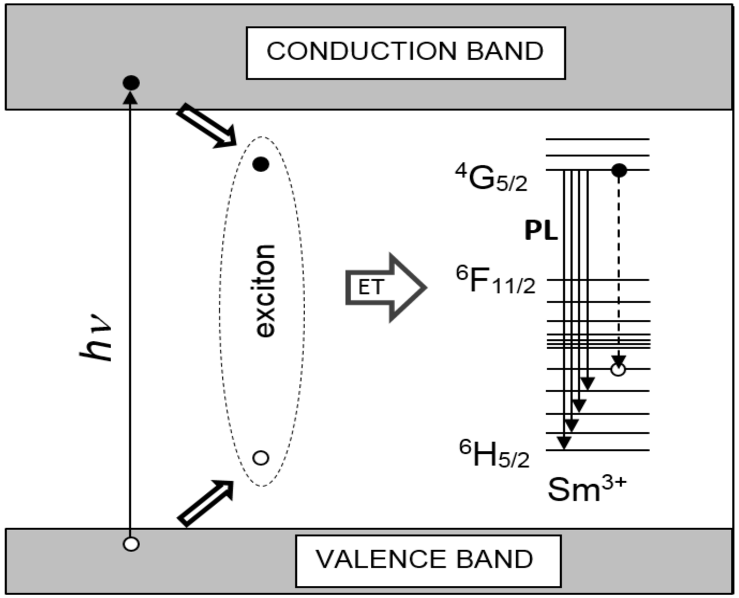
as the optical transitions within 4f electron manifold are parity-forbidden

2. Are the PL transduction mechanisms efficient enough?

Fortunately there is a solution to the first problem – excitation via host



thickness 1 mm – 1cm



thickness < 100 nm

- Excitation of the host via fundamental absorption with $h\nu > E_g$
- Energy transfer to rare earth impurity

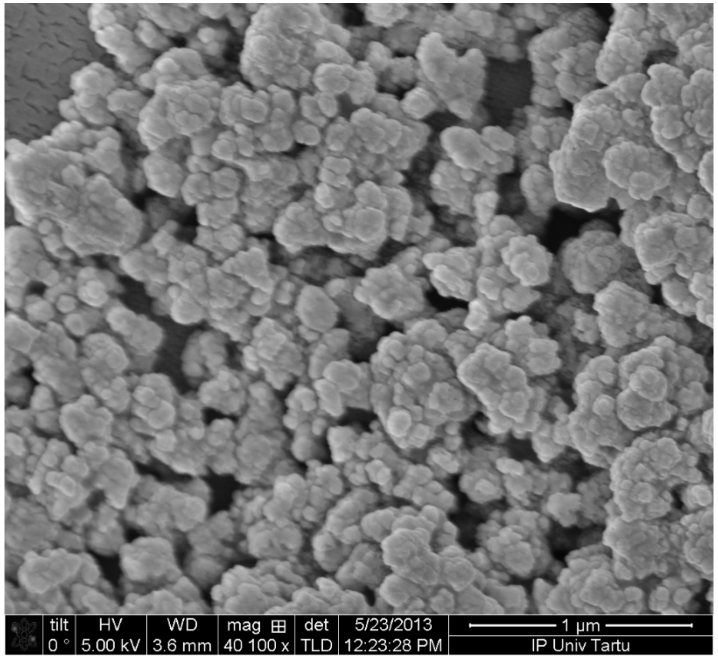
Materials studied

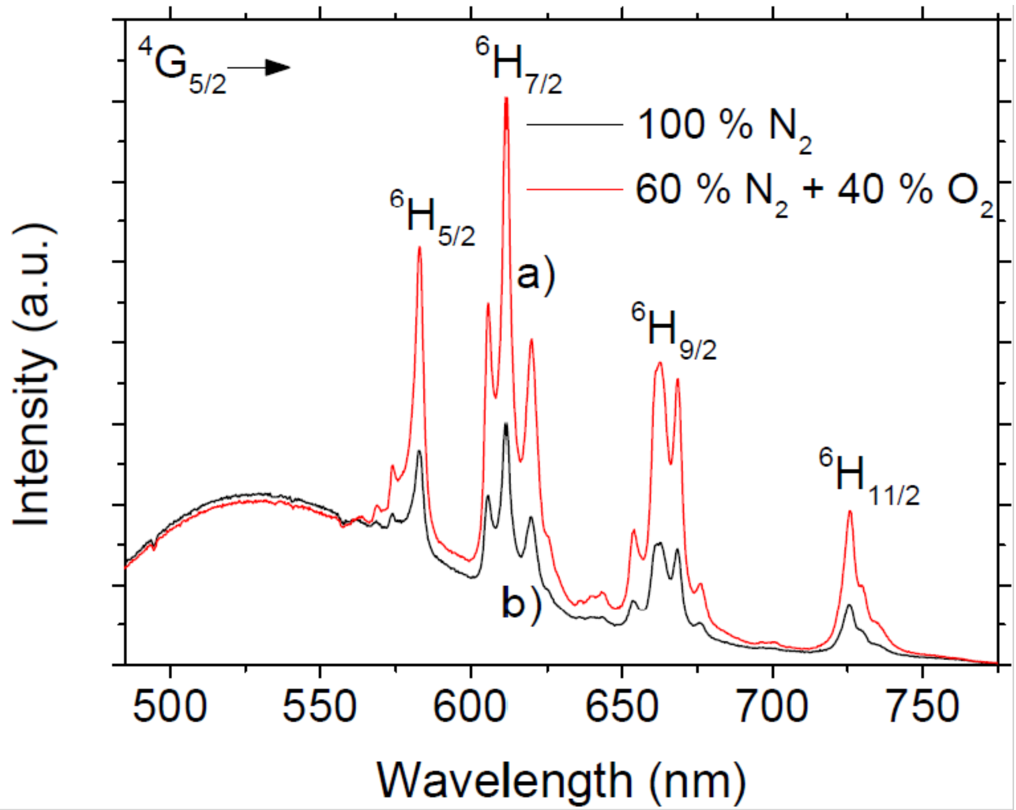
Host	RE	Eg	E_{ex} / λ_{ex}	λ_{PL} (nm)
TiO_2 anatase	Sm	3.2 eV	3.5 eV 355 nm	~610 nm
SnO_2	Eu	3.7 eV	4.7 eV 266 nm	~610 nm

Nanopowders – prepared by sol-gel technique, annealed

Thin films - pulsed laser deposition or spin-coating (sol-gel), annealed

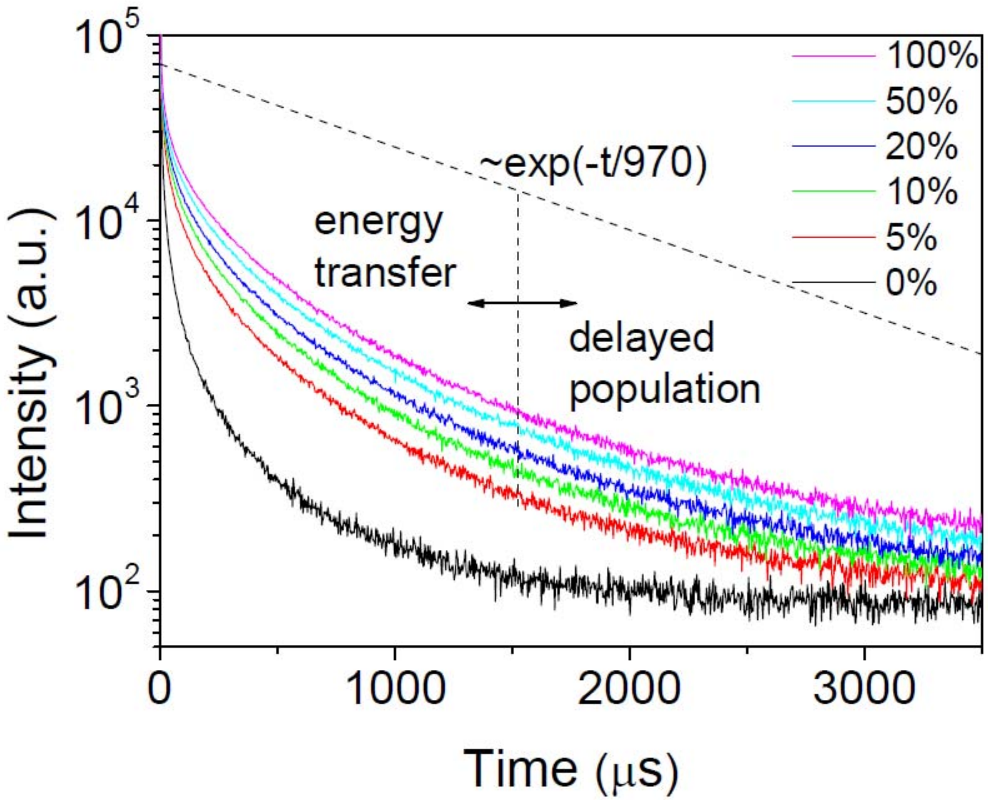
Sm^{3+}(1at%) in TiO_2 nanopowder





M. Eltermann, K. Utt, S. Lange, R. Jaaniso. Optical Materials **51**, 24-30 (2016).

PL decay at different O_2 vol%

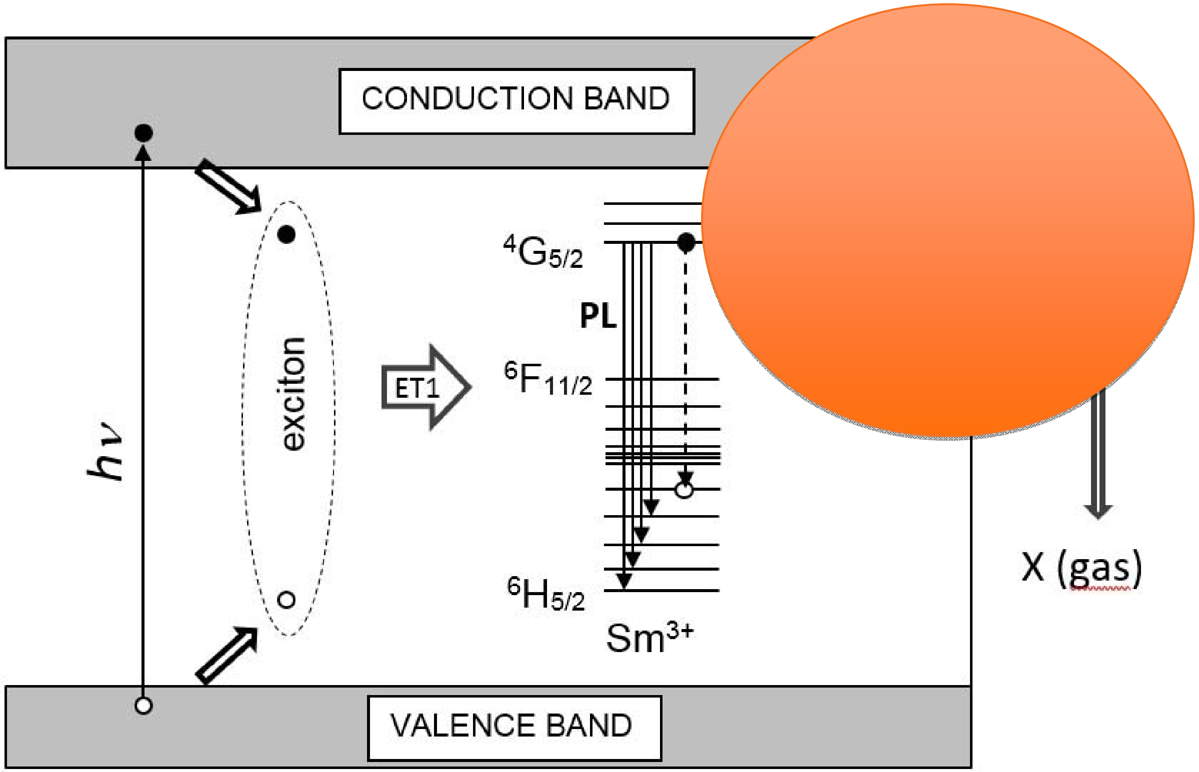


Lifetime based sensing

is insensitive to several sources of drifts, e.g. the drifts of excitation or detection electronics, contamination of optical paths, etc.

M. Eltermann, K. Utt, S. Lange, R. Jaaniso. Optical Materials **51**, 24-30 (2016).

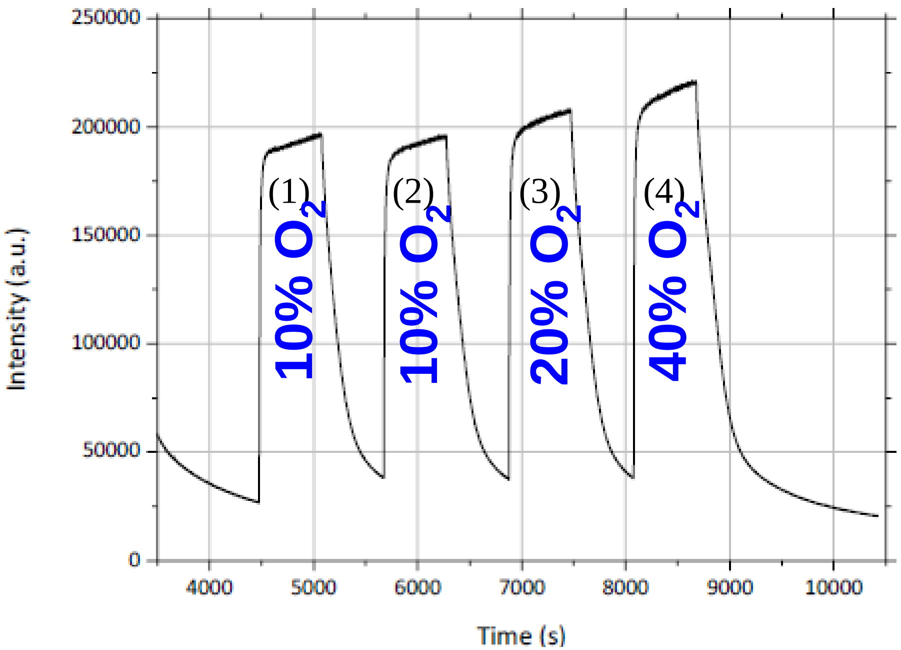
Transduction mechanism I

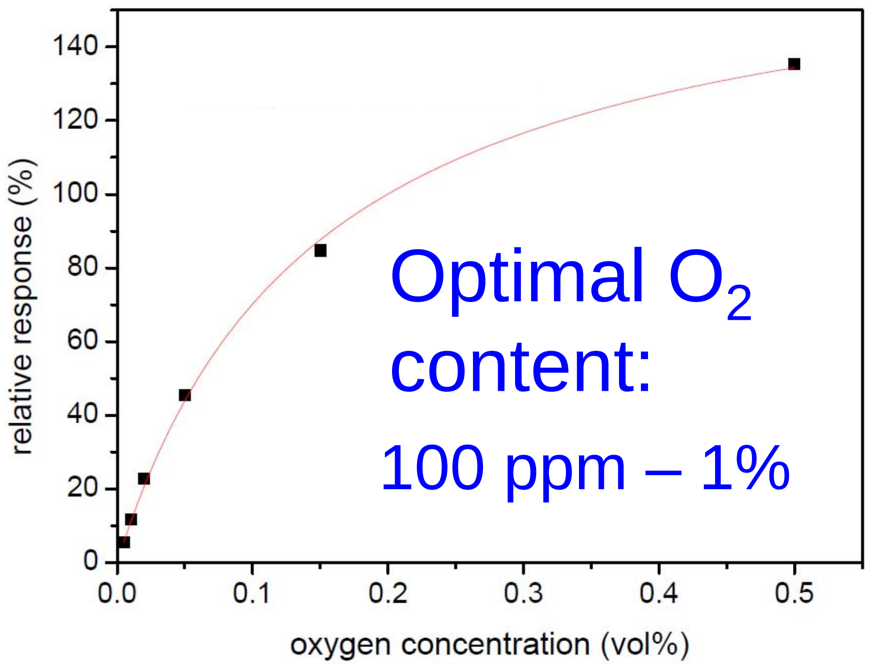


PL quenching due to surface-charge-switched excitation energy transfer.

Thin films of $Sm^{3+}:TiO_2$:

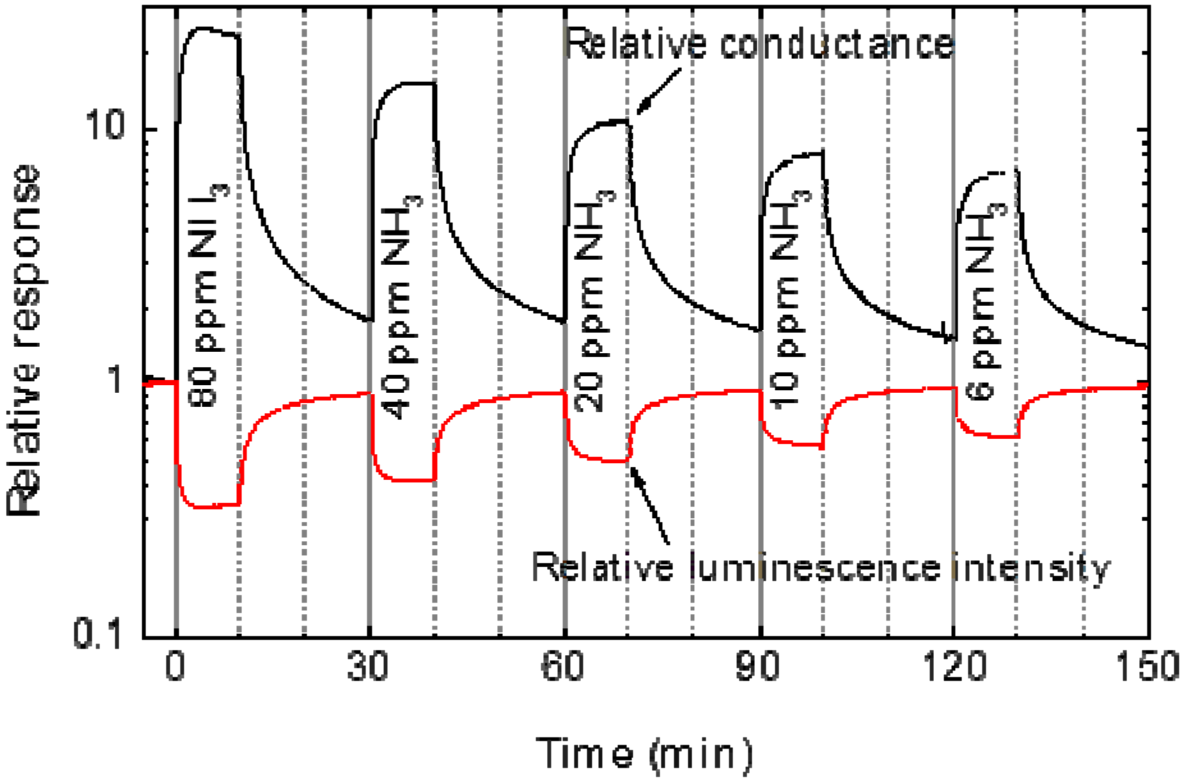
trace O_2 sensing

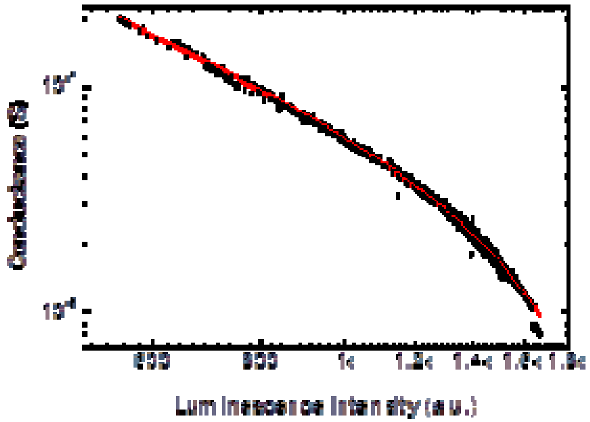




Signal becomes almost saturated at oxygen contents over 1% in O_2/N_2 mixture. Another remarkable property - short response time!

Dual sensing of NH_3

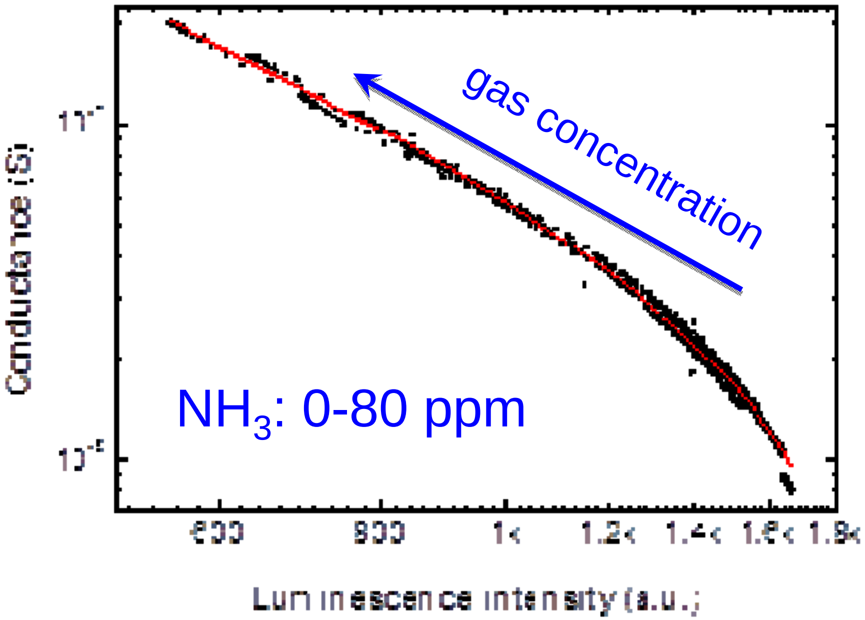


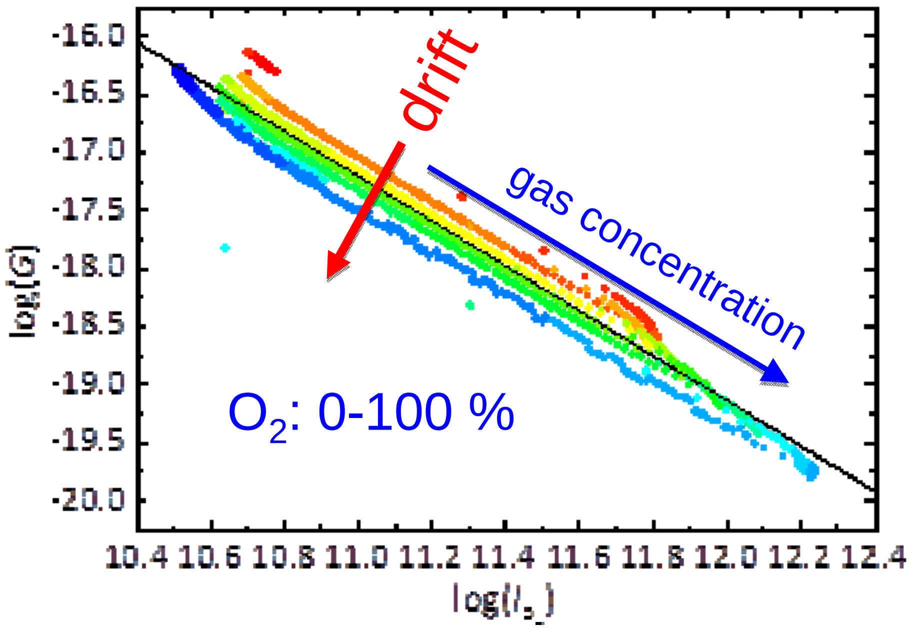


Sm: TiO_2

T=150 ºC

Luminescence *versus* conduction





Relation $(I_{PL}-I_{PL0})=G^n$ holds at every time moment!

Sm:TiO$_2$

cost
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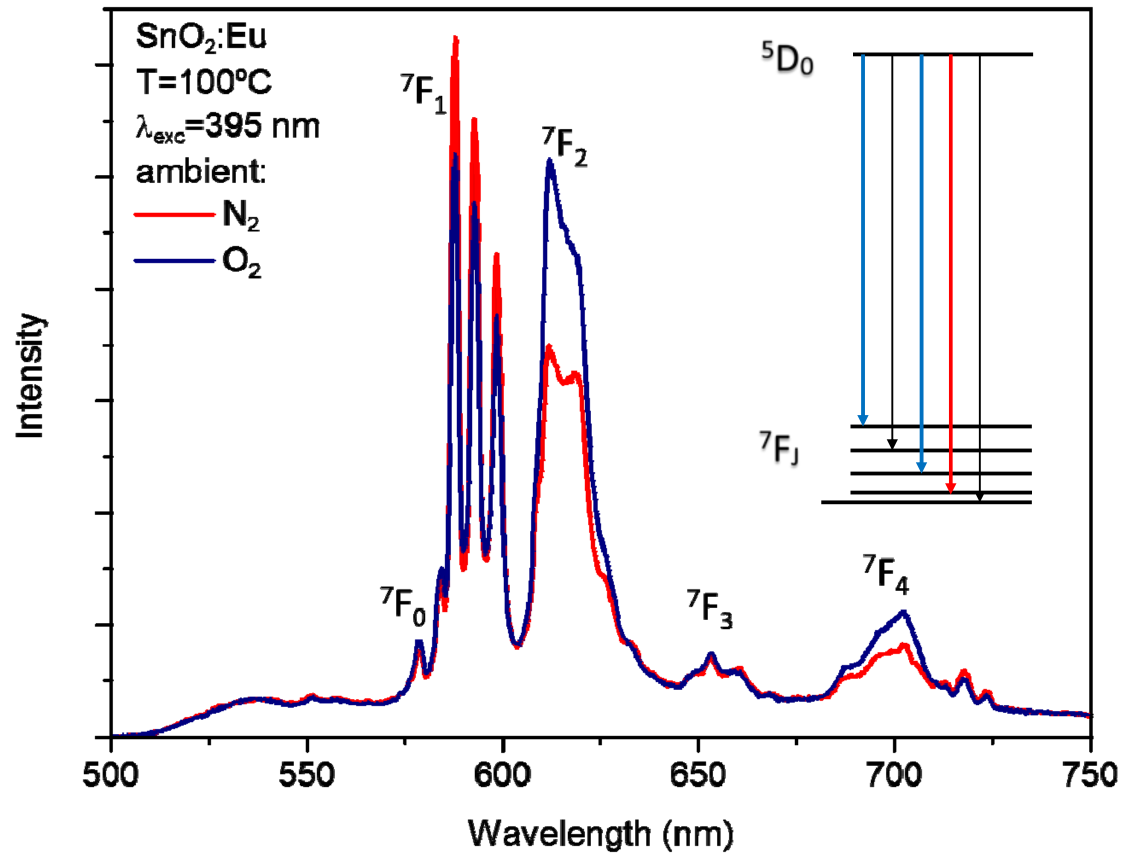
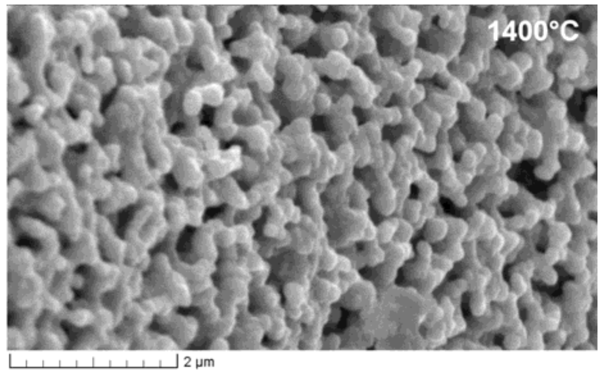
$Eu:SnO_2$ - Transduction mechanism II





Effect of local fields on the stengths of (ultra)sensitive 4f-4f transitions.

Ratiometric $^7F_2/^7F_1$ sensing!

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Summary

- RE ions in nanoscale oxides can be efficient optical probes of gas sorption
- Different transduction mechanisms are possible
- Lifetime based sensing is demonstrated
- Dual mode (conduction+PL) sensing can enhance performance and help to understand underlying mechanisms

Collaborators and support

Team:

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Thank you very much for your attention!