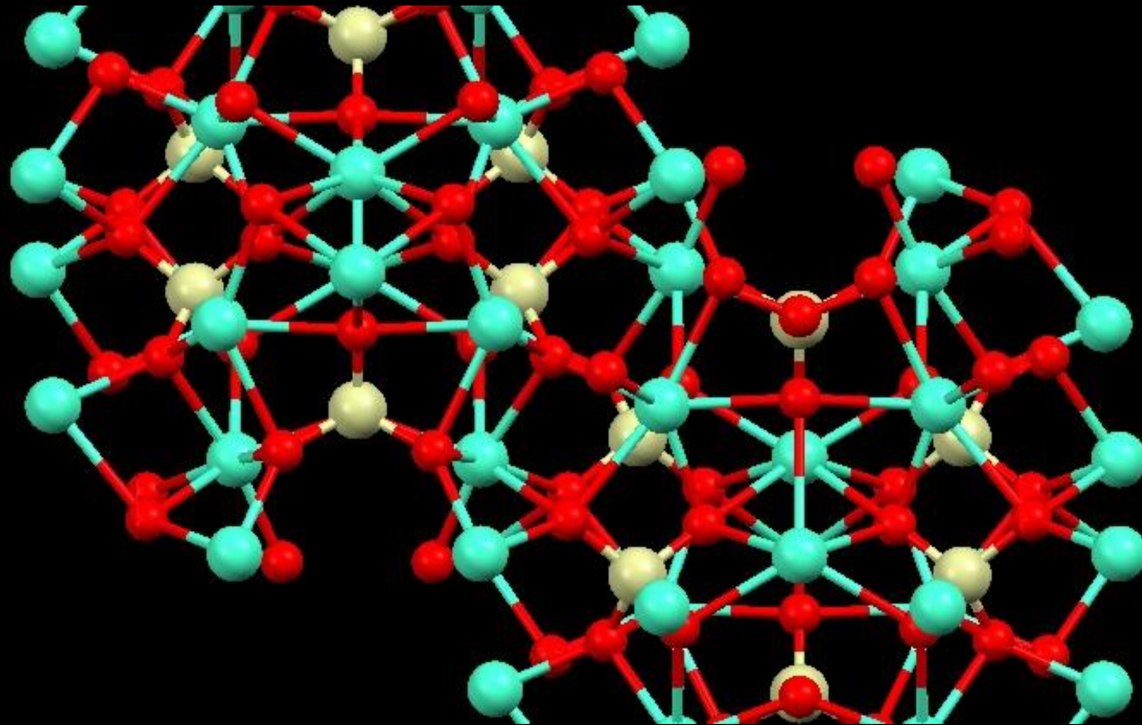


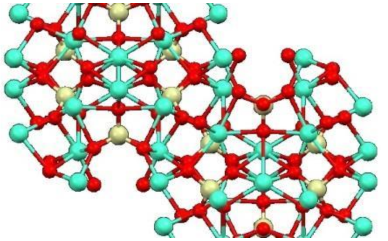
Luminescence properties of new phosphors: $Ca_3M_2Si_3O_{12}$:Tb,Eu

Irene Carrasco Ruiz

Luminescent Materials Group. UNIVR

LUMINET Meeting Tartu 2015

MOTIVATION



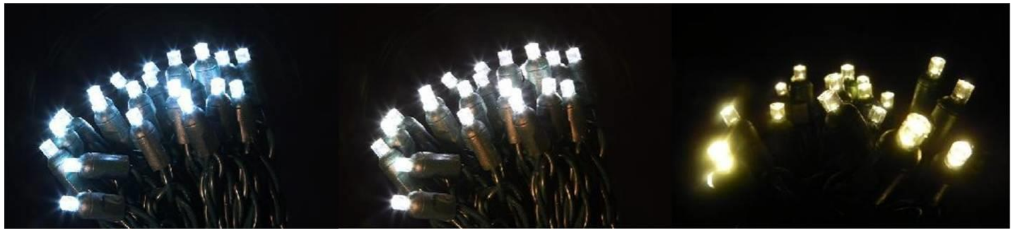
Rare earth phosphors are light-emitting materials with wide variety of applications.

Plasma display panels

White LEDs

Blue LED chip + yellow-emitting phosphor ➡ Cool light

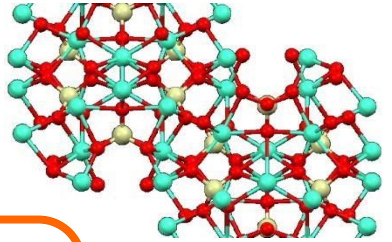
White LEDs:
High brightness
Low energy consumption
High reliability
Long lifetime
Eco-friendly



Cool white **Pure white** **Warm white**

UV-LED chip + tricolor emitting phosphors ➡ Warm light

New phosphors to improve UV-excited white LEDs



Silicate phosphors:

Good transparency in UV-VIS

Favorable luminescent properties

High chemical stability

Simple synthesis process

Silico-carnotite type structure:

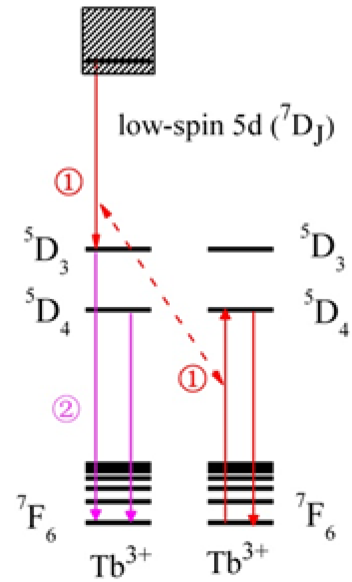
Orthorombic space group, *Pnma*

Good stability for RE doping from Eu-Lu ions

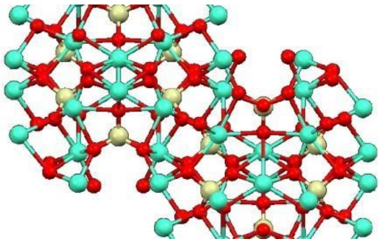
- Both Tb^{3+} and Eu^{3+} exhibit absorption bands in the UV
- Green emission from Tb^{3+} and red emission from Eu^{3+} have many applications in lighting and displays
- Tb is an excellent sensitizer for Eu

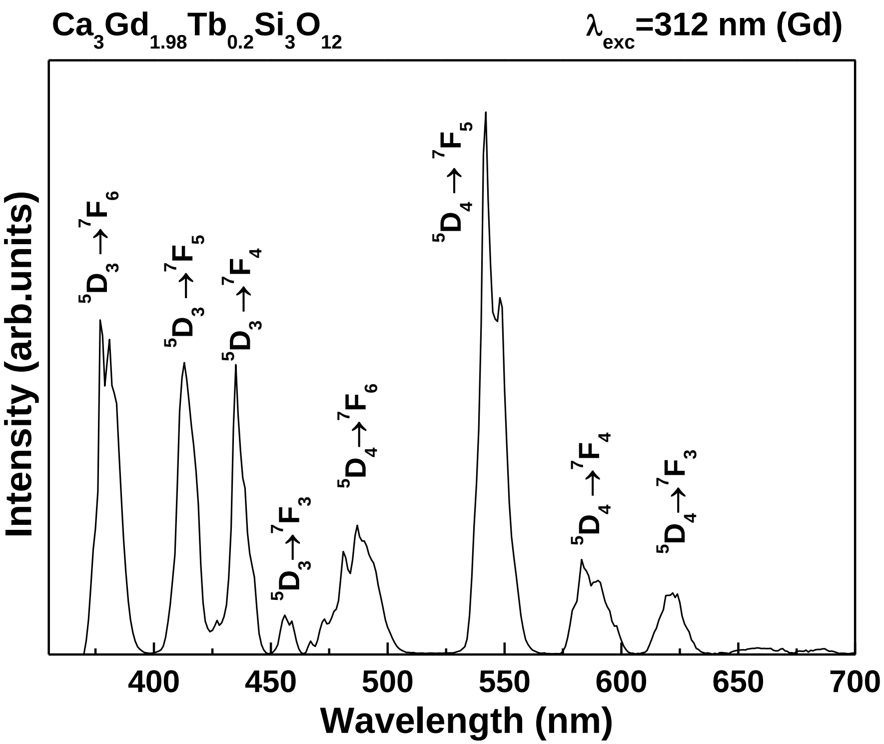
Blue emission of Tb^{3+} is quenched due to cross relaxation processes

Silico-carnotite structure allows efficient Tb^{3+}-Eu^{3+} energy transfer

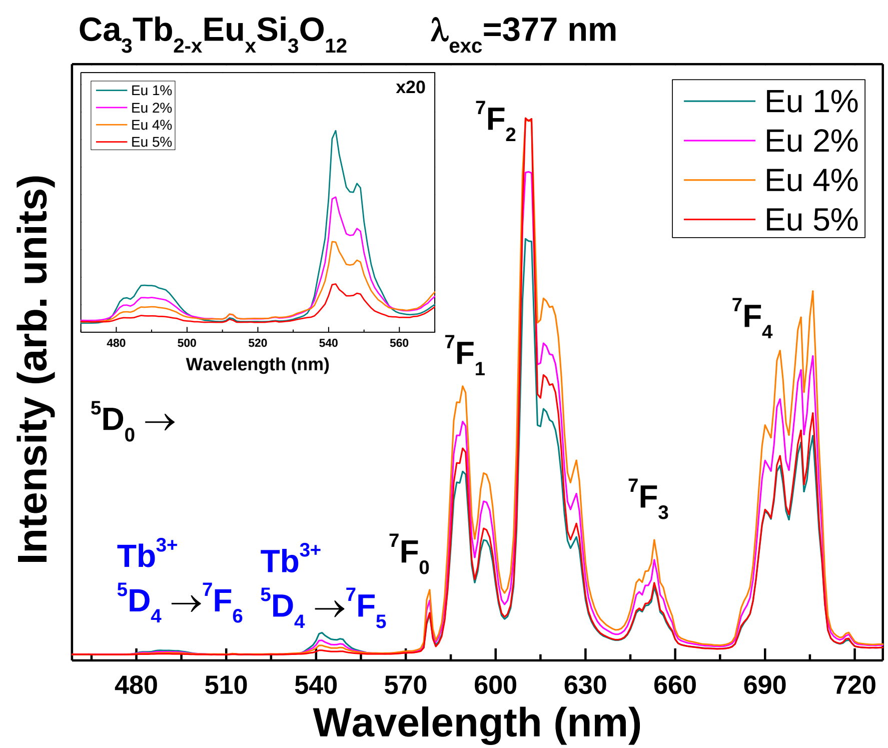


In diluted compounds it is possible to minimize cross relaxation

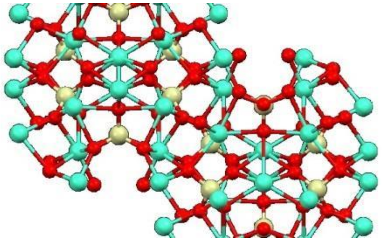




Tb-Eu energy transfer can be controlled adjusting doping concentration



Tb^{3+} - Eu^{3+} silico-carnotite materials are very interesting and promising for white LEDs



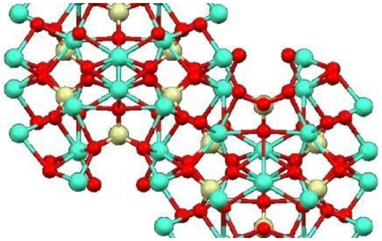
OBJECTIVE

Investigate the luminescent properties of various silico-carnotite phosphors in order to obtain white emission.

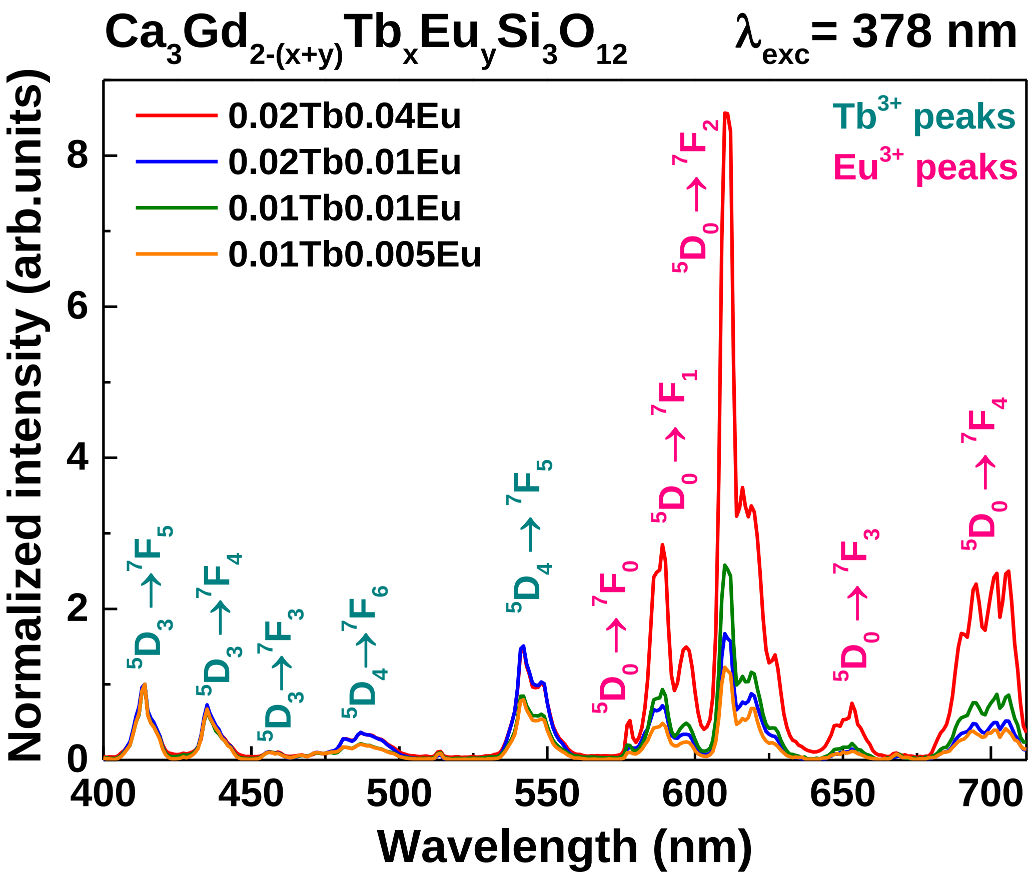
METHODOLOGY

- **Synthesis of phosphors via a conventional solid state reaction (1450^{o} C x 3h)**
- **RT luminescence experiments**

Gadolinium silicates



EMISSION

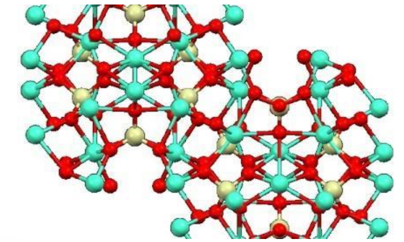


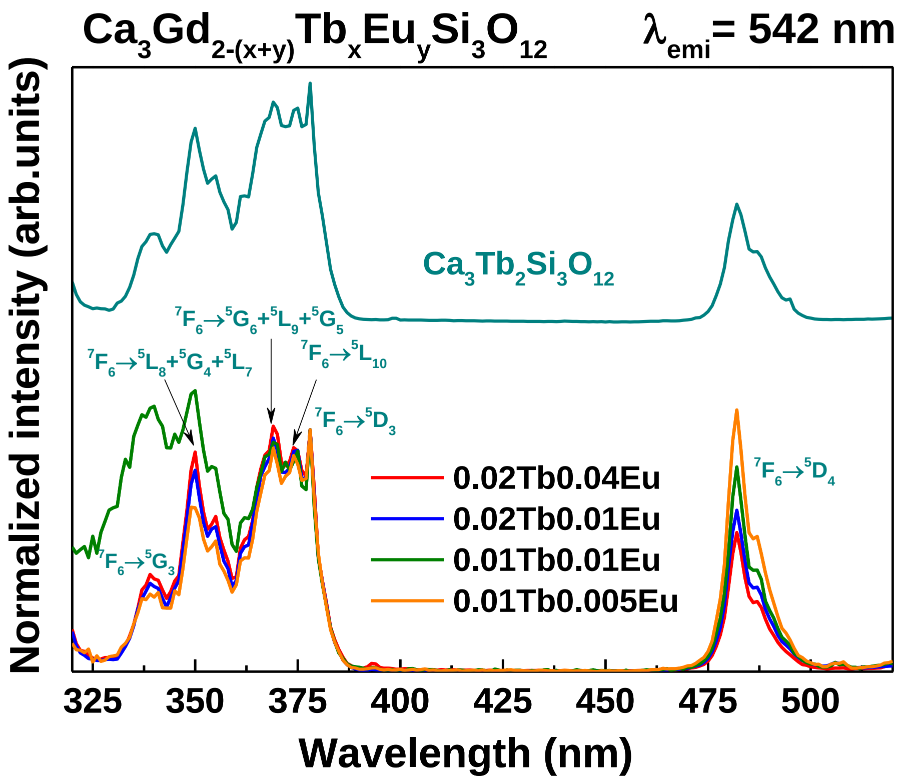
Emission B+G+R

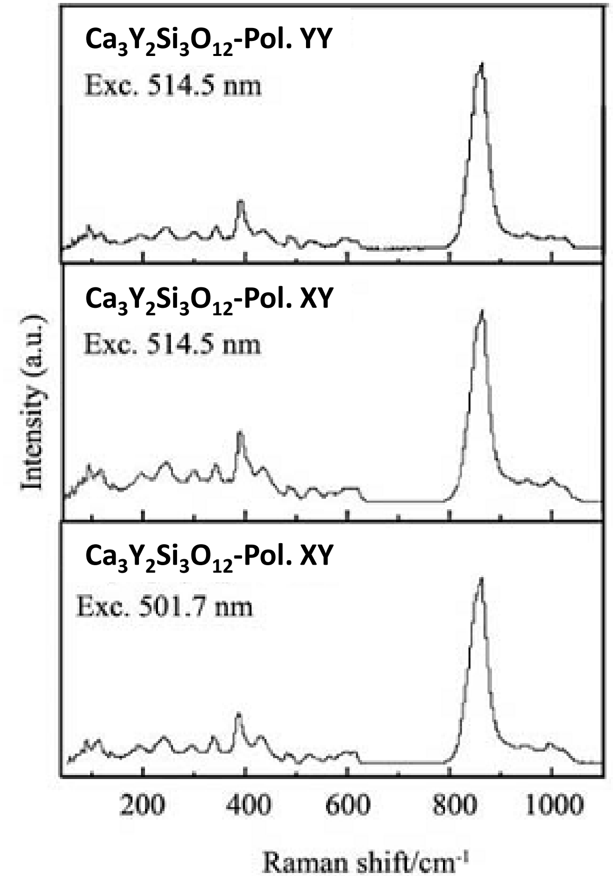
Evidences of relaxation from $^5D_3$ to $^5D_4$ (Tb^{3+} levels)

Gadolinium silicates

EXCITATION





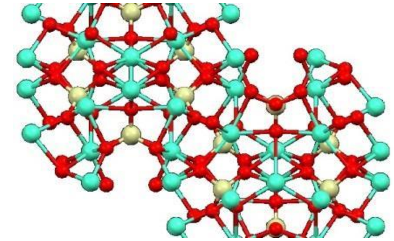


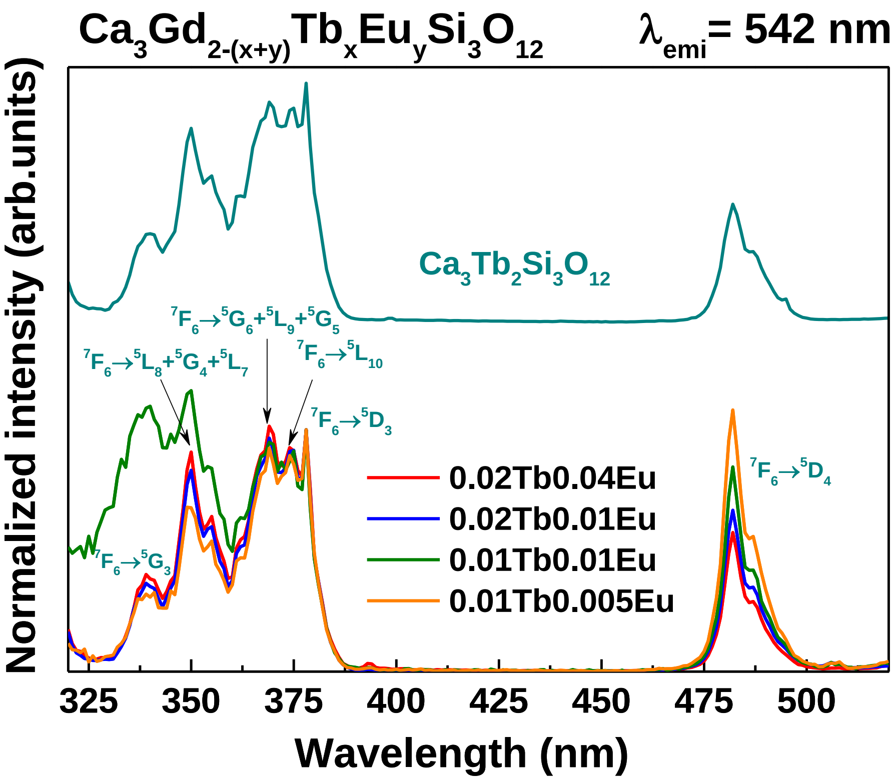
F. Piccinelli, JOURNAL OF RARE EARTHS, Vol. 27, No. 4, Aug. 2009, p. 555.

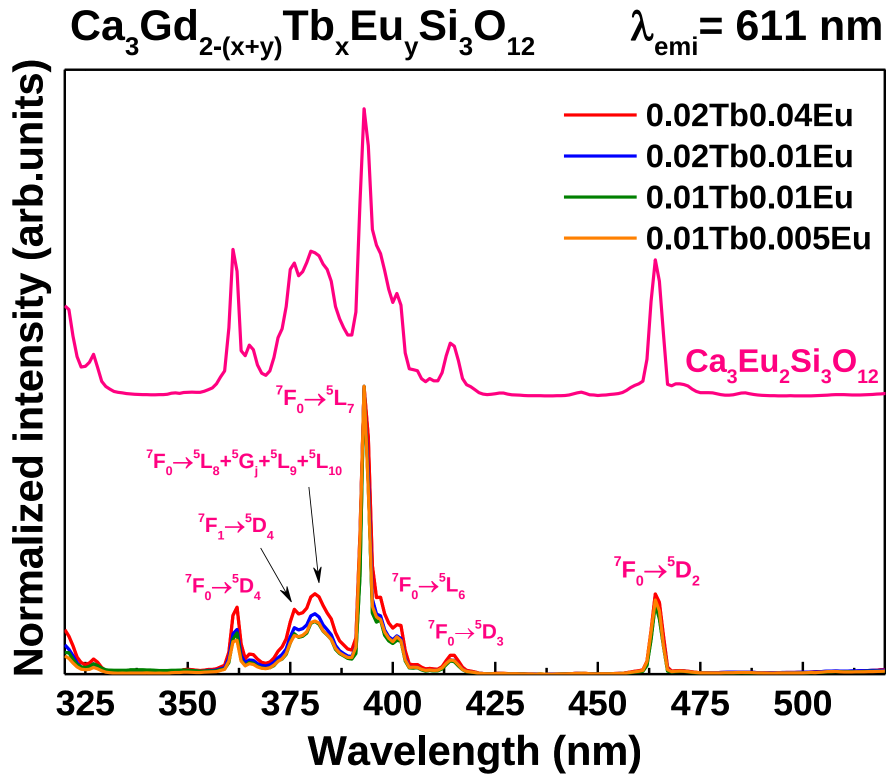
Vibrational cut-off is about 1050 cm^{-1} . Energy gap between $^5D_3$ and $^5D_4$ levels is about 5750 cm^{-1}. It is possible to populate $^5D_4$ from $^5D_3$ by multiphonon relaxation.

Gadolinium silicates

EXCITATION





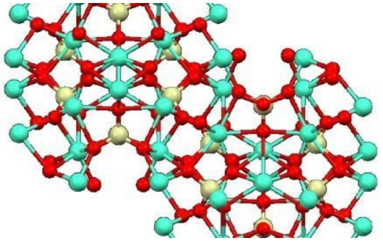


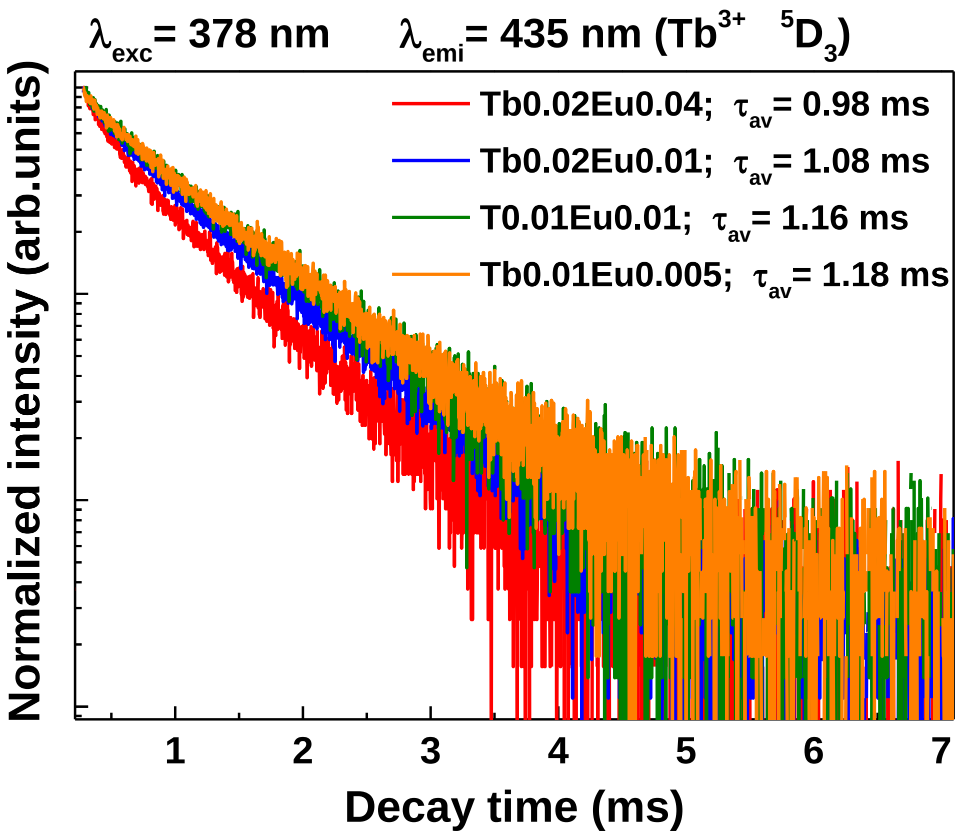
The spectra show evidences of multiphonon relaxation from $^5D_3$ to $^5D_4$

No evidences of Tb-Eu energy transfer

Gadolinium silicates

DECAY CURVES

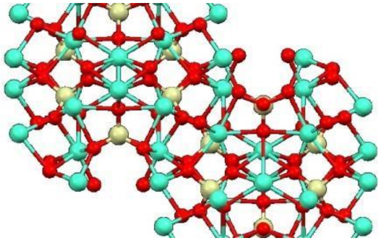


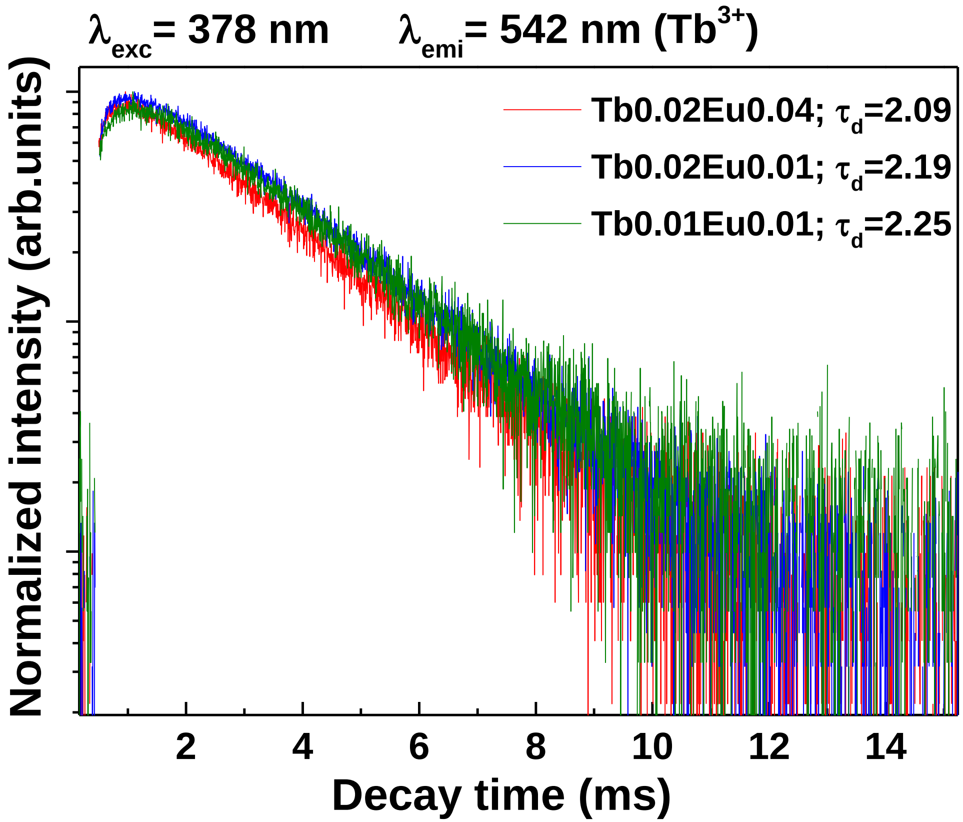


- Non exponential curves due to the presence of disorder
- Decay constant is in practice not affected by Eu^{3+} concentration

Gadolinium silicates

DECAY CURVES

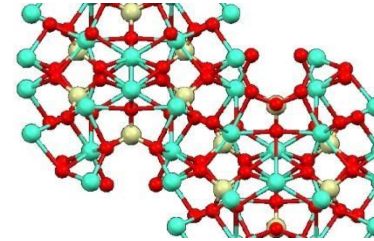


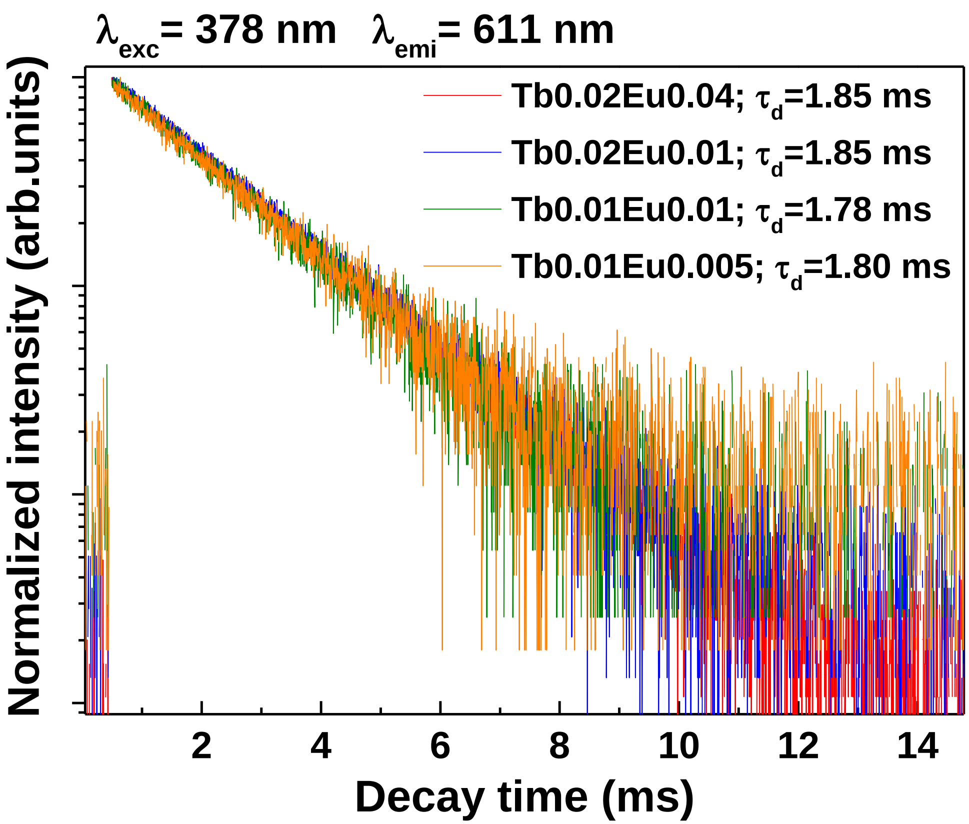


- Slow initial buildup due to the multiphonon relaxation from $^5D_3$ to $^5D_4$
- Decay constant is in practice not affected by Eu^{3+} concentration

Gadolinium silicates

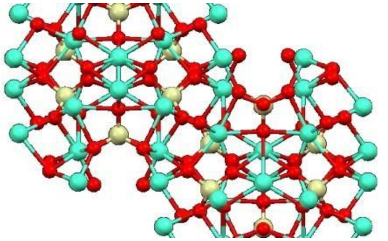
DECAY CURVES

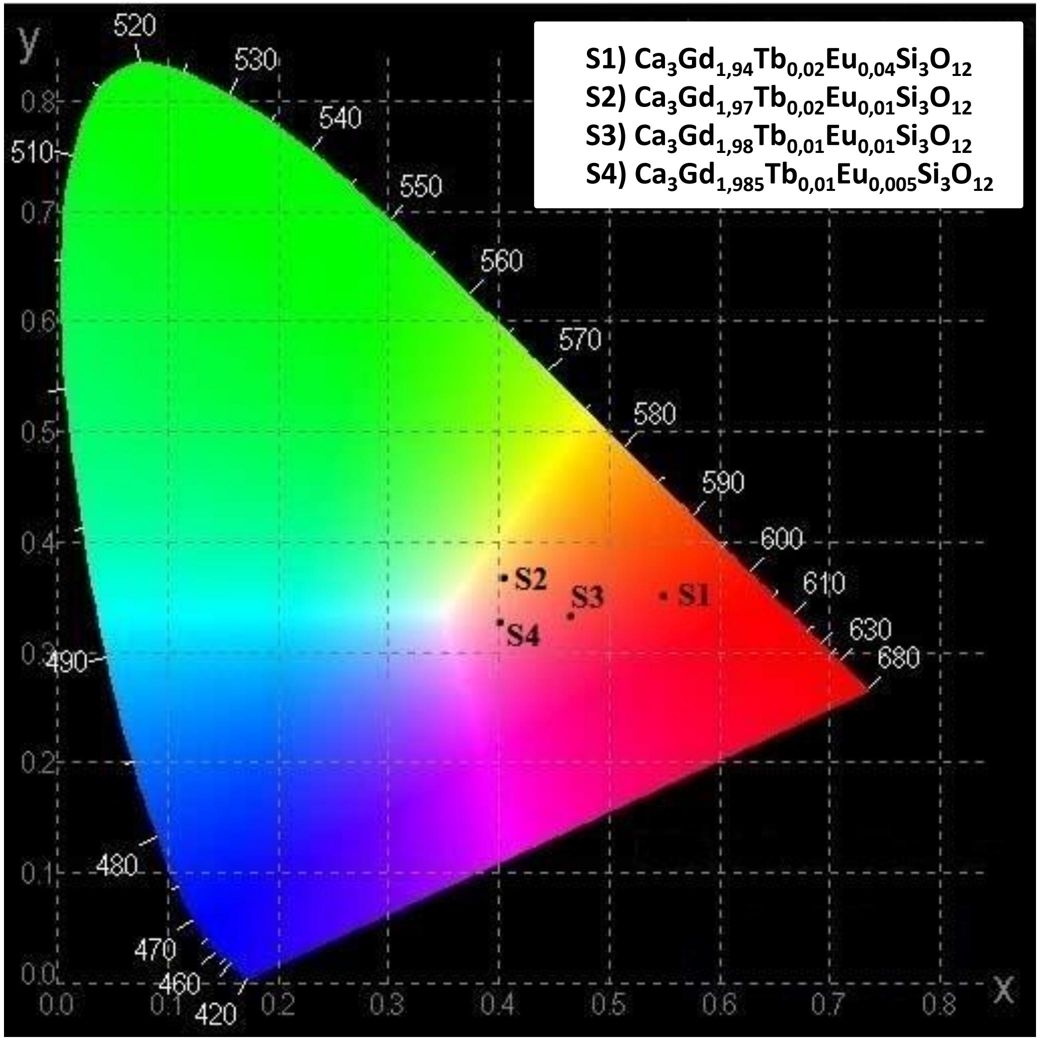




- **Exponential curves**
- **Decay constant is not significantly affected by changing the dopant concentration**

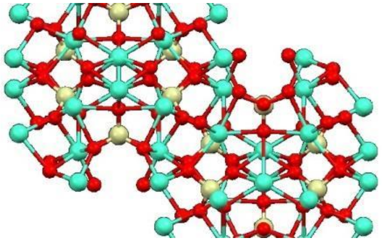
Gadolinium silicates
CIE COORDINATES





- **Emission colour depends on the Tb-Eu ratio, not only on the total dopant concentration**
- **Samples S2 and S4 present very interesting properties**

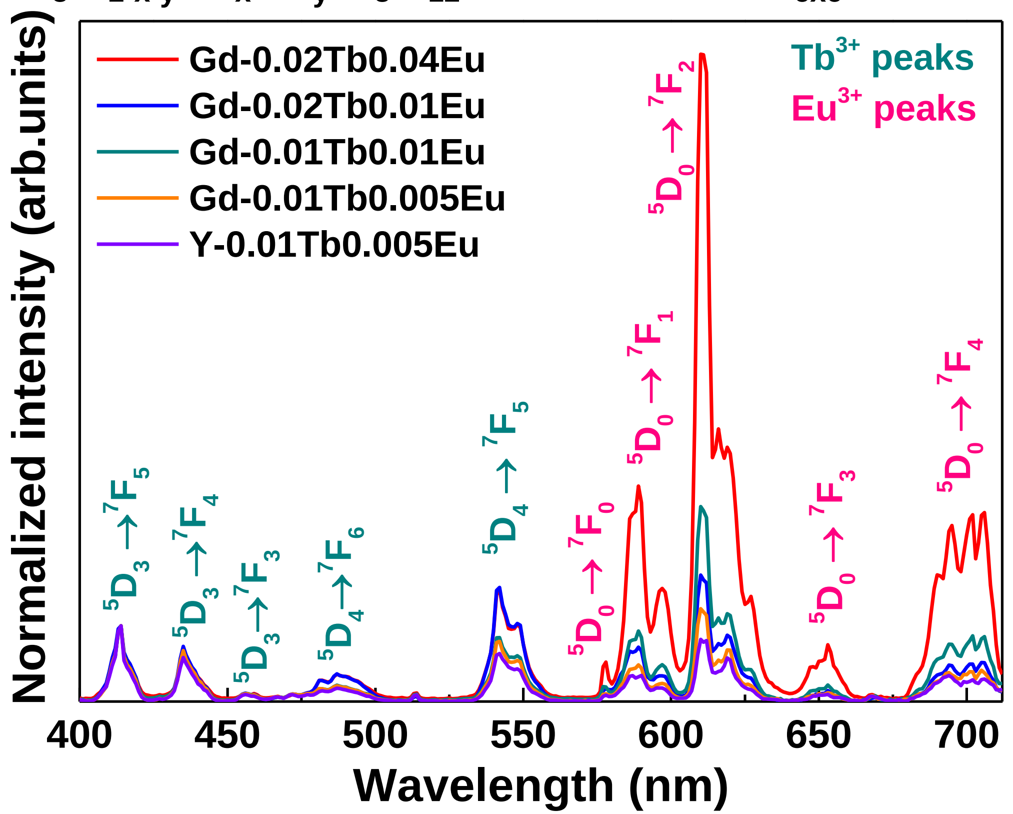
NEW GOAL
Explore other hosts starting from these results (yttrium silicate)



Yttrium silicate

EMISSION

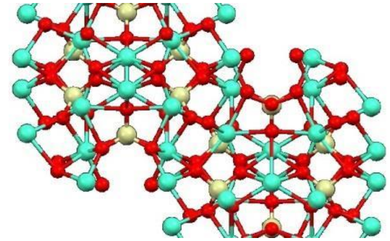
$Ca_3M_{2-x-y}Tb_xEu_ySi_3O_{12}$ (M= Gd, Y) λ_{exc}= 378 nm



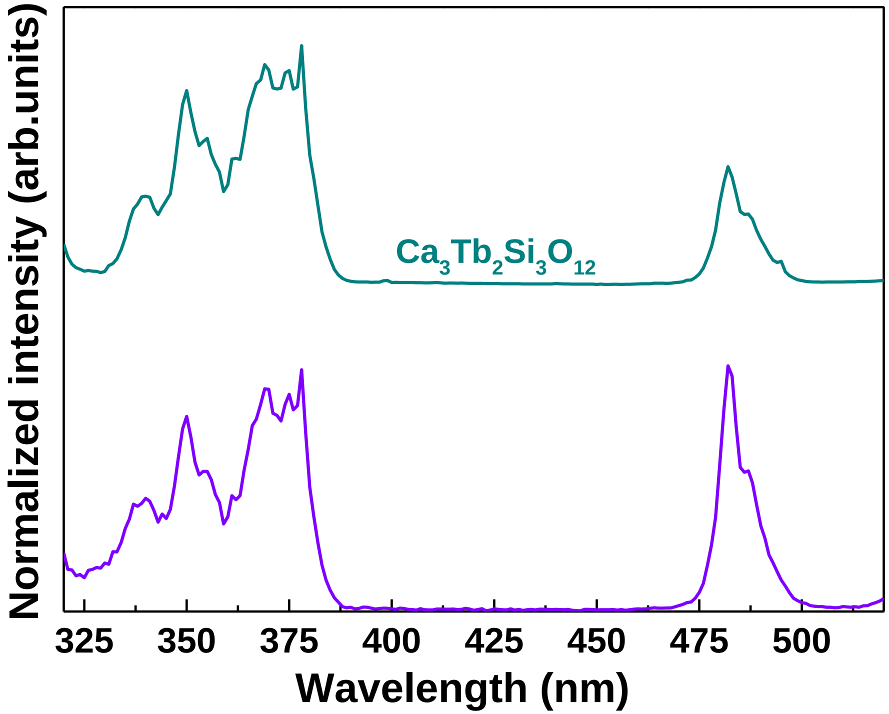
The spectrum is almost identical to the one recorded for the S4 Gd-silicate

Yttrium silicate

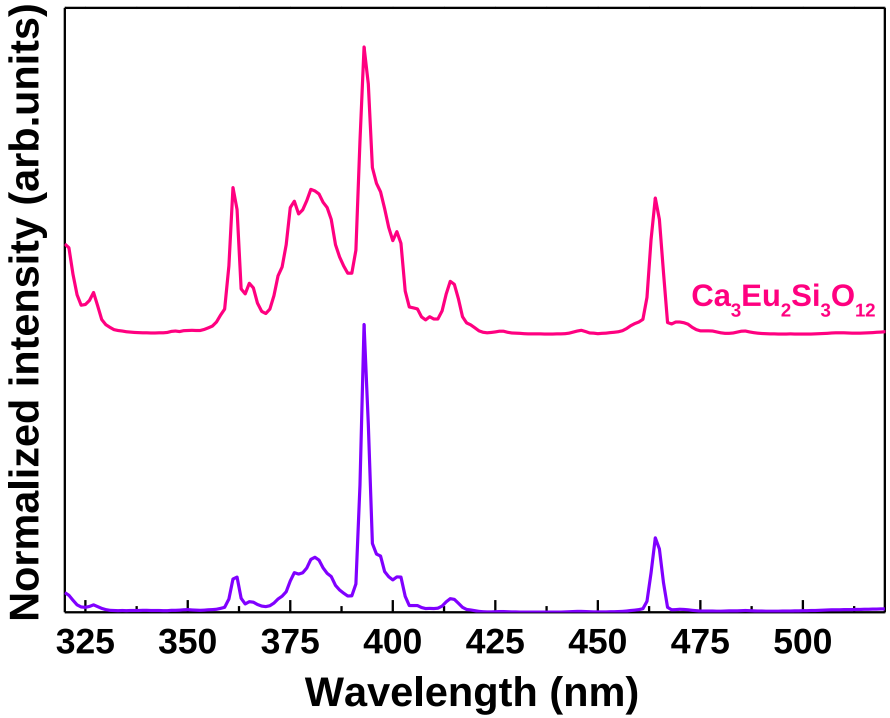
EXCITATION



$Ca_3Y_{1.985}Tb_{0.01}Eu_{0.005}Si_3O_{12}$ λ_{emi}= 542 nm



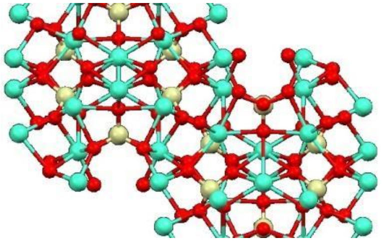
$Ca_3Y_{1.985}Tb_{0.01}Eu_{0.005}Si_3O_{12}$ λ_{emi}= 611 nm

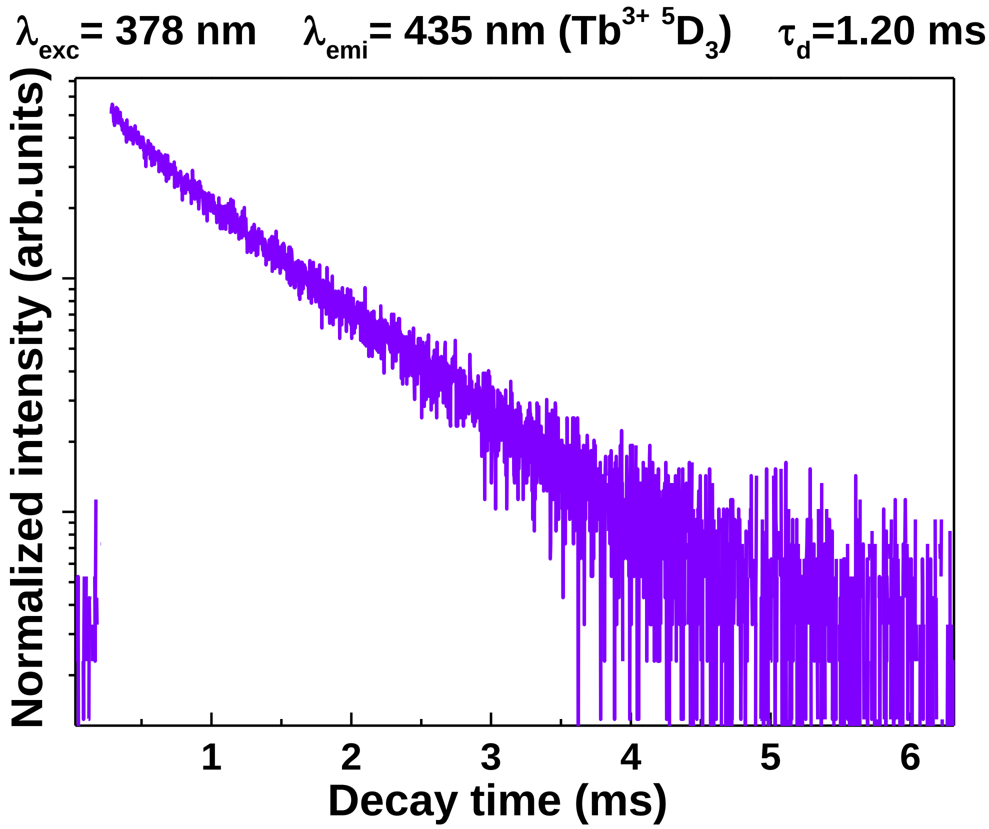


The spectra are in good agreement with the results obtained for the Gd-silicate: evidences of relaxation from $^5D_3$ to $^5D_4$, and no evidences of transfer from Tb to Eu

Yttrium silicate

DECAY CURVES

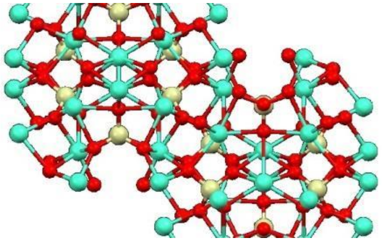




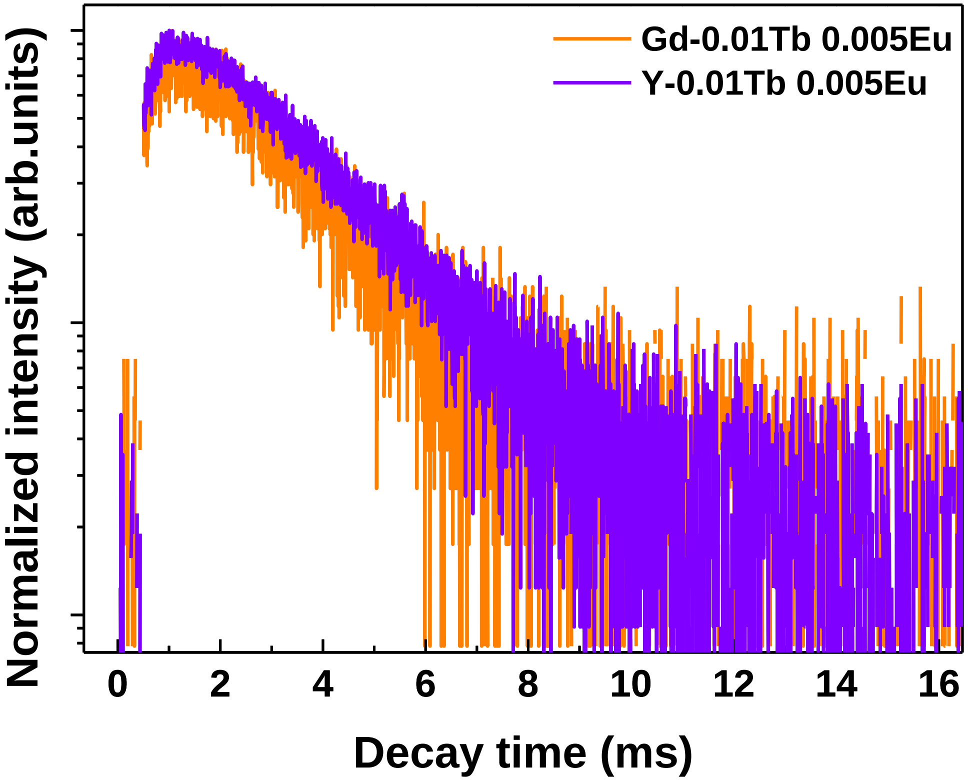
- Non exponential curves due to the presence of disorder
- Decay constant is consistent with the values obtained for Gd phosphors

Yttrium silicate

DECAY CURVES



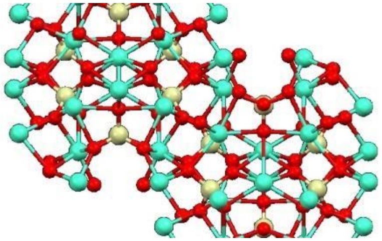
λ_{exc}= 378 nm λ_{emi}= 542 nm (Tb^{3+} $^5D_4$) τ_d=2.29 ms

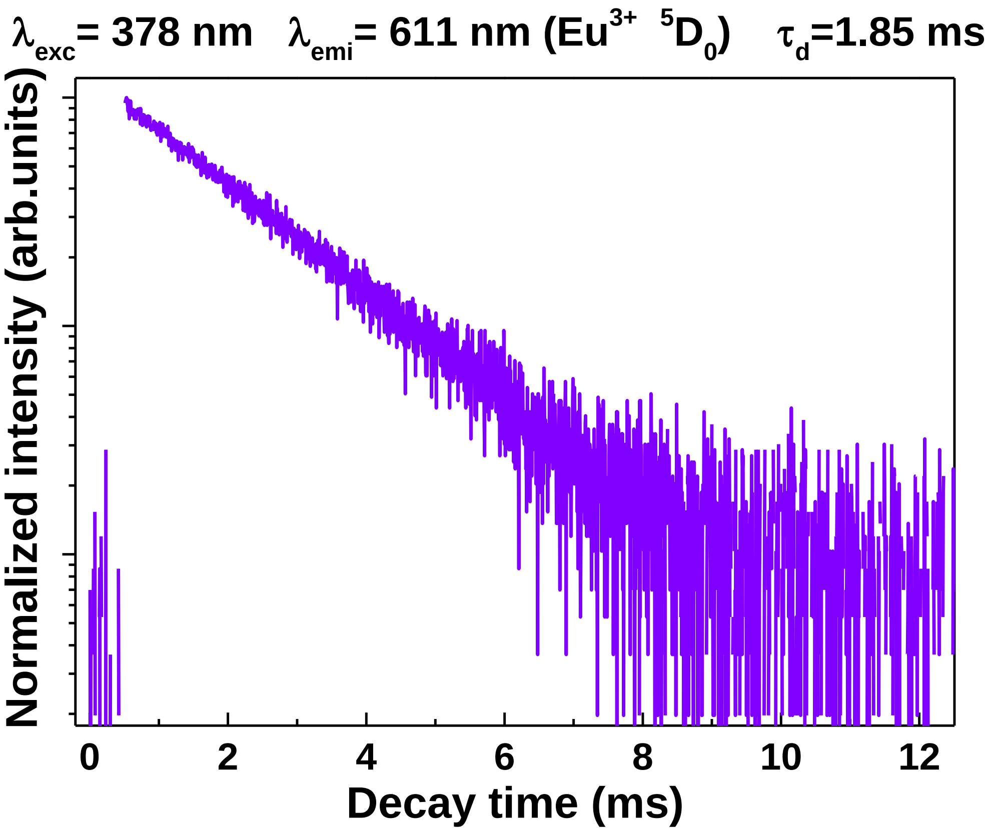


- Slow initial buildup due to the multiphonon relaxation from $^5D_3$ to $^5D_4$
- Decay constant is consistent with the values obtained for Gd-phosphors

Yttrium silicate

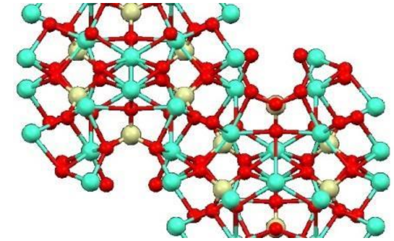
DECAY CURVES

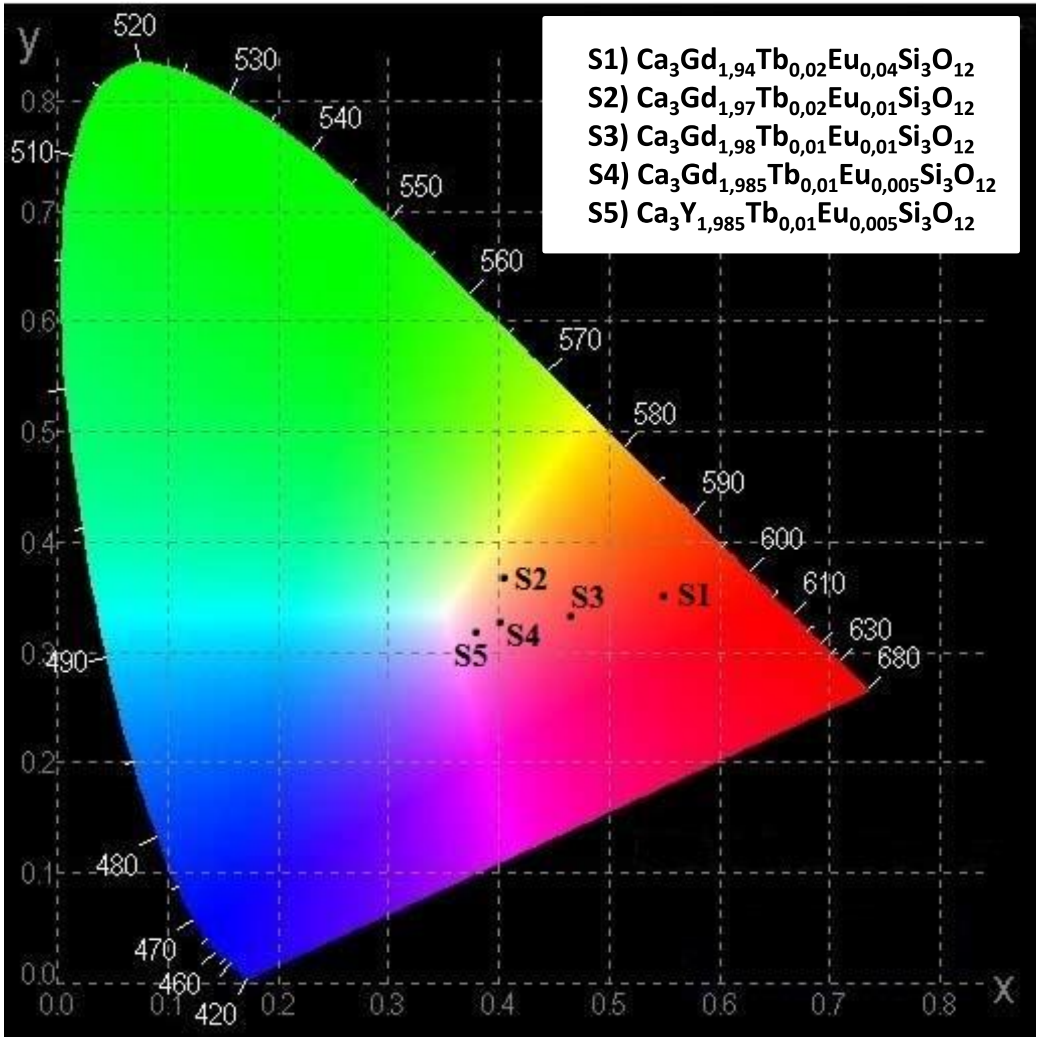




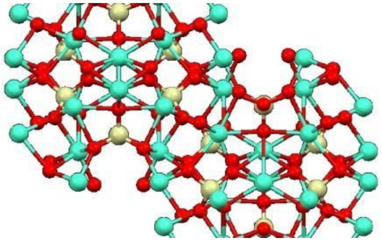
- Exponential curves
- Decay constant is consistent with the values obtained for Gd-phosphors

Yttrium silicate
CIE COORDINATES





S2 and S5 present promising properties for developing white phosphors



CONCLUSIONS

Tb^{3+} $^5D_3$-$^5D_4$ cross relaxation can be minimized in diluted compounds

No clear evidence of Tb^{3+}-Eu^{3+} energy transfer

Emission colour depends on the Tb-Eu ratio, not only on the total dopant concentration

Control of Tb-Eu doping leads to close-to-white emission in various silico-carnotite phosphors

FUTURE WORK

Different dopings in $Ca_3Y_2Si_3O_{12}$ to improve the colour, based on the results obtained for samples S2 and S5

Thank you for your attention