Investigation of the quantum cutting properties of Tb^{3+}/Yb^{3+} co-doped silica-hafnia glass and glass-ceramics obtained by sol-gel technology

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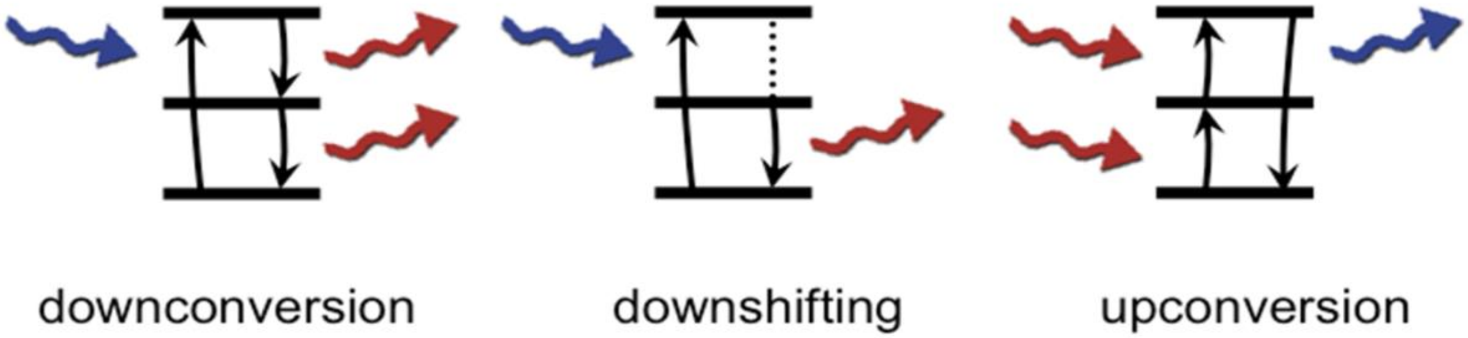
Outline

- Introduction
- Sample preparation
- Structural and optical characterization
- Silver addition for rare-earth sensitization
- Conclusions and perspectives

Photon management with RE^{3+}-ions

- Specific energy levels
- Relatively long lifetimes (µs-ms)

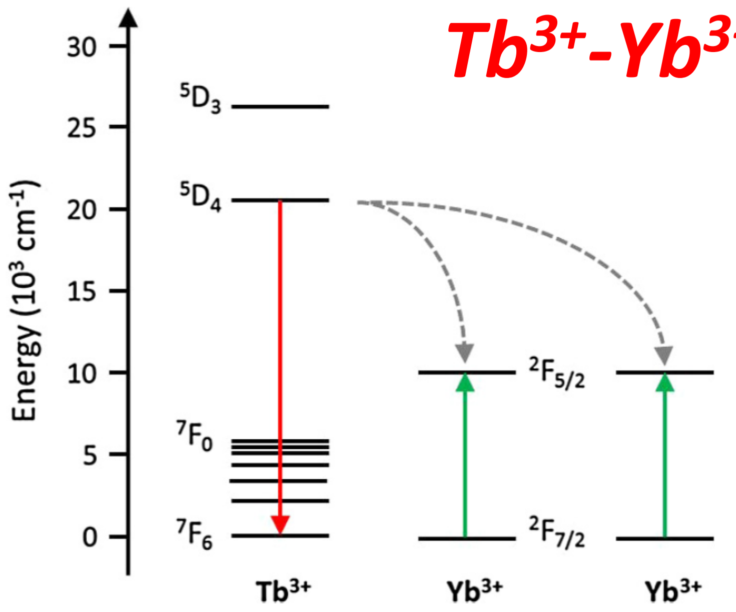


+

- Low losses materials
- Low phonon energy materials

proper choice of
RE couple and matrix

Choice of the rare earths



Tb^{3+}-Yb^{3+}

One blue photon @ 488nm

Two infrared photons @ 980 nm

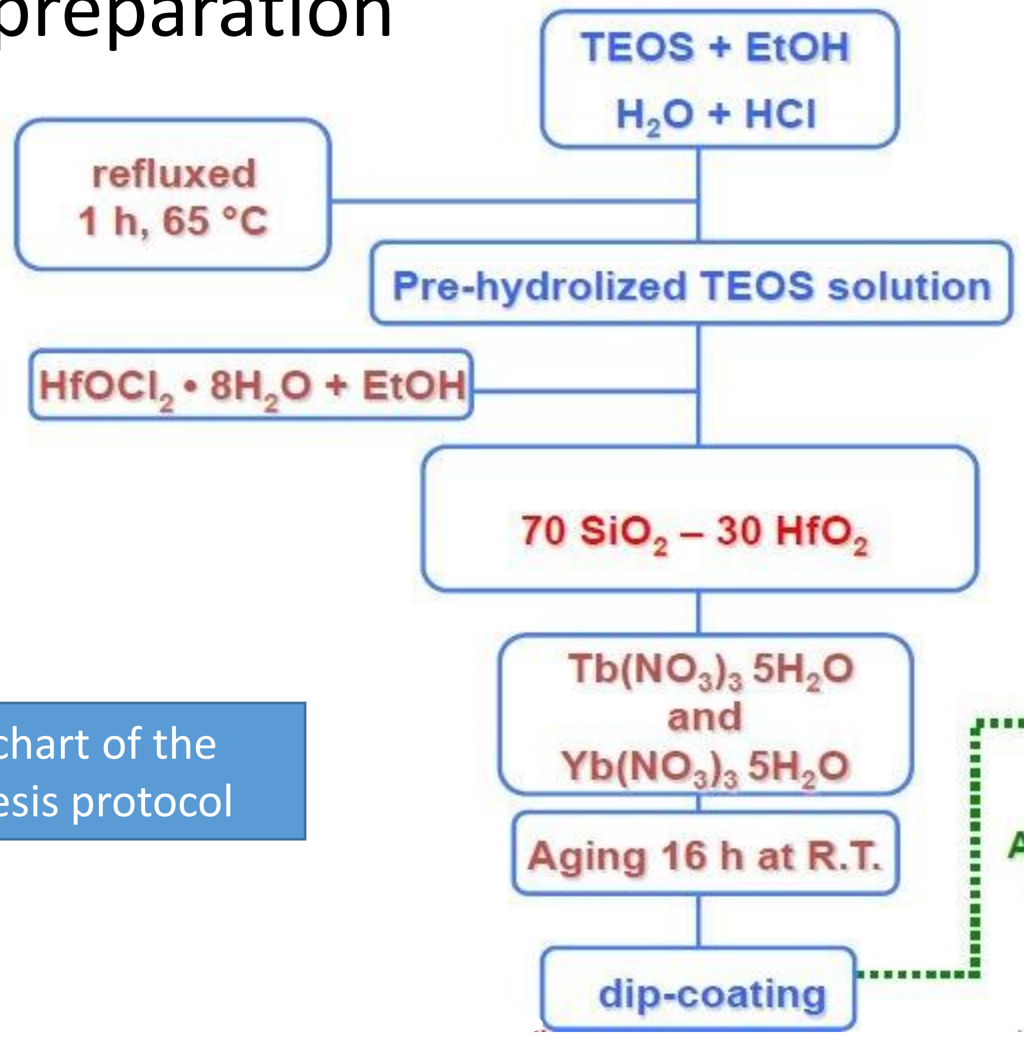
Choice of the host material

SiO_2-HfO_2 glass-ceramics

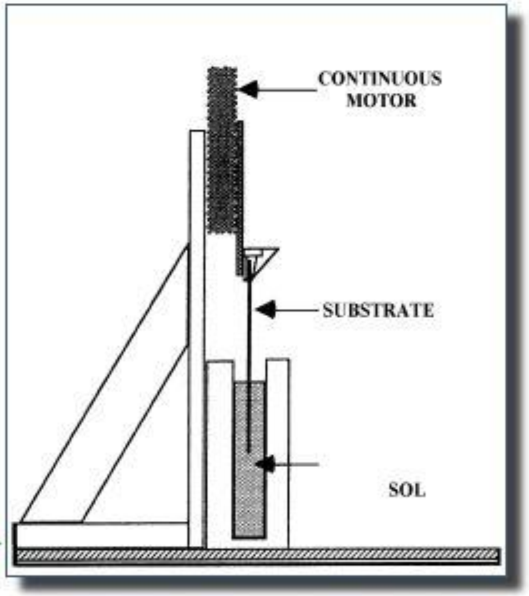
- ✓ Combine the advantages of glasses and the better spectroscopic properties of crystals
  - Silica-based waveguides and fibers
  - HfO_2 low phonon energies (~700 cm^{-1})
  - HfO_2 high refractive index (~2.1 vis. range)

Binary system – can be tailored

Sample preparation



Flowchart of the synthesis protocol



50" at 900 °C after each dip.
A heat treatment of 900 °C for 5 min after 30 dips. An additional heat treatment was performed of 1000 °C for 30 min in order to nucleate nanocrystals

GLASS (G)

GLASS-CERAMICS (GC)

G. Alombert-Goget et al., Proc. SPIE 7598 (2010) 75980P–1/9.
G. Alombert-Goget et al., Opt. Mater. 33 (2010) 227–230.

Samples general properties

[Tb] : [Yb] = 1 : 4 (best rate from previous studies)

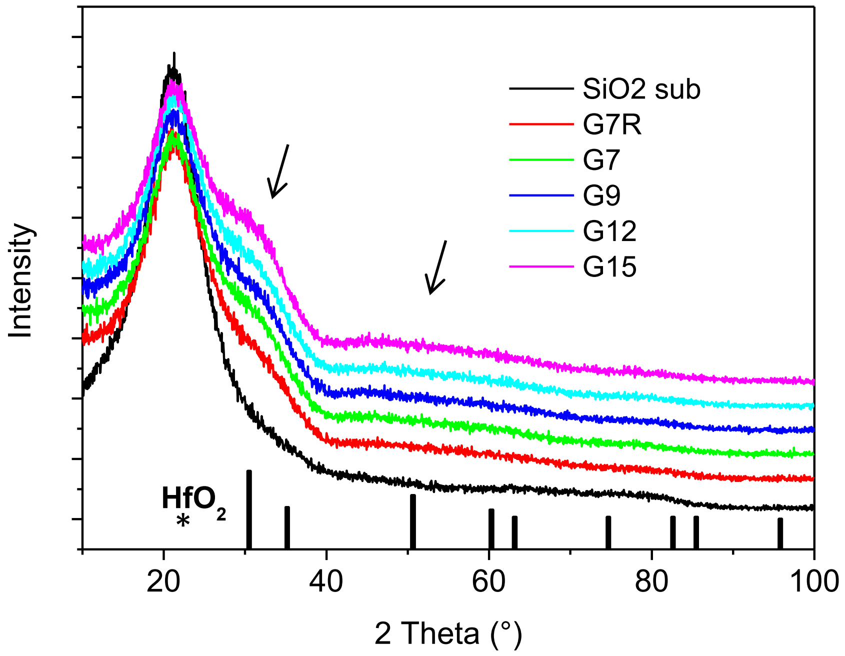
[Tb]+[Yb] = 7 ÷ 15 (in previous studies 1 ÷ 9)

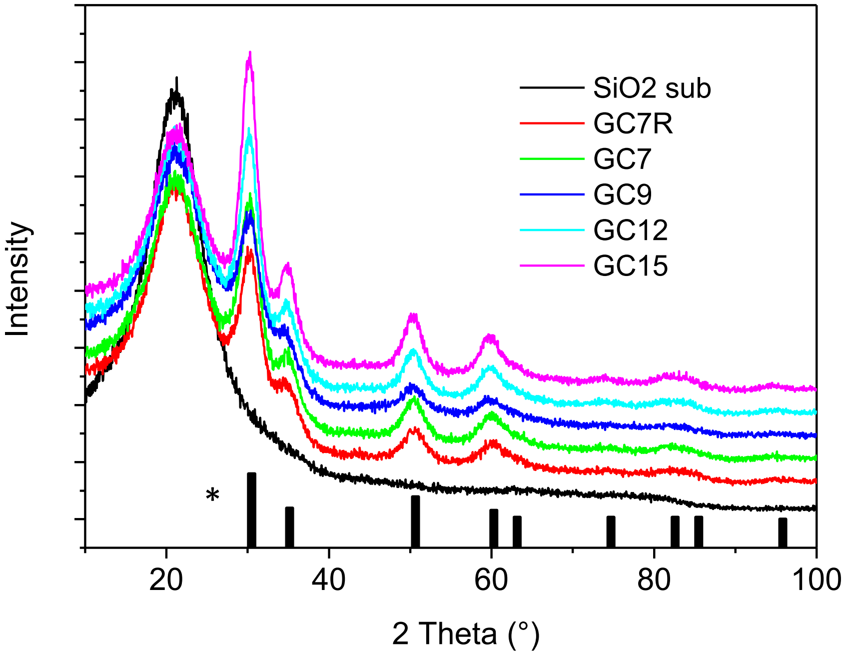
G (900 °C ann.) and GC (1000 °C ann.) samples

Layer thickness ~ 0,7 – 0,8 µm

G. Alombert-Goget et al., Proc. SPIE 7598 (2010) 75980P–1/9.
G. Alombert-Goget et al., Opt. Mater. 33 (2010) 227–230.
A. Bouajaj et al., Opt. Mat., 2016,52, 62-68

Structural characterization



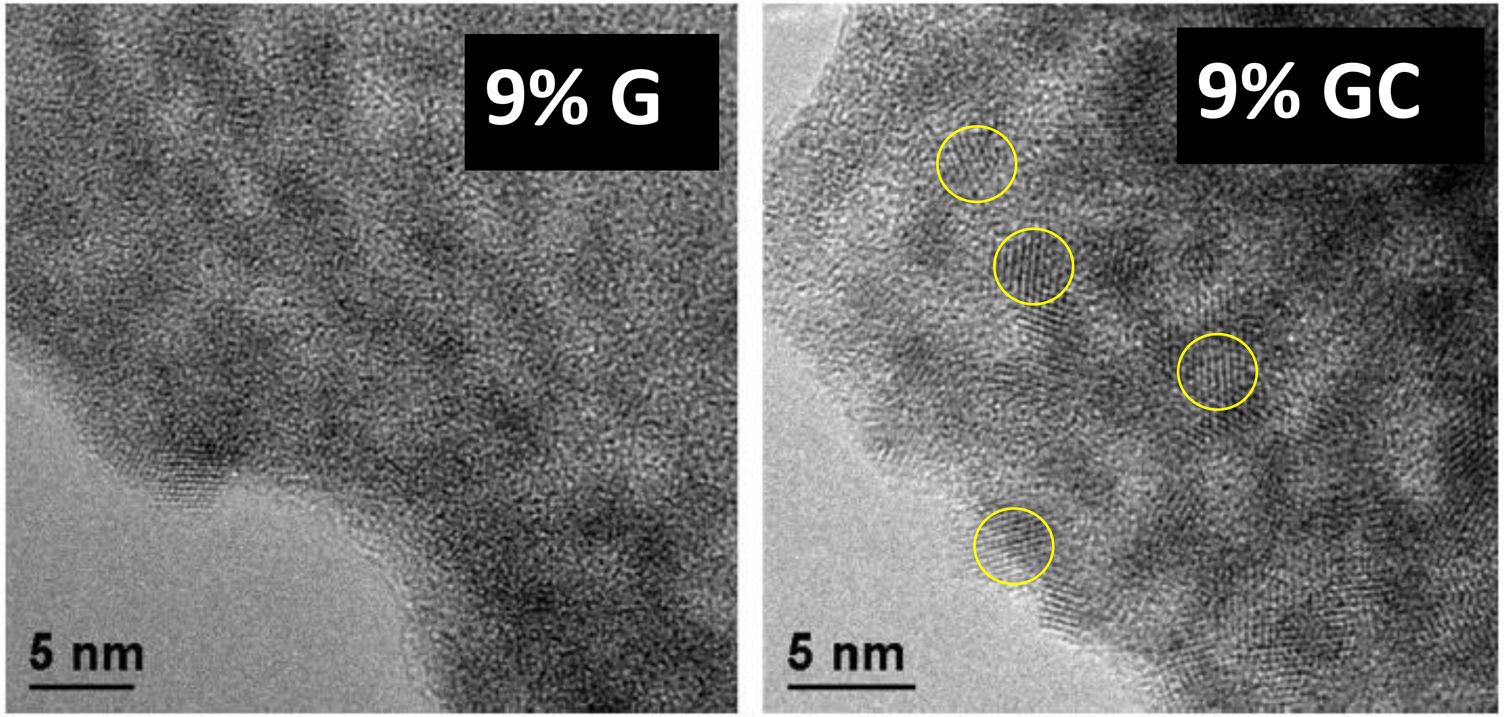


- ✓ Broad signals suggest that initial nucleation stages could be present also in G samples
- ✓ Phase separation and formation of HfO_2 nanocrystals of about 3-4 nm in GC samples

*** tetragonal HfO_2 (ICSD card No 85322)**

A. Bouajaj et al., Opt. Mat., 2016,52, 62-68

Structural characterization



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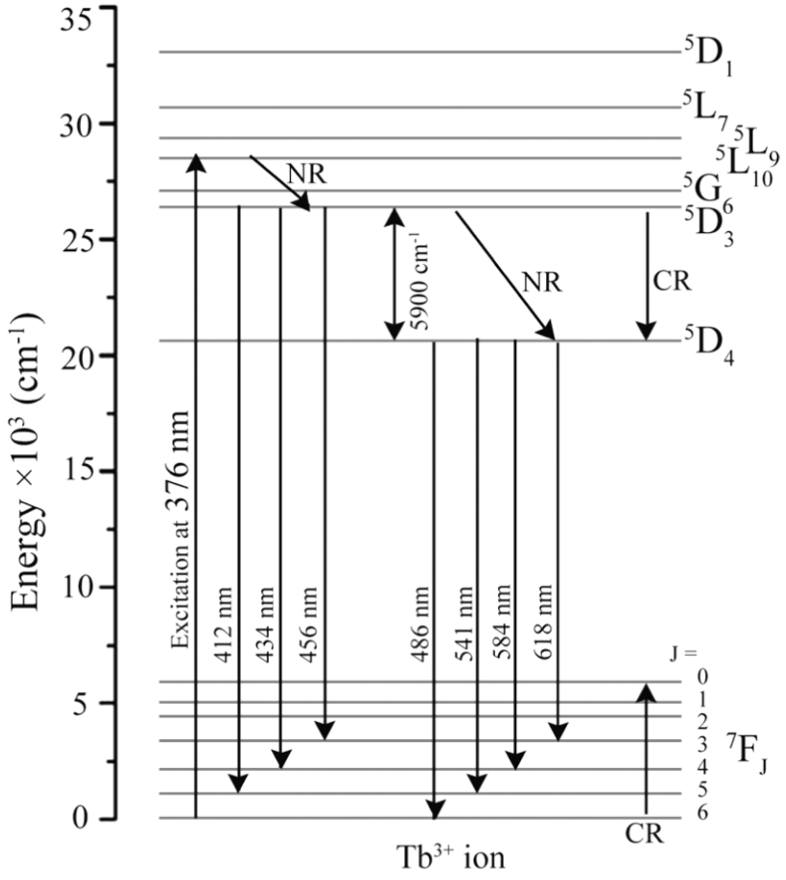
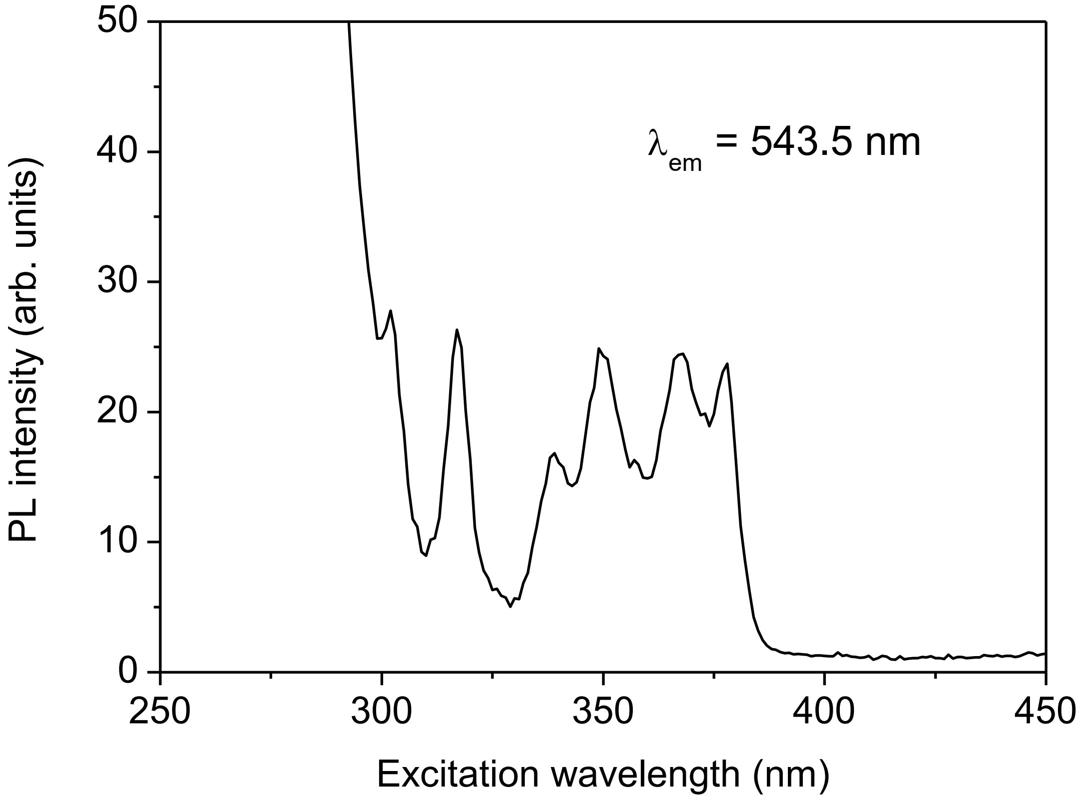
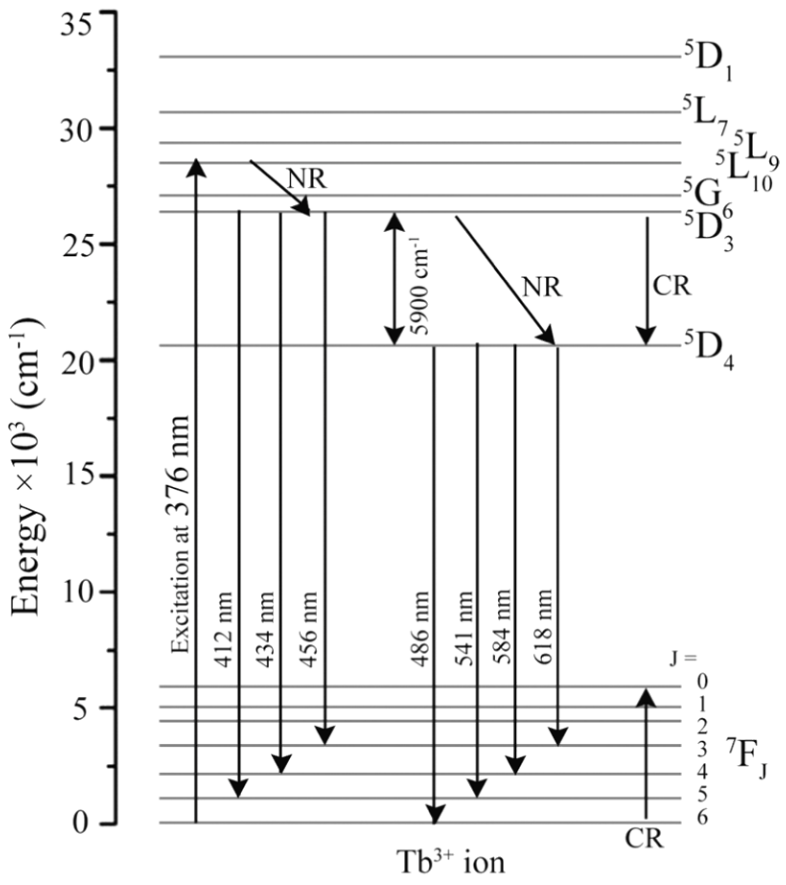
A. Bouajaj et al., Opt. Mat., 2016,52, 62-68

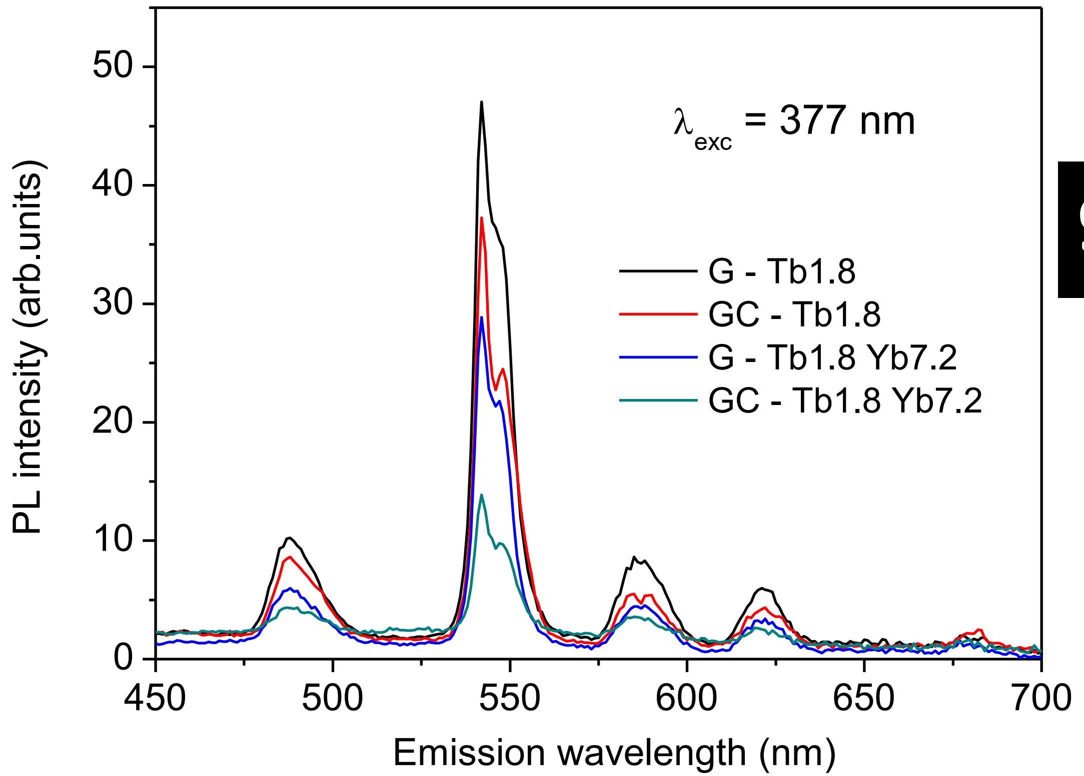
Optical characterization





Optical characterization



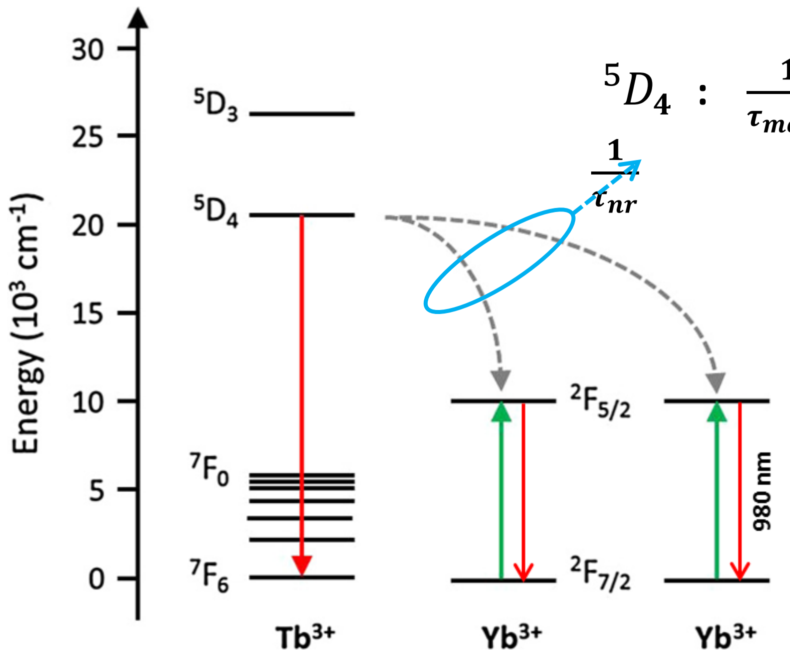


9% G

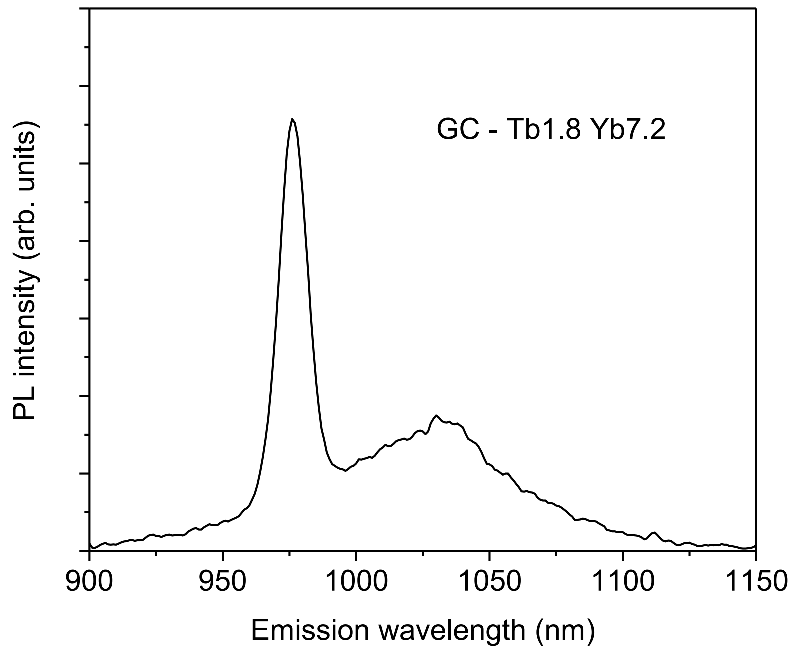
- ✓ Tb^{3+} emission decrease from G to GC
- ✓ Tb^{3+} emission decrease when Yb^{3+} is added

Energy transfer, in particular in GC matrix

Optical characterization



$$^5D_4 \; : \; \frac{1}{\tau_{meas}} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}}$$

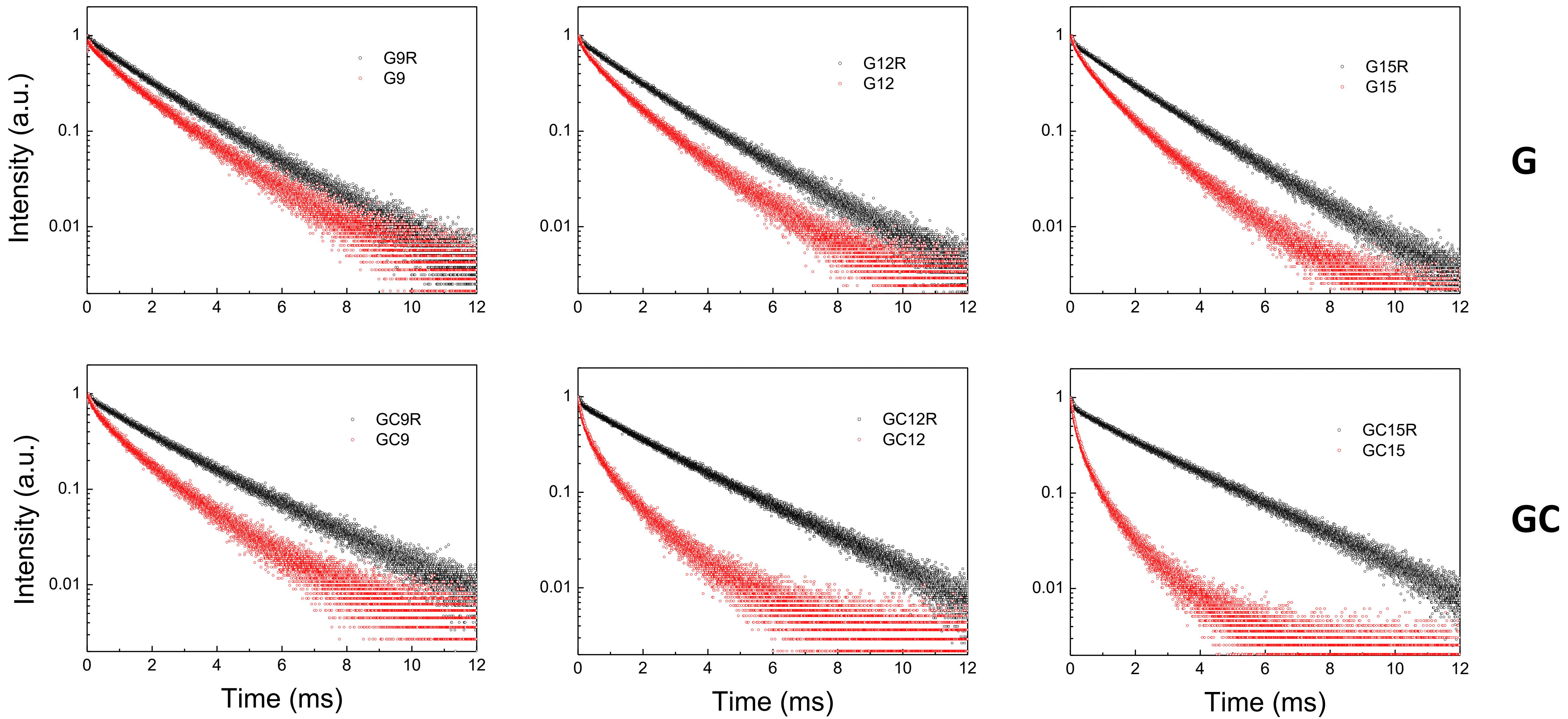


$$\eta_{tot} = \eta_{r,Tb}\,(1 - \eta_{ET}) + 2\,\eta_{ET} \approx 1 + \eta_{ET}$$

$$\eta_{ET} = 1 - \frac{\int I_{Tb+Yb}\,dt}{\int I_{Tb}\,dt}$$

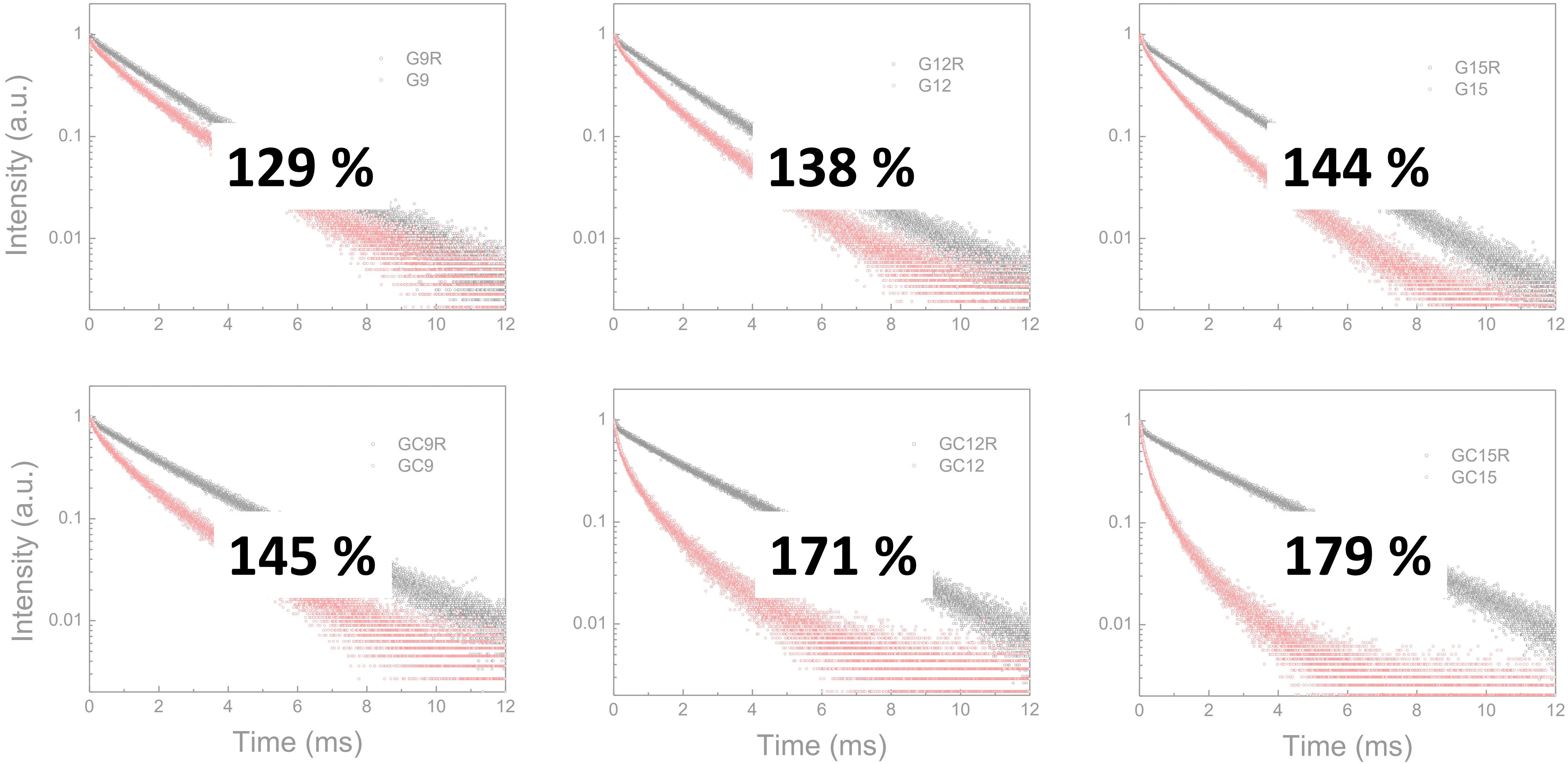
Optical characterization

$^5D_4 \longrightarrow {}^7F_J$ λ_{exc} = 355 nm λ_{em} = 543.5 nm



Optical characterization

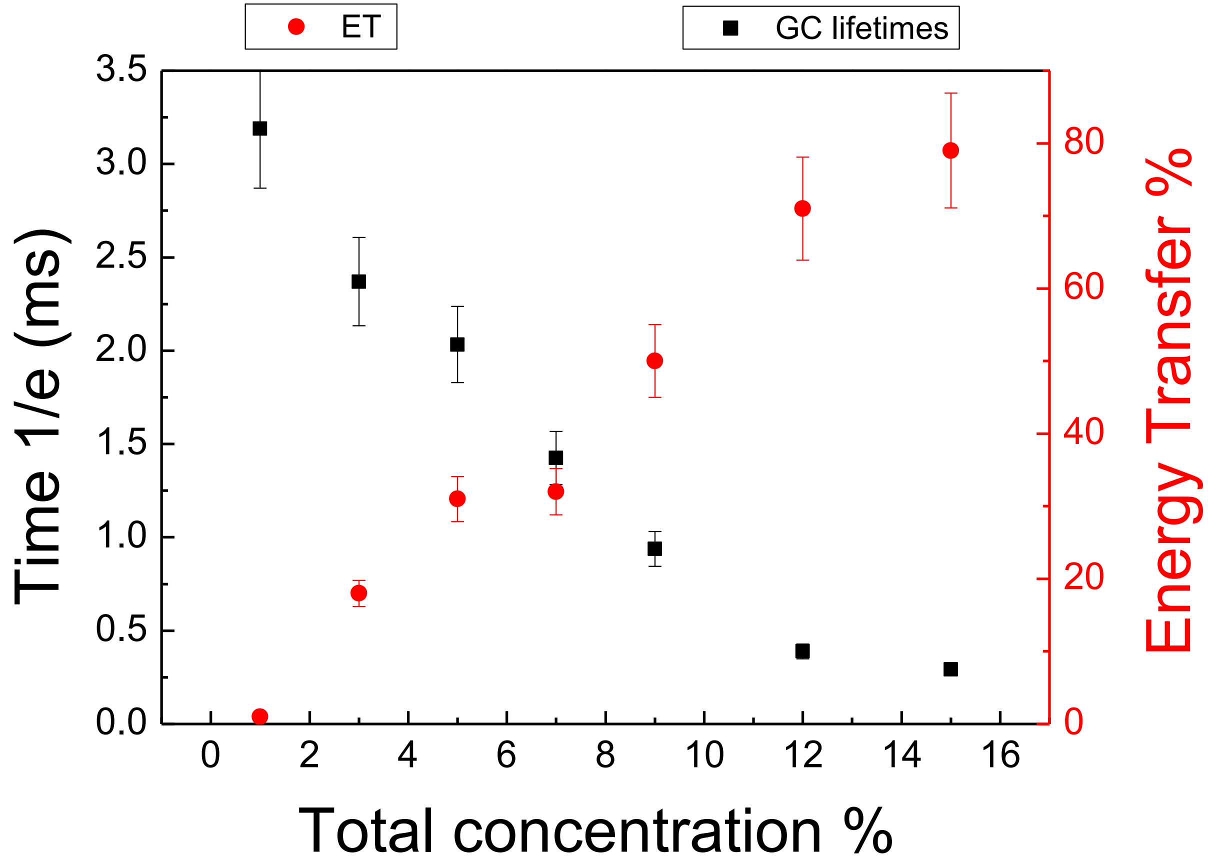
$^{5}D_{4} \longrightarrow {}^{7}F_{J}$ λ_{exc} = 355 nm λ_{em} = 543.5 nm



G

GC

Optical characterization



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Why Ag doping? Energy transfer

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Applied Physics A
Materials Science & Processing

Silver-sensitized erbium-doped ion-exchanged sol–gel waveguides

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Mechanisms of Ag to Er energy transfer in silicate glasses: A photoluminescence study

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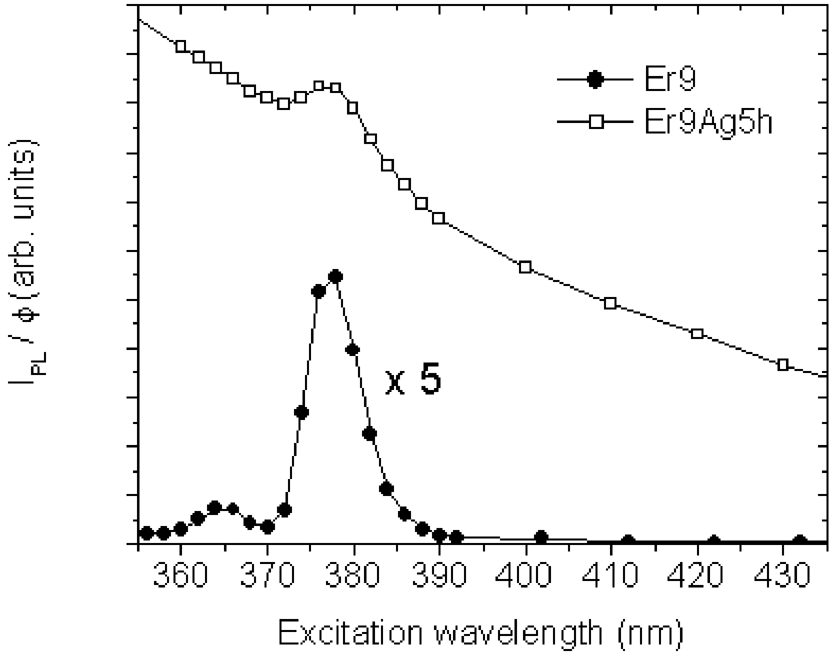
Ag introduction by ion exchange

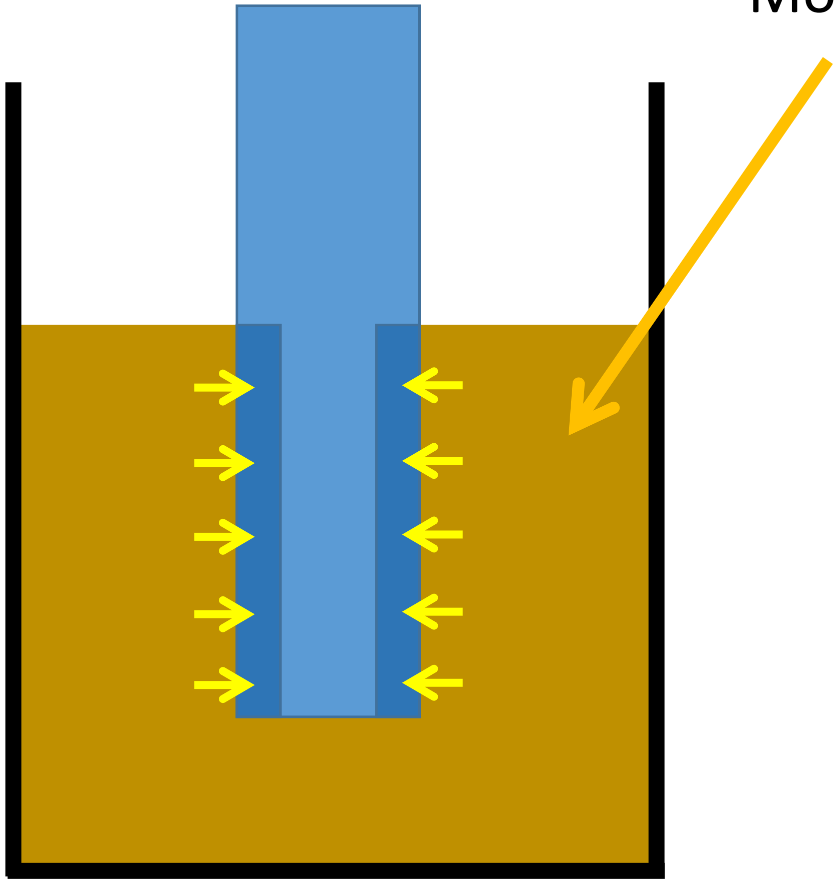
⬇

Broadband excitation of Er^{3+} ions

1.54 µm emission



Ag doping



Molten salt bath 1 mol% of $AgNO_3$ in $NaNO_3$

1h @ 350 °C

Diffusion and/or substitution process

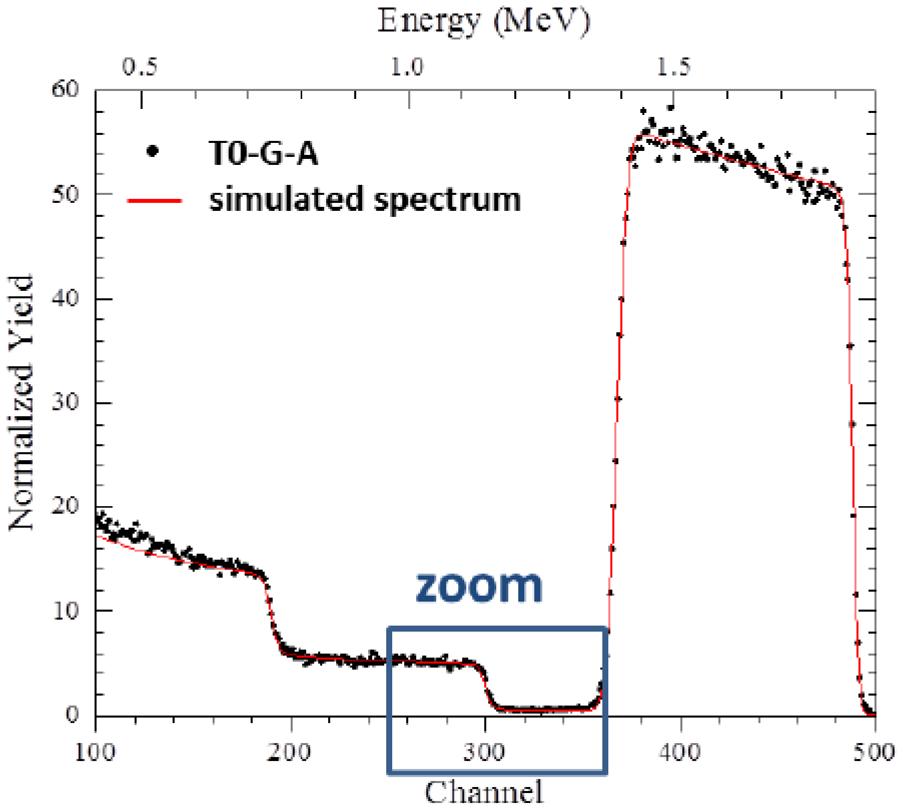
Followed by thermal annealing in air

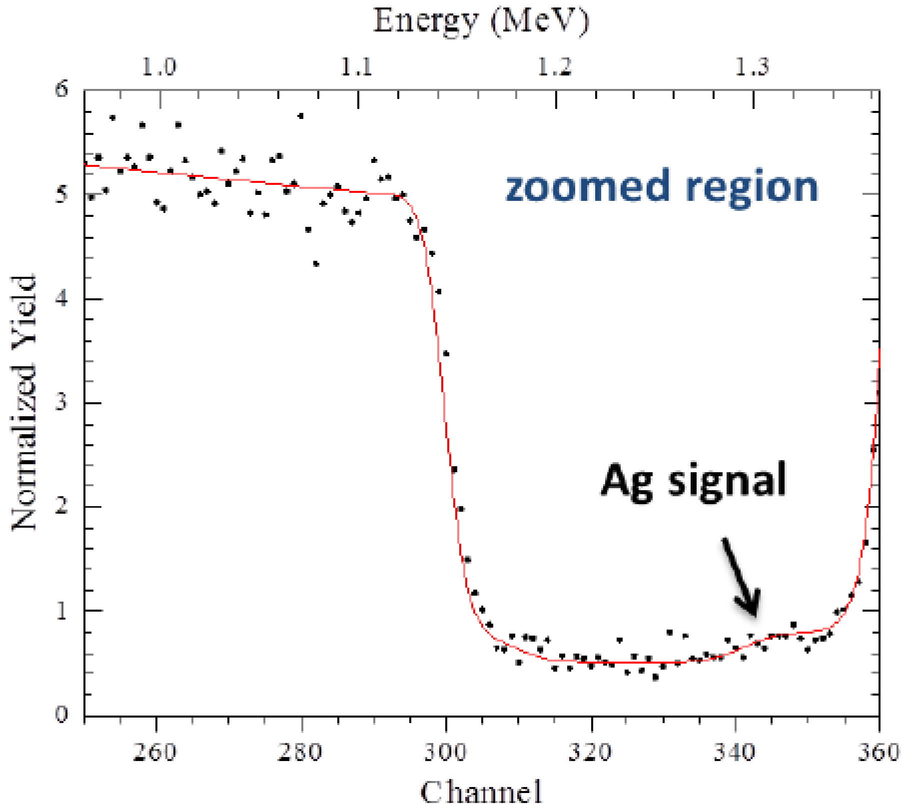
1h @ 380 °C

1h @ 440 °C

Ag aggregation and precipitation

Ag doping



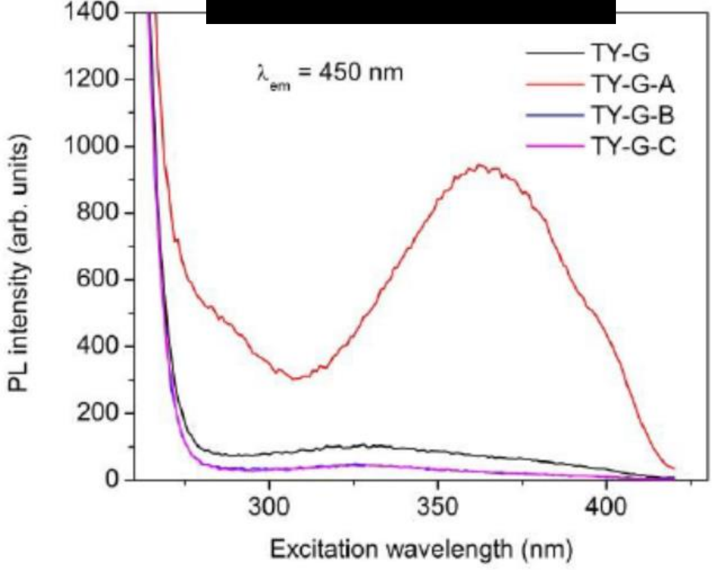


0.2 at.% Ag

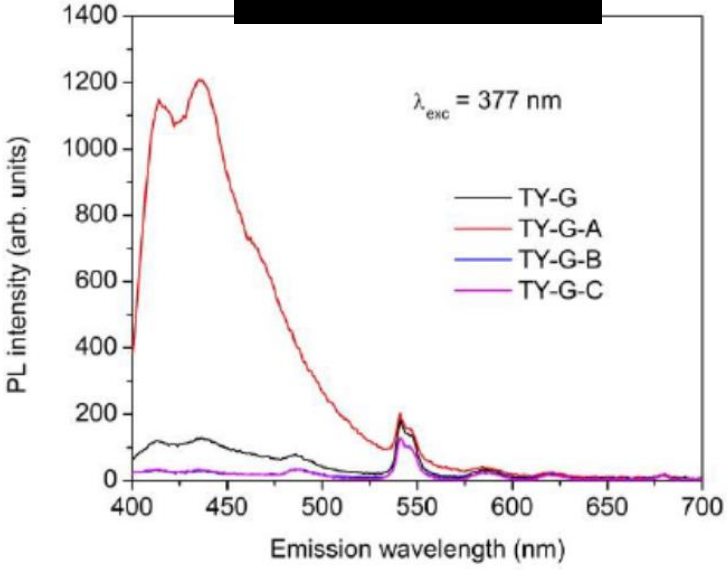
In the different samples from 0.2 at.% to 1 at.% Ag

Ag doping

5% G - PLE



5% G - PL



broad excitation band in the UV region only for «as-exchanged» samples

broad emission band in the blue region only for «as-exchanged» samples

reasonably related to oxygen-deficiency centers

Conclusions and perspectives

- Successful downconversion in Tb^{3+} + Yb^{3+} codoped SiO_2-HfO_2 glass-ceramics
- Efficiency trend increasing with concentration, up to 179 % for 15 at.% [Tb+Yb]
  - higher RE concentration
  - deeper investigation of the ET process via rate-equation modelling
  - direct efficiency measurement by an integrating sphere
- Low amount of silver introduction, only for glass samples
  - Na^+ addition in the matrix for efficient Ag^+-Na^+ ion exchange

Thank you!

MAECI bilateral project PLESC - Centro Fermi Italy / University of Witwatersrand South Africa 2015-18

CNR Italy / CNRST-Morocco bilateral project 2014-15

VINNMER Marie Curie Incoming Project - Nano2solar 2016-18

Sample label	[Tb] (mol%)	[Yb] (mol%)	n@543.55 nm [±0.001]		n@632.8 nm [±0.001]		Layer thickness [±0.2 μm] (μm)
			TE_0	TM_0	TE_0	TM_0	
BR3G	1	0	1.589	1.576	1.575	1.561	0.7
BR3GC	1	0	1.599	1.583	1.585	1.568	0.7
B3G	1	4	1.590	1.580	1.578	1.565	0.7
B3GC	1	4	1.610	1.598	1.596	1.582	0.7
BR4G	1.4	0	1.578	1.569	1.566	1.558	0.8
BR4GC	1.4	0	1.591	1.579	1.579	1.565	0.7
B4G	1.4	5.6	1.592	1.581	1.579	1.566	0.7
B4GC	1.4	5.6	1.619	1.607	1.606	1.592	0.7
B5RG	1.8	0	1.602	1.590	1.590	1.576	0.7
B5RGC	1.8	0	1.611	1.592	1.597	1.576	0.7
B5G	1.8	7.2	1.589	1.577	1.577	1.565	0.8
B5GC	1.8	7.2	1.610	1.583	1.598	1.583	0.8

R

5% (B3G, B3GC)

7% (B4G, B4GC)

9% (B5G, B5GC)

Ag doping

label sample	[Tb] mol%	[Yb] mol%	Ag doping	Annealing T (°C)	Thickness (nm)	n@544	n@632
T0-G	1	0	-	-	705	1.626	1.621
T0-G-A	1	0	✓	-	665	1.670	1.662
T0-G-B	1	0	✓	380	665	1.684	1.675
T0-G-C	1	0	✓	440	670	1.666	1.658
TY-G	1	4	-	-	710	1.641	1.634
TY-G-A	1	4	✓	-	695	1.678	1.673
TY-G-B	1	4	✓	380	675	1.709	1.703
TY-G-C	1	4	✓	440	690	1.700	1.697
TY-GC	1	4	-	-	655	1.677	1.672
TY-GC-A	1	4	✓	-	660	1.676	1.671
TY-GC-B	1	4	✓	380	650	1.693	1.689
TY-GC-C	1	4	✓	440	655	1.683	1.678

Choice of rare-earth couples

Donor: absorbs incident photons from the sun and transfer its energy to the acceptor rare-earth :

Pr^{3+}, Tm^{3+}, Tb^{3+}, relatively strong absorption in the blue

Er^{3+} : many mean or weak absorption bands in the UV-blue-green

Acceptor: emits the photons that will be absorbed by the PV cell

Yb^{3+}, single excited state - Emission at ~1000 nm absorbed efficiently by Si solar cell

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