# The bright side of defects: Chemistry and physics of persistent and storage phosphors

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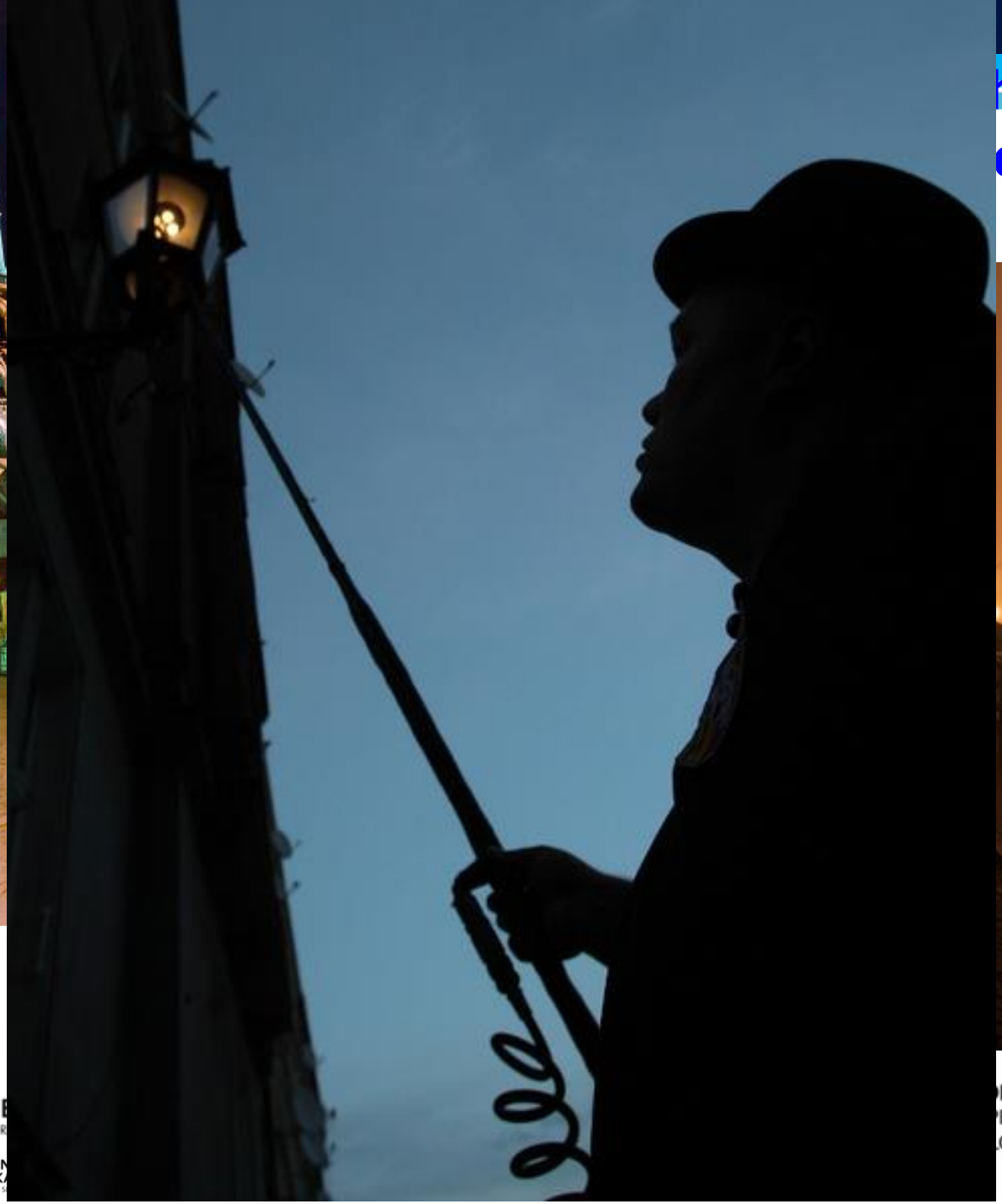

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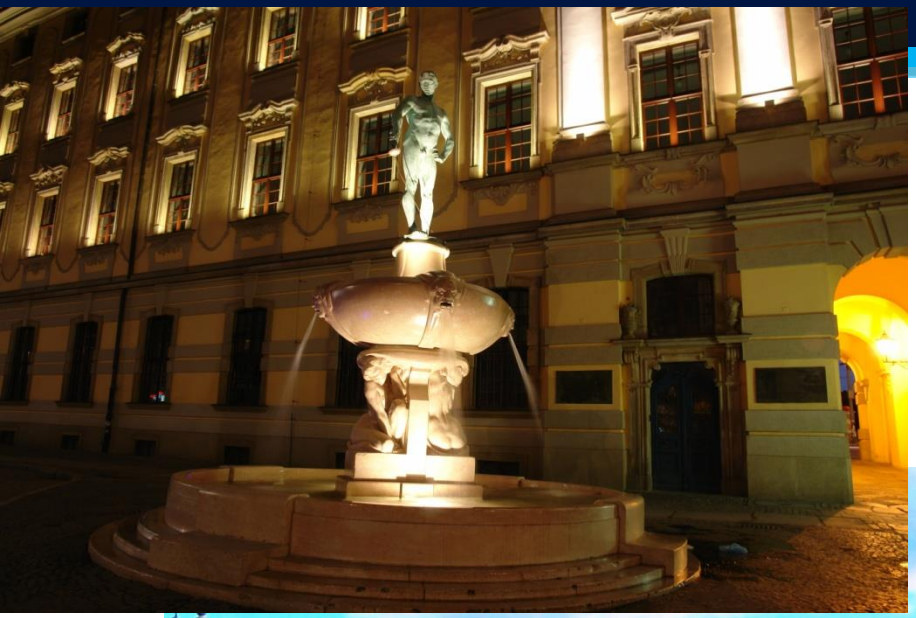
# 1945 vs. nowadays

# 1702
# the Beginning of the University of Wroclaw


## The Bull establishing the University

# University just after the World War II

# University Nowadays



# University Nowadays

# Graduation

# Faculty of Chemistry

| | |
|---|---|
| Researchers | ~110 |
| PhD Students | ~100 |
| Students | ~600 |

# Luminescent Materials Research Group

# The nice part

# is over

# The bright side of defects: Chemistry and physics of persistent and storage phosphors

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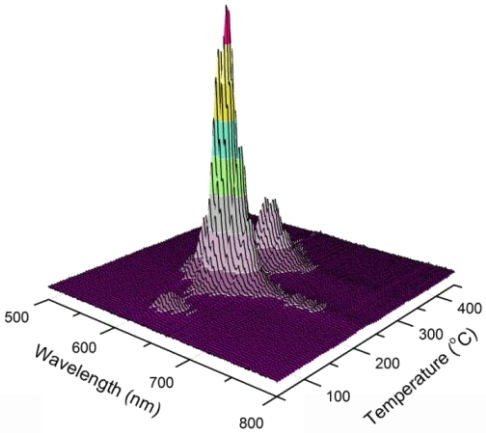
# Colin Humphreys

"Crystals are like people,

it is the defects in them

which tend to make them interesting!"



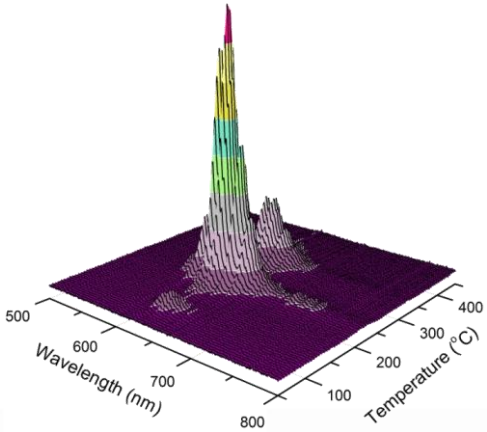
# Defect Types
# a simplified approach

**Intrinsic defects:** Schottky and Frenkel defect (thermally created)

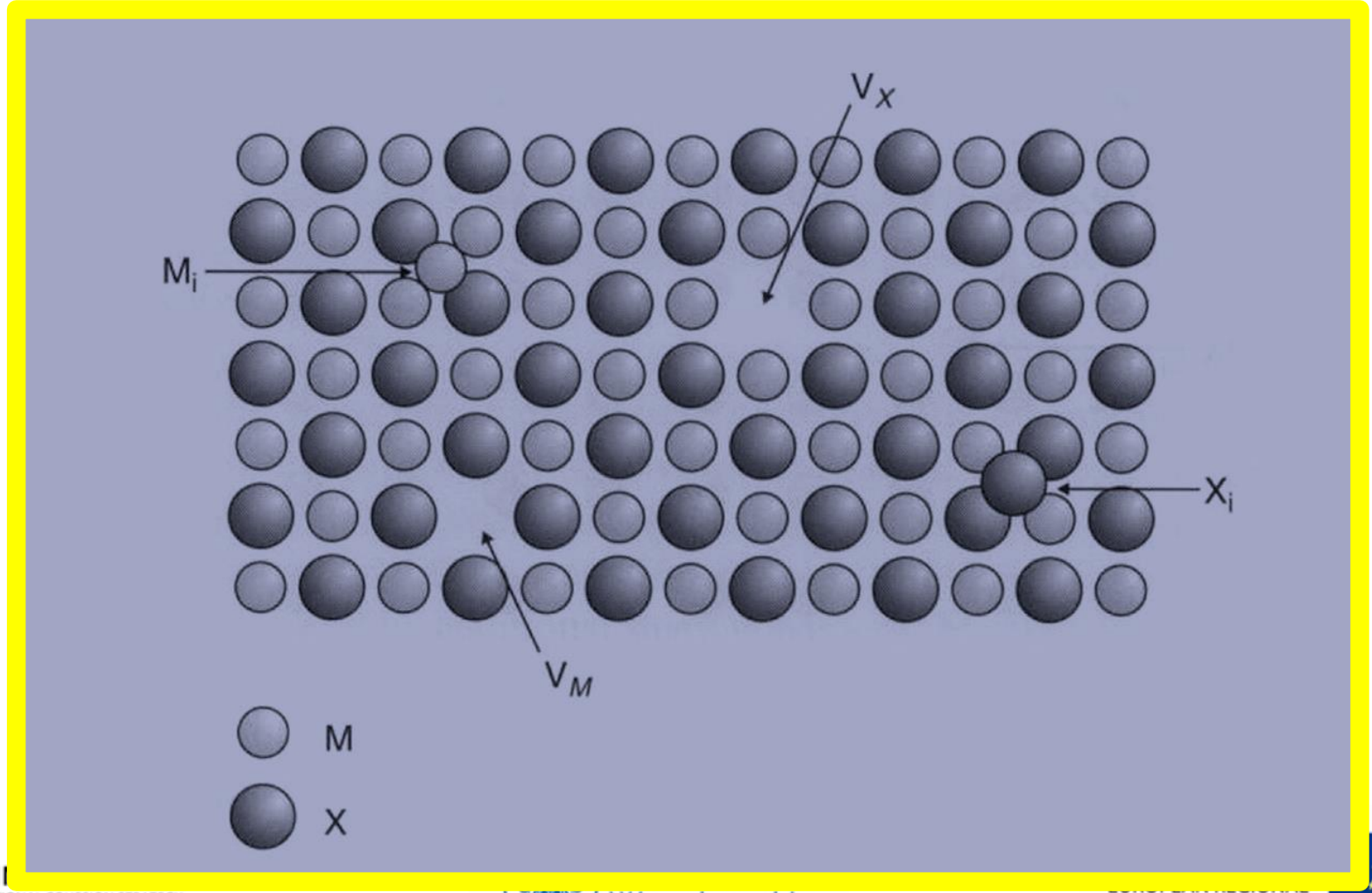
**Extrinsic defects:** Impurities (intentional or unintentional dopants)

And these two lines can be easily developed into:

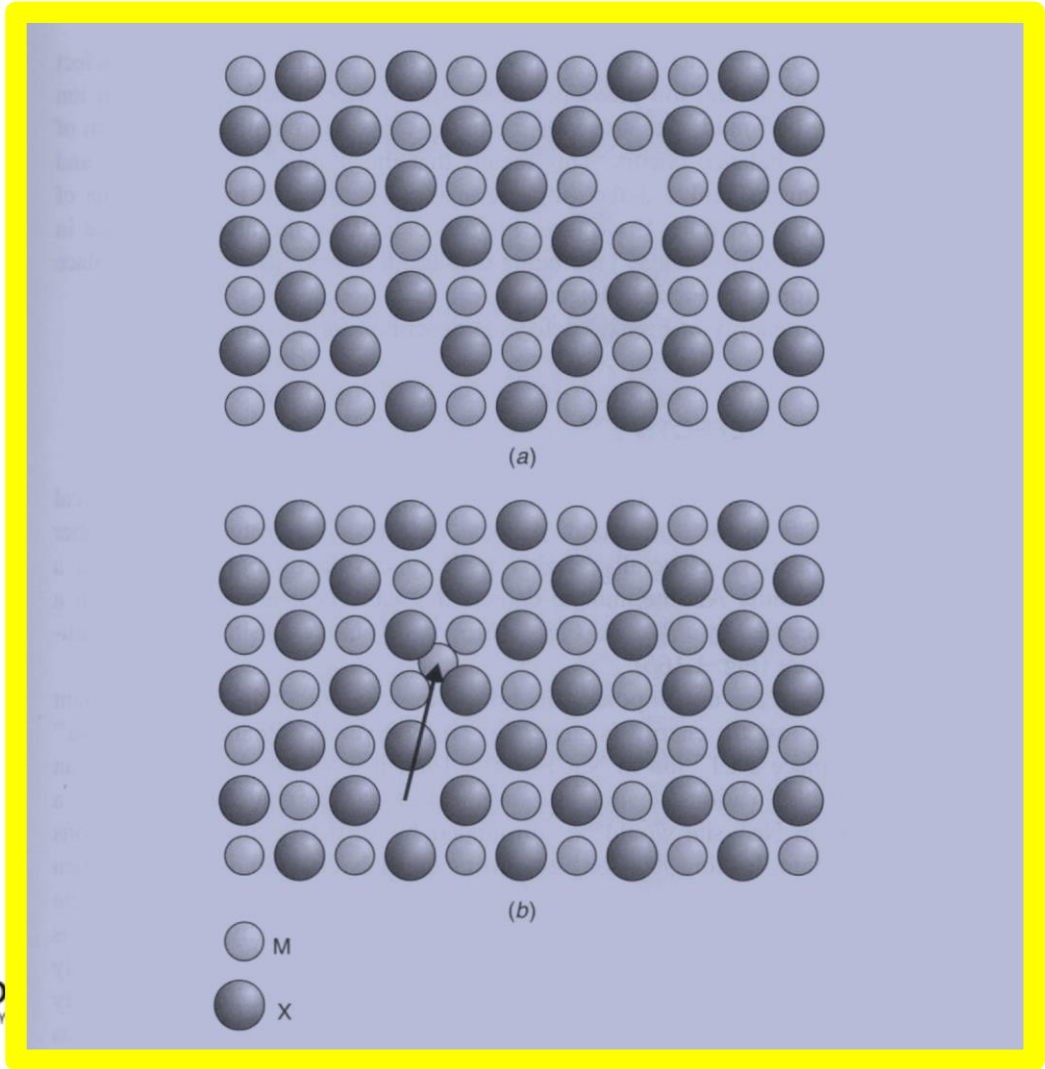
- An article
- A book chapter
- A book



# Types of Defects in Crystalline Solids



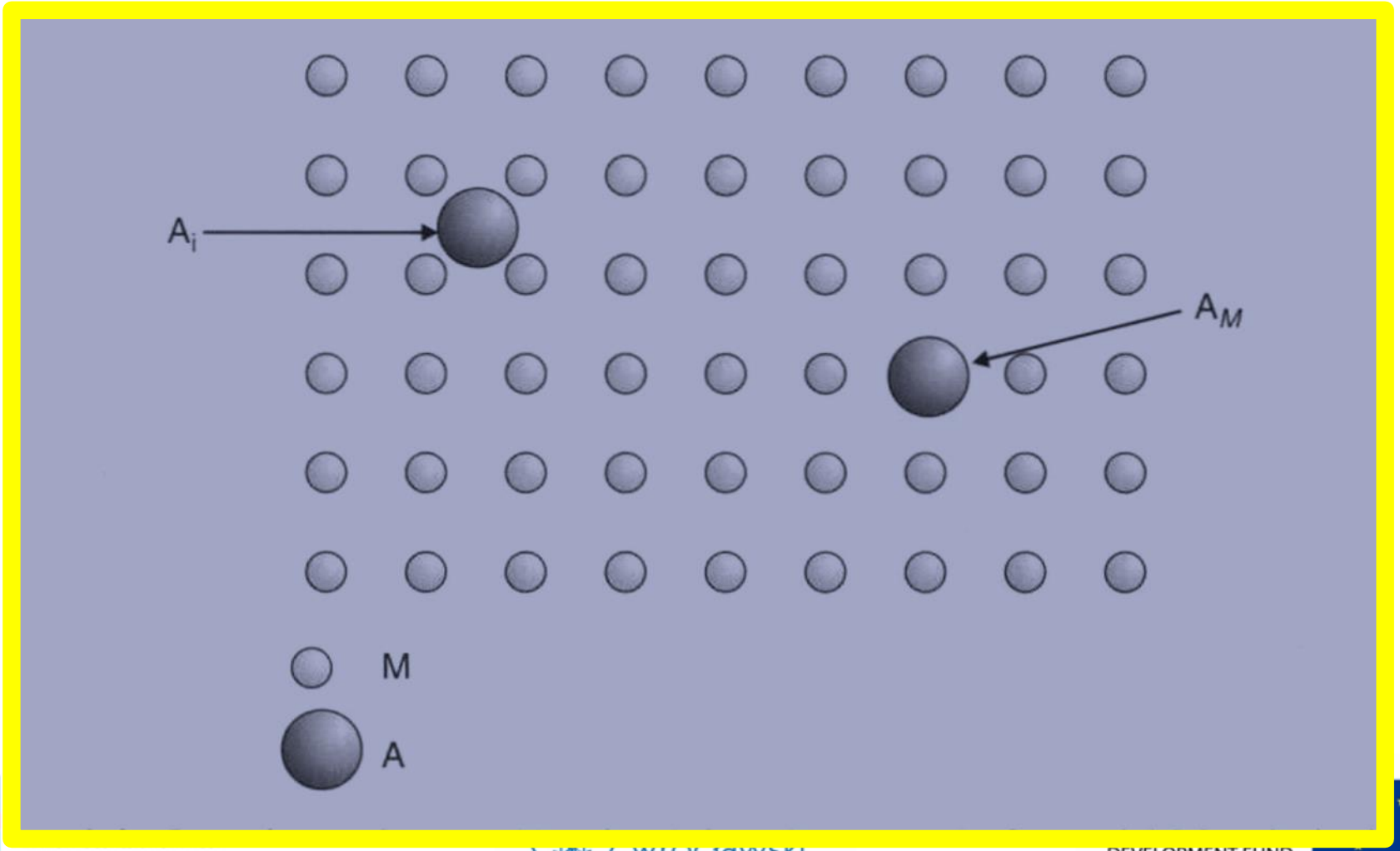
# Pair Defects: Schottky and Frenkel Defects. Their Populations Increases with Temperature




**Schottky**

**Frenkel**

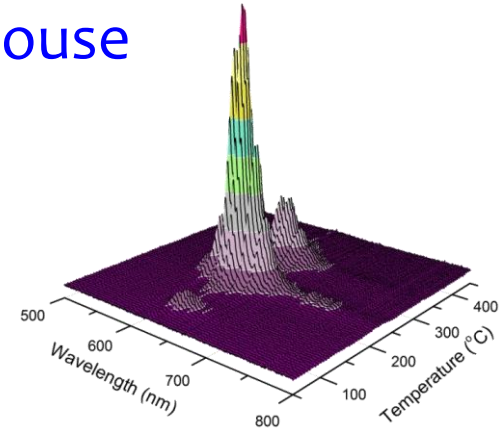
# Impurity Point Defects



# Erice, Sicily, Italy, 2014

**Andries Meijerink: „We, who research luminescence, need to learn more about the NATURE of DEFECTS”**

During the discussion at
Prof. Baldassare (Rino) Di Bartolo’s Family House



# What happens in

# Storage (and persistent) phosphors?

# Defects

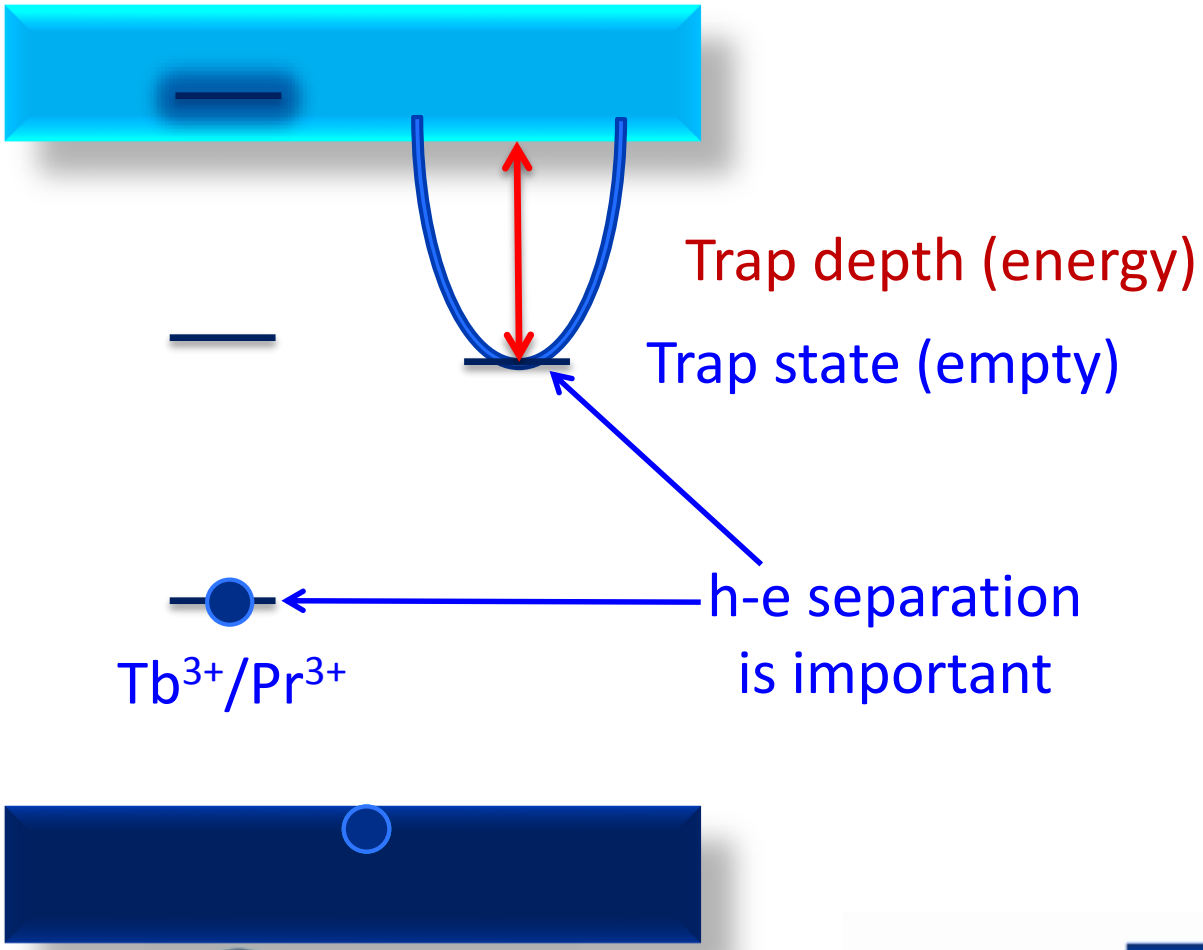
# play their game

# A story on

$Lu_2O_3$:Tb,M;
$Lu_2O_3$:Pr,M;

M=Sr/Ca, Hf, Ti, Ta, Nb

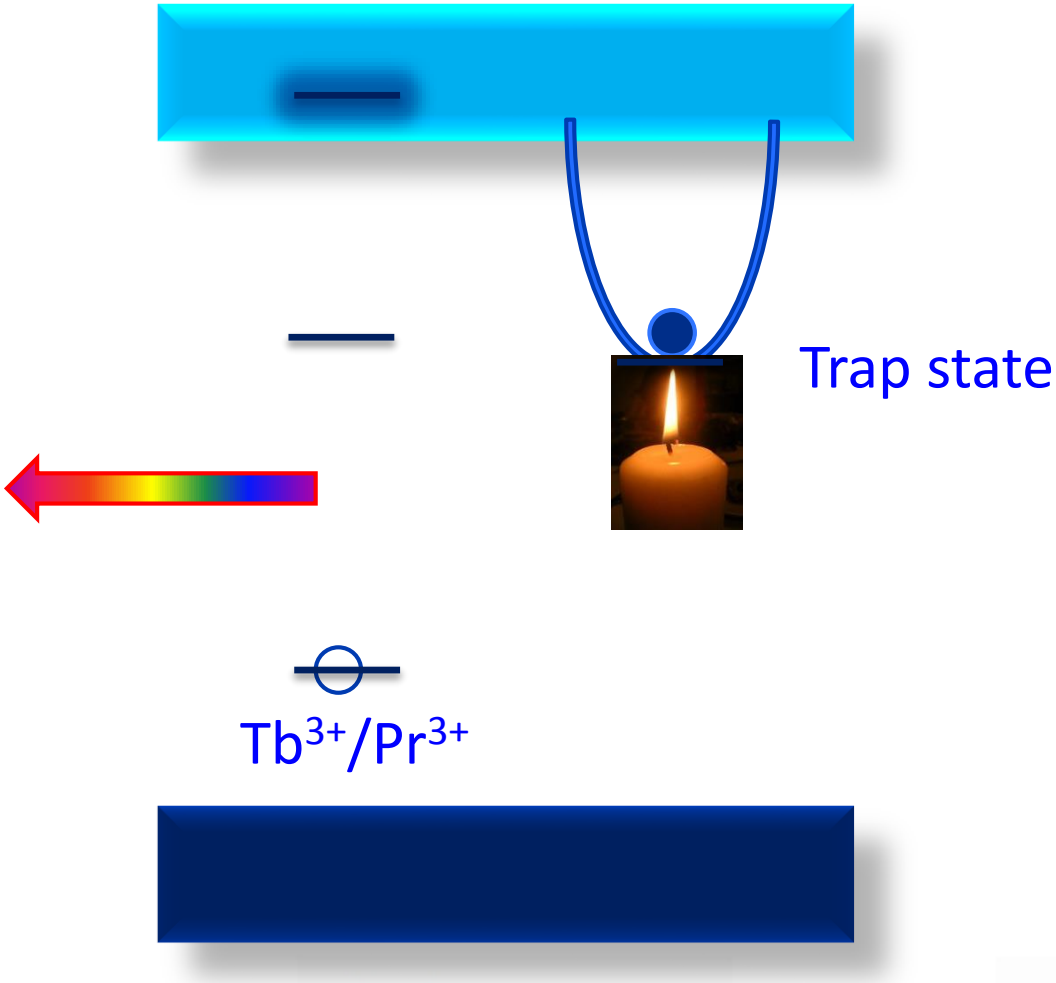
# Energy storing
# = immobilizing carriers in excited states



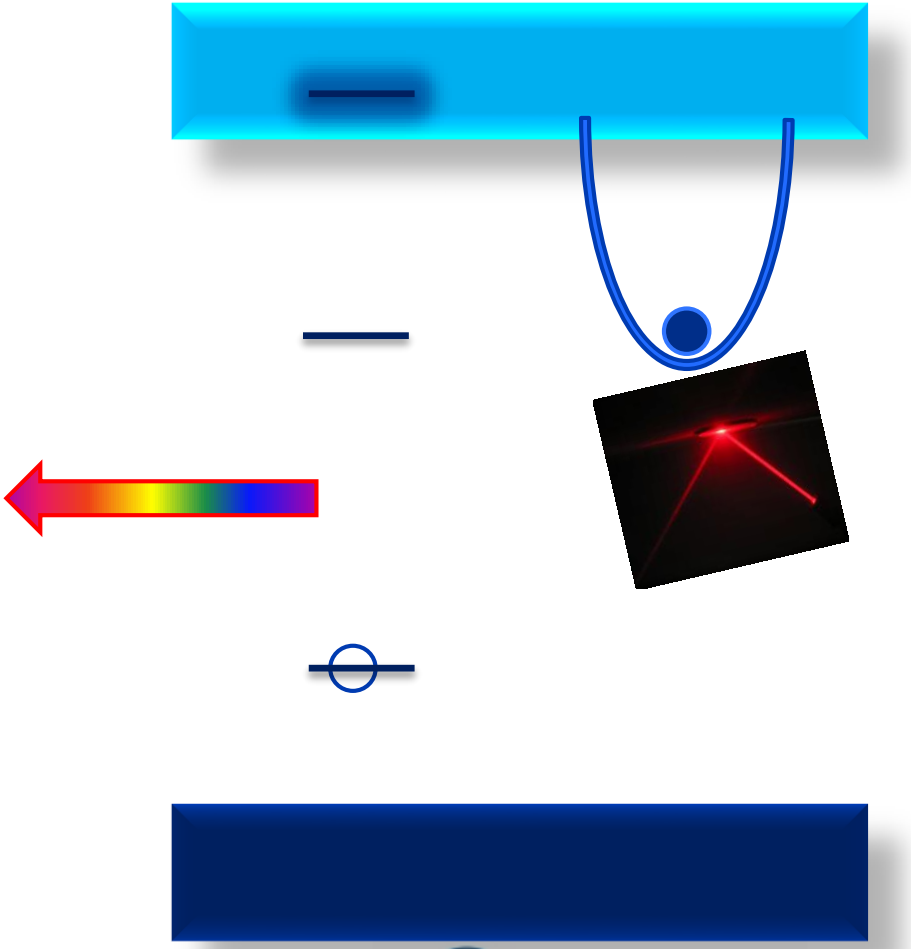
# Energy releasing

# Thermoluminescence

# Energy releasing - thermoluminescence

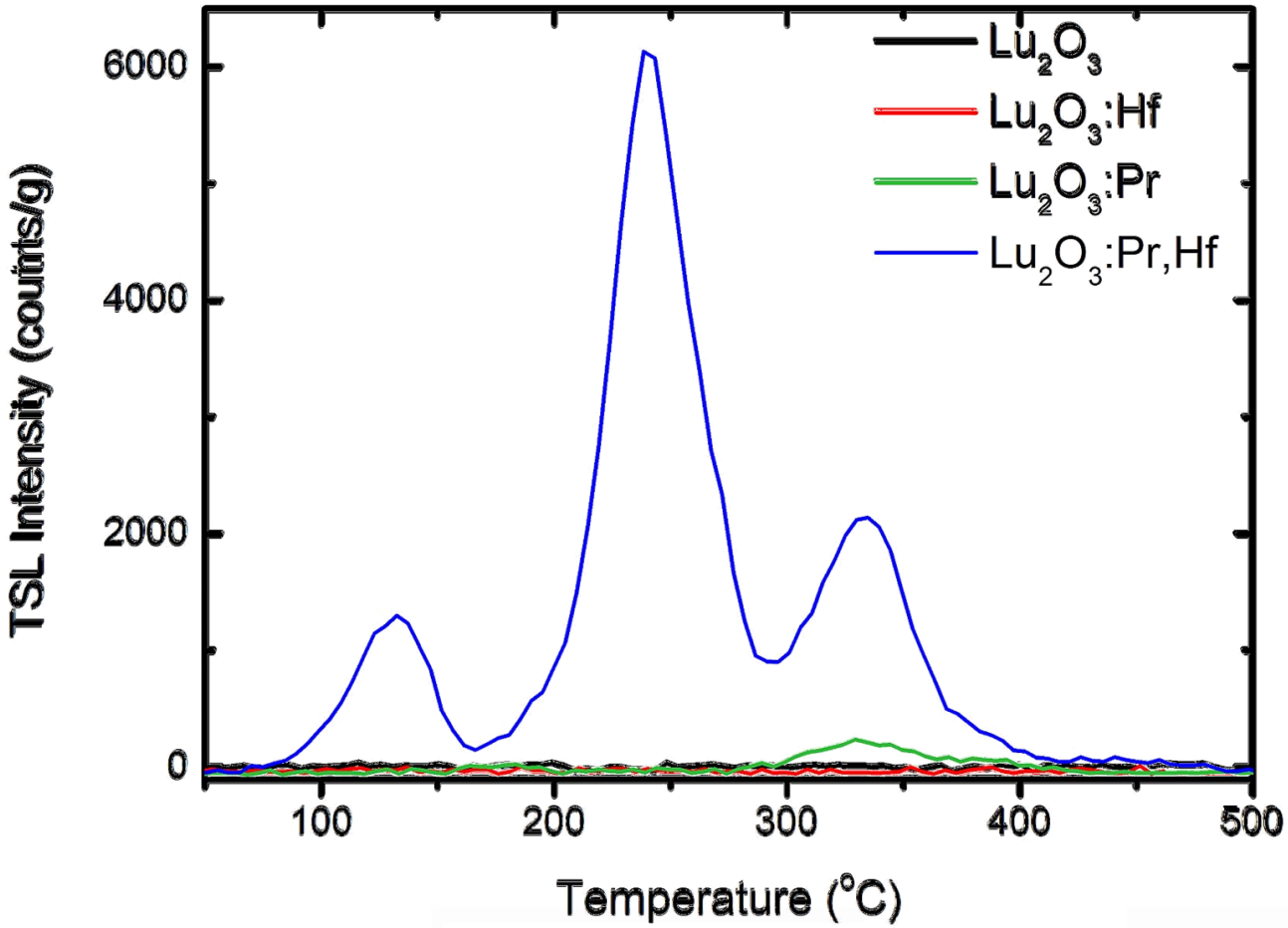


# Energy releasing Optically Stimulated Luminescence



# TL – a combined effect of dopants

## $Lu_2O_3$:Pr,Hf

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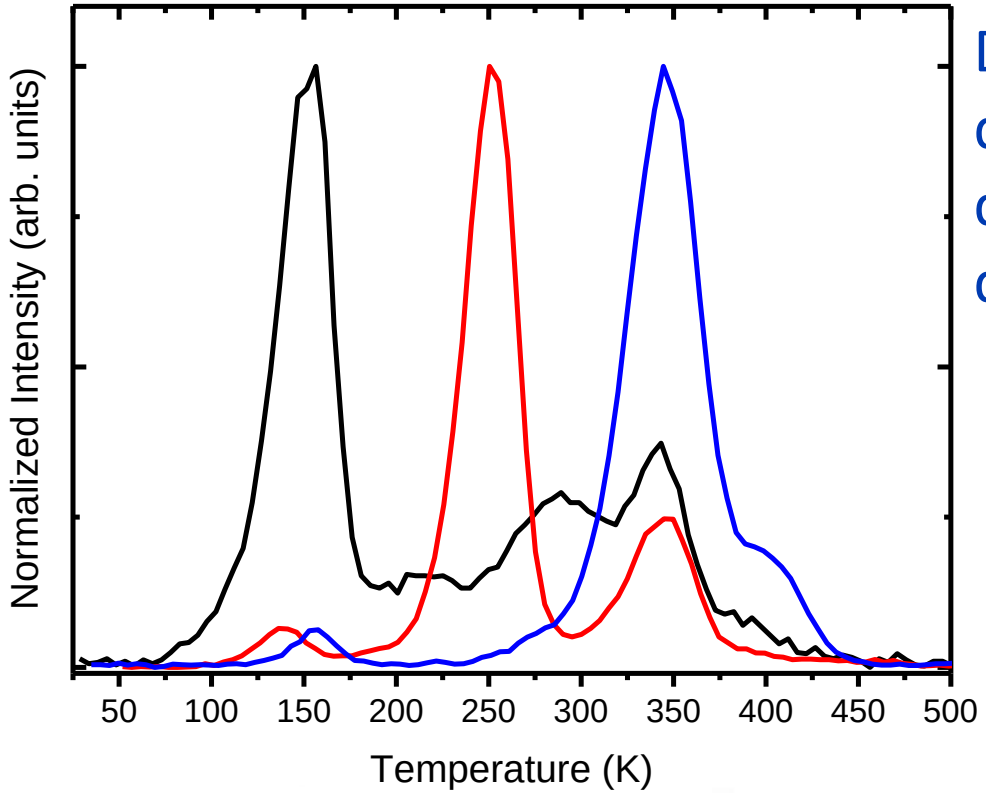
# Lu2O3:Pr,M - co-dopant define the trap depth(s)?

**Sr(II)<Hf(IV)<Nb(V)**




Does the co-dopant **charge** define the trap depth?

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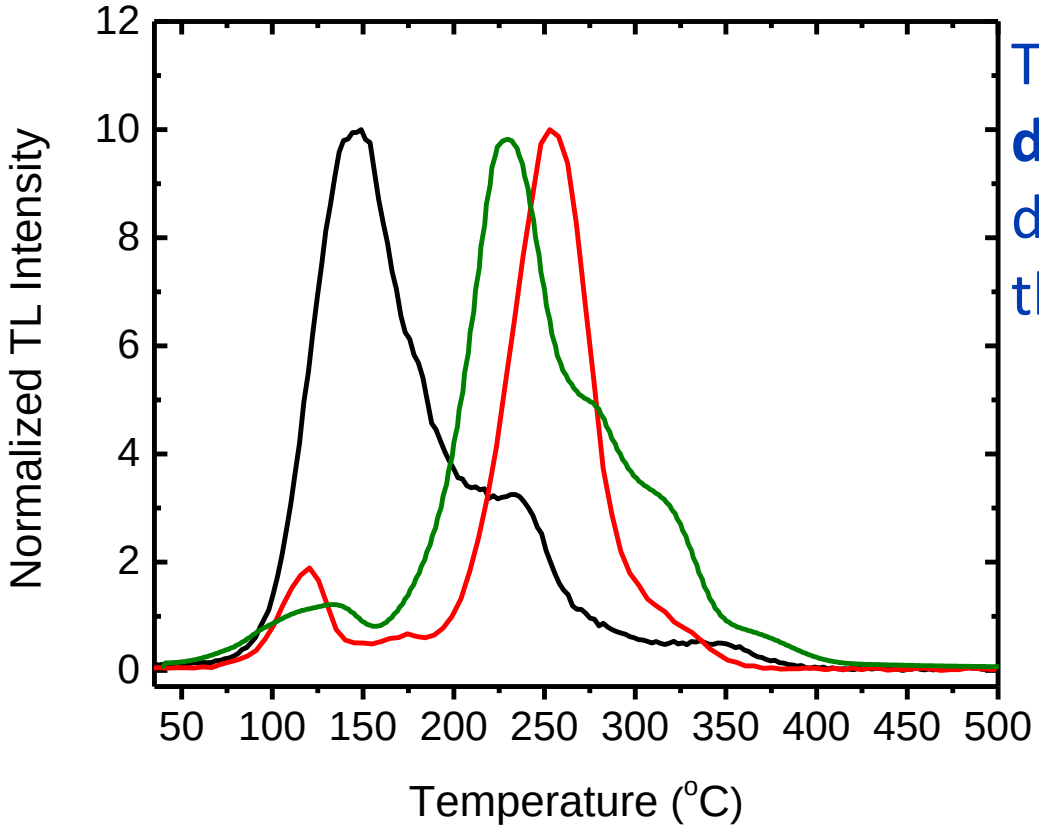
# Lu2O3:Tb,M - co-dopant and the trap depth(s) !!!

**Ca(II)< Nb(V)<Hf(IV)**

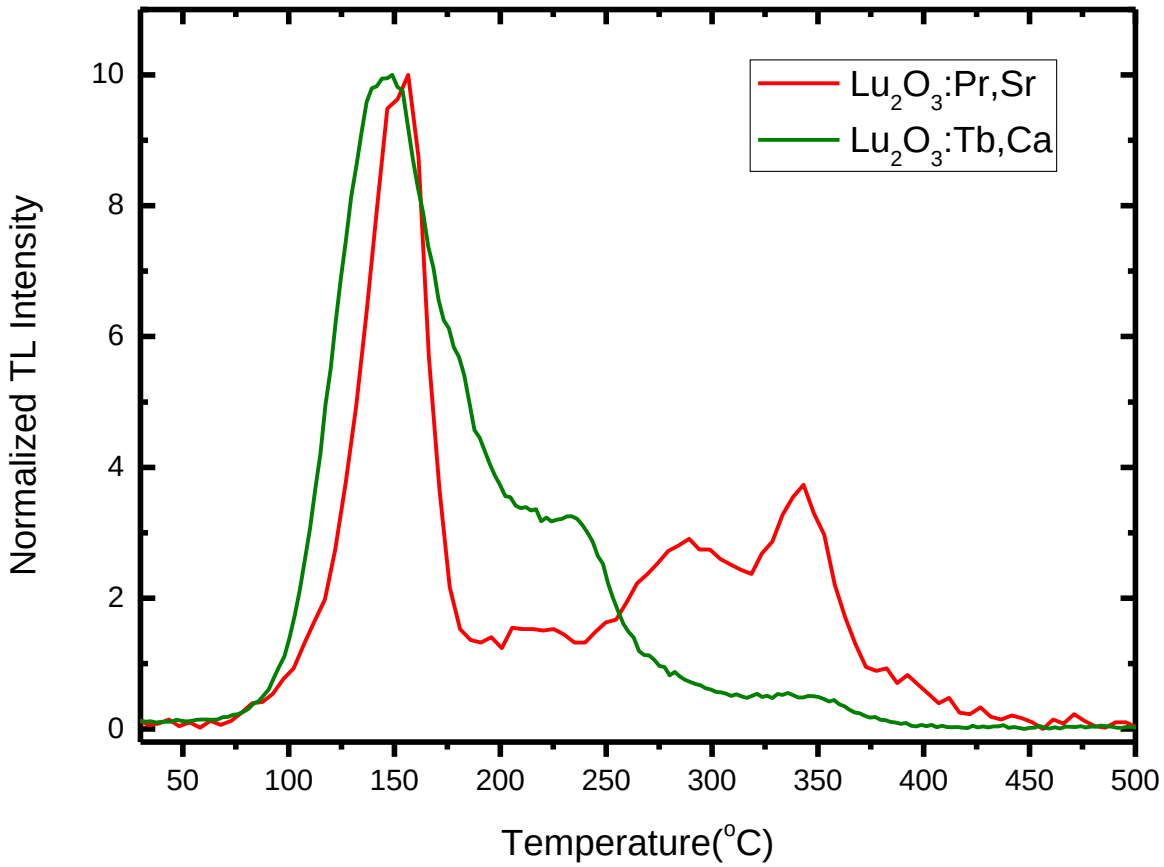



The charge **does not** directly define the trap depth

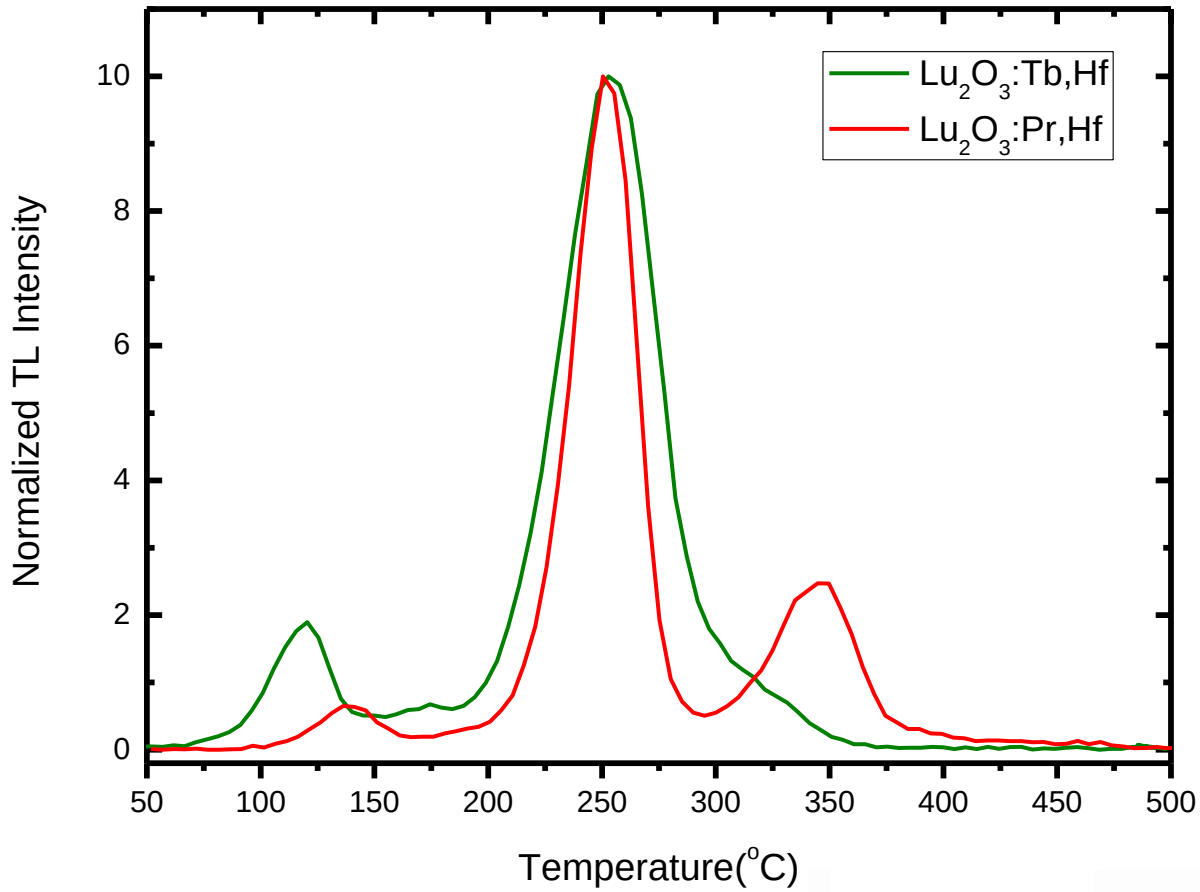
# Comparison of TL

# $Lu_2O_3$:Pr,M vs. $Lu_2O_3$:Tb,M

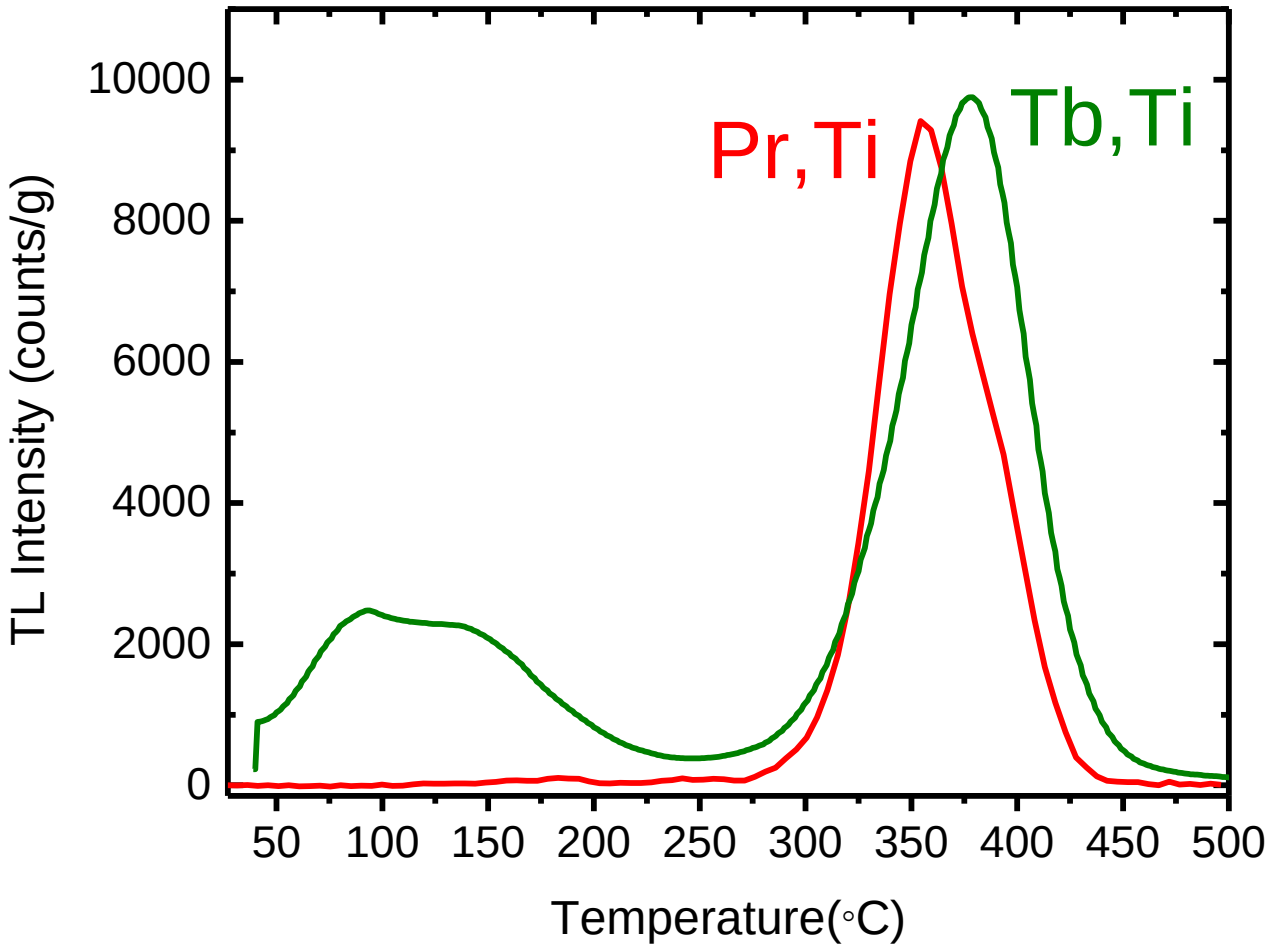
# Pr,Sr vs. Tb,Ca



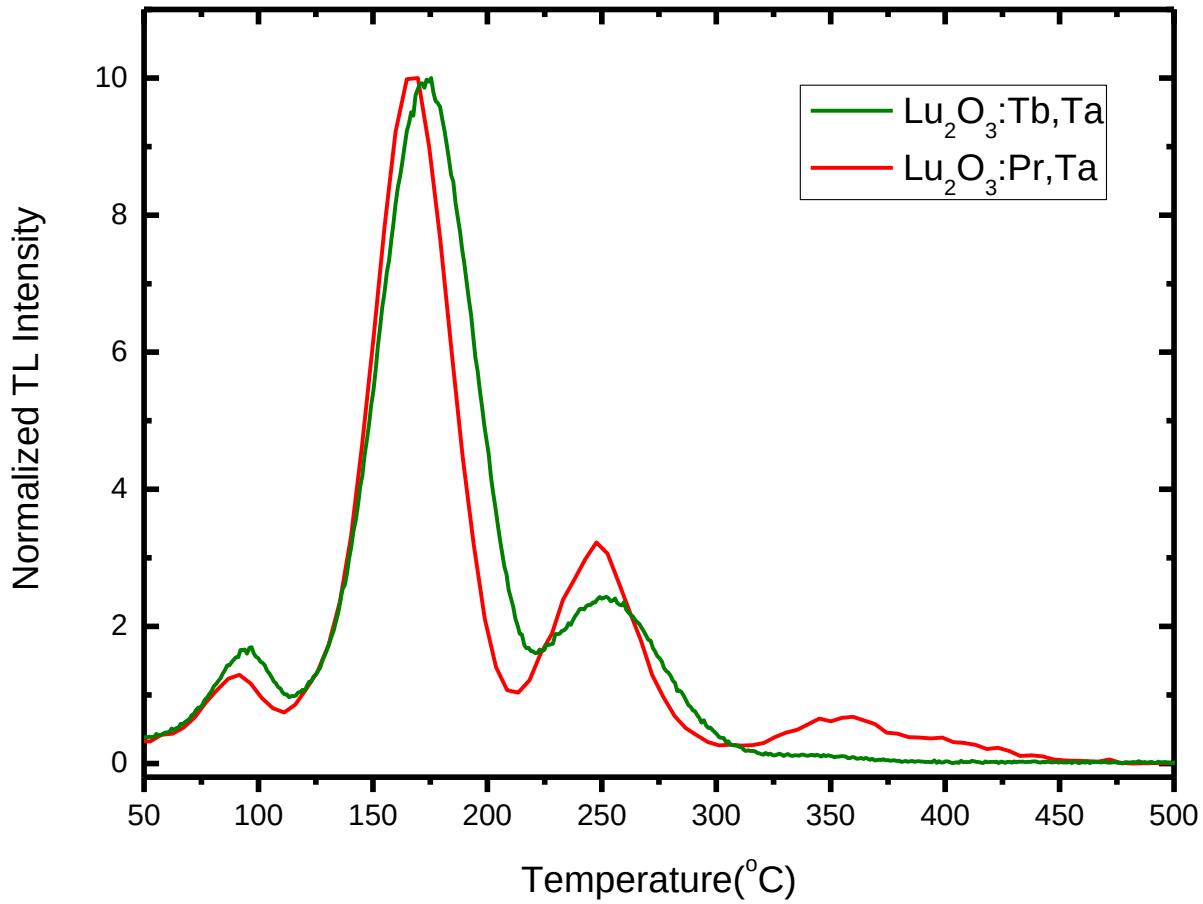
# Pr,Hf vs. Tb,Hf



# Pr,Ti vs. Tb,Ti

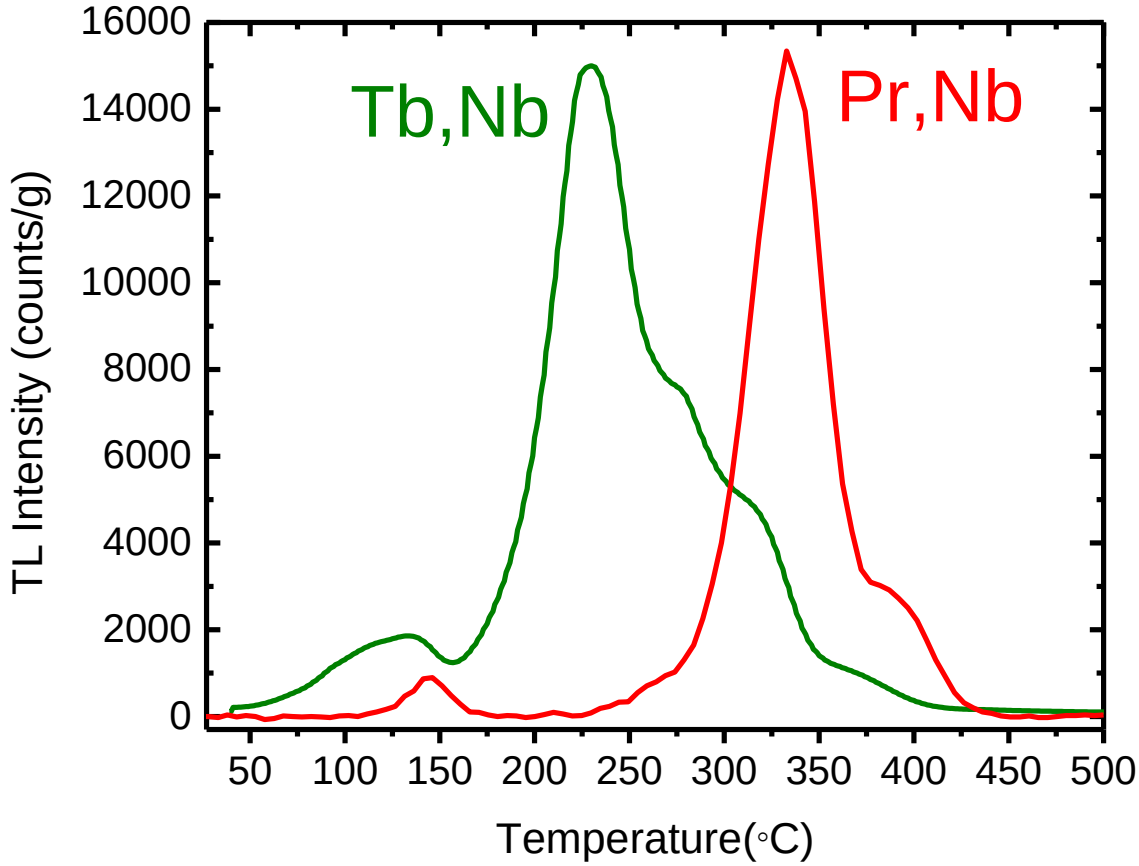

Pr,Ti
Tb,Ti
TL Intensity (counts/g)
10000
8000
6000
4000
2000
0
50
100
150
200
250
300
350
400
450
500
Temperature(◦C)

# Pr,Ta vs. Tb,Ta


Lu2O3:Tb,Ta
Lu2O3:Pr,Ta
Normalized TL Intensity
Temperature(°C)
0
2
4
6
8
10
50
100
150
200
250
300
350
400
450
500

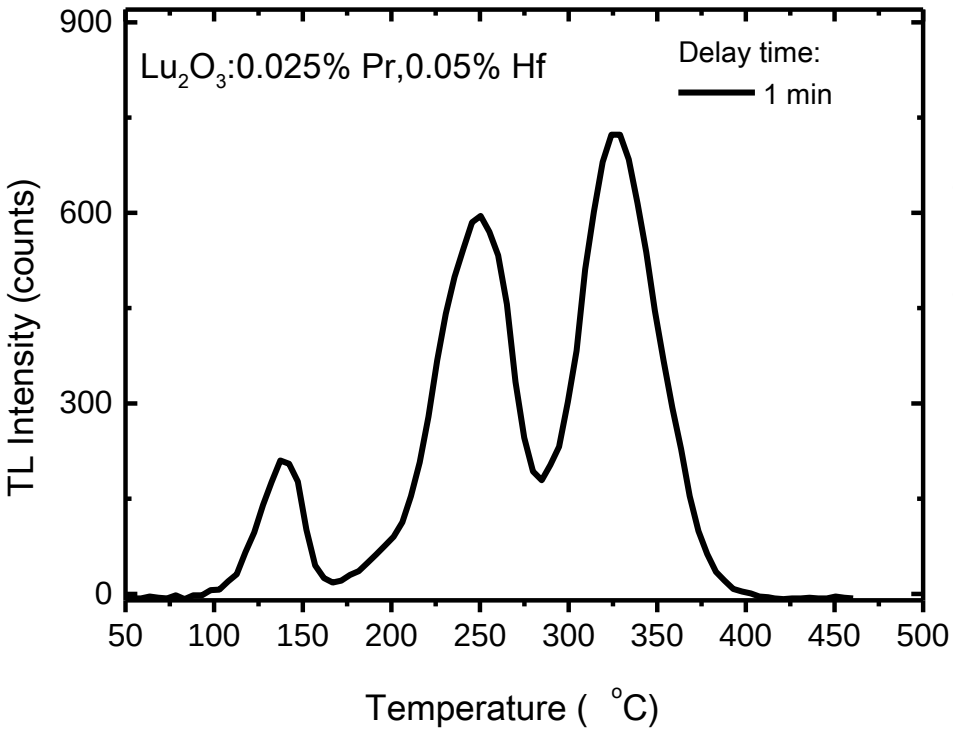
# Pr,Nb vs. Tb,Nb

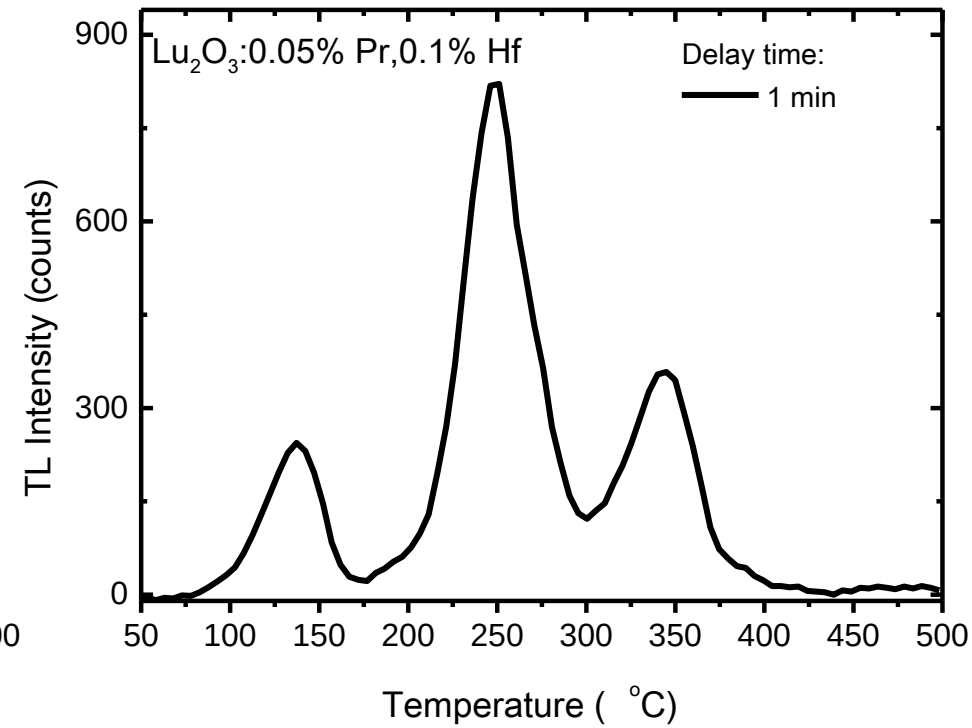
?


Tb,Nb
Pr,Nb
TL Intensity (counts/g)
16000
14000
12000
10000
8000
6000
4000
2000
0
50
100
150
200
250
300
350
400
450
500
Temperature(◦C)

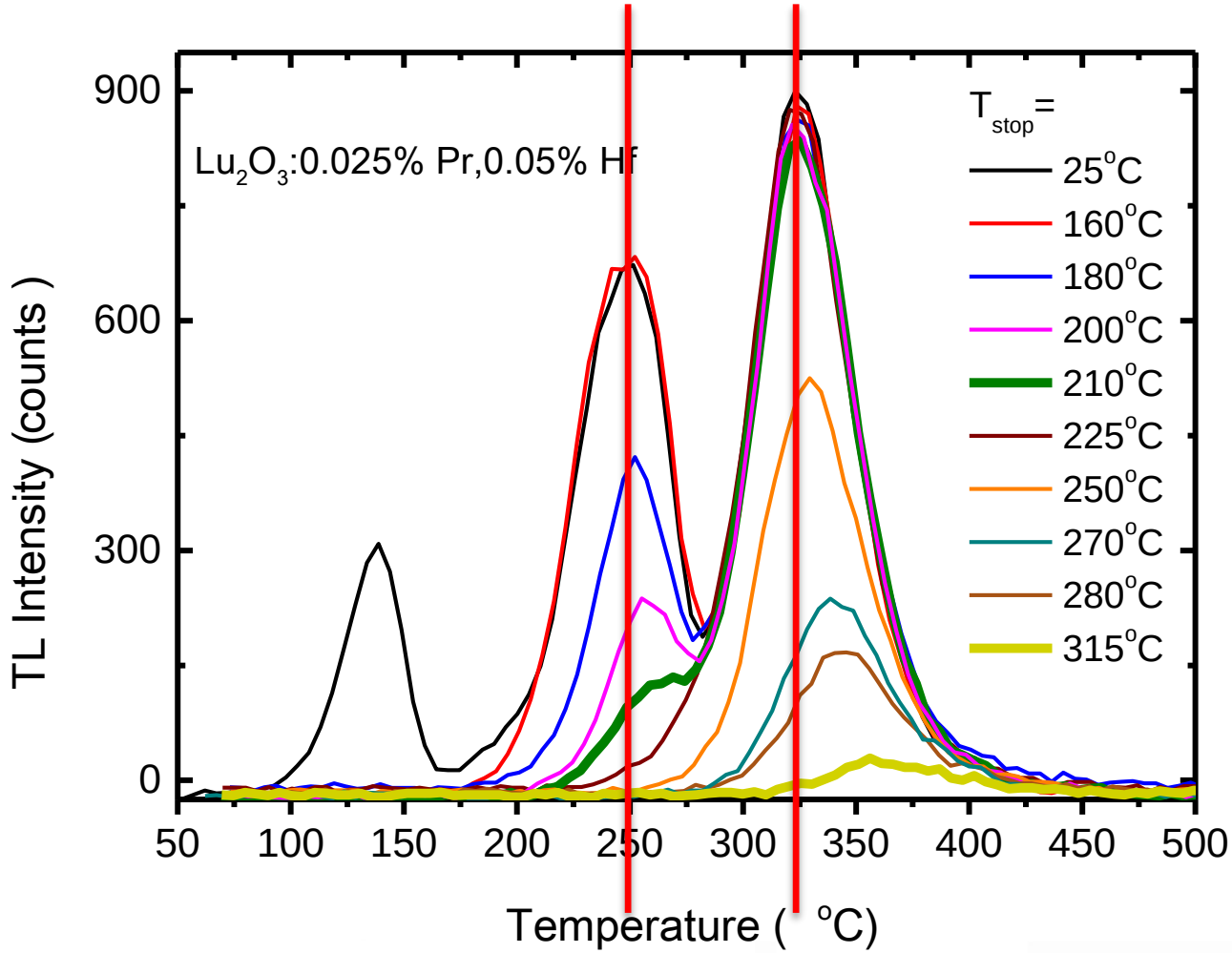
?

# Concentrations are very important

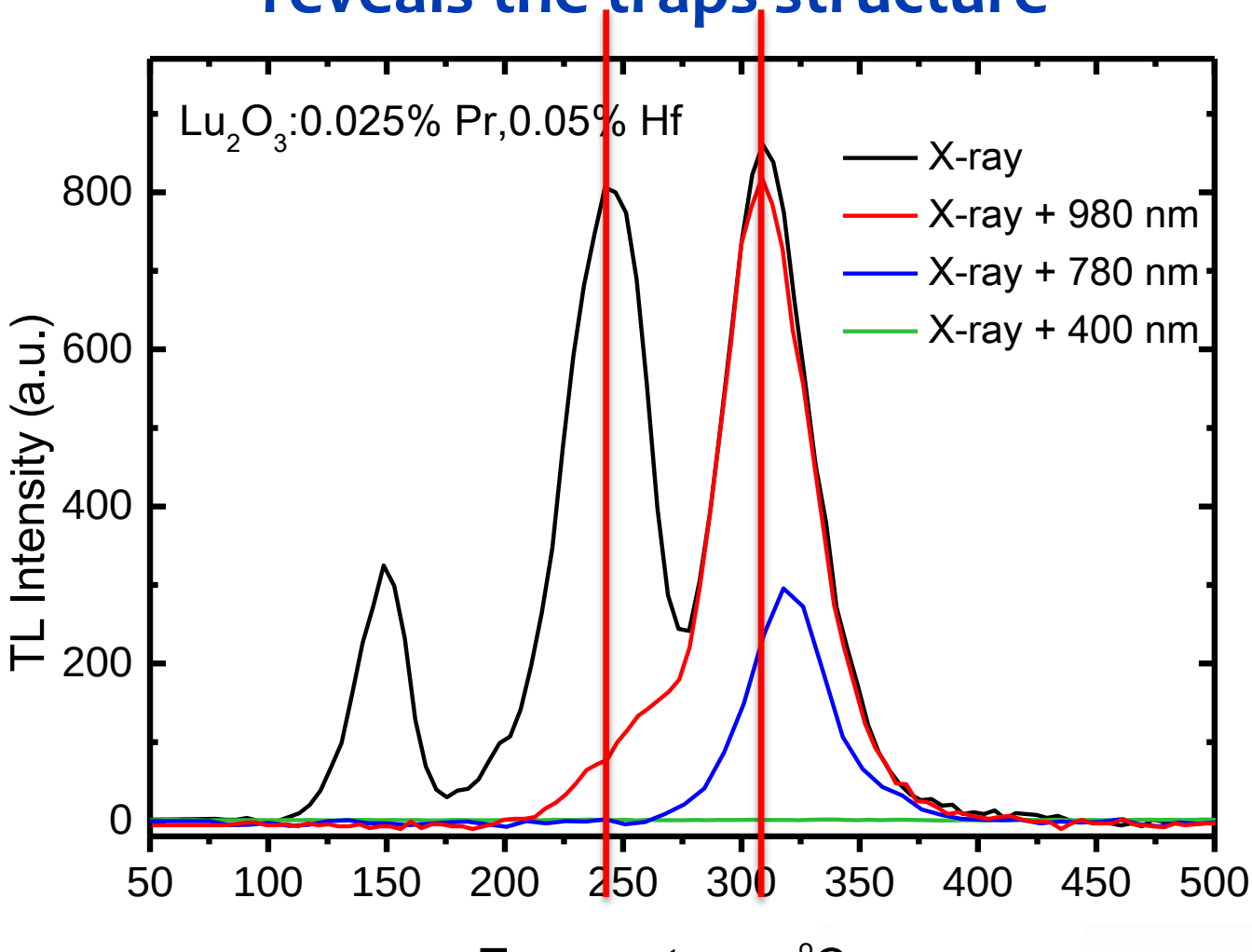


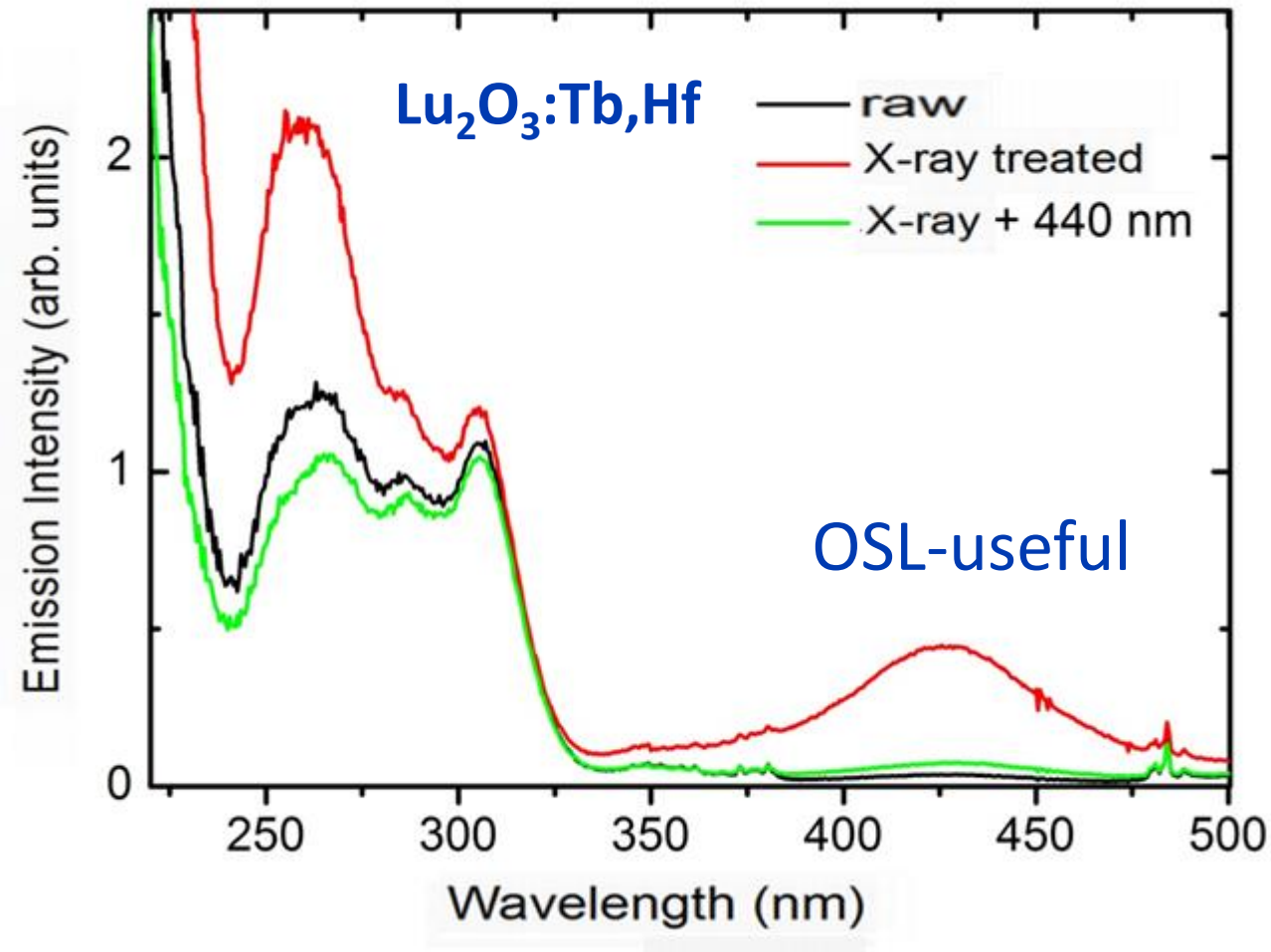
# Thermal „partial cleaning" reveals the traps' structure



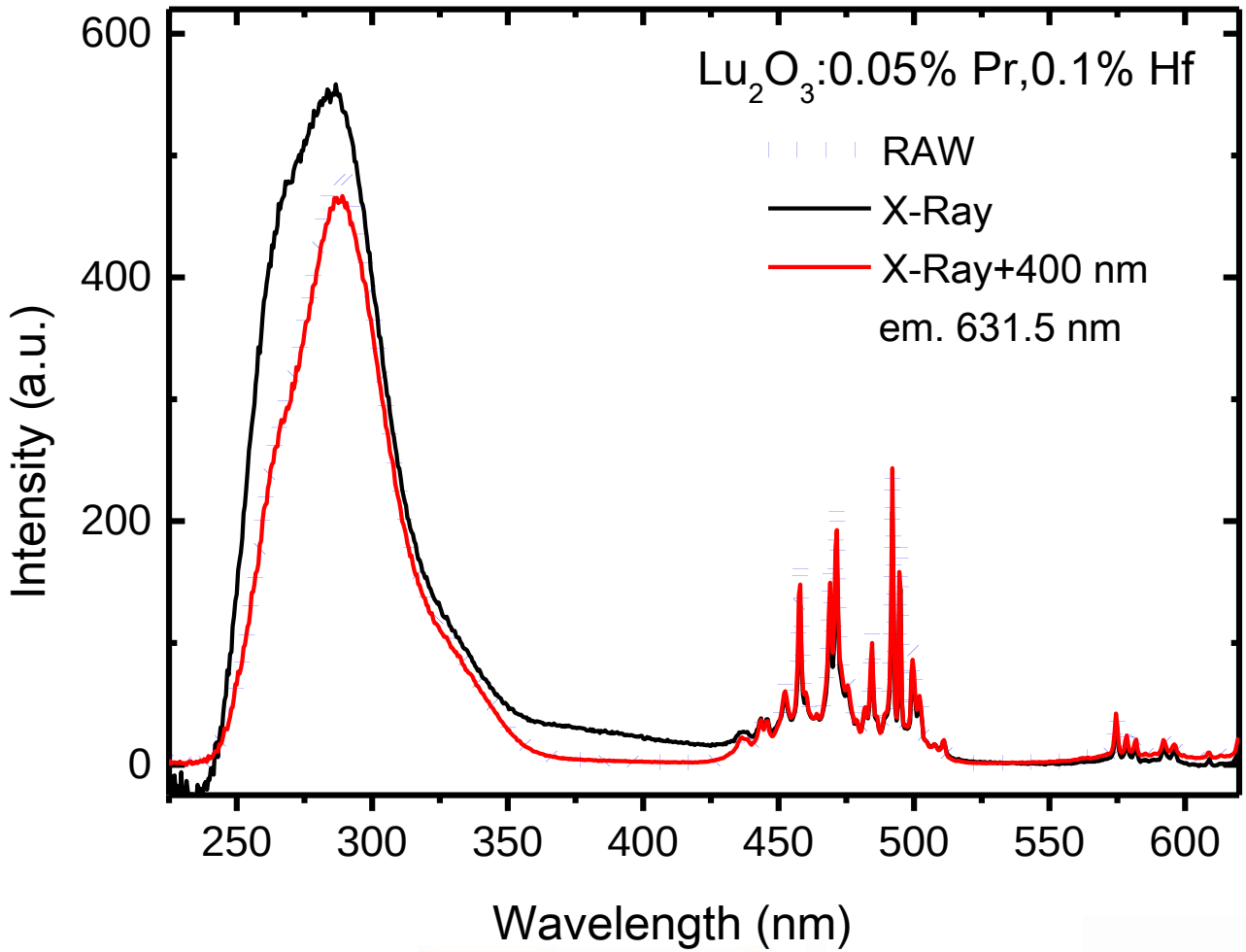
# Optical „partial cleaning" reveals the traps structure



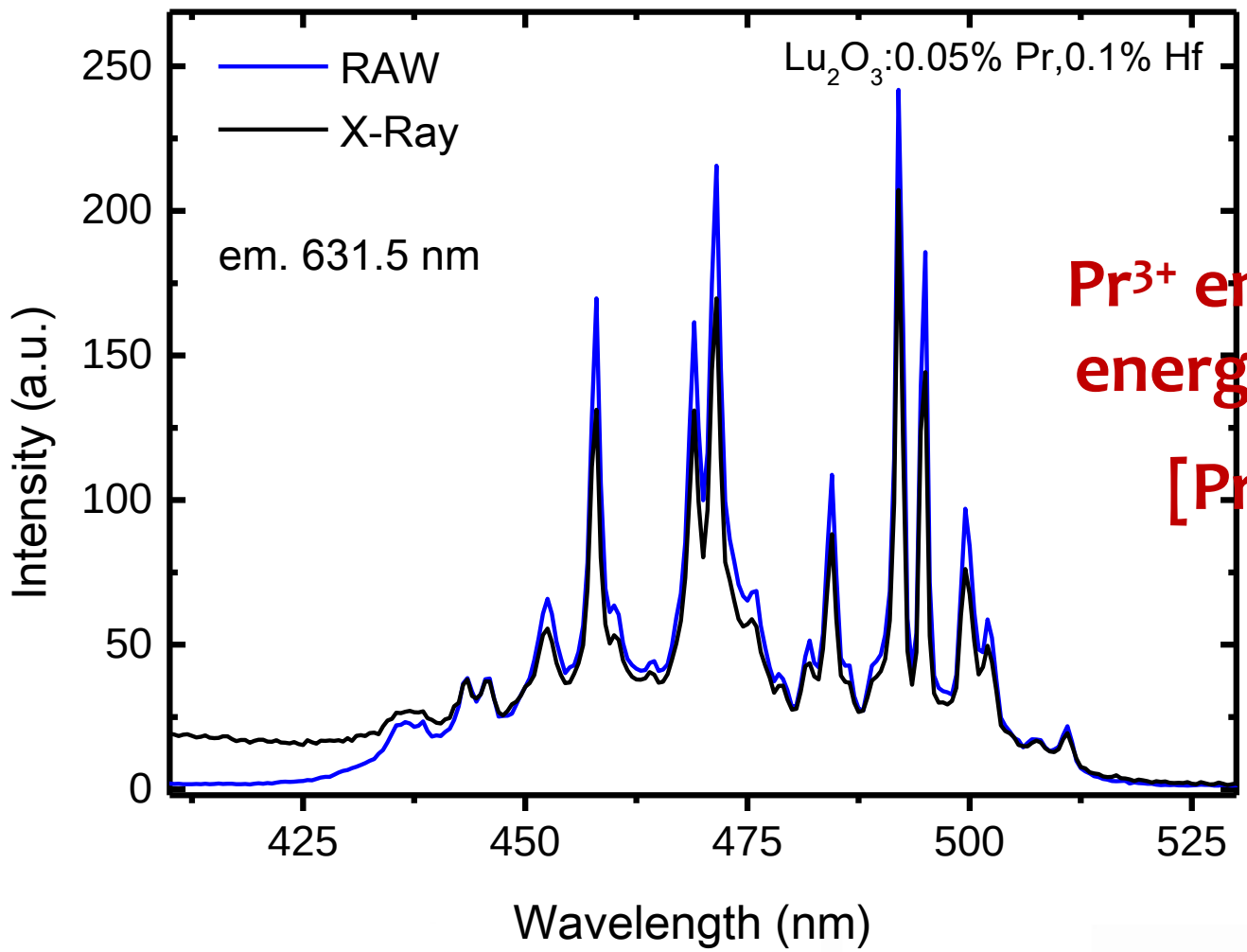
# Changes are seen in excitation spectra and are reversable



# Changes are seen in excitation spectra and are reversable



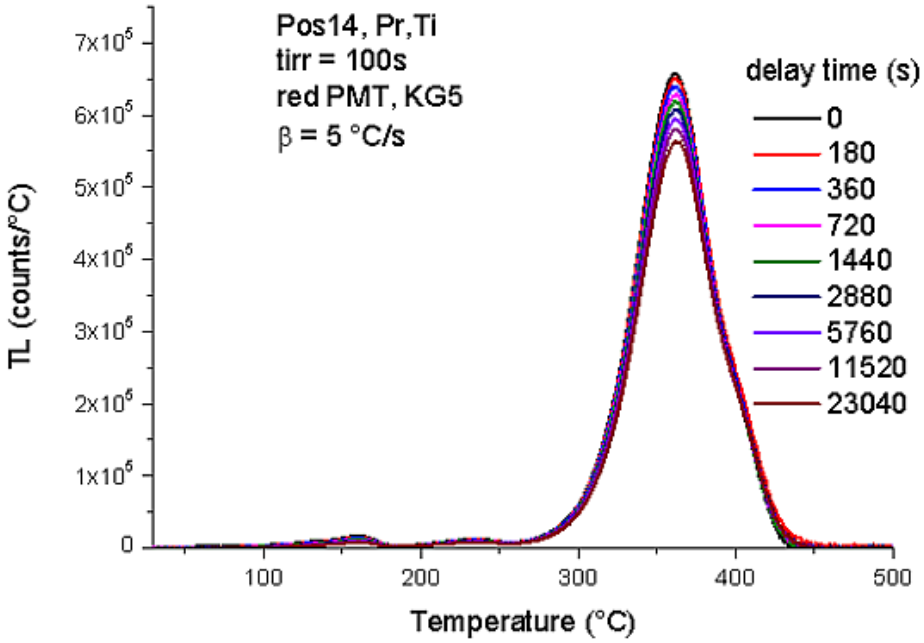
# Changes are seen in excitation spectra and are reversible

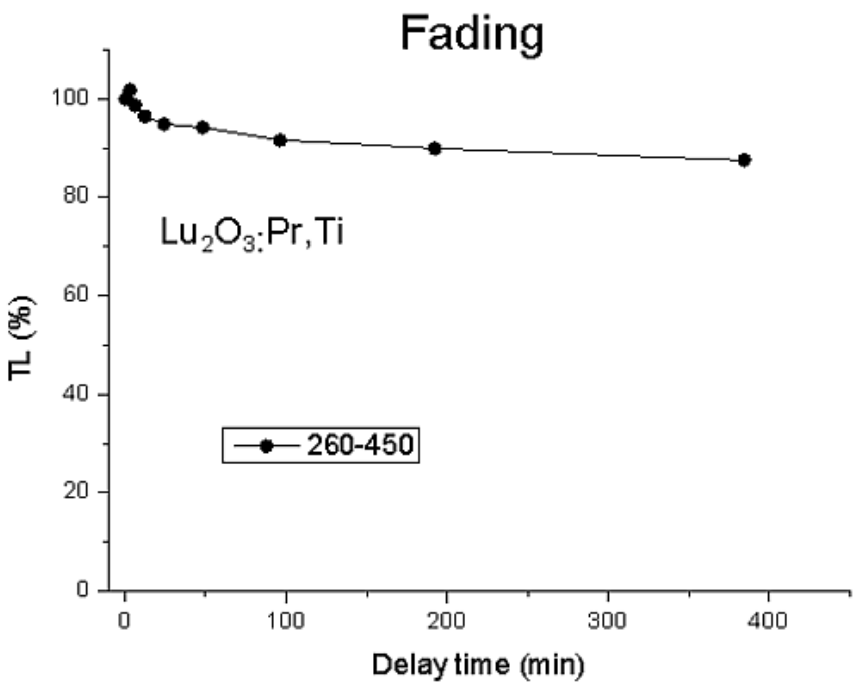



**$Pr^{3+}$ engaged in energy storing**

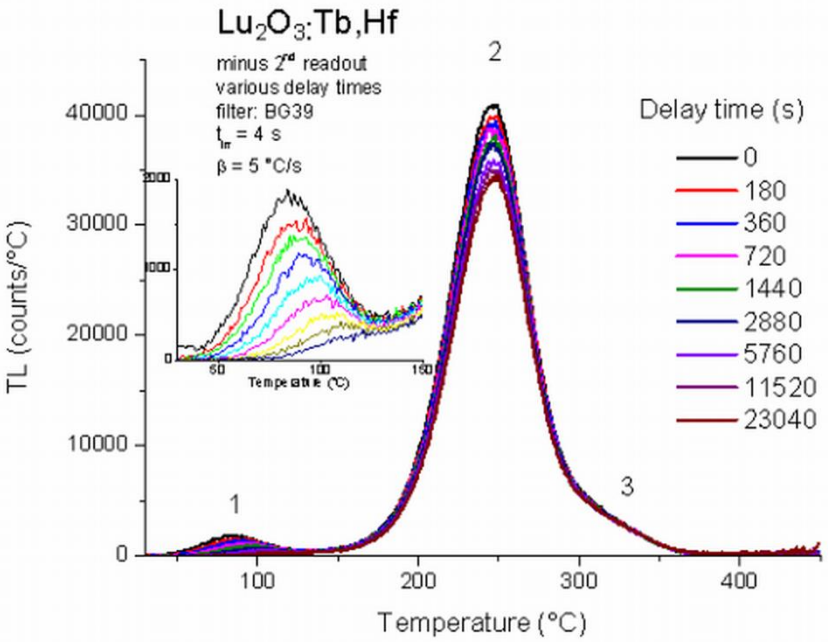
**$[Pr^{3+}+h]$?**

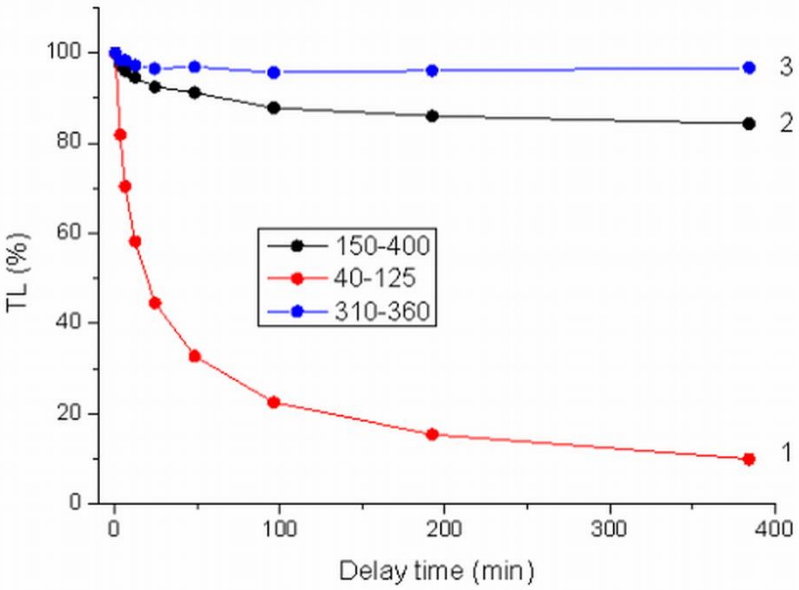
# Lu2O3:Pr,Ti – fading



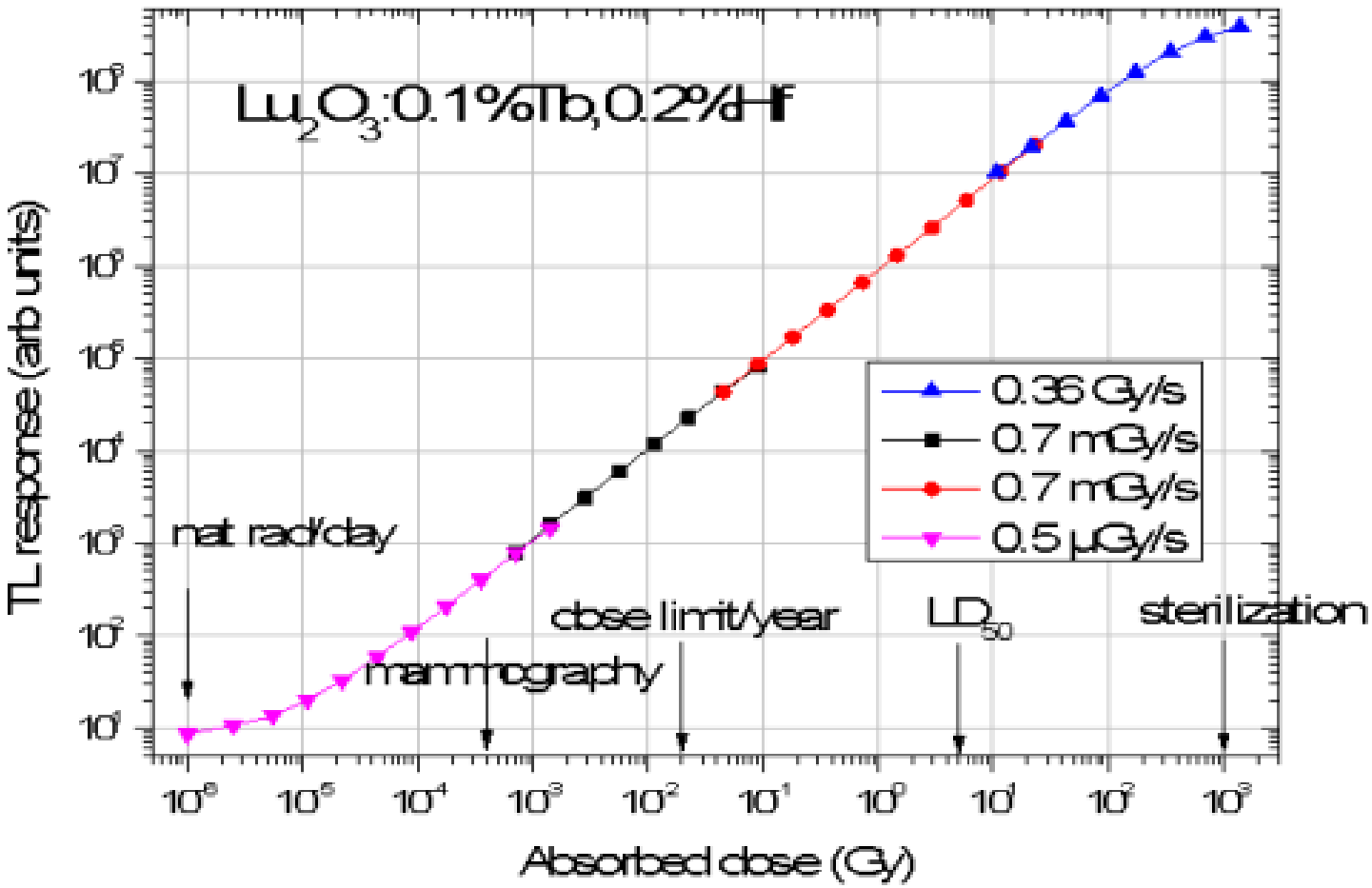
# Lu2O3:Tb,Hf – fading



# Lu2O3:Tb,Hf – range of „linear" response

## 7 orders of magnitude – exceptional




environmental, personal, radiotherapy, sterilization

# Summary

- Two families of storage phosphors were discovered: green-emitting $Lu_2O_3$:Tb,M and red-emitting $Lu_2O_3$:Pr,M
- Response - dose „linear" dependence covers >7 orders of magnitude
- No radiation damage observed up to at least 1 kGy range of doses

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**Paulina Bolek (PhD student)**
**and Dr. Adrie Bos (Delft TU)**

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# Thank you

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