

# EAGLES

International Conference on  
Rare-Earth Doped Glass Materials and Fibre Lasers  
MPNS COST Action MP1401



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## Rare earth activated silica-hafnia glass and glass ceramics to improve the efficiency of photovoltaic solar cells

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**CSMFO LAB.** CHARACTERIZATION and DEVELOPMENT of MATERIALS for PHOTONICS and OPTOELECTRONICS Laboratory



**DSFTM**  
Dipartimento di Scienze Fisiche e Tecnologie della Materia



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**FONDAZIONE  
BRUNO KESSLER**



*This project is part of a CNRST-Morocco / CNR-Italy agreement*

Photovoltaic cells will be delivered by the company:

***MeridionaleImpianti***

Address: Strada provincial Belpasso Bivio Aspro - Piano Tavola 95121 CATALANA Italy

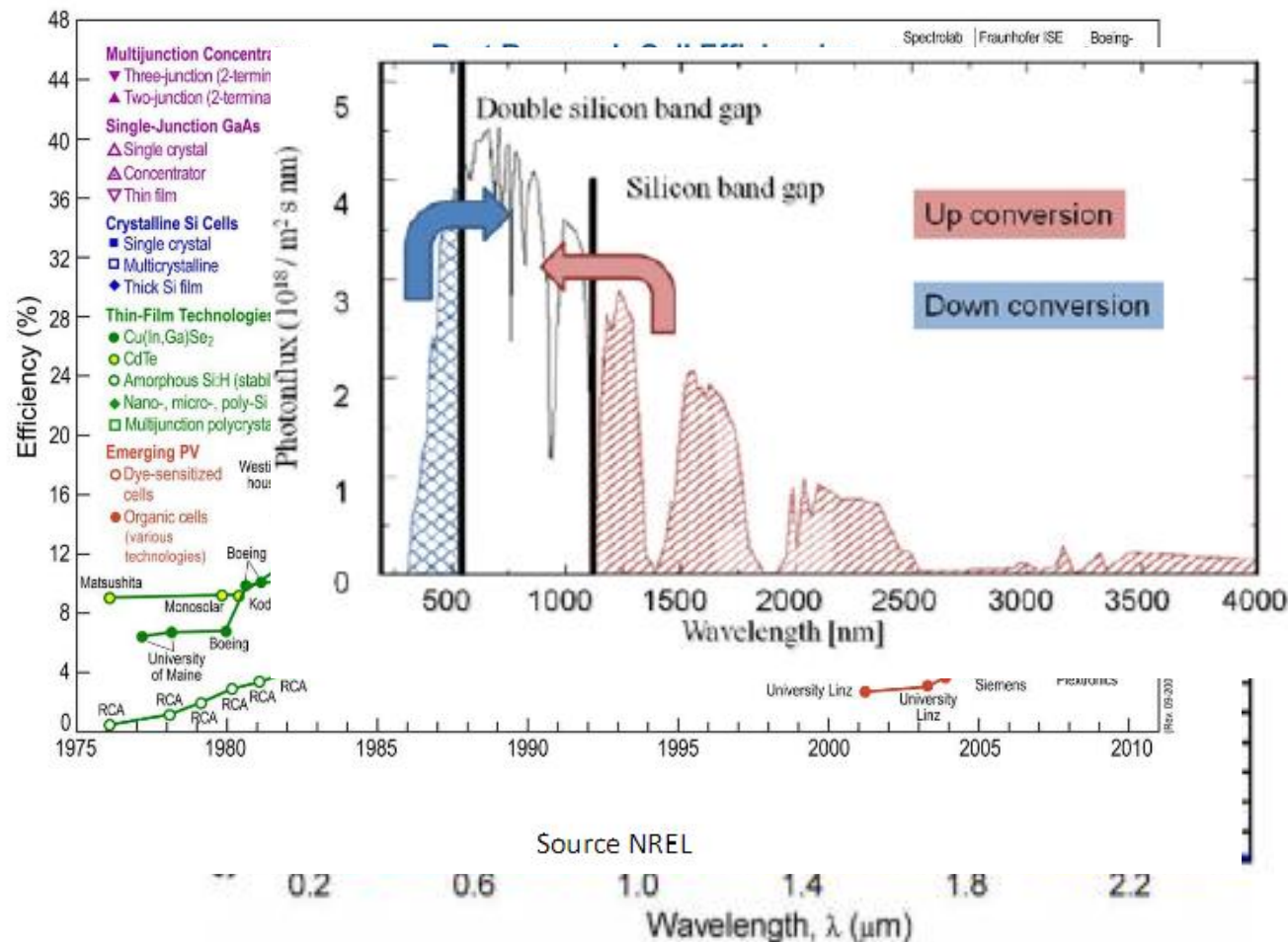
# Introduction

Recent years have seen the development of large research on renewable energy and in particular photovoltaic.

- For the multijunction based on GaAs the conversion efficiency reaches more than 40%.
- The conversion efficiency between 20 and 25% crystalline Si.
- while organic emerging sectors the conversion efficiency does not exceed 7- 8%.

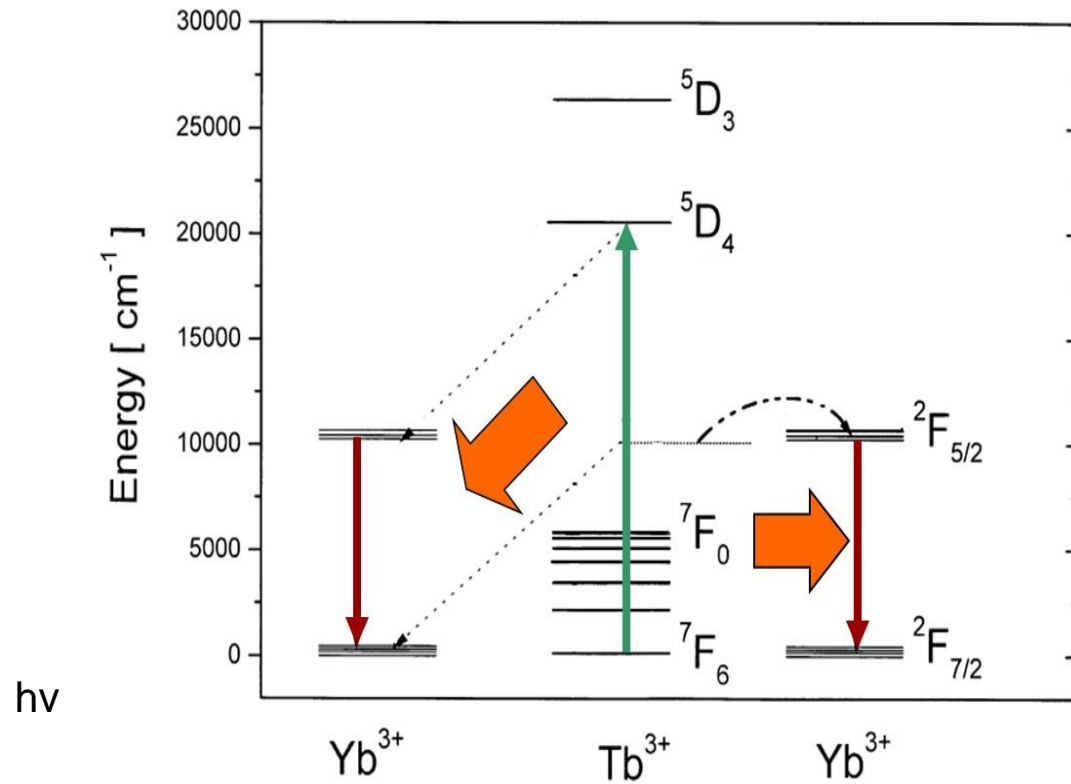
• Photons with energies smaller than the silicon band gap are not absorbed, and their energy is totally wasted.

• Photons with energies larger than twice the silicon band gap are absorbed, but the excess energy is lost to heating.



# Down and up converter layer for solar cells

## Energy transfer with Tb<sup>3+</sup> / Yb<sup>3+</sup>



One blue photon @ 488nm → Two infrared photon @ 980nm

Down conversion shifts photons from a high-energy band to the maximum absorption band of silicon.

Donor/acceptor	Frequency conversion
Pr <sup>3+</sup> /Yb <sup>3+</sup>	Blue (440nm) → NIR (2 emitted photons: 1000 nm)
Tm <sup>3+</sup> /Yb <sup>3+</sup>	Blue (478nm) → NIR (2 emitted photons: 1000 nm)
Tb <sup>3+</sup> /Yb <sup>3+</sup>	Blue (485nm) → NIR (2 emitted photons: 1000 nm)
Ce <sup>3+</sup> /Yb <sup>3+</sup>	UV-blue (4f-5d 330 borate to 450 nm YAG) → NIR
Ho <sup>3+</sup> /Yb <sup>3+</sup>	Blue (~450 nm) → NIR (2 emitted photons: 985+1180 nm)
Er <sup>3+</sup> /Yb <sup>3+</sup>	Violet-Blue-Green → NIR MP relaxation (2 emitted photons: 1000 + 1500 nm)

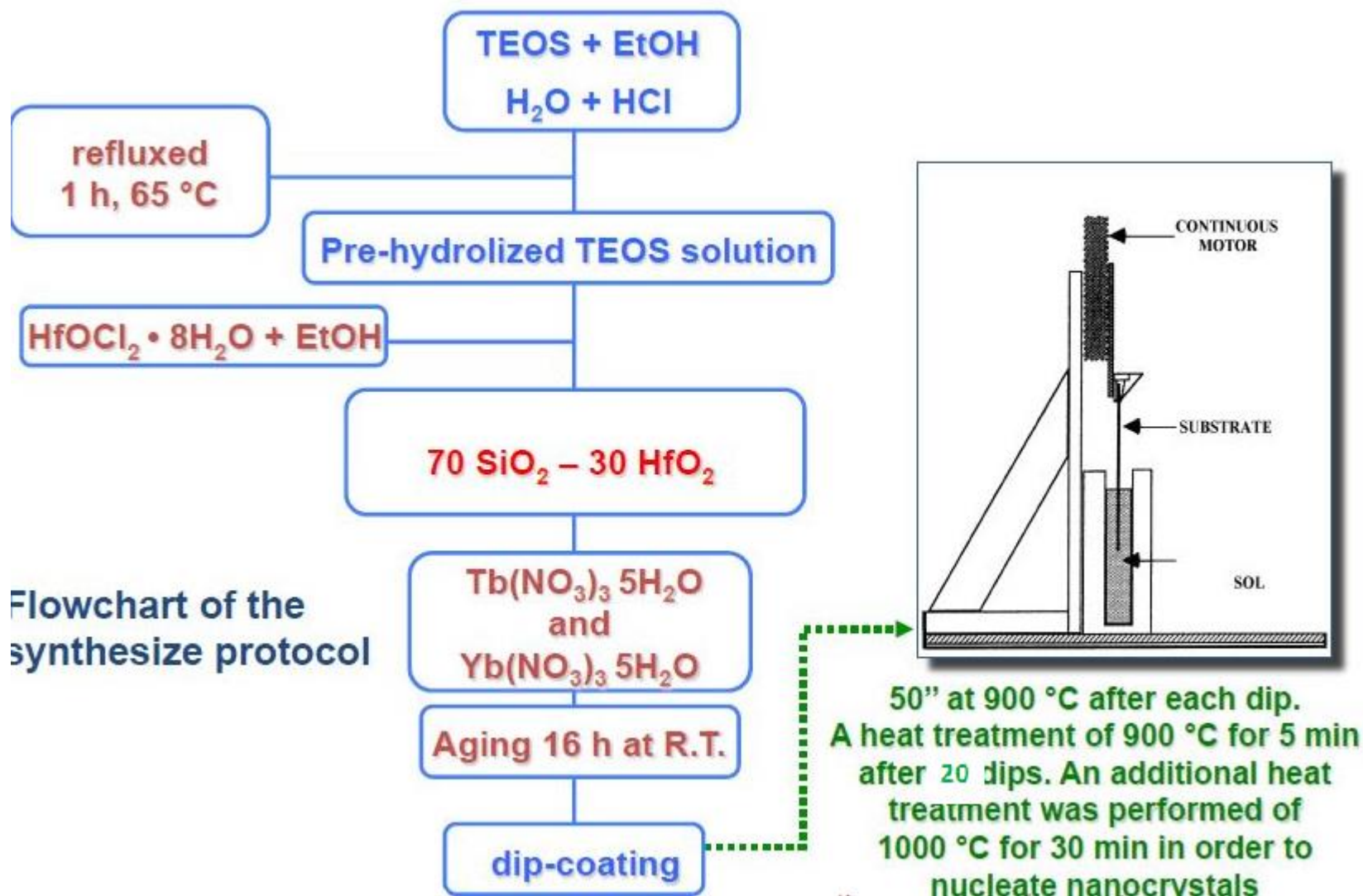
Up conversion shifts photons from a low-energy band to the maximum absorption band of silicon.

## Choice of the rare-earth host

### Glass Ceramics

- Combine the advantages of glasses and crystals
- Better spectroscopic properties than glasses
- Transparency

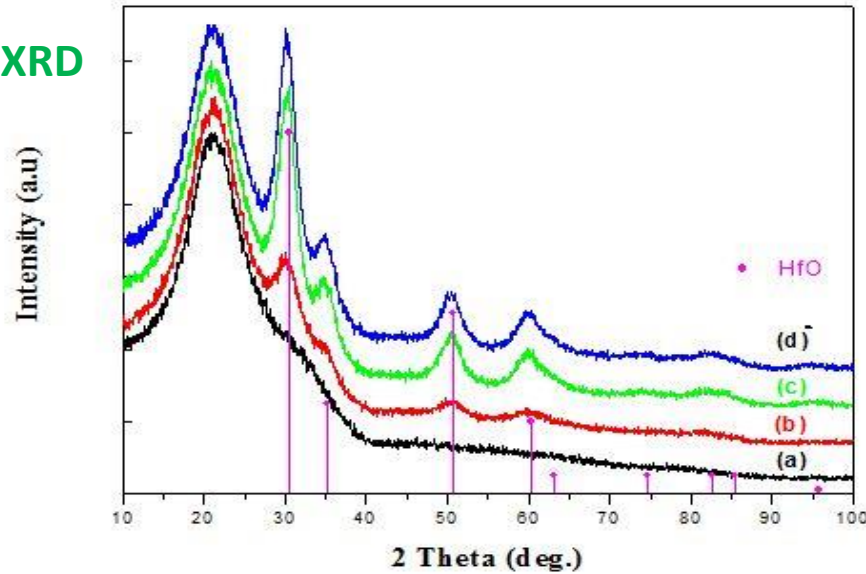
## Experimental: synthesize protocol





# Structural characterization

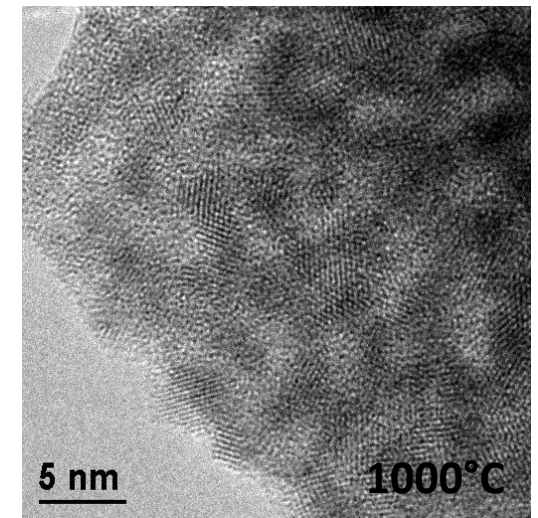
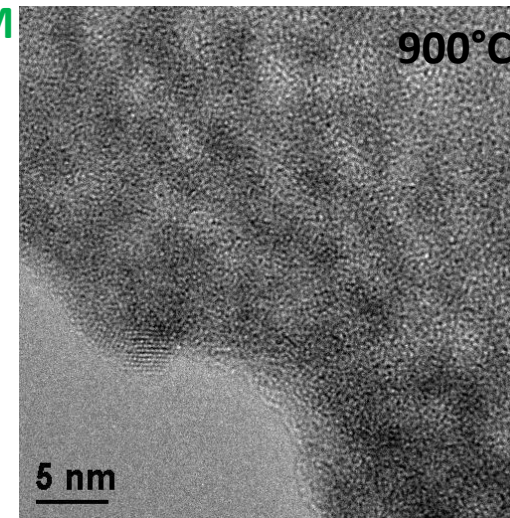
## XRD



- Non-crystalline phase (hump centred at  $2\theta \approx 21^\circ$ ) is contributed to the amorphous structure of silica.
- Thin film treated at  $900^\circ\text{C}$  is completely amorphous
- Crystallization occurs after heat treatment at  $1000^\circ\text{C}$  for 30 min.
- Diffraction peaks become more intensive by increasing the concentration of rare earth → **rare earth ions are embedded in hafnia nanocrystals.**

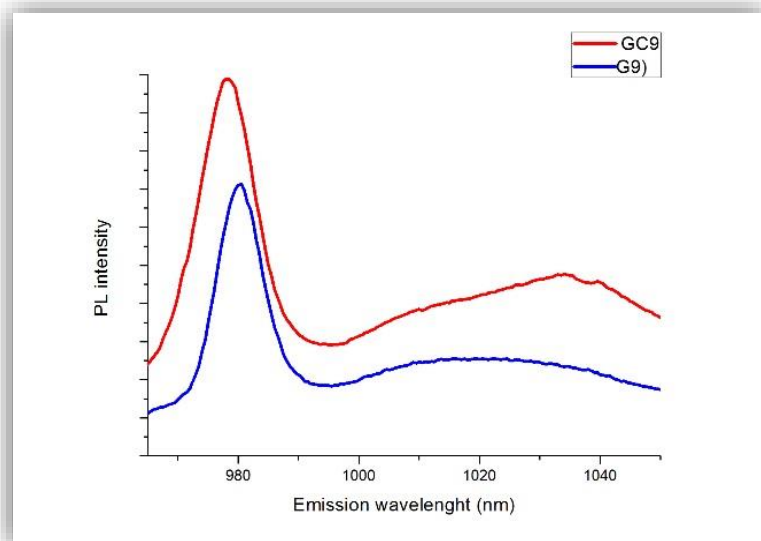
- The difference in the two samples is the final annealing temperature at  $900^\circ\text{C}$  or  $1000^\circ\text{C}$ .
- Sample treated at lower temperature is amorphous
- Higher temperature treatment induces the precipitation of small crystallites whose size is of the order of 2-3 nm.

## TEM



## Photoluminescence spectrum

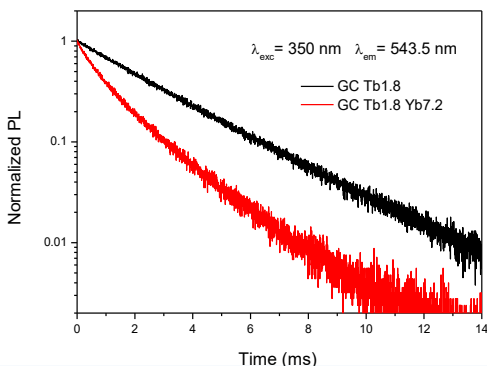
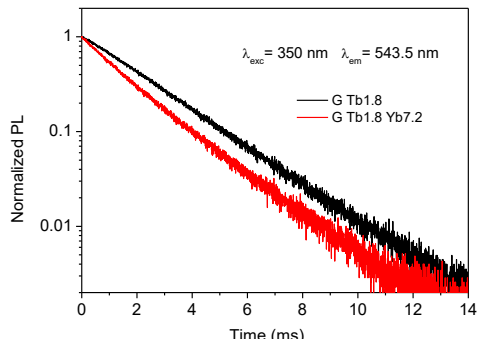
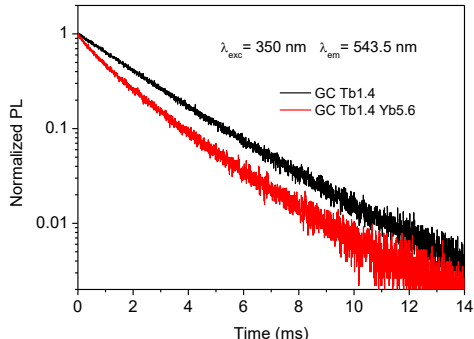
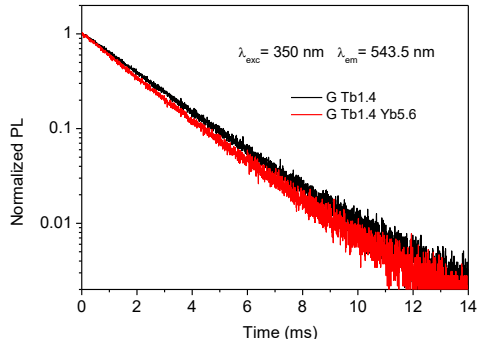
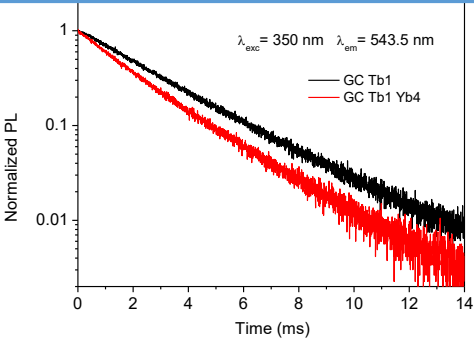
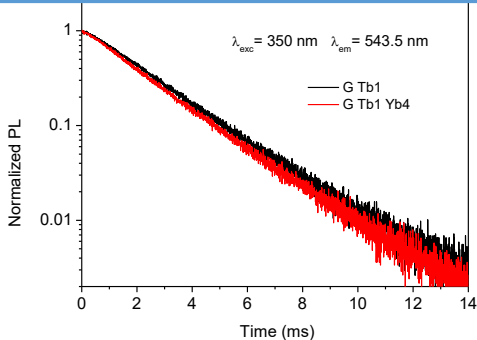
Room temperature photoluminescence spectrum of the  $^2F_{5/2} \rightarrow ^2F_{7/2}$  transition of  $\text{Yb}^{3+}$  ions after excitation at 476 nm



The emission of the  $\text{Yb}^{3+}$  ion after excitation at 476 nm is an indication of the presence of an **efficient energy transfer from  $\text{Tb}^{3+}$  to  $\text{Yb}^{3+}$** .



# Decay curves analysis



The evaluation of the energy transfer efficiency between Tb<sup>3+</sup> and Yb<sup>3+</sup> can be obtained by comparing the luminescence decay of terbium with and without ytterbium co-doping ions.

**Energy transfer efficiency** between Tb<sup>3+</sup> and Yb<sup>3+</sup> :

$$\eta_{RE-Yb} = 1 - \frac{\int I_{RE-Yb} dt}{\int I_{RE} dt}$$

The relation between the transfer efficiency and the **effective quantum efficiency is linear and is defined as:**

$$\eta_{EQE} = \eta_{RE-r}(1-\eta_{RE-Yb})+2\eta_{RE-Yb}$$

**G**

Composition (Tb+Yb concentration in mol %)	5%	7%	9%
Transfer efficiency	8.4%	10.3%	26.4%
Effective quantum efficiency	108.4%	110.3%	126.4%

**GC**

Composition (Tb+Yb concentration in mol %)	5%	7%	9%
Transfer efficiency	24.6%	32.3%	54.6%
Effective quantum efficiency	124.6%	132.3%	154.6%

## Conclusion & perspectives

- efficient quantum cutting in  $\text{Tb}^{3+}:\text{Yb}^{3+}$  co-doped  $70\text{SiO}_2\text{-}30\text{HfO}_2$  glass and glass-ceramic waveguides deposited by a sol-gel
- A fixed concentration rate  $[\text{Yb}]/[\text{Tb}] = 4$  and increasing rare earths total amounts  $[\text{Tb}+\text{Yb}] = 5, 7, 9$  have been studied. Structural investigation by XRD and TEM shows that the precipitation of small hafnia nanocrystals
- The waveguiding properties of the films are confirmed and a clear NIR photoluminescence emission around 980 nm is detected, due to the  $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$  transition of  $\text{Yb}^{3+}$  ions.
- The energy transfer efficiency, estimated from the PL decay curves of the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition at 543.5 nm of  $\text{Tb}^{3+}$  ions, increases when increasing the total  $[\text{Tb} + \text{Yb}]$  concentration.
- The best performance is almost 55% and it is obtained for the most doped glass-ceramic sample, while it is only 26% in the glass sample with the same rare earth concentration.

### **Future work will focus on:**

- **Increasing the concentration rare earth ions to increase the effective quantum efficiency**
- **The use of other rare earth couple : Pr/Yb and Er/Yb**

**THANK YOU**