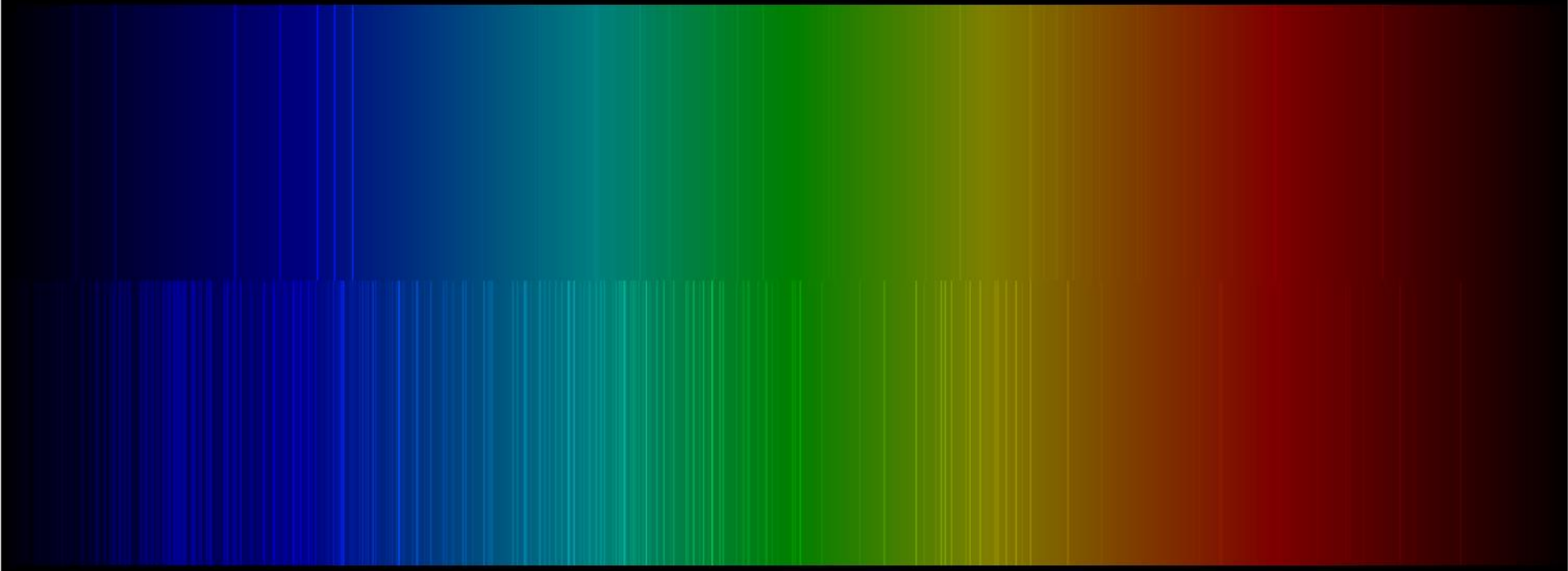


Energy transfer processes in $Ca_3Tb_2Si_3O_{12}:Eu^{3+}$

Irene Carrasco Ruiz
Luminescent Materials Group. UNIVR

Verona 2015

OUTLINE

Motivation

Sample details

Results:

- **-RT luminescence experiments**
- **-8K-330K luminescence experiments**

Conclusions

Future work

MOTIVATION

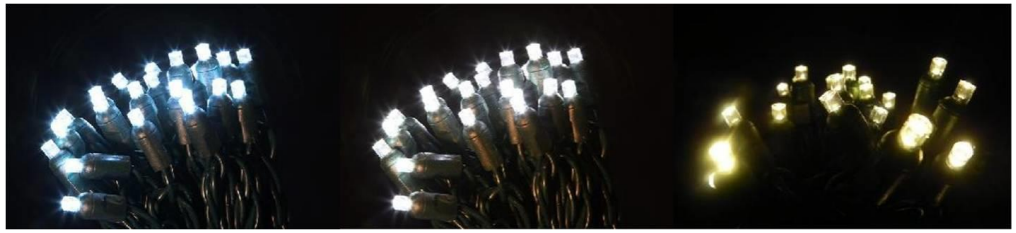
Rare earth phosphors are light-emitting materials with wide variety of applications.

Plasma display panels

White LEDs

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

Blue LED chip + yellow-emitting phosphor ➞ Cool light



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

UV-LED chip + tricolor emitting phosphors ➞ Warm light

New phosphors to improve UV-excited white LEDs

Sensitization is a traditional way to enhance luminescence efficiency

Tb^{3+} is a very good sensitizer for Eu^{3+}

Both ions exhibit absorption bands in the UV

Green emission from Tb^{3+} and red emission from Eu^{3+} have many applications in lighting and displays

Silicate phosphors:
Good transparency in UV-VIS
Favorable luminescent properties
High chemical stability
Low cost

Silico-carnotite type structure:
Orthorombic space group, *Pnma*
Good stability for RE doping from Eu-Lu ions

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

OBJECTIVE

Study the Tb^{3+}-Eu^{3+} energy transfer processes in $Ca_3Tb_2Si_3O_{12}:Eu^{3+}$.

METHODOLOGY

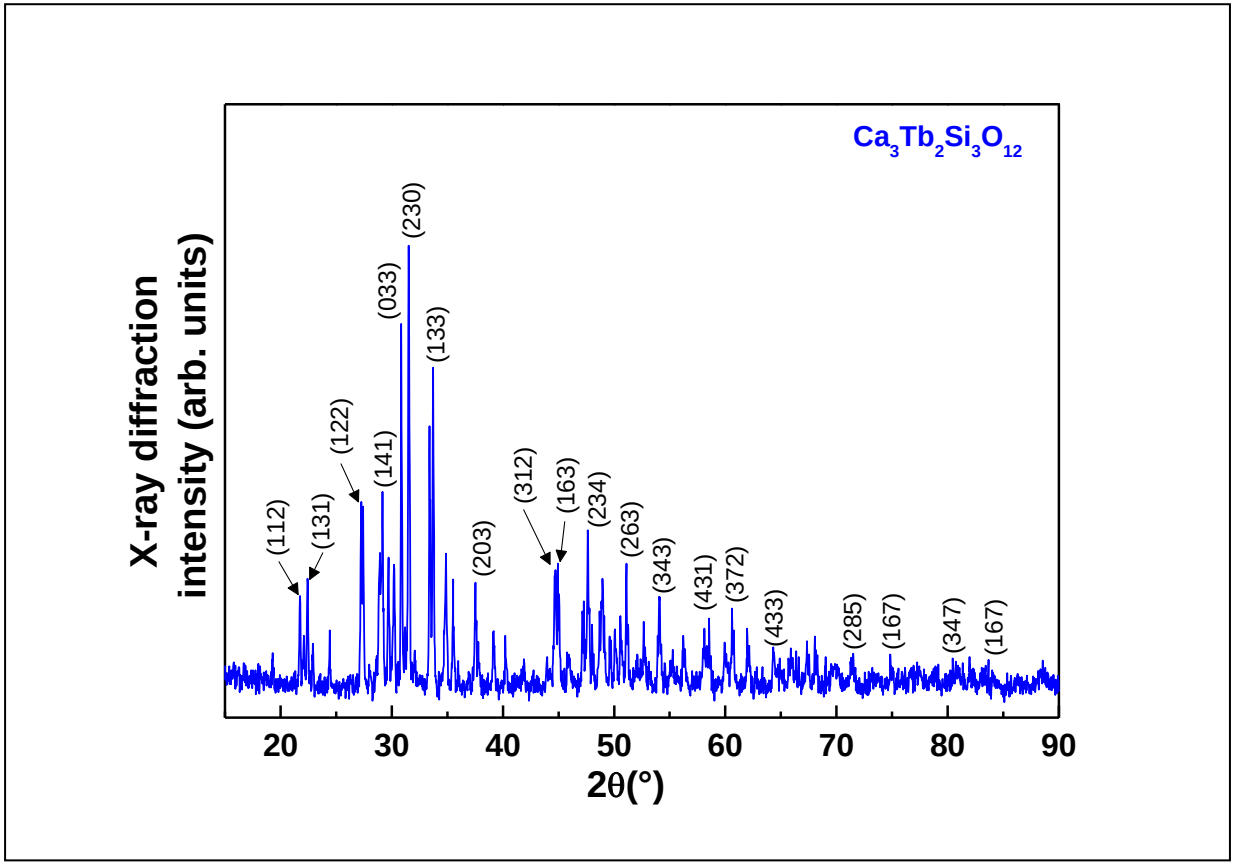
Performing luminescence and decay time experiments in $Ca_3Tb_2Si_3O_{12}$, $Ca_3Tb_2Si_3O_{12}:Eu^{3+}$ and in $Ca_3Eu_2Si_3O_{12}$ powders.

SAMPLE DETAILS

$Ca_3Tb_2Si_3O_{12}$,$Ca_3Eu_2Si_3O_{12}$ and $Ca_3Tb_2Si_3O_{12}:Eu^{3+}$ (5 mol%)

Synthesized by SSR (III TT at 1450 ^oC x 3h)

Homogeneus white powders.*Pure phase*



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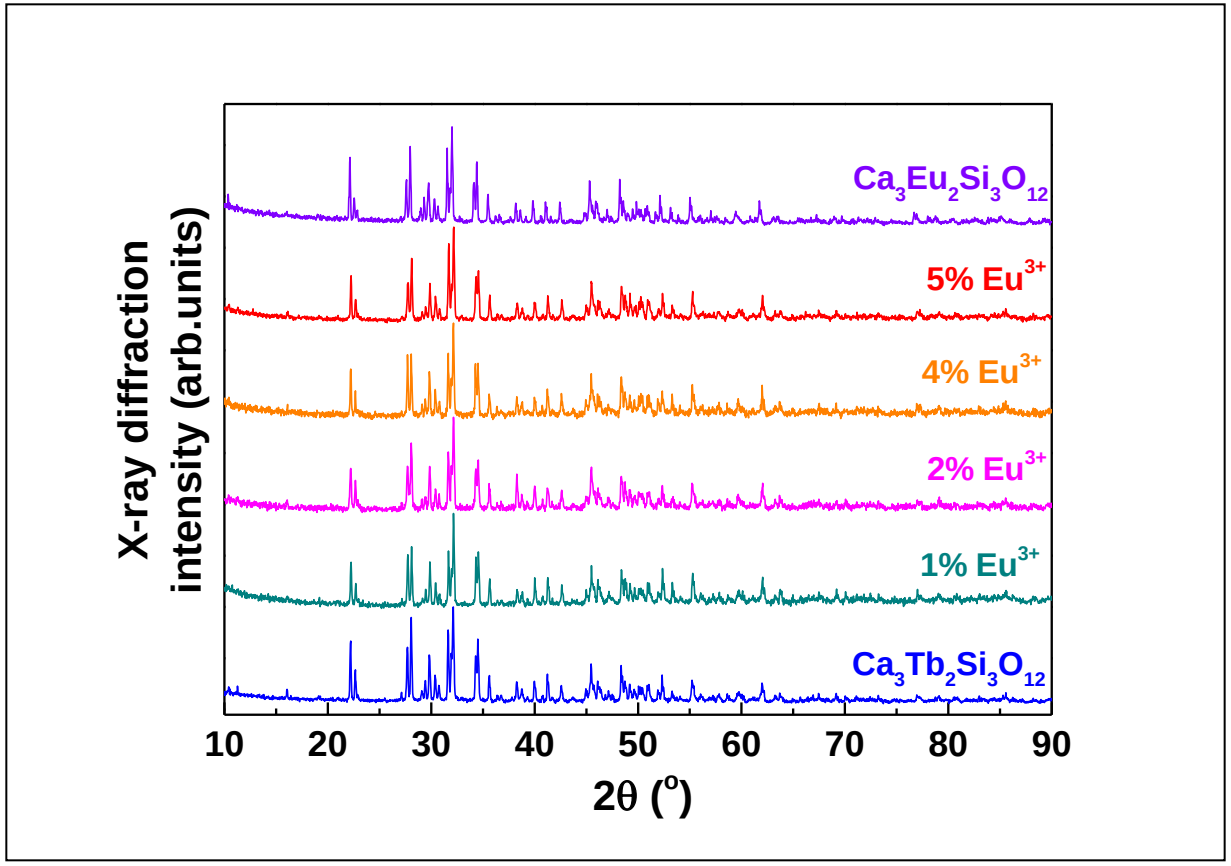
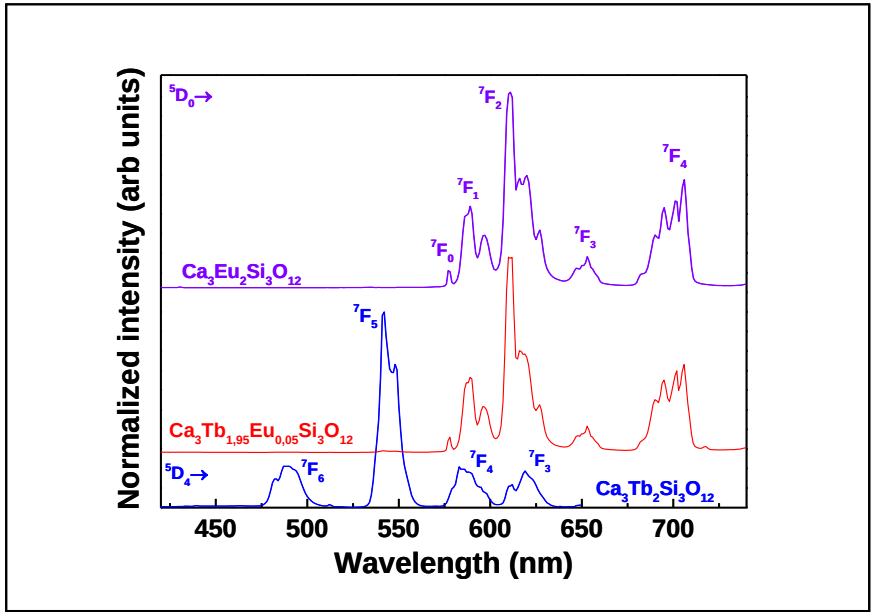


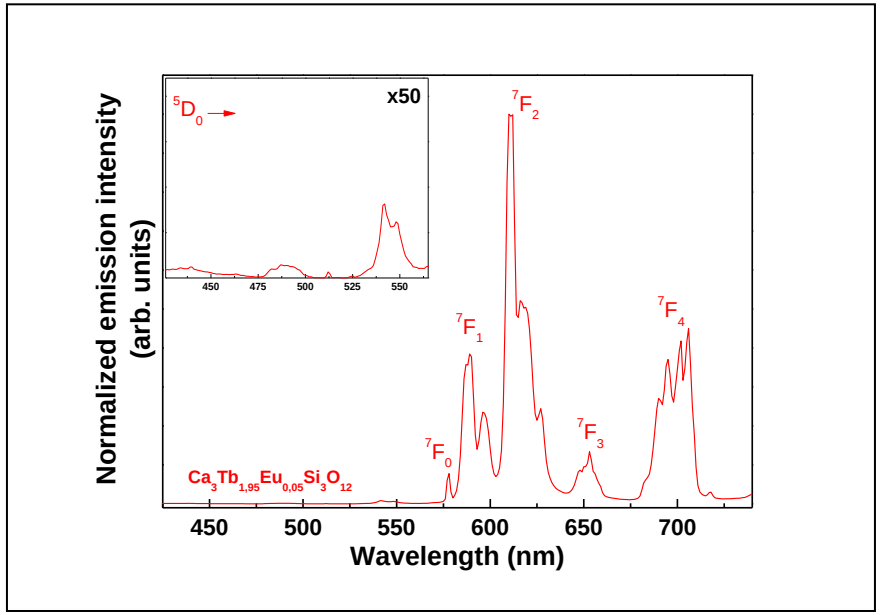
PHOTOLUMINESCENCE RESULTS

RT EMISSION

$Ca_3Tb_2Si_3O_{12}$ and $Ca_3Tb_2Si_3O_{12}:Eu^{3+}$: λ_{exc} =377 nm $^5D_3$ (Tb^{3+})

$Ca_3Eu_2Si_3O_{12}$: λ_{exc} =393 nm $^5L_7$ (Eu^{3+})



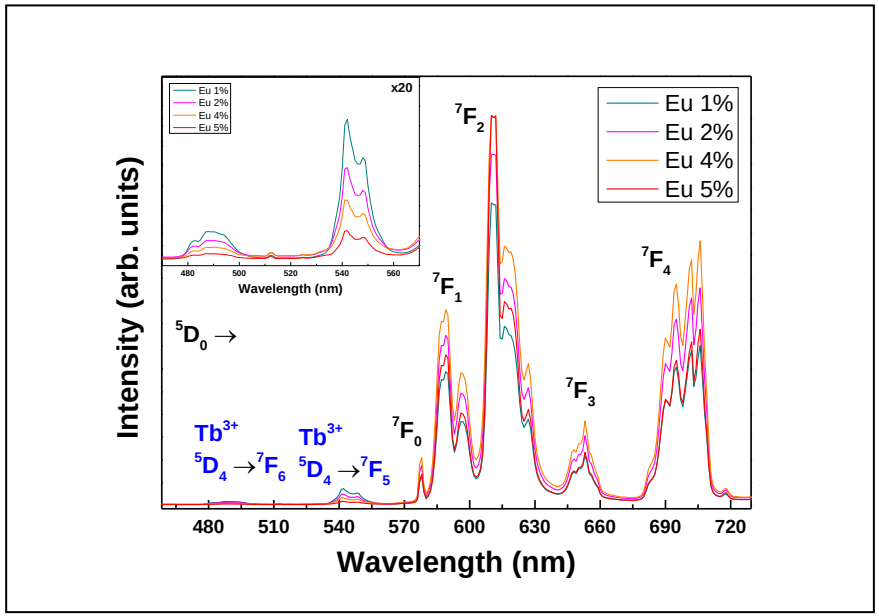


Very efficient energy transfer from Tb^{3+} to Eu^{3+}

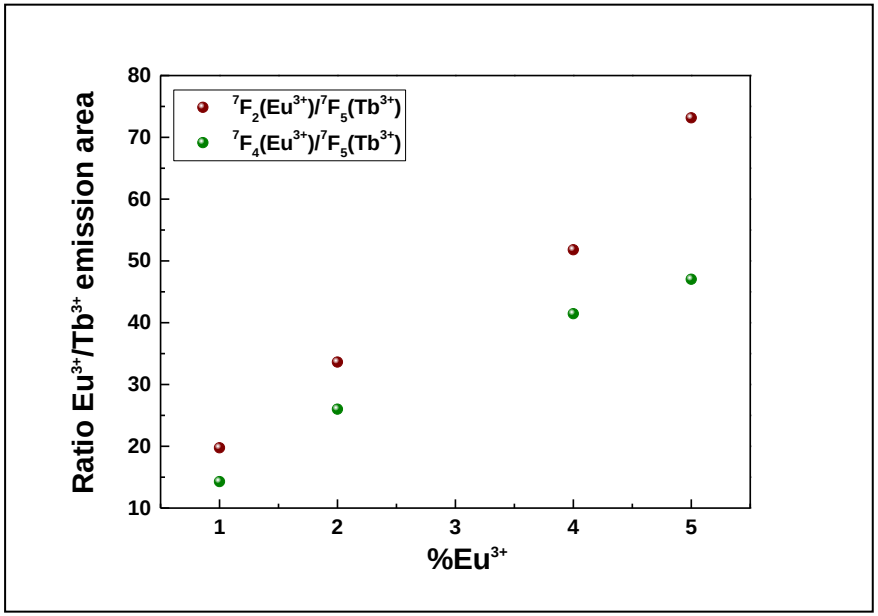
PHOTOLUMINESCENCE RESULTS

RT EMISSION

λ_{exc} =377 nm $^5D_3$ (Tb^{3+})



$$\frac{I\,{}^7F_J(Eu^{3+})}{I\,{}^7F_5(Tb^{3+})}; J = 2,4$$

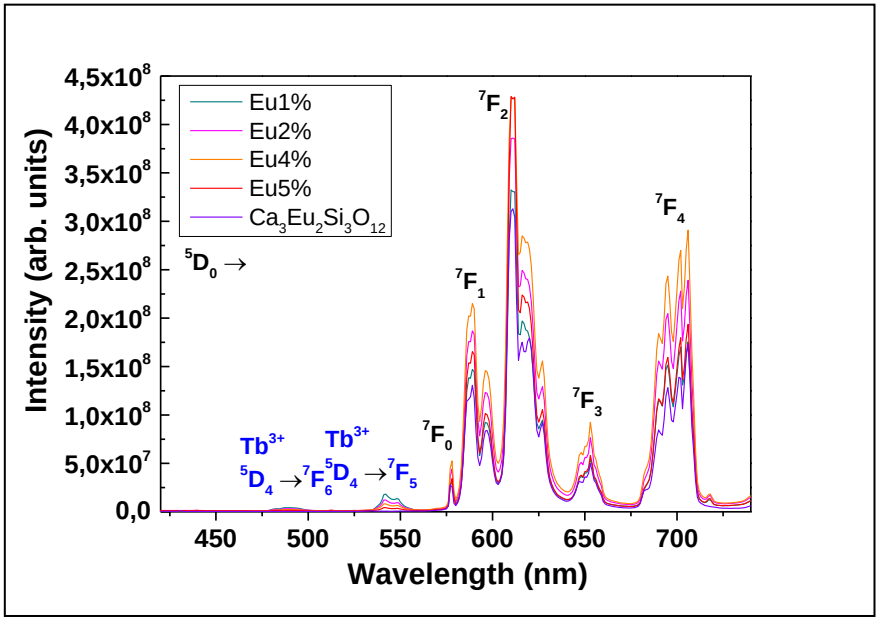


PHOTOLUMINESCENCE RESULTS

RT EMISSION

$Ca_3Tb_2Si_3O_{12}:Eu^{3+}$
λ_{exc} =377 nm $^5D_3$ (Tb^{3+})

$Ca_3Eu_2Si_3O_{12}$:
λ_{exc} =393 nm $^5L_7$ (Eu^{3+})



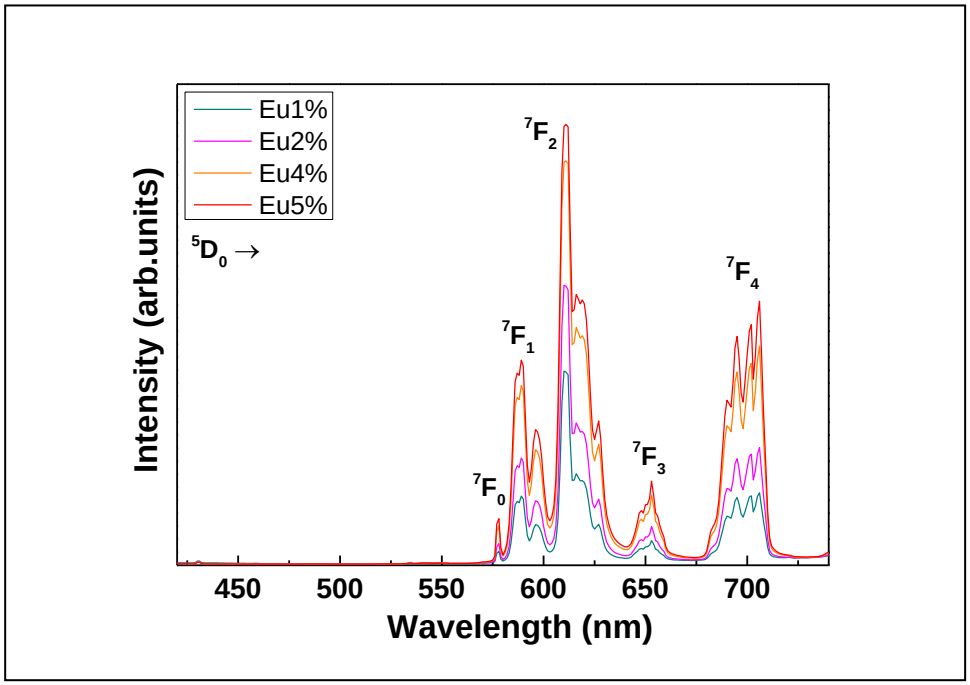
Eu^{3+} concentration (%)	$\frac{Emission\ Ca_3Tb_2Si_3O_{12}:Eu^{3+}}{Emission\ Ca_3Eu_2Si_3O_{12}}$
1	1.2
2	1.5
4	1.8
5	1.3

Enhancement of Eu^{3+} luminescent.

PHOTOLUMINESCENCE RESULTS

RT EMISSION

λ_{exc} =393 nm $^5L_7$ (Eu^{3+})

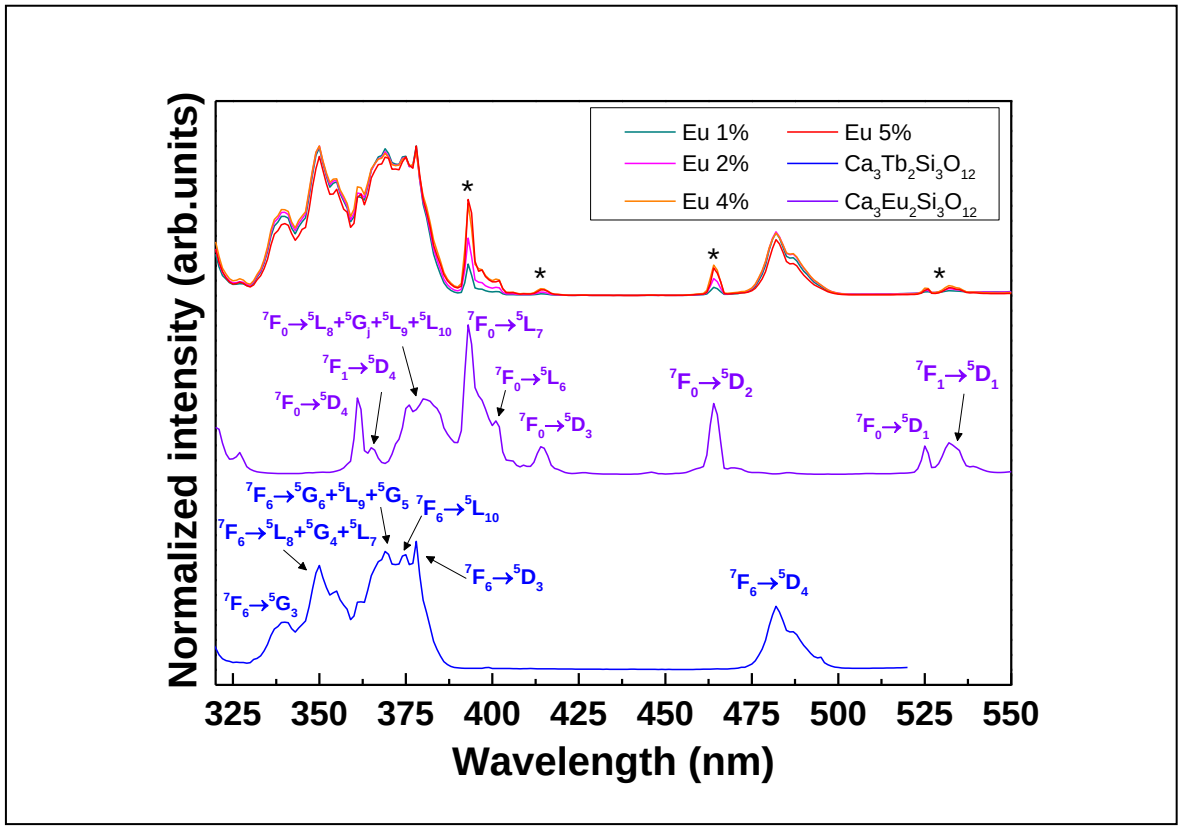


No Tb^{3+} emission bands are observed under direct excitation into Eu^{3+}

These results prove no $Eu^{3+} \longrightarrow Tb^{3+}$ energy transfer is present
No spectral shift under different excitations.

PHOTOLUMINESCENCE RESULTS

RT EXCITATION



Only a few Eu^{3+} excitation bands are observed (labeled with *)

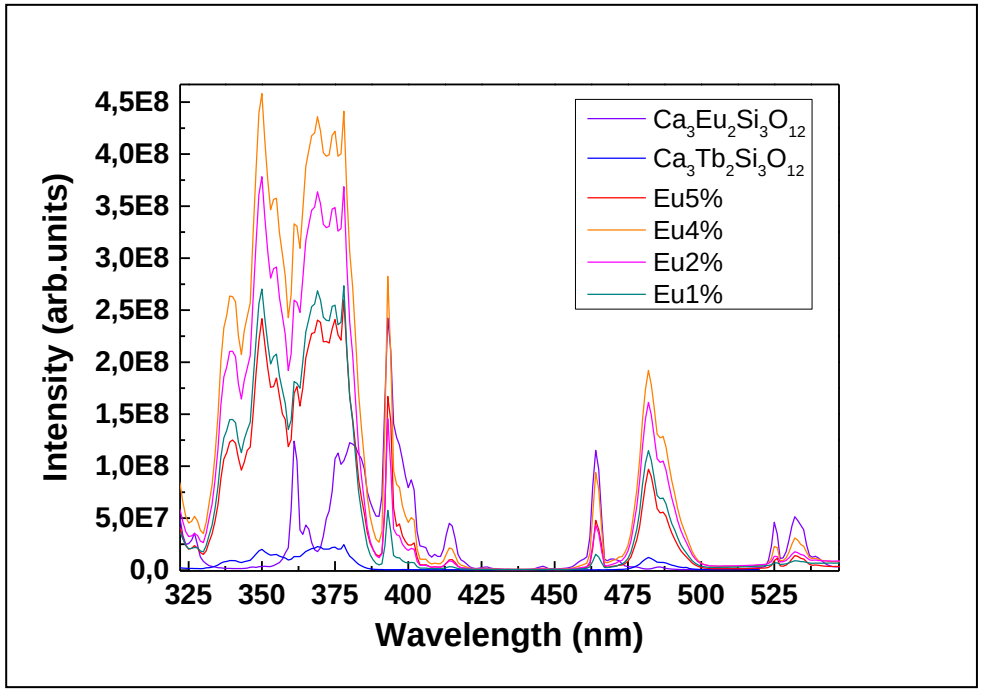
These results confirm the $Tb^{3+} \longrightarrow Eu^{3+}$ energy transfer

PHOTOLUMINESCENCE RESULTS

RT EXCITATION

$Ca_3Tb_2Si_3O_{12}$: λ_{emi} =542 nm (Tb^{3+})

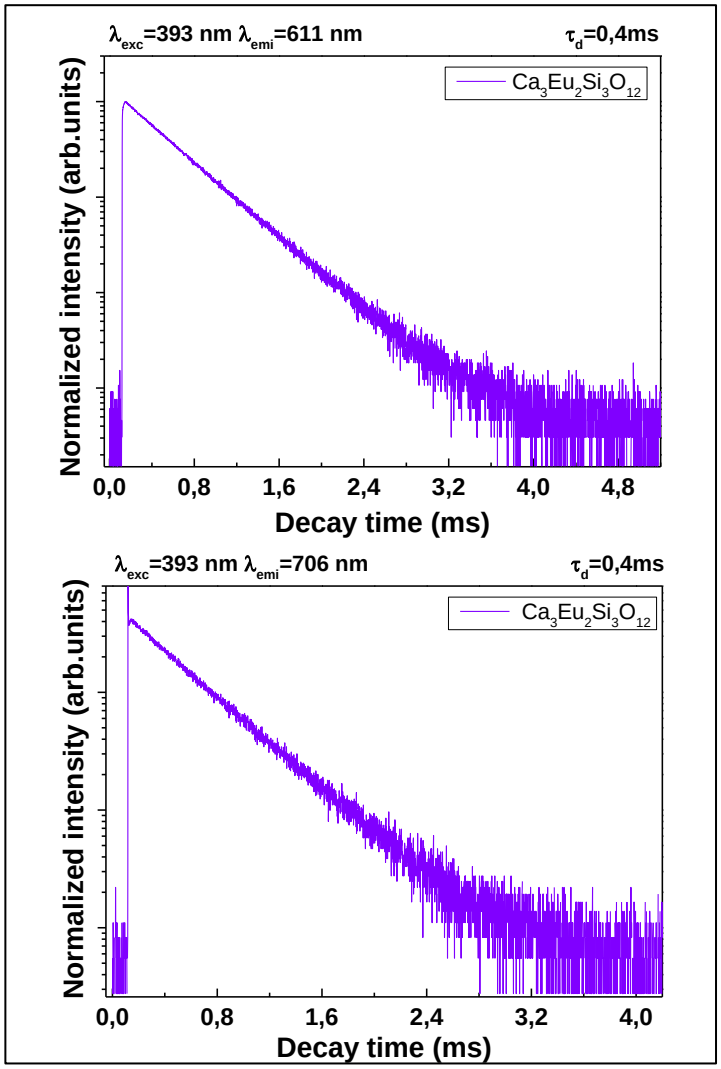
$Ca_3Eu_2Si_3O_{12}$and $Ca_3Tb_2Si_3O_{12}$:Eu^{3+} λ_{emi} =611 nm (Eu^{3+})

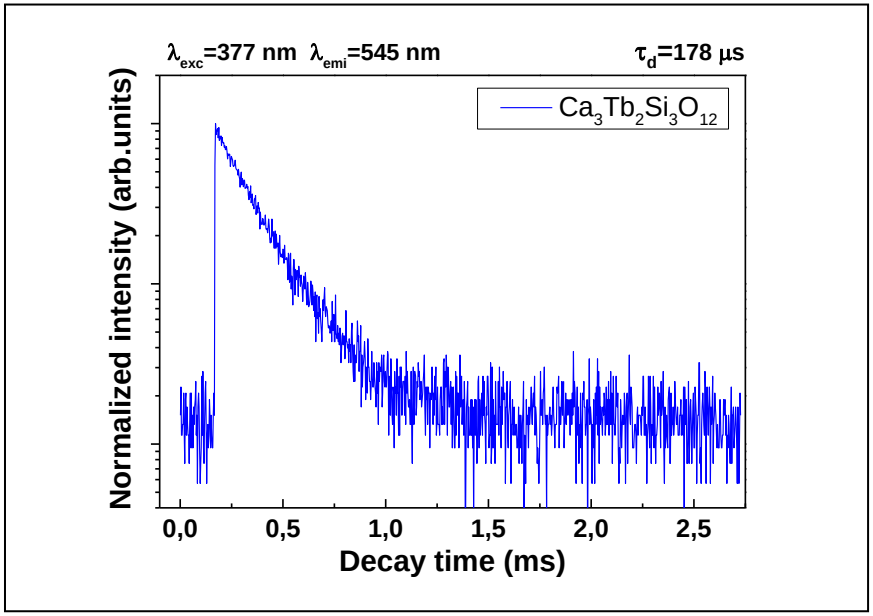


Intensity of excitation bands is enhanced, specially in near UV region

PHOTOLUMINESCENCE RESULTS

RT DECAY KINETICSOF $Ca_3Eu_2Si_3O_{12}$ AND $Ca_3Tb_2Si_3O_{12}$

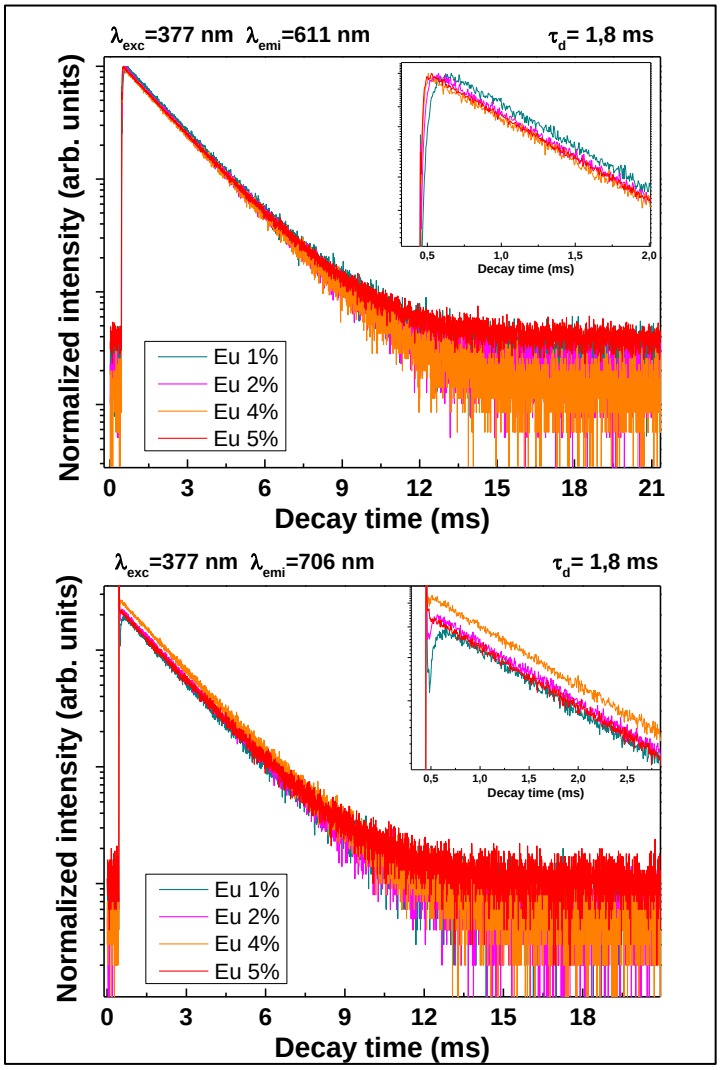


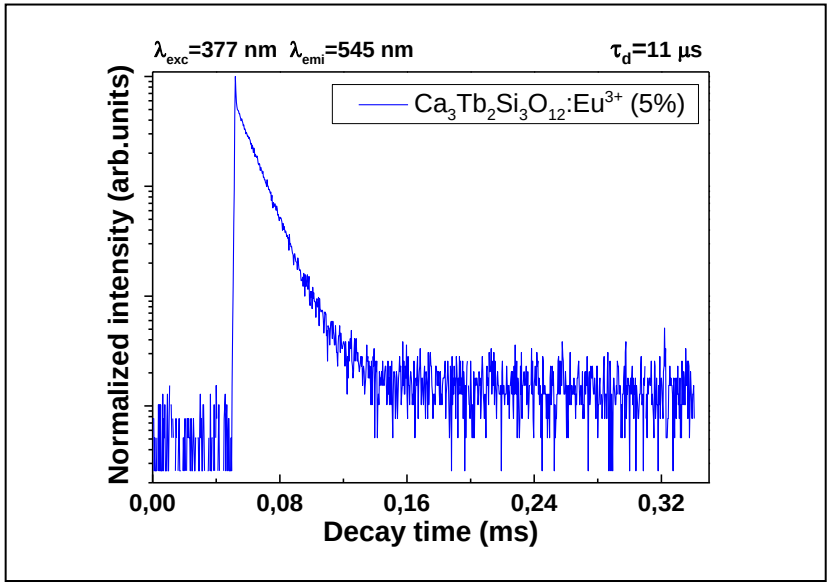


Short time constant probably due to energy migration along Ln^{3+} ions, because of high concentration

PHOTOLUMINESCENCE RESULTS

RT DECAY KINETICS OF $Ca_3Tb_2Si_3O_{12}:Eu^{3+}$



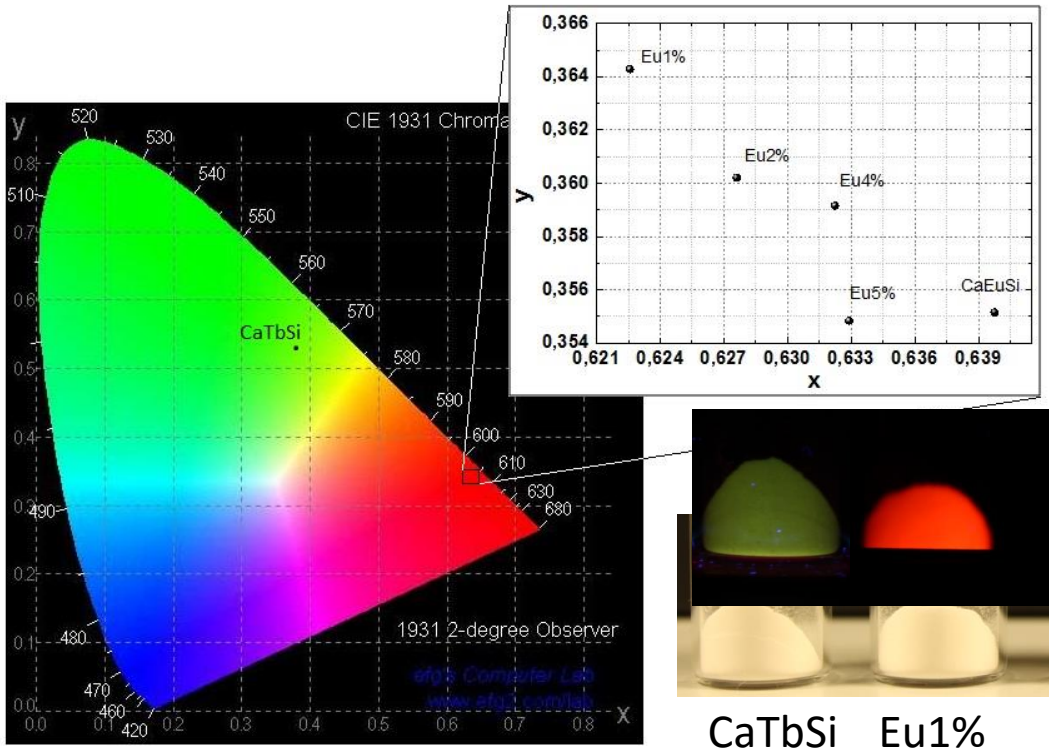


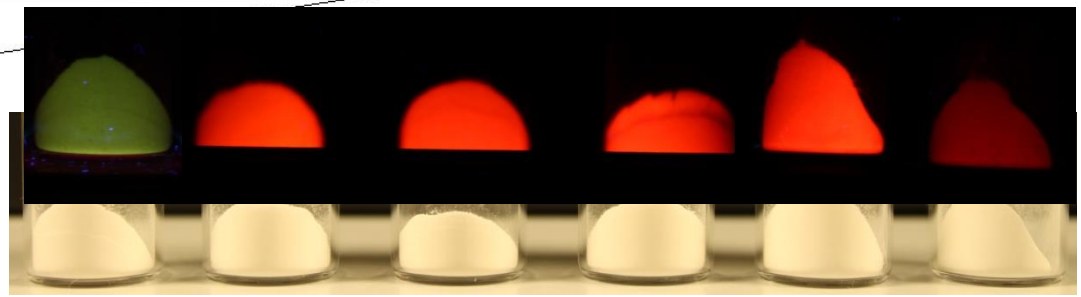
$$\eta_{RT} = 1 - \frac{\tau_{Tb-Eu}}{\tau_{Tb}} = 0.94$$

Longer time constant for Eu^{3+} emission.
Very efficient Tb^{3+}- Eu^{3+} energy transfer.

PHOTOLUMINESCENCE RESULTS

CIE chromaticity coordinates





CaTbSi Eu1% Eu2% Eu4% Eu5% CaEuSi

UV excitation at 365 nm

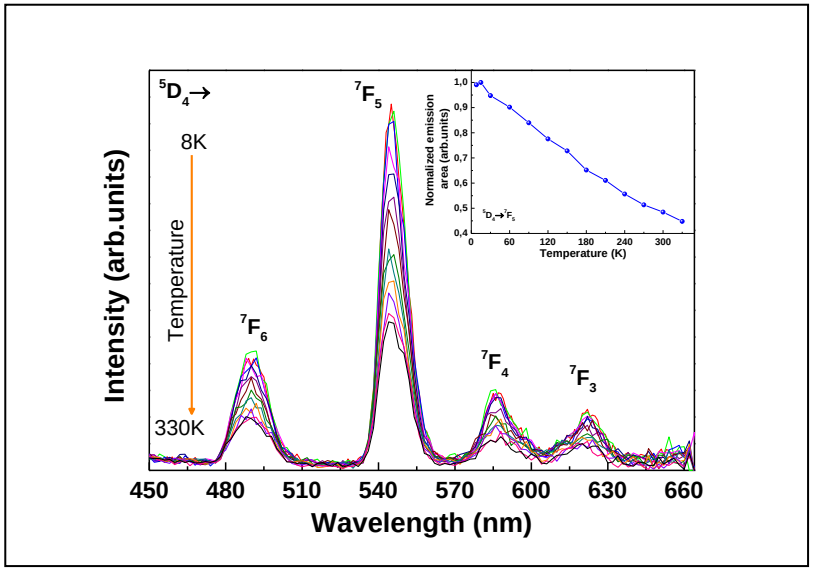
Emission colour of $Ca_3Tb_{2-x}Eu_xSi_3O_{12}$ phosphors could be tuned effectively from green to red by adjusting Eu^{3+} concentration

PHOTOLUMINESCENCE RESULTS

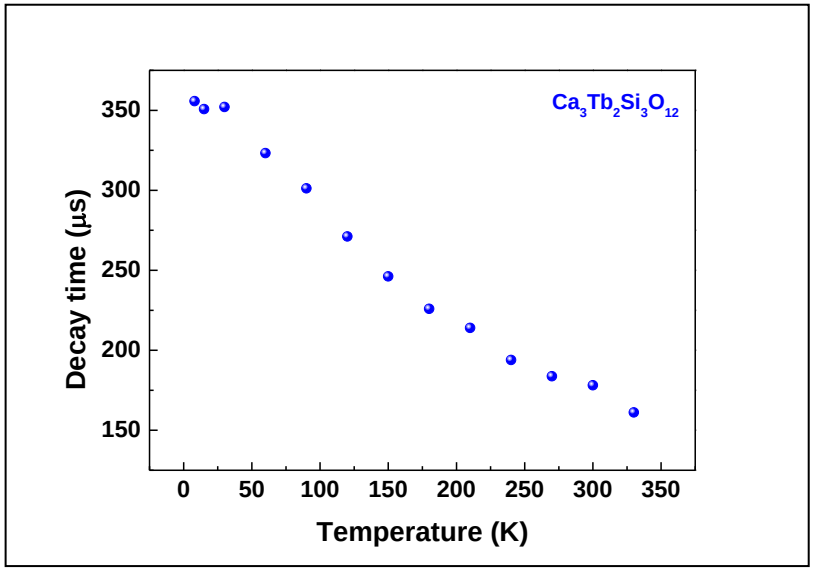
TEMPERATURE STUDY OF $Ca_3Tb_2Si_3O_{12}$

λ_{exc} =370 nm into $^5D_3$ level of Tb^{3+}

Emission



Decay kinetics (λ_{emi} =545 nm)



$$\Delta EA(Tb^{3+}) = 55\%$$

$$\Delta\tau(Tb^{3+}) = 55\%$$

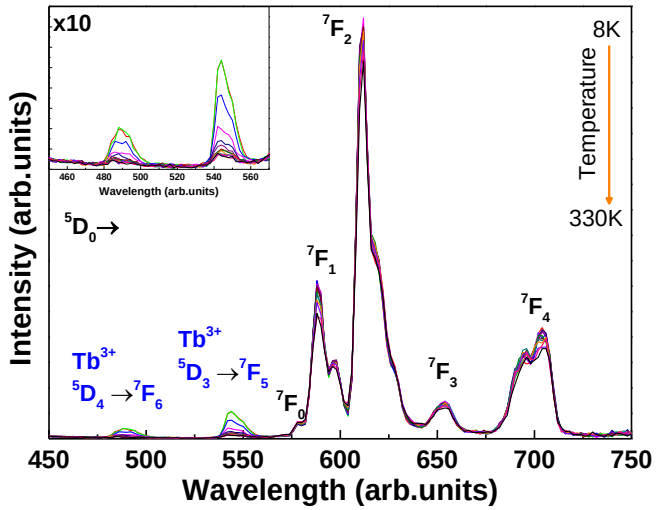
Results confirm very fast energy migration among Tb^{3+} ions above 50K

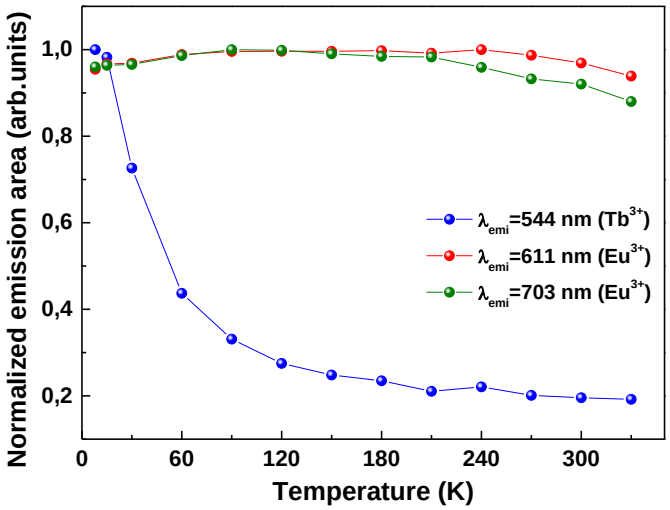
PHOTOLUMINESCENCE RESULTS

TEMPERATURE STUDY OF $Ca_3Tb_2Si_3O_{12}:Eu^{3+}$ (5%)

λ_{exc} =370 nm into $^5D_3$ level of Tb^{3+}

Emission



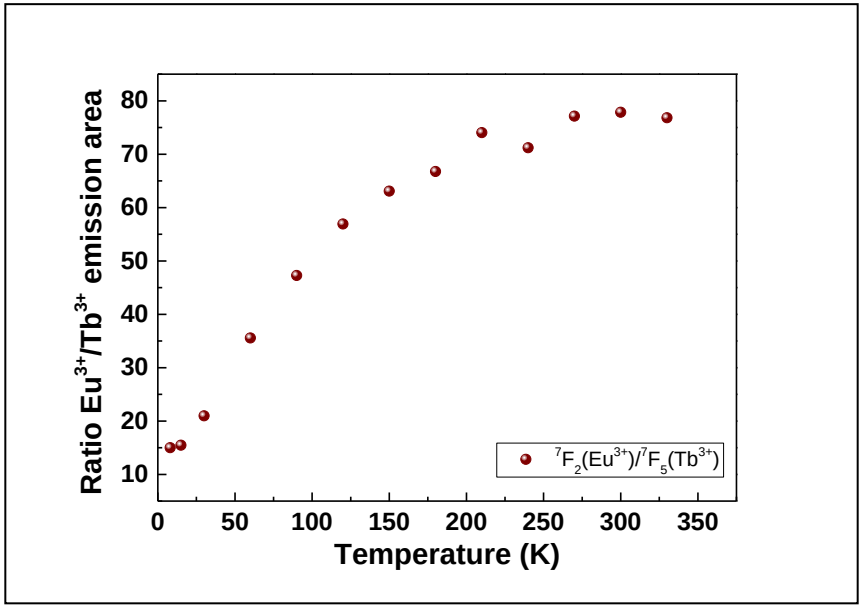


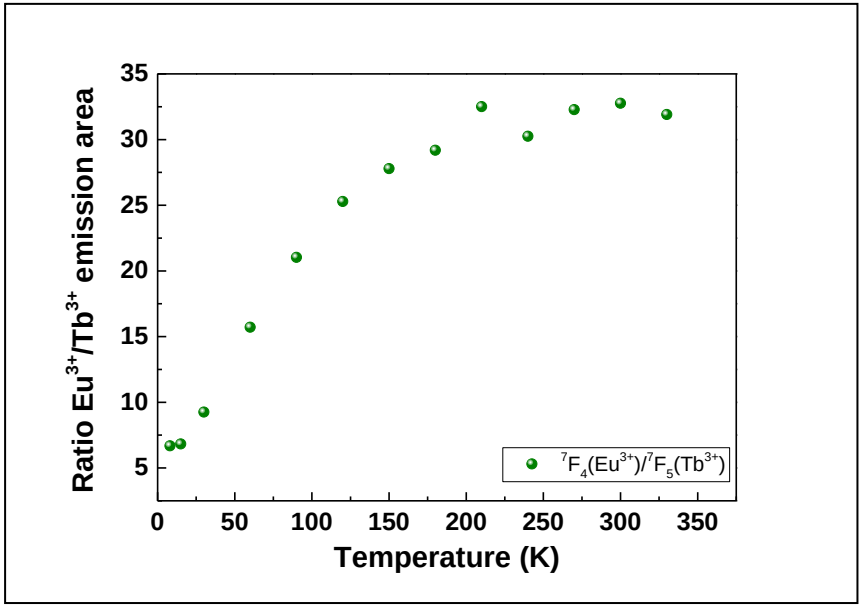
$$\Delta EA\ (Tb^{3+}) = 80\%$$

$$\Delta EA\ (Eu^{3+}) < 10\%$$

PHOTOLUMINESCENCE RESULTS

TEMPERATURE STUDY OF $Ca_3Tb_2Si_3O_{12}:Eu^{3+}$ (5%)





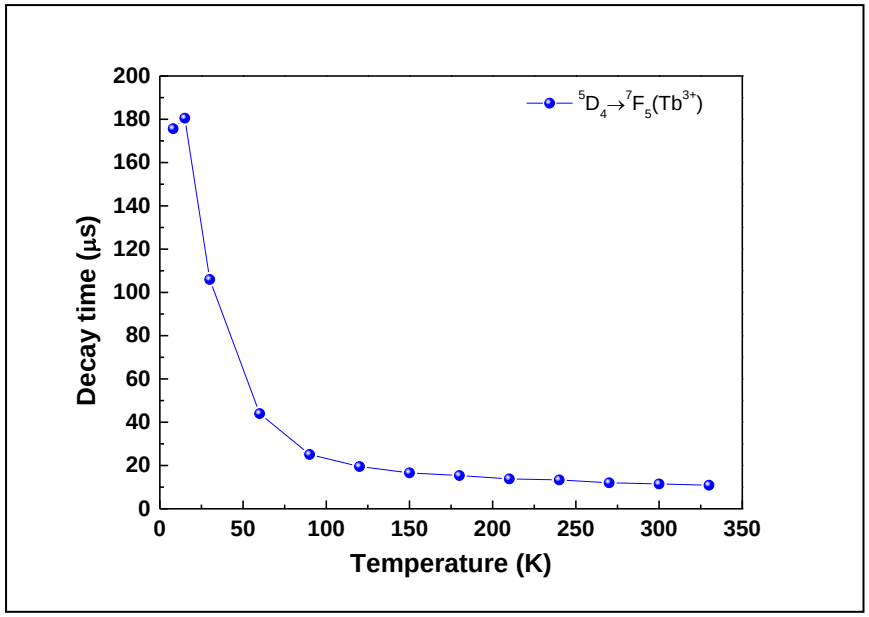
As temperature increases and energy migration among Tb^{3+} ions becomes faster, the larger is Tb^{3+} - Eu^{3+} emission ratio.

PHOTOLUMINESCENCE RESULTS

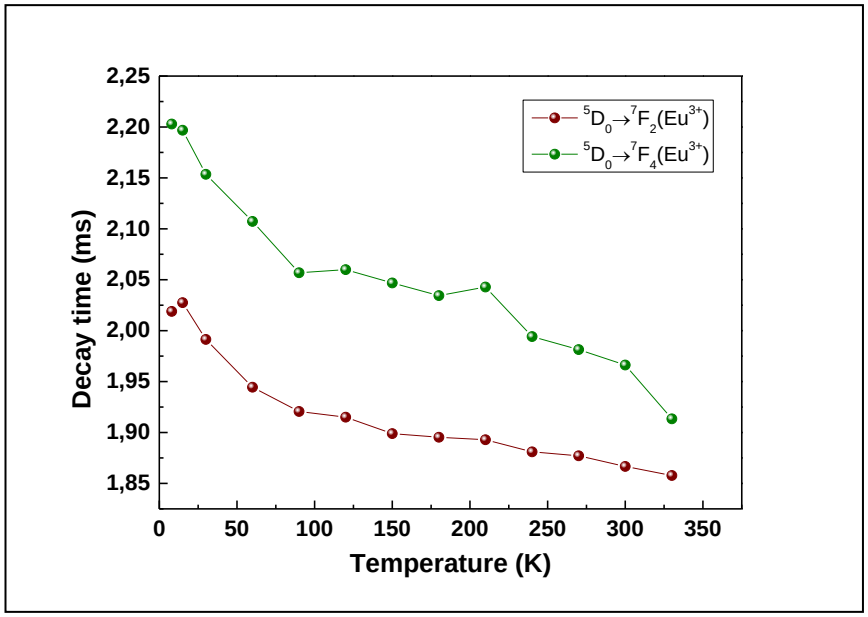
TEMPERATURE STUDY OF $Ca_3Tb_2Si_3O_{12}:Eu^{3+}$ (5%)

λ_{exc} =370 nm into $^5D_3$ level of Tb^{3+}

Decay kinetics (λ_{emi} =544 nm)



Decay kinetics (λ_{emi} =611, 702 nm)



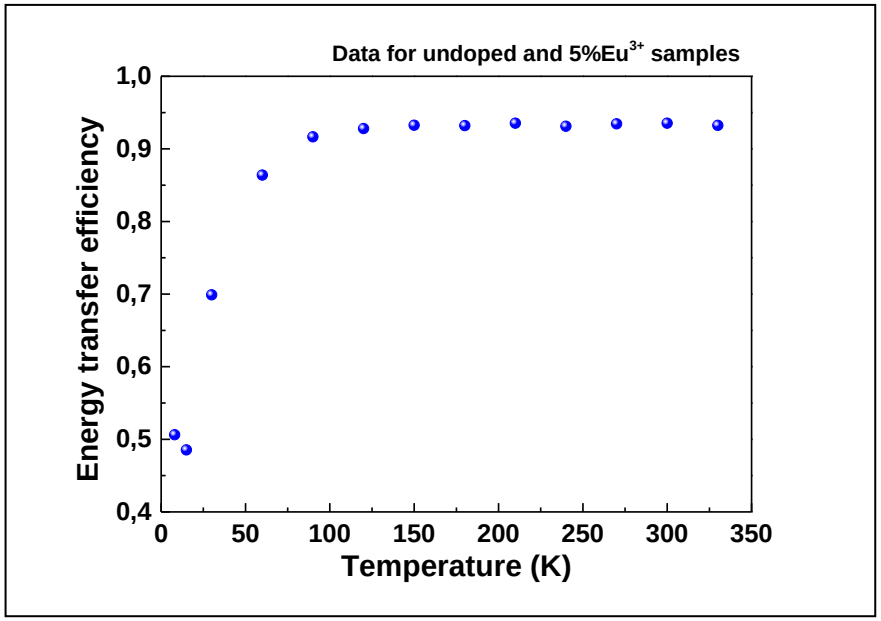
$$\Delta\tau(Tb^{3+}) = 94\%$$

$$\Delta\tau(\,^5D_0 \rightarrow {}^7F_2\,Eu^{3+}) = 9\%$$

$$\Delta\tau(\,^5D_0 \rightarrow {}^7F_4\,Eu^{3+}) = 13\%$$

PHOTOLUMINESCENCE RESULTS

EFFICIENCY OF ENERGY TRANSFER



$$\eta(T) = 1 - \frac{\tau_{Tb-Eu}(T)}{\tau_{Tb}(T)}$$

$$\eta(LT) = 0.51 \quad \eta(RT) = 0.94$$

Efficiency of Tb^{3+} - Eu^{3+} energy transfer is more than 90% from 100 K to 350K

CONCLUSIONS

Clear evidences of energy transfer from Tb^{3+} to Eu^{3+}

Tb^{3+} emission almost quenched and very strong Eu^{3+} emission

Efficient changes in the emission colour of the material by the addition of Eu^{3+}

Tb^{3+} - Eu^{3+} energy transfer enhances Eu^{3+} luminescence

Energy migration among Tb^{3+} ions enhance Tb^{3+} - Eu^{3+} energy transfer

FUTURE WORK

Experiments at higher T to test thermal stability

Decay curves for Tb^{3+} emission in 1%, 2% and 4% Eu-doped samples to stimate efficiency of the transfer

Synthesis of diluted samples in order to avoid Tb^{3+} concentration quenching

Thank you for your attention

LUMINESCENT MATERIALS LAB