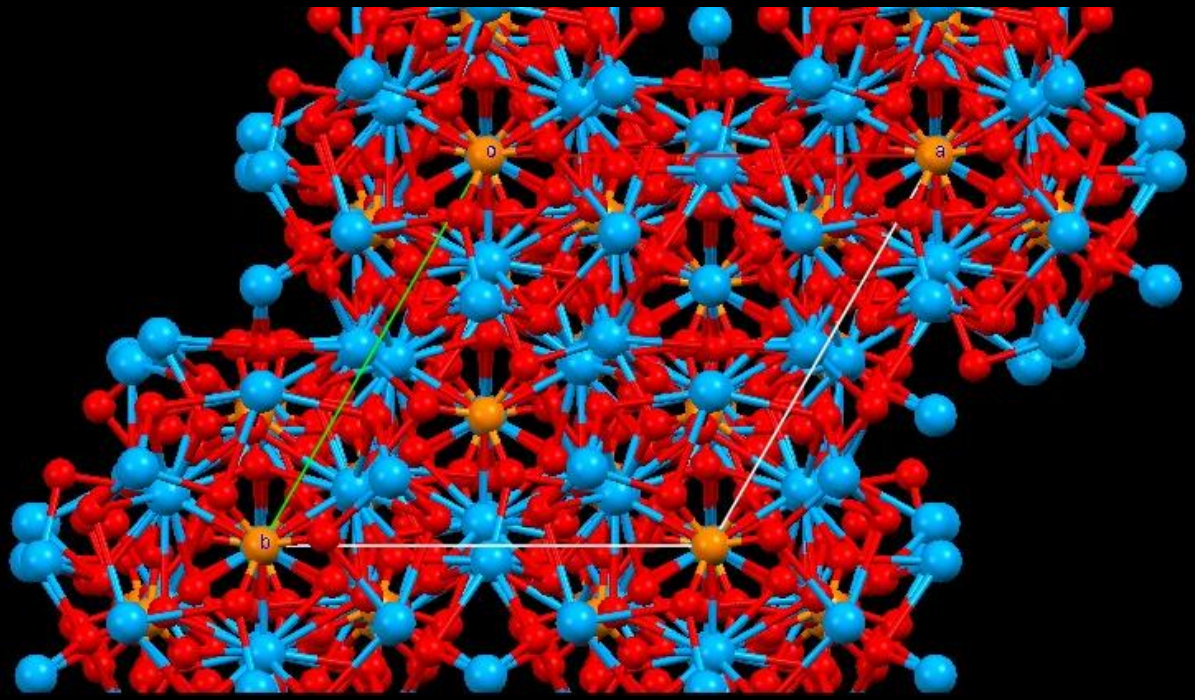

Luminescence properties of new phosphor $Ca_9Tb(PO_4)_7$ doped with Eu^{3+}

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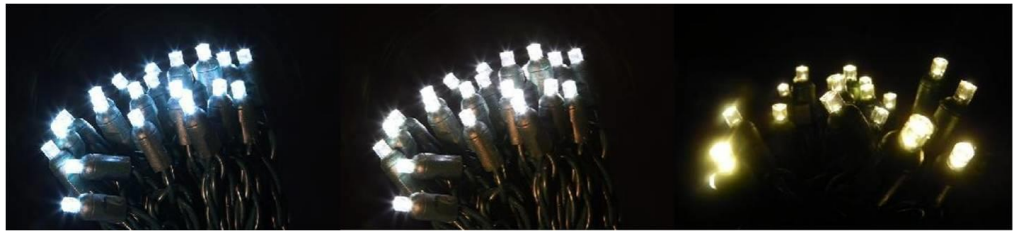
LUMINET Meeting Aveiro 2016

MOTIVATION

New environmentally friendly and energy efficient lighting devices are strongly required: solid state lighting.

Blue and near UV LEDs led to the development of devices capable to produce white light in a reliable and efficient way based on inorganic phosphors

Blue LED chip
+
yellow phosphor
Cool light



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

UV-LED chip
+
RBG phosphors
Warm light

Red phosphors for LEDs are relatively difficult to develop: New approaches may be useful.

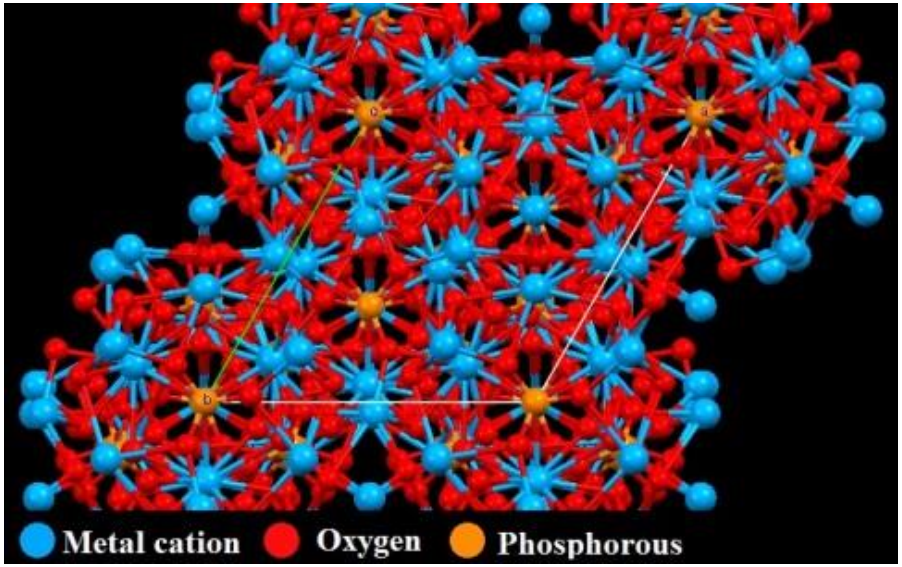
Energy transfer processes are very interesting from both a fundamental and an applied point of view and are crucial in many technological applications.

Tb^{3+} is a very good sensitizer for Eu^{3+} and both ions exhibit absorption bands in the UV: Tb^{3+} - Eu^{3+} materials are very interesting and promising for w-LEDs

Whitlockite-type structure

Rhombohedral crystal structure
Cell volume: 3533 Å^3

Space group *R*3*c*
Very flexible structure for Ln^{3+} doping



Four possible cation sites for the Ln^{3+} dopants in the host, due to the similarity between the ionic sizes of the Ca^{2+} and most of Ln^{3+} ions. For Tb^{3+} and Eu^{3+} three crystal sites are partially occupied by both Ca^{2+} and Ln^{3+}

Used in scintillation applications , X-ray-excited long-lasting phosphorescence materials (for application in biological imaging)

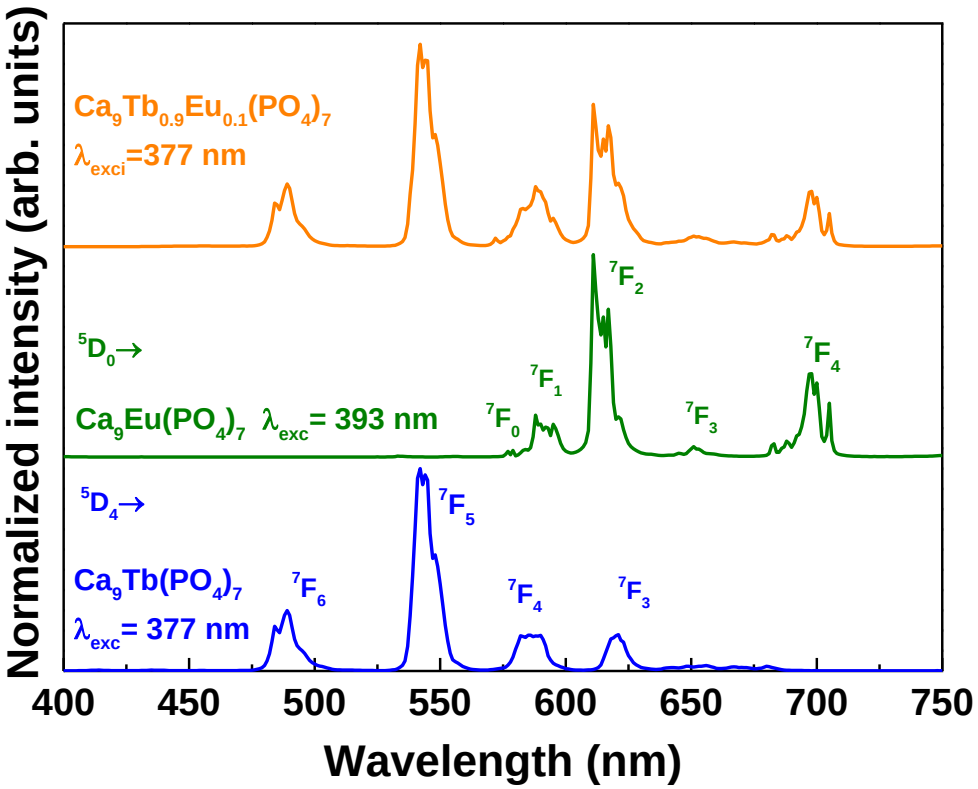
OBJECTIVE

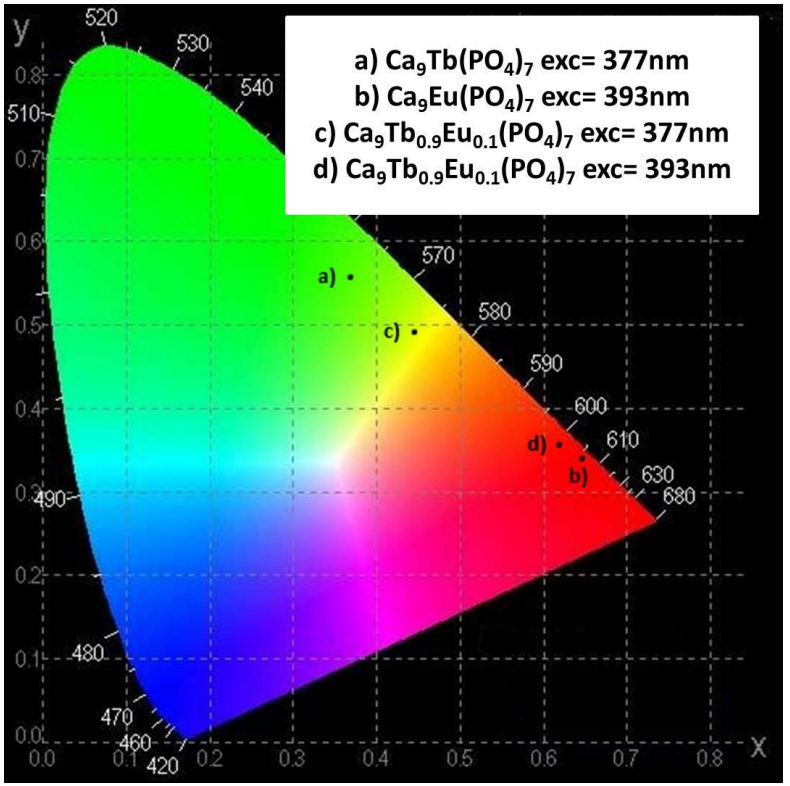
Study the luminescent properties of various whitlockite phosphors doped with europium in order to investigate the Tb-Eu energy transfer process

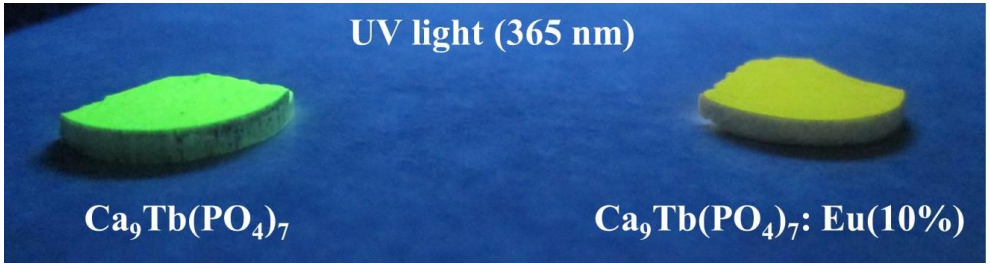
METHODOLOGY

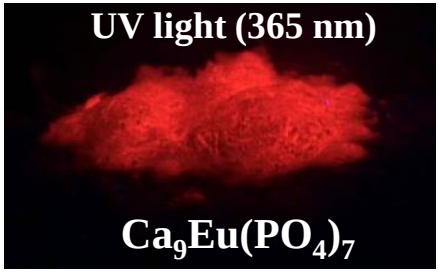
- **Synthesis of various whitlockite phosphors via a high temperature solid state reaction**
- **RT luminescence experiments**

EMISSION

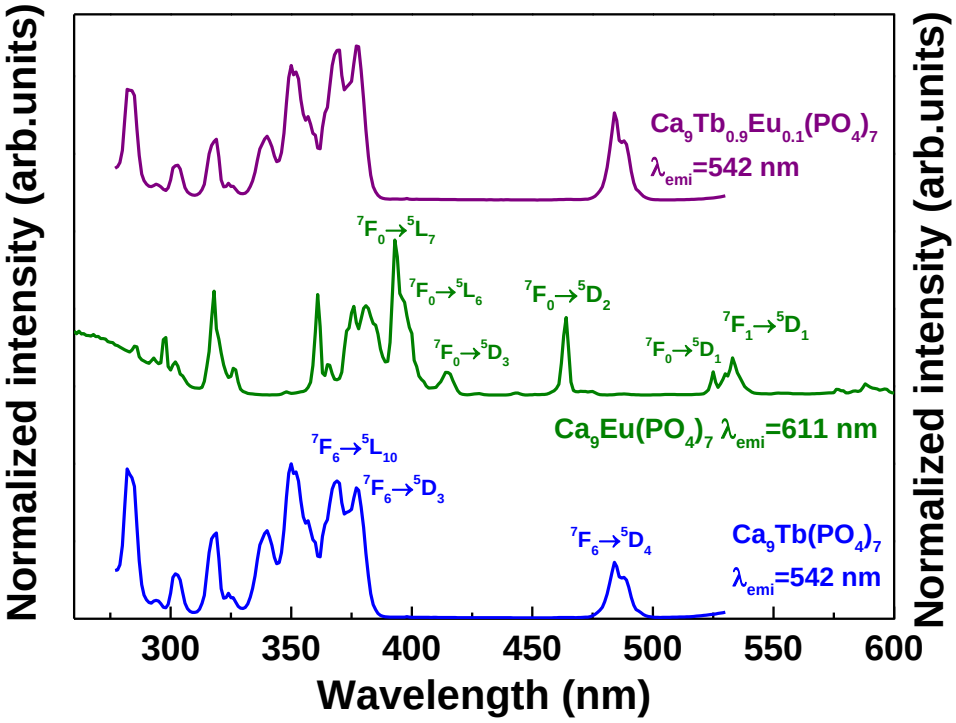

Normalized intensity (arb. units)
Ca9Tb0.9Eu0.1(PO4)7
λexci=377 nm
5D0→
Ca9Eu(PO4)7 λexc= 393 nm
7F0
7F1
7F2
7F3
7F4
5D4→
Ca9Tb(PO4)7
λexc= 377 nm
7F6
7F5
7F4
7F3
400
450
500
550
600
650
700
750
Wavelength (nm)

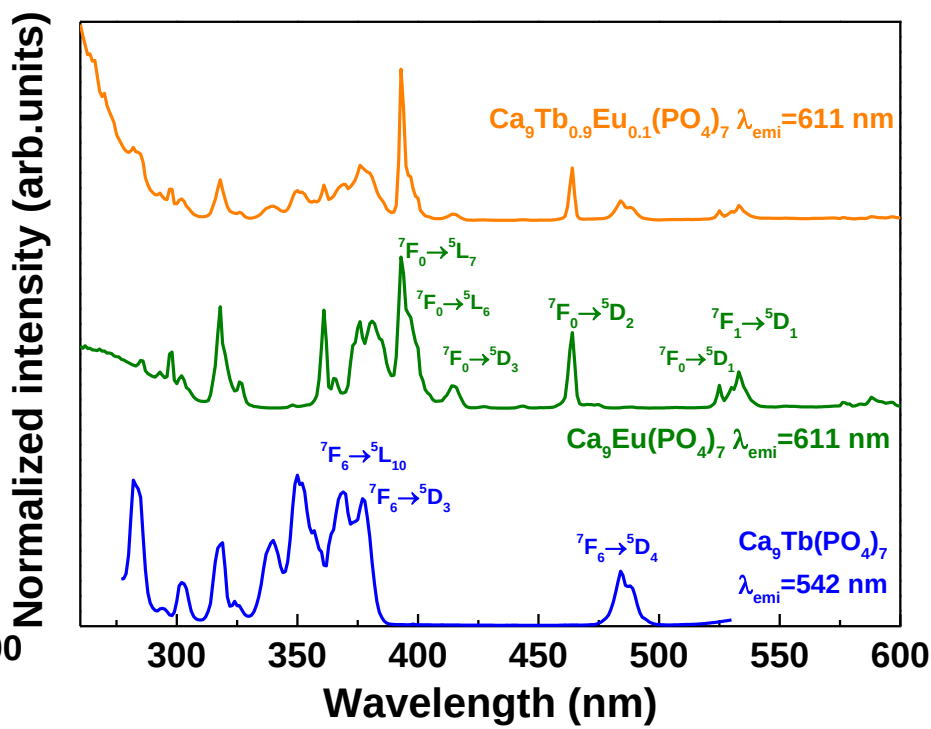

a) Ca9Tb(PO4)7 exc= 377nm
b) Ca9Eu(PO4)7 exc= 393nm
c) Ca9Tb0.9Eu0.1(PO4)7 exc= 377nm
d) Ca9Tb0.9Eu0.1(PO4)7 exc= 393nm
y
x
520
530
540
510
570
580
590
600
610
630
680
490
480
470
460
420
a)
b)
c)
d)


UV light (365 nm)
Ca9Tb(PO4)7
Ca9Tb(PO4)7: Eu(10%)


UV light (365 nm)
Ca9Eu(PO4)7

EXCITATION

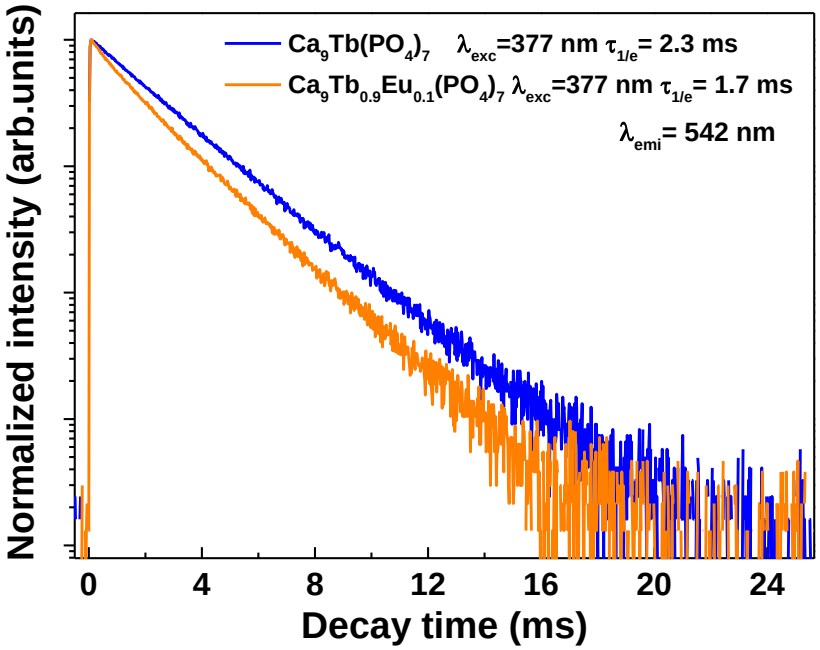


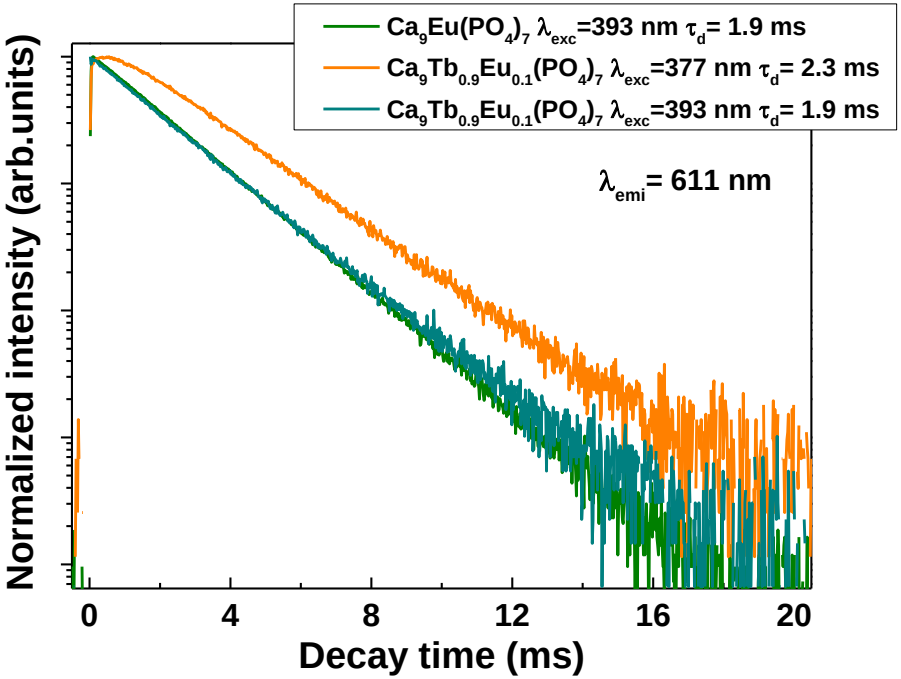


The spectra show evidence of $^5D_3$ - $^5D_4$ cross relaxation

Evidence of weak Tb-Eu energy transfer

DECAY KINETICS



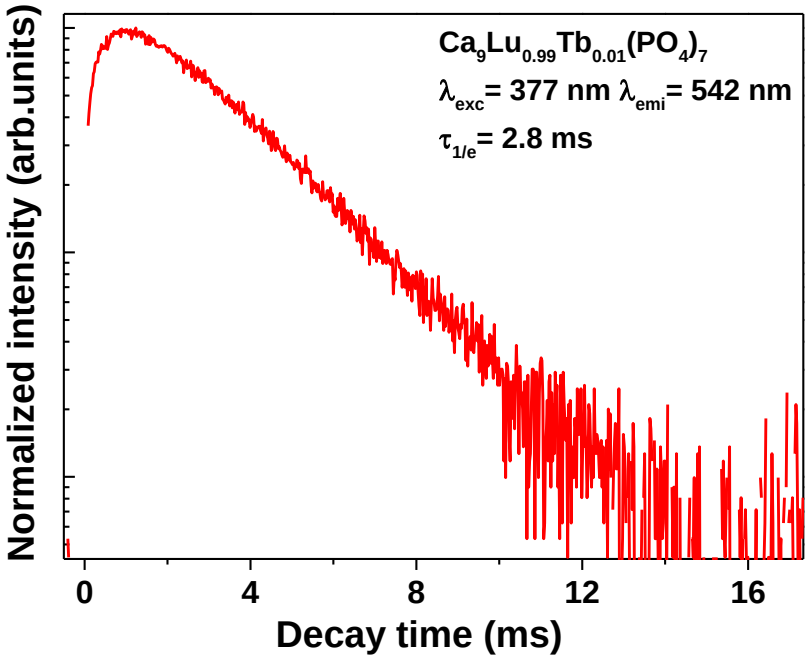


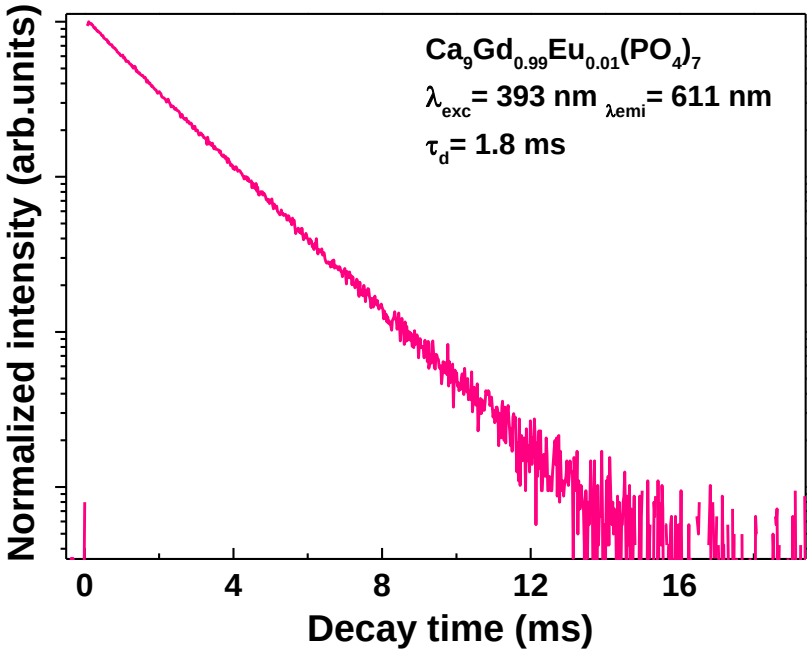
Non exponential decay curves

Decay constant slightly shortens in the Eu-doped samples

Same decay constant for neat Eu and Tb-Eu samples when exciting at 393 nm

Rise at short times when exciting into 377 nm



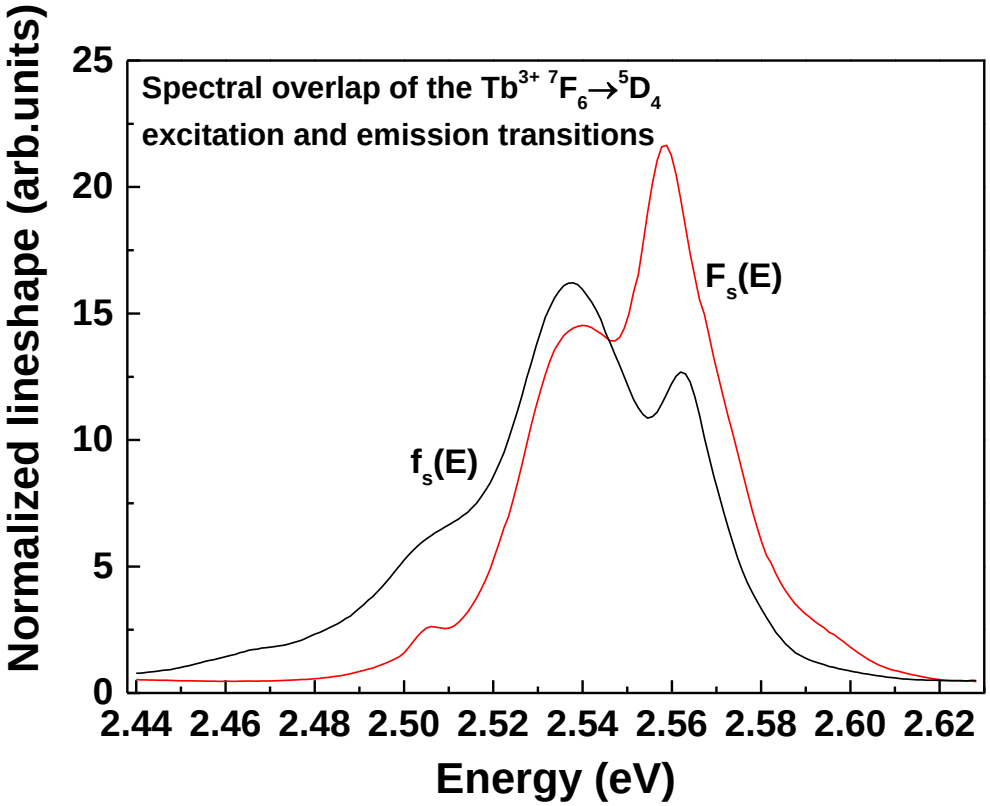


Decay constant slightly shortens in concentrated Tb compounds compared to diluted one

Same decay constant for concentrated and diluted Eu compounds

Weak or neglectable energy migration along Ln^{3+} ions

Energy migration in the Tb^{3+} subset of ions



For $Ca_9Tb(PO_4)_7$ the critical distance of dipole-dipole energy transfer was evaluated using the equation:

$$R_c^6 = 3 \cdot 10^{12} f_d \int \frac{f_s(E) F_s(E)}{E^4} dE$$

$$f_d(Tb^{3+}) = 3 \cdot 10^{-7}$$

$R_c \approx 7.8$ Å is estimated. If compared with the minimum Tb-Tb distance of about 5.2 Å, a fast migration is predicted, but the experimental results show only a weak effect when comparing diluted and neat Tb compounds

J. M. P. J. Vestegen, J. L.Sommerdijk and J. G. Verriet, *J. Lumin.***1973**, 6, 425.

Silico-carnotite (Tb^{3+} $^5D_4$ emission)

$Ca_3Y_{1.98}Tb_{0.02}Si_3O_{12}$ τ_d= 2.50 ms

$Ca_3Tb_2Si_3O_{12}$ τ_d= 0.18 ms

$Ca_3Tb_{1.9}Eu_{0.1}Si_3O_{12}$ τ_d= 0.01 ms

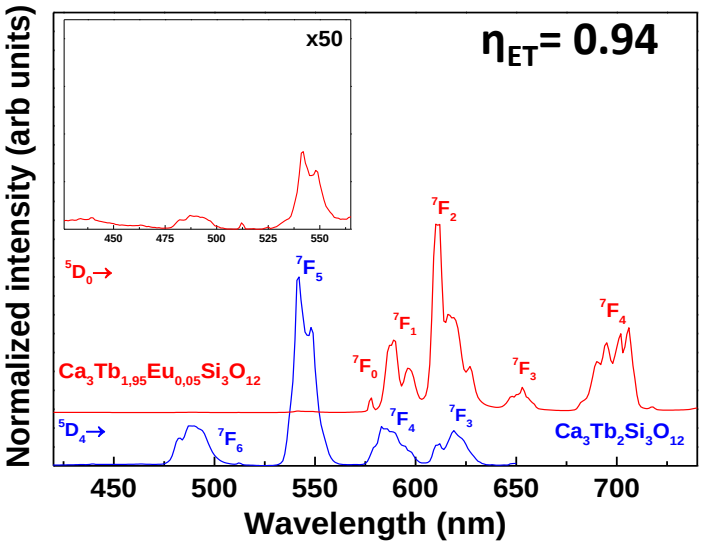
Eulytite (Tb^{3+} $^5D_4$ emission)

$Sr_3Y_{0.99}Tb_{0.01}(PO_4)_3$ τ_d= 2.98 ms

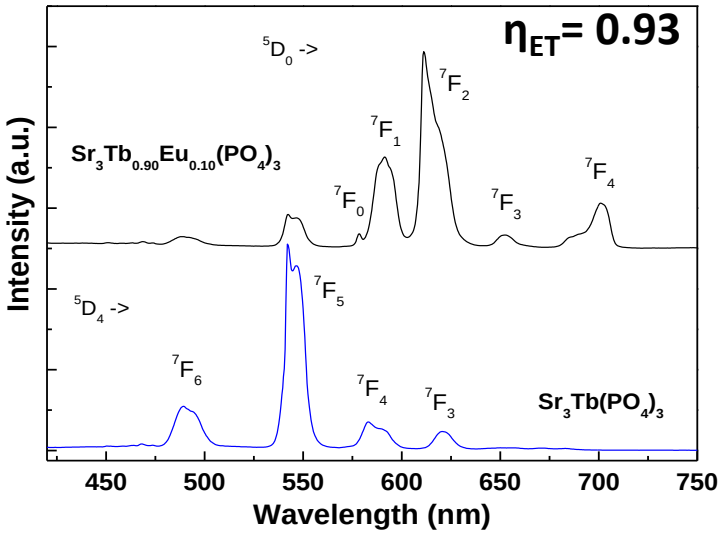
$Sr_3Tb_3(PO_4)_3$ τ_d= 2.68 ms

$Sr_3Tb_{0.9}Eu_{0.1}(PO_4)_3$ $\tau_{1/e}$= 0.20 ms

Tb-Eu energy transfer enhanced via Tb-Tb energy migration



I.Carrasco et.al, *Opt. Mat.* **48** (2015) 252-257



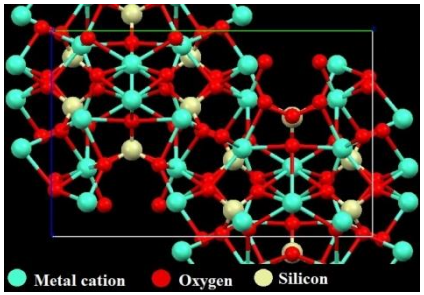
M. Bettinelli et.al, *Opt. Mat.* **33** (2010) 119-122

Compound	Rc (Å)	d (Å)
$Ca_3Tb_2Si_3O_{12}$	7.4	3.1
$Sr_3Tb(PO_4)_3$	7.6	4
$Ca_9Tb(PO_4)_7$	7.8	5.1

Why the behaviour of Tb/Eu is so different in the whitlockite?

$Ca_3Tb_2Si_3O_{12}$

(Silico-carnotite)

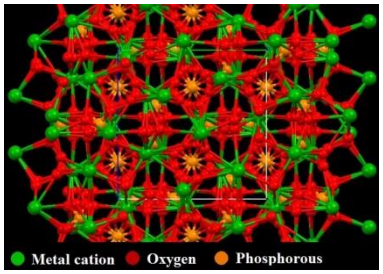


Cell volume:1038 Å^3

Three available crystal sites for Tb ions

$Sr_3Tb(PO_4)_3$

(Eulytite)

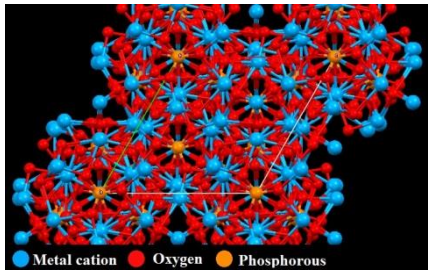


Cell volume: 1033 Å^3

The pairs of cations are disordered on a single crystallographic site

$Ca_9Tb(PO_4)_7$

(Whitlockite)



Cell volume: 3533 Å^3

Four possible cation sites for the Tb ions in the host

No clear explanation: various hypothesis

CONCLUSIONS

Slight change in the emission colour of the material by the addition of Eu^{3+}

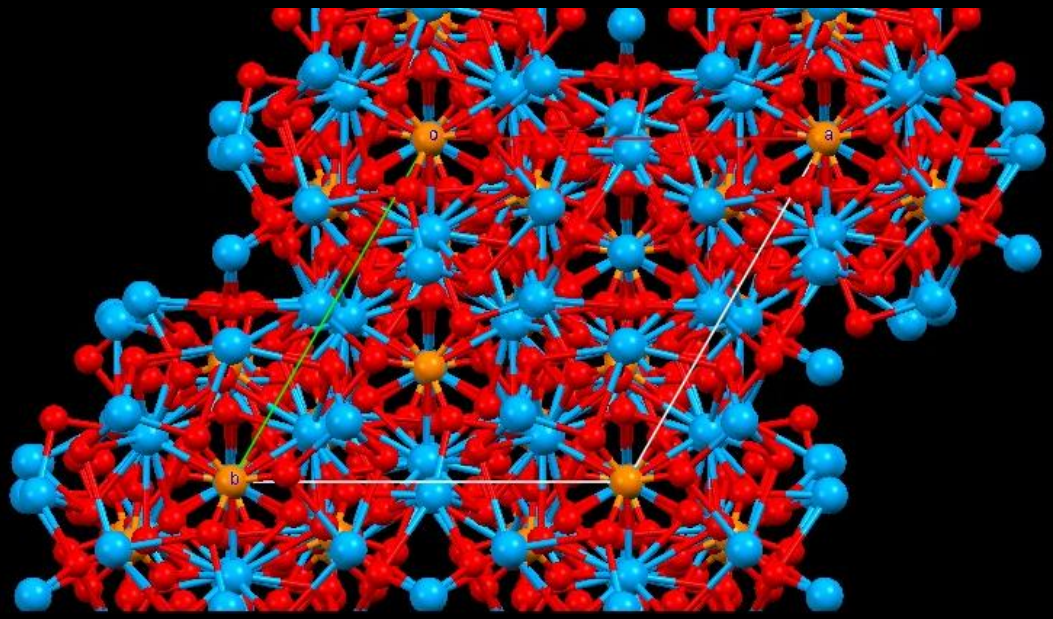
Evidence of weak Tb^{3+}-Eu^{3+} energy transfer and Tb^{3+}-Tb^{3+} energy migration processes

The mechanisms involved in the energy transfer (Tb-Tb and Tb-Eu) process are not clear

FUTURE WORK

Further analysis of the measured data to better understand the phenomena (exploration of suitable models to describe the processes)

Thank you for your attention



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