Thermoluminescence and Defect Structure of Eu^{2+} and Mn^{2+} doped $BaMgAl_{10}O_{17}$

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Outline

- **Application areas of BAM**
- **Crystal structure and luminescence spectra of BAM**
- **Problem setting**
- **Thermoluminescence analysis**
  - **BAM:Eu**
  - **BAM:Mn**
- **Interpretation and conclusions**

Application Areas of $BaMgAl_{10}O_{17}$:Eu(Mn)

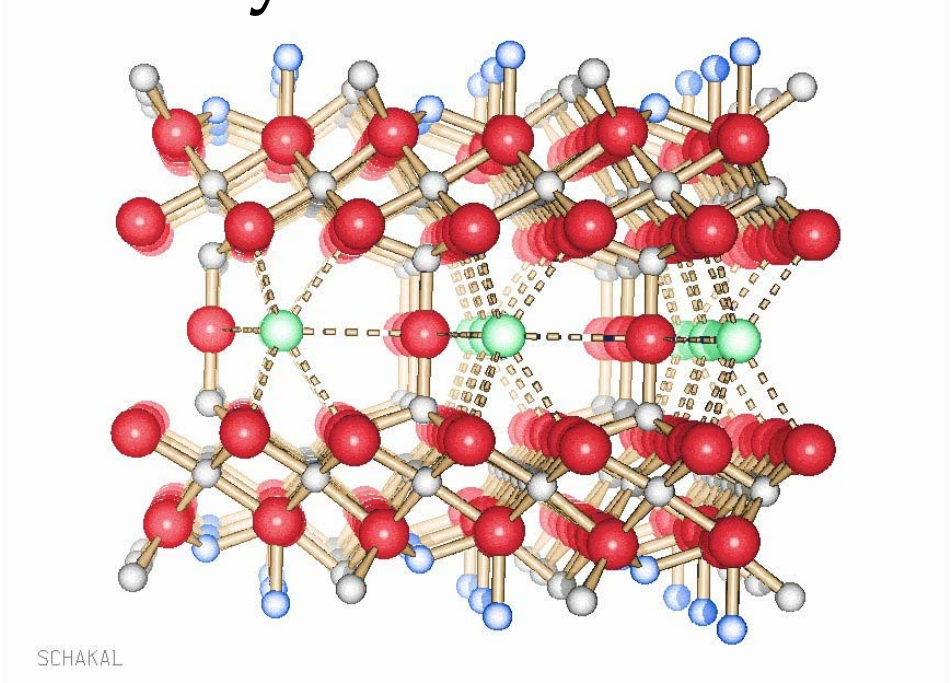
Fluorescent Lamps

Plasma Displays

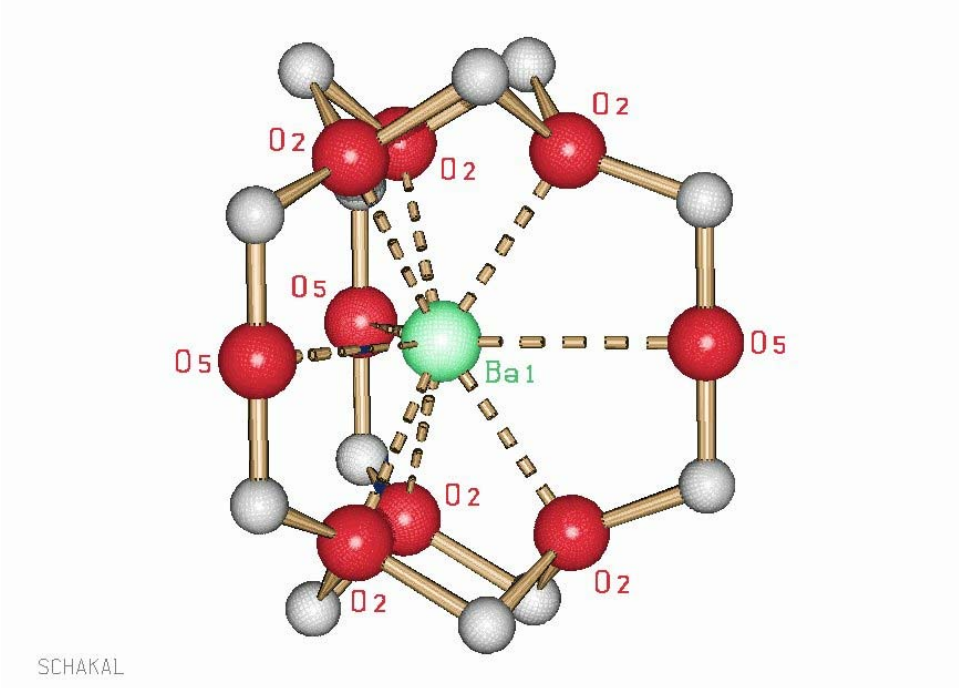
High photoluminescence efficiency and perfect color point for tricolor lamps and emissive displays

Structure of $BaMgAl_{10}O_{17}$ (BAM)

Layer structure



Ba^{2+} coordination sphere

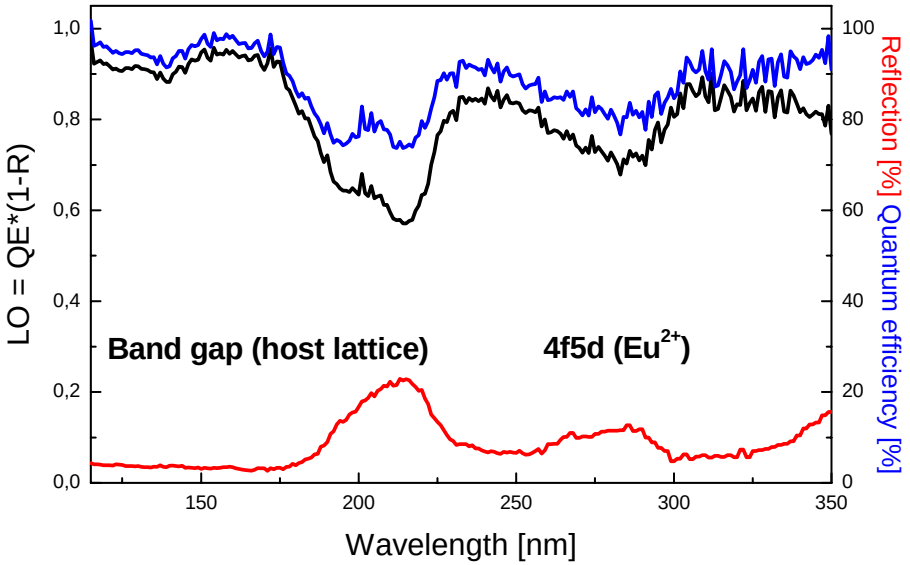


Eu^{2+} occupies Ba^{2+} sites in the conduction layers

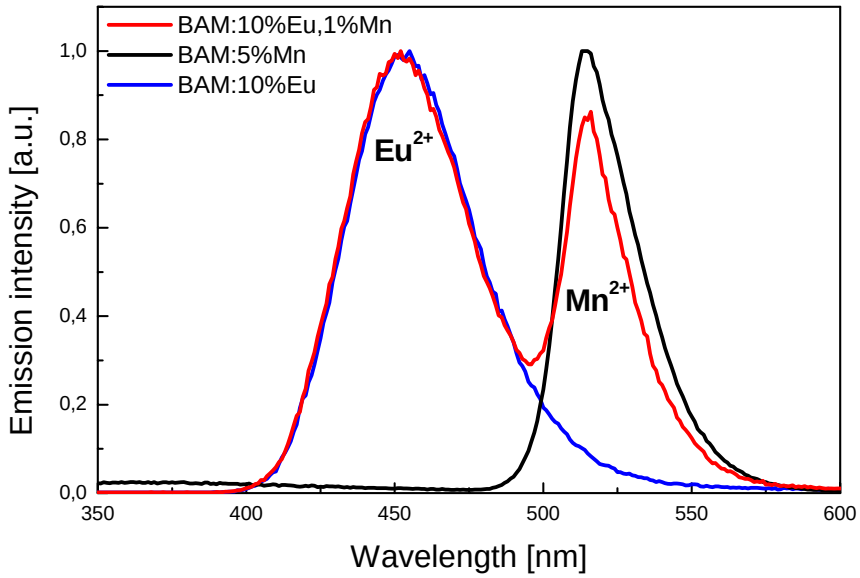
Mn^{2+} occupies Mg^{2+} sites in the spinel blocks

Luminescence Spectra of BAM:Eu and BAM:Mn

Excitation and reflection spectra



Emission spectra

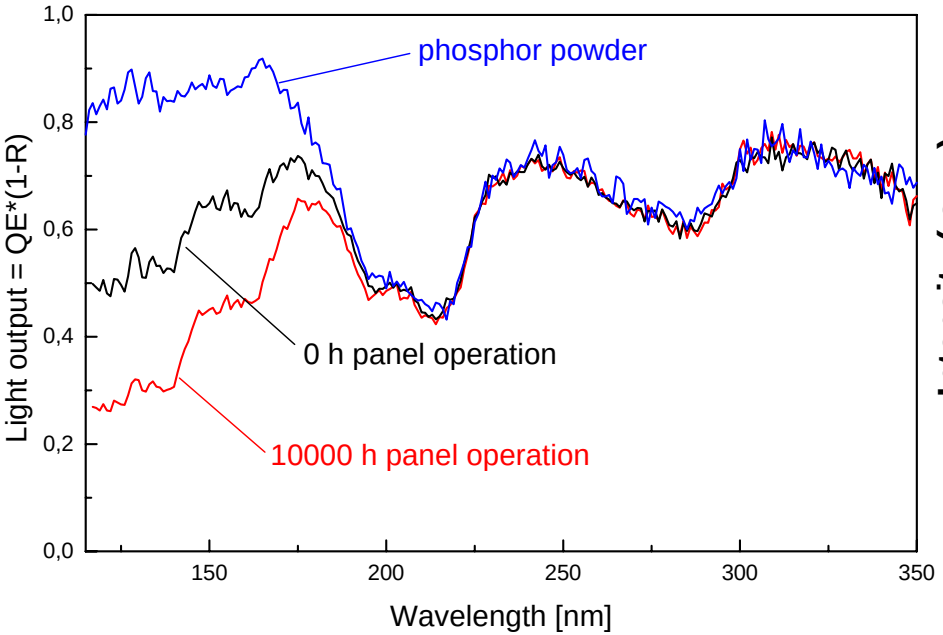


Excitation bands: 170 nm (host lattice)
230 nm (4f5d Eu^{2+})
320 nm (4f5d Eu^{2+})

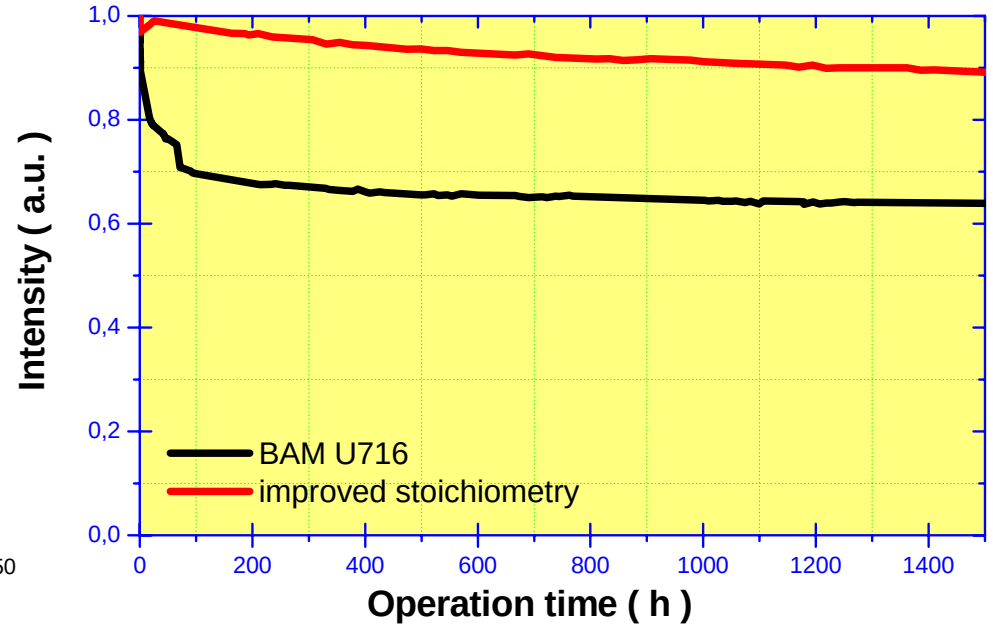
Emission band: 453 nm (5d4f Eu^{2+})
515 nm (5d5d Mn^{2+})

Problem Setting

Change of spectral light output



Time dependence of light output

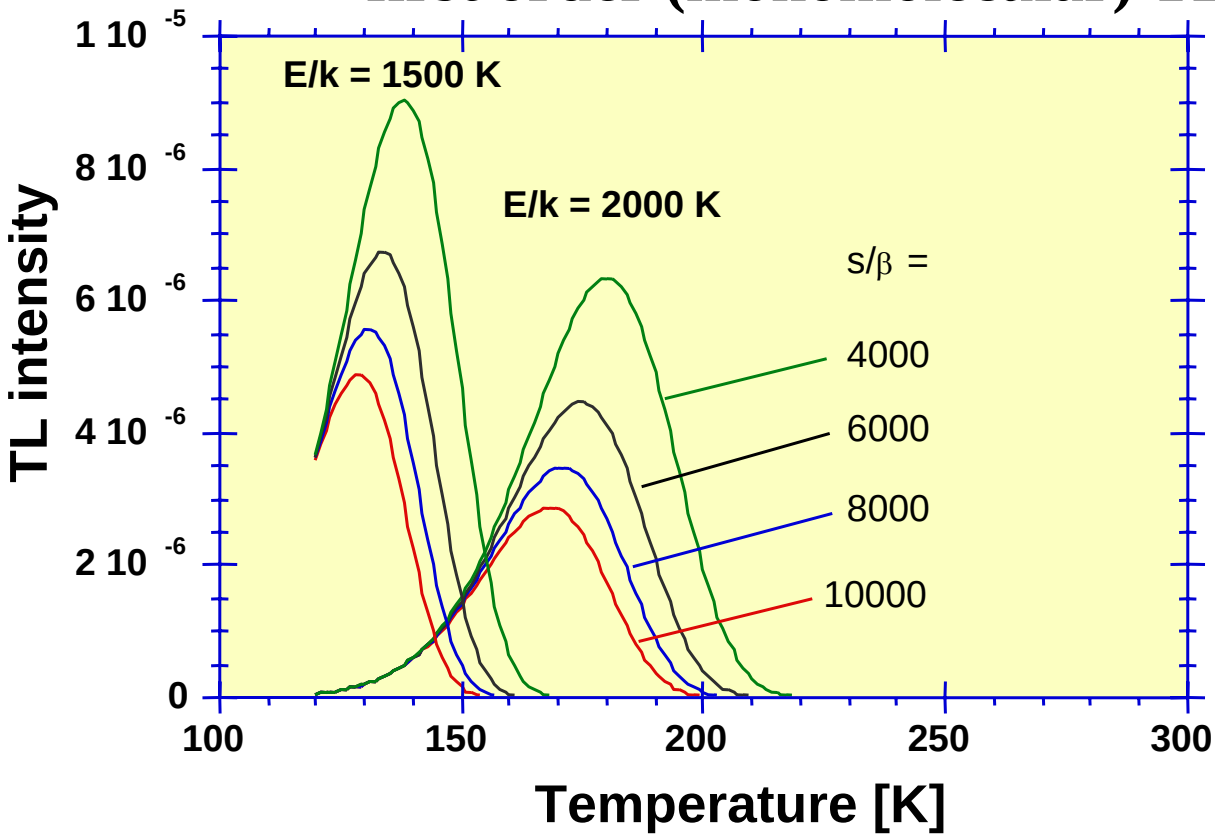


Strong degradation during device operation related to

- **Eu^{3+} formation**
- **Powder quality (crystallinity) and Ba/Mg/Eu/Al ratio**

Thermoluminescence Analysis

first order (monomolecular) TL kinetics



N_{T_0} : number of trapped electrons

s : decay frequency

b : heating rate

E : energy trap depth below excited state

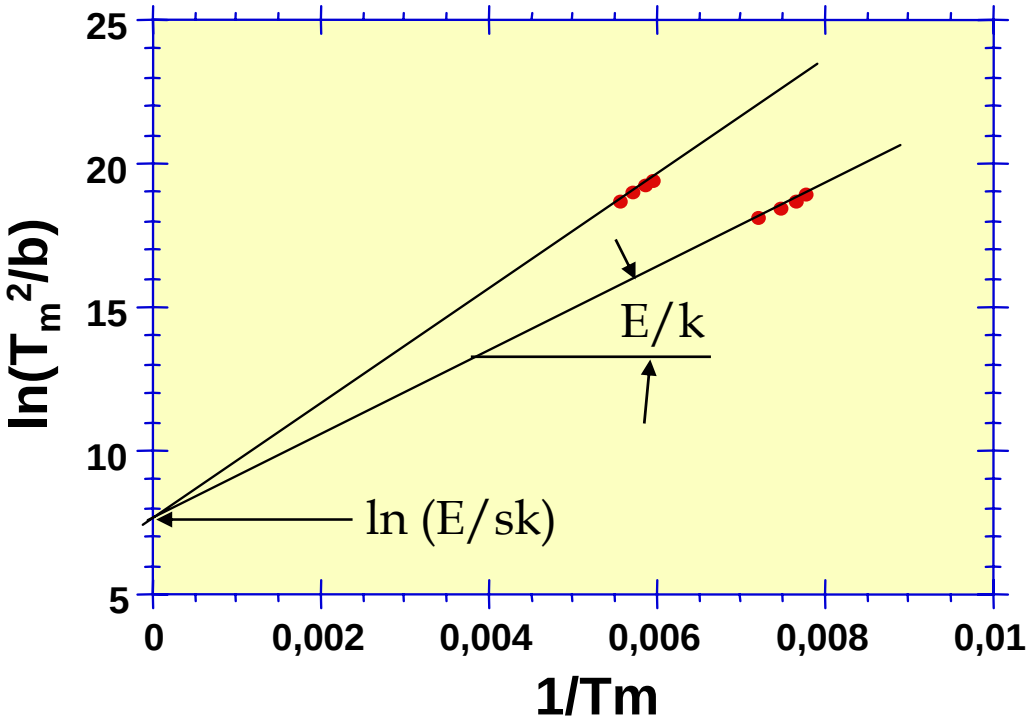
$$I_{TL} = N_{T_0} s \exp(-E/kT) \cdot \exp\left[-s/\beta \int_{T_0}^{T} \exp(-E/kT)\,dT\right]$$

Randall, Wilkins 1945

Thermoluminescence Analysis

first order (monomolecular) TL kinetics

$$I_{TL} = N_{T_0} s \exp(-E/kT) \cdot \exp\left[- s/\beta \int_{T_0}^{T} \exp(-E/kT)dT \right]$$

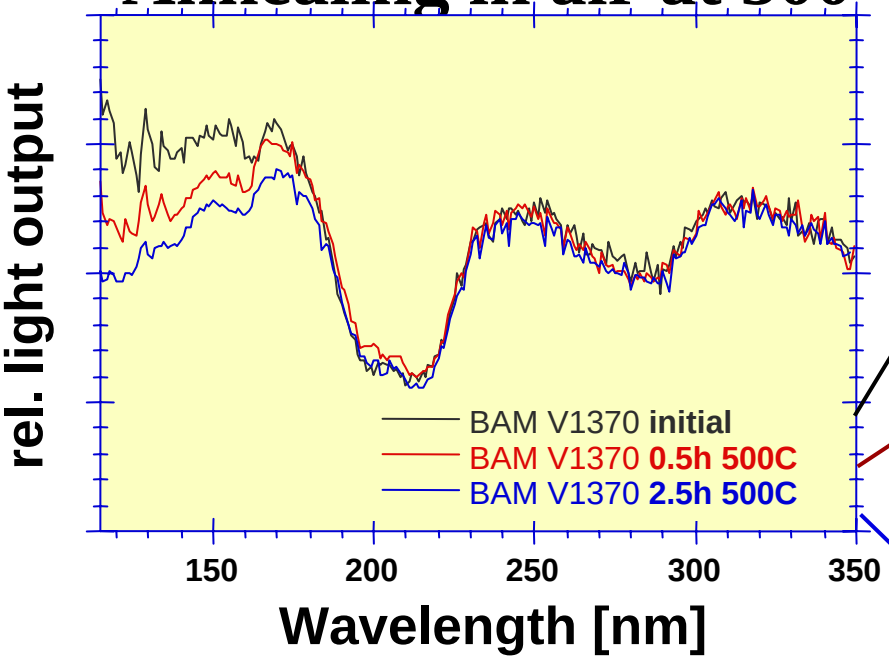


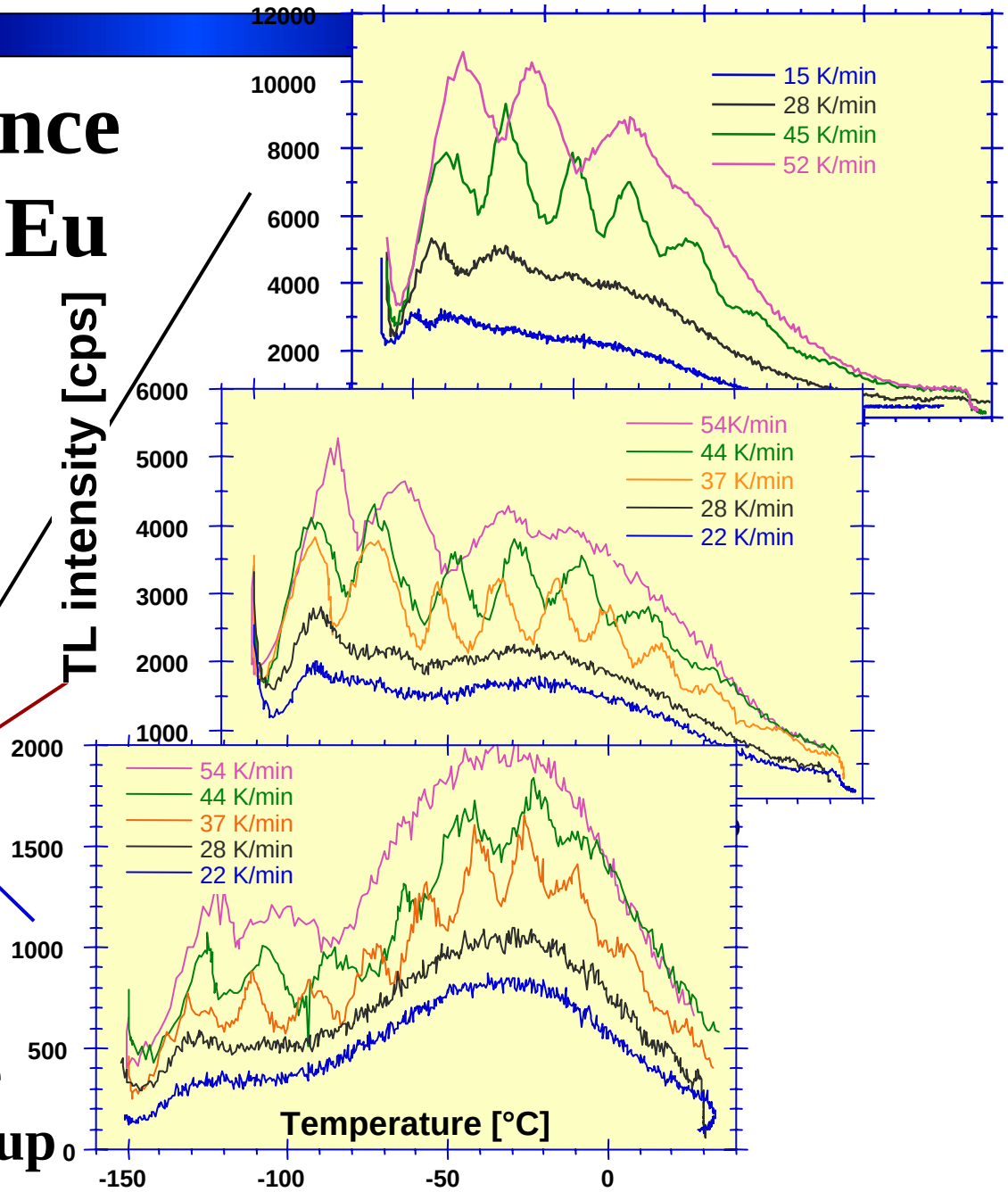
$$\frac{dI_{TL}}{dT} = 0 \quad \text{at} \quad T = T_m$$

$$\frac{\beta \cdot E}{k\, T_m^2} = s \cdot \exp(-E/k\, T_m)$$

Thermoluminescence Analysis of BAM:Eu

Annealing in air at 500°C





TL intensity decreases

Peak structure does not change

High temperature band shows up

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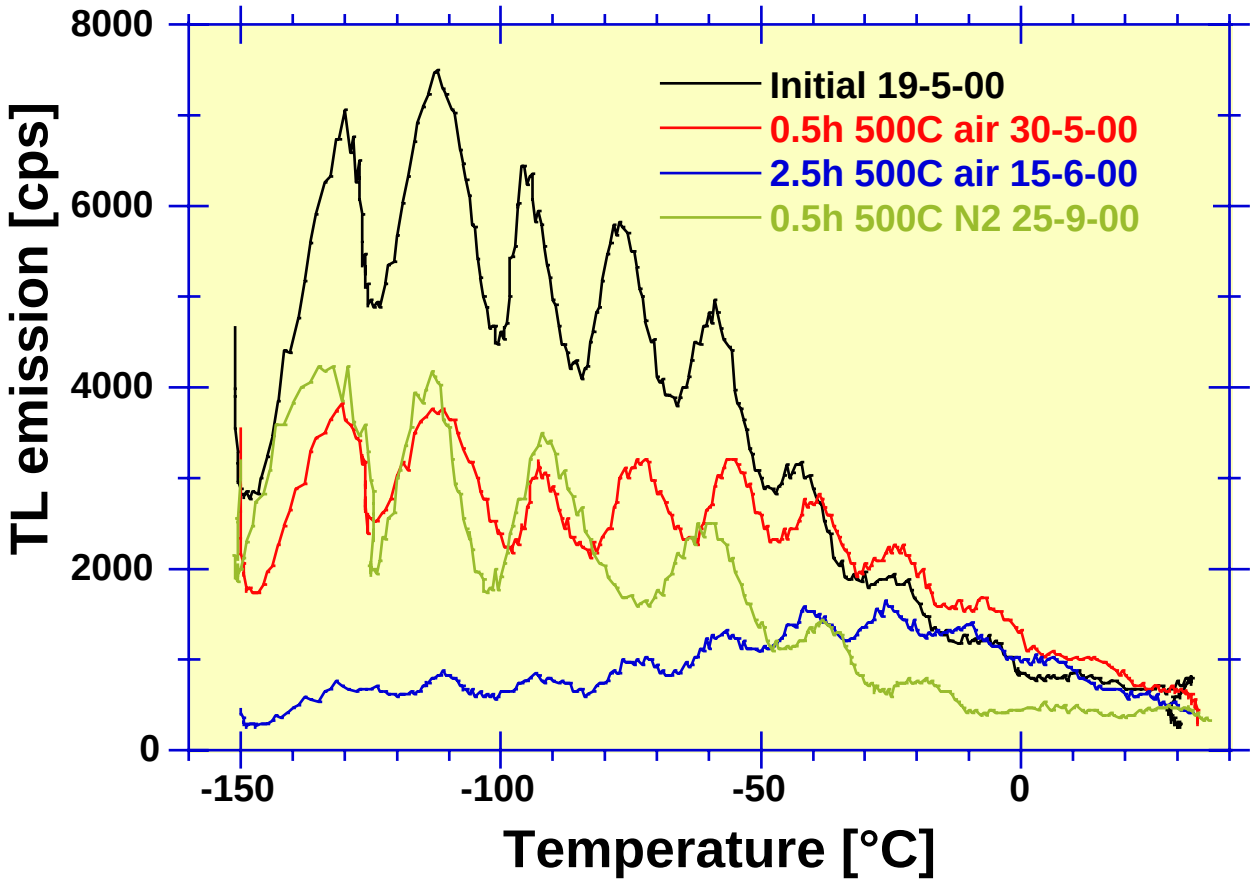
Thermoluminescence Analysis of BAM:Eu

Annealing in air or Nitrogen



Annealing in air

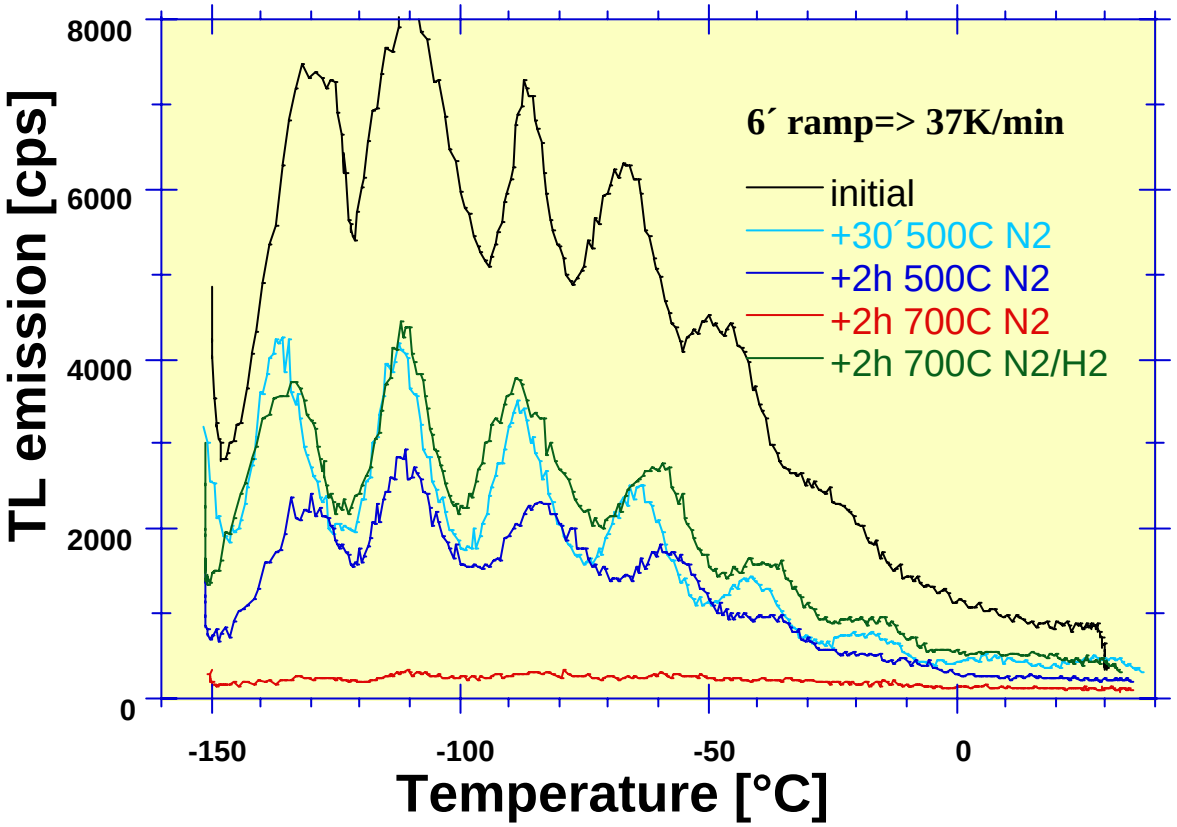
- **Density of shallow traps decreases**
- **Density of deep trap (0.3 eV) increases**

Annealing in Nitrogen

- **Deep trap does not show up**

Thermoluminescence Analysis of BAM:Eu

Annealing in N_2 or N_2/H_2



Annealing in Nitrogen

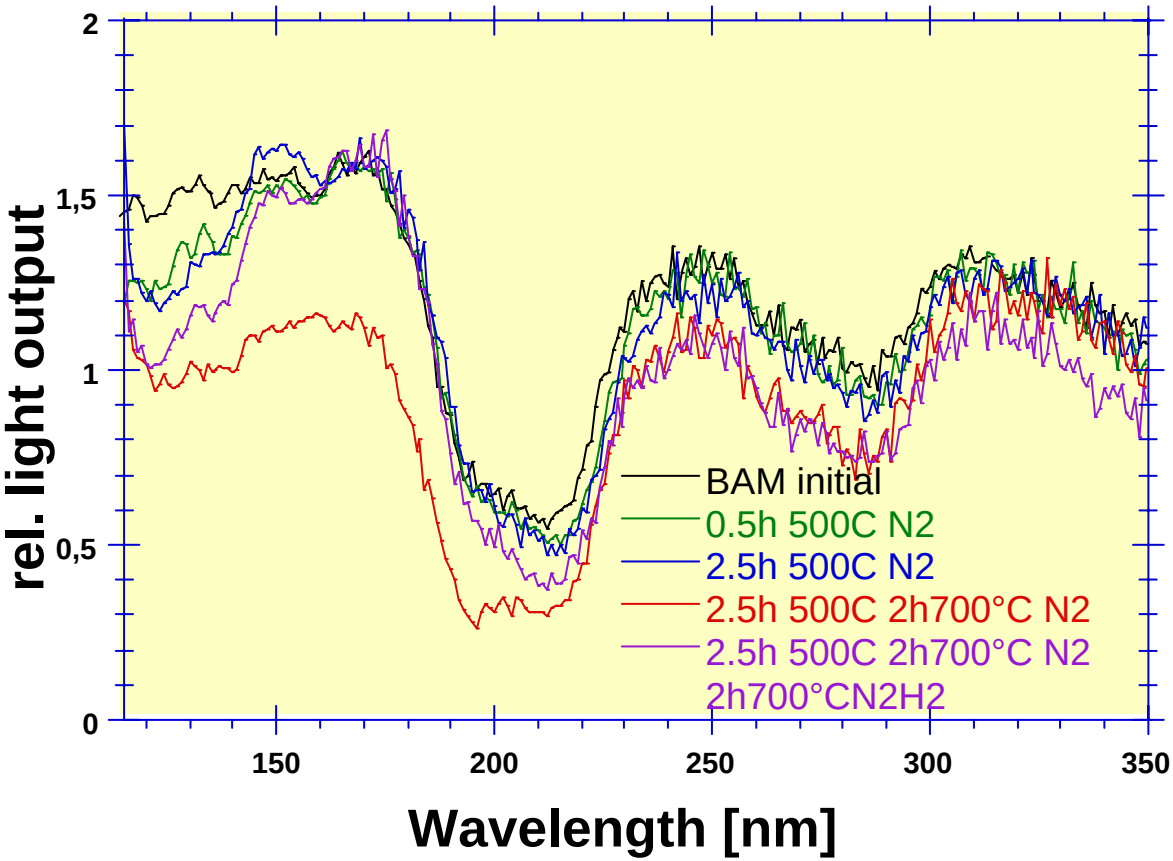
- **Density of shallow traps decreases**

Annealing in N_2/H_2

- **Density of shallow traps decreases again**
- **Deep trap does not show up**

Light Output of BAM:Eu

Annealing in N_2 or N_2/H_2 at 700°C

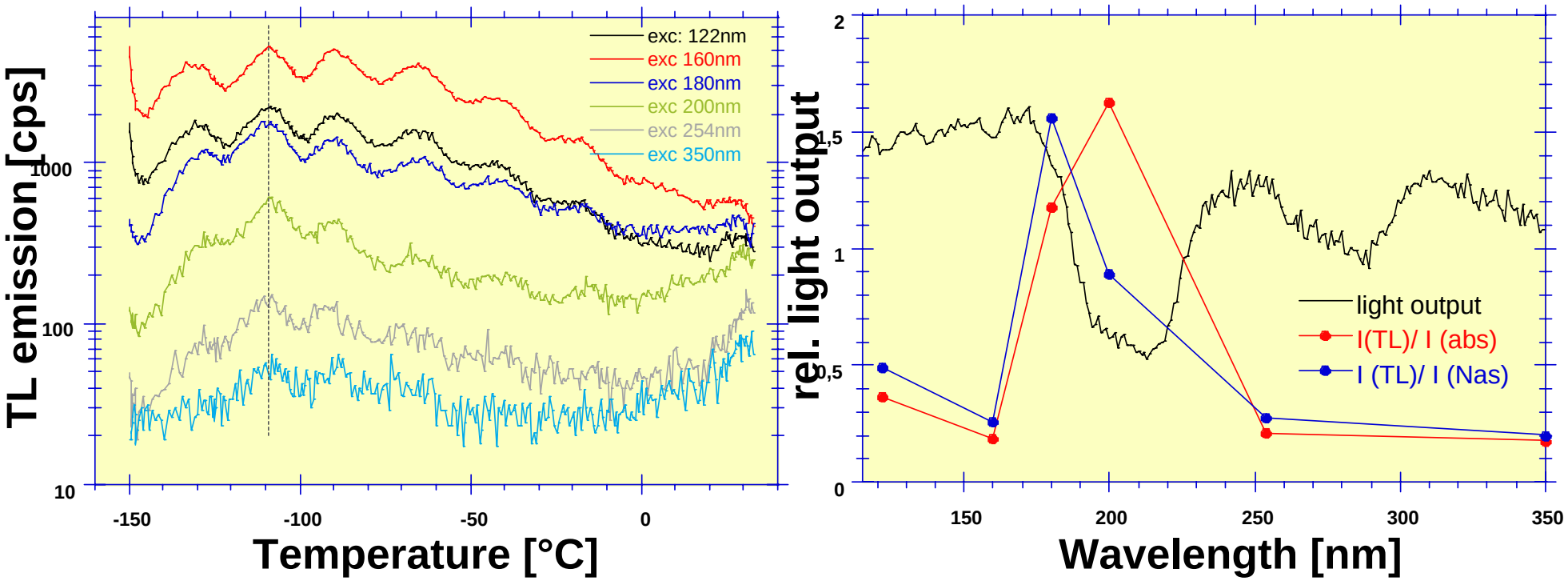


<u>Annealing in Nitrogen</u>
Reduces its efficiency over the complete wavelength range

<u>Annealing in N_2/H_2</u>
Restores initial efficiency

Thermoluminescence Analysis of BAM:Eu

Thermoluminescence vs. Excitation Wavelength



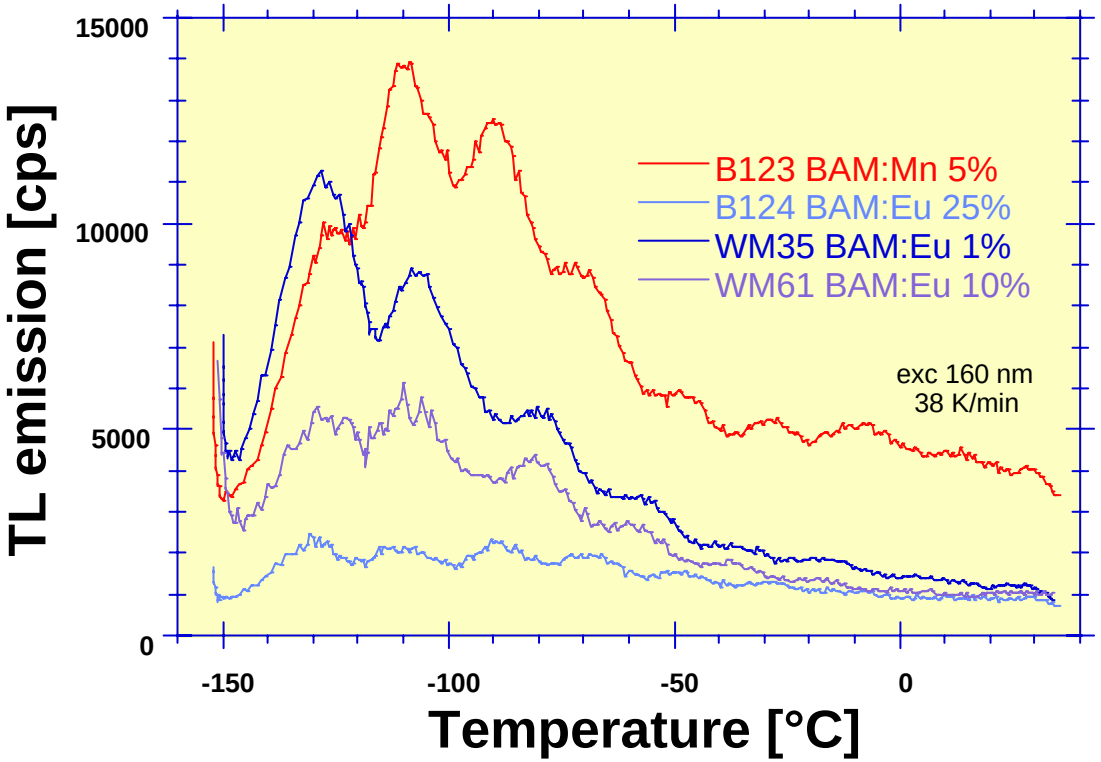
shallow trap structure is independent of excitation energy

deep trap glow peak only due to low energy excitation (λ > 180 nm)

TL is most intense under band gap excitation

Thermoluminescence Analysis of BAM:Mn

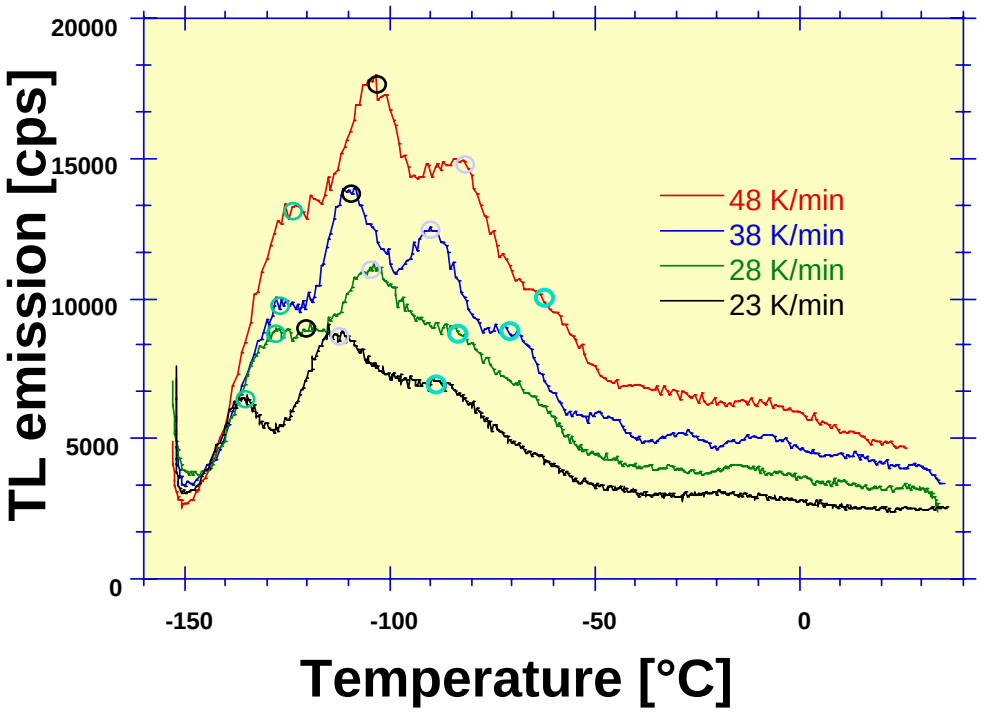
Comparison between BAM:Eu and BAM:Mn

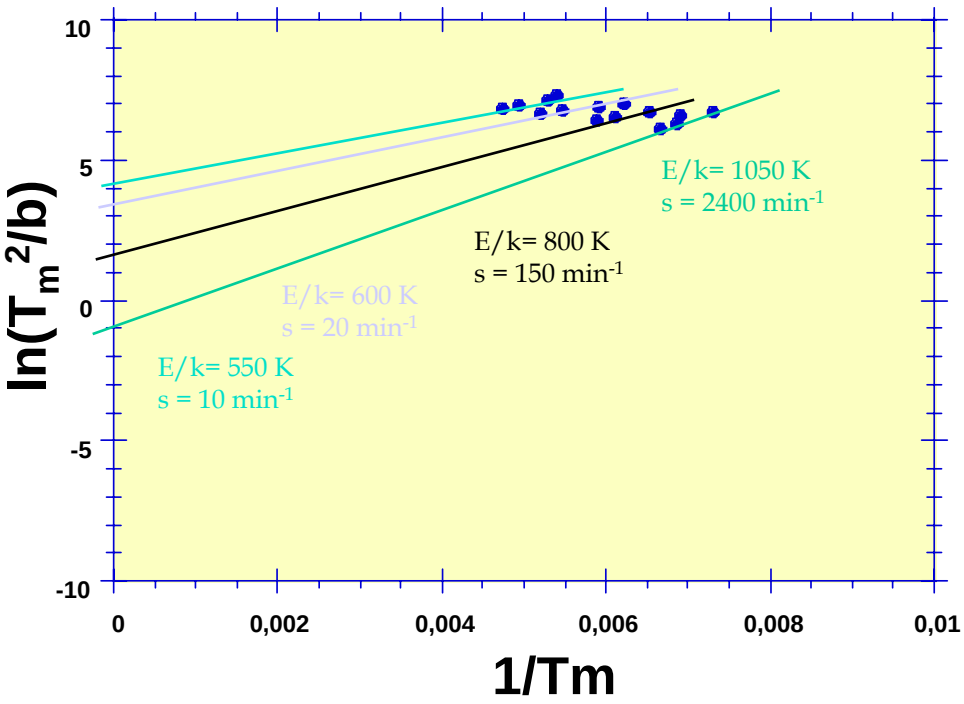


BAM:Mn exhibits similar peak structure than BAM:Eu → **trap levels are lattice and not activator related**

Thermoluminescence Analysis of BAM:Mn

BAM:5%Mn



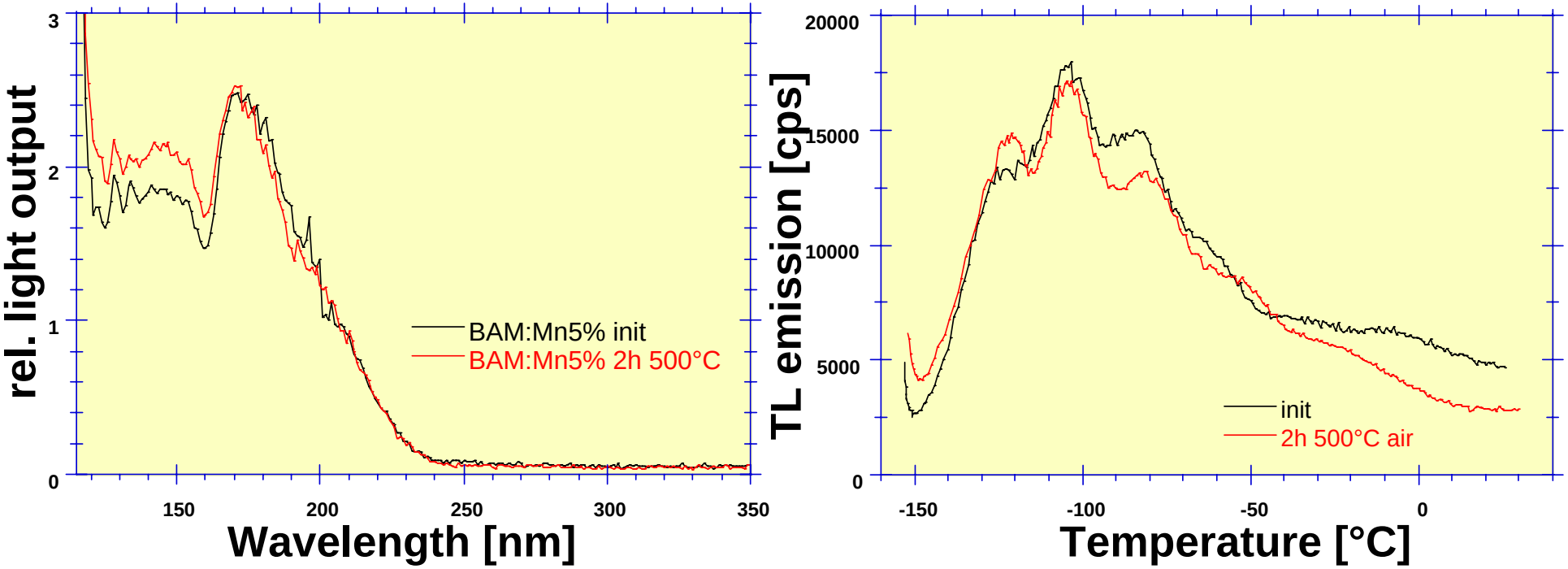


TL-intensity is 2.2 times higher than for BAM:Eu

Trap depth energy is 0.04 eV smaller than for BAM:Eu

Thermoluminescence Analysis of BAM:Mn

BAM:5%Mn - thermal treatment in air



Light output for λ < 170 nm slightly increases

TL fine structure remain unchanged => trap structure unchanged

TL fine structure intensity unchanged => trap density unchanged

Interpretation of TL Spectra of BAM

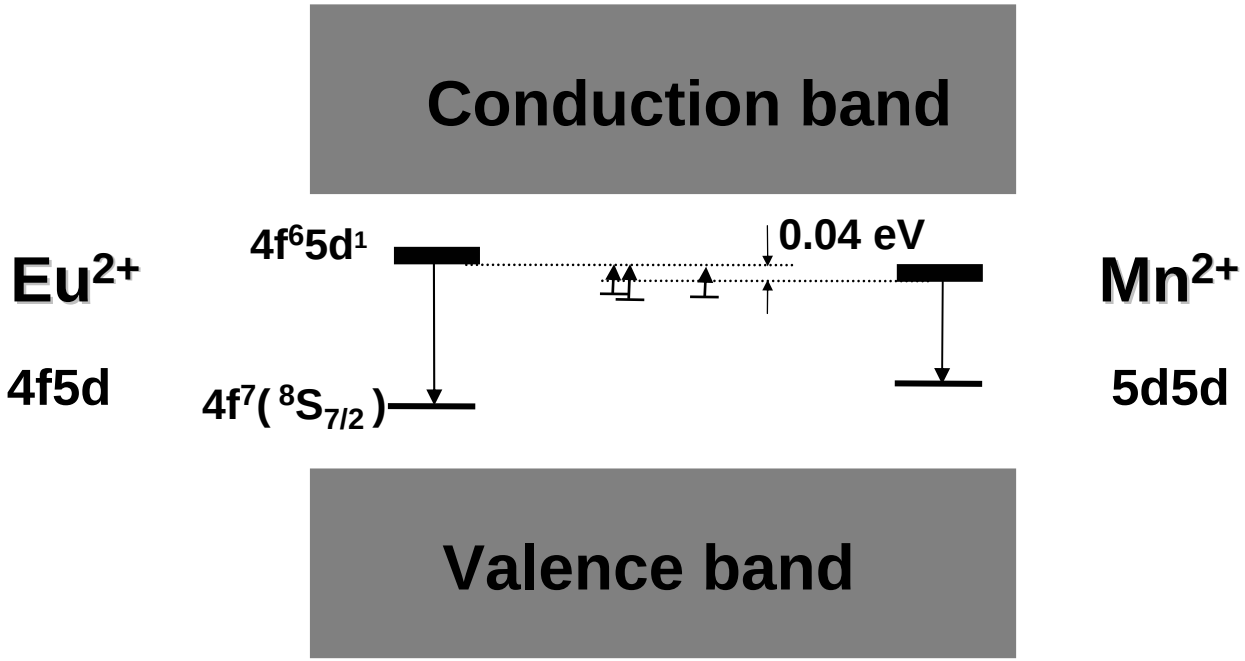
Annealing experiments

- In air at 500°C
  - reduction of shallow trap density due to diffusion (within the conduction layers)
  - Formation of oxygen vacancies due to annealing in N_2/H_2 during synthesis
  - oxidation of Eu^{2+} to Eu^{3+} (trap at 0.3 eV, color centre), not for Mn^{2+}
- In N_2 at 500°C
  - reduction of oxygen vacancy density due to diffusion
  - no oxidation of Eu^{2+}
- TL spectrum after annealing in N_2/H_2 at 500 or 700°C
  - Increase of oxygen vacancy density due to removal of Oxygen

TL spectra dependent on excitation energy

- Photon energy >> band gap: band excitation and efficient ET to Eu^{2+}
- Photon energy ~ band gap: exciton formation and elctron trapping on defects
- Photon energy < band gap: 4f5d excitation of Eu^{2+}

Thermoluminescence Model for BAM



Shallow traps are located in the band gap, 0.1 to 0.2 eV below the excited state of Eu^{2+} and Mn^{2+}

Conclusions

Light output reduction and deep trap formation (0.3 eV) only occur in presence of Oxygen (only for BAM:Eu)
$\Rightarrow$ related to Eu^{3+} formation

Annealing in reducing atmosphere improves VUV light output and deep traps disappear (reduction of Eu^{3+} to Eu^{2+})

$\Rightarrow$ Degradation of BAM:Eu is largely caused by oxidation of the redoxsensitive activator Eu^{2+}