TAMPERE UNIVERSITY OF TECHNOLOGY

United Nations Educational, Scientific and Cultural Organization

International Year of Light 2015

# Nanoparticles containing glasses prepared using direct doping method

**L. Petit*, N. Ojha, H. Nguyen-** Tampere University of Technology (Finland)

**P. Lopez-Iscoa, D. Pugliese, D. Milanese** - Politecnico Di Torino (Italy)

*Representing nLIGHT Corp, Lohja (Finland)

As part of CoACH-ETN program

POLITECNICO DI TORINO 1859 1906

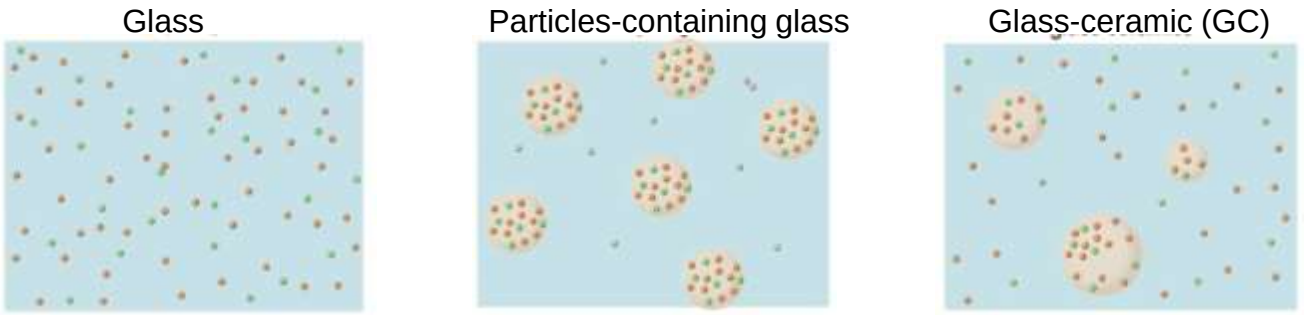
# Outline

**Main objective: To improve the spectroscopic properties (absorption, emission and lifetime) of $Er^{3+}$-doped phosphate glasses**

- To control the site of the rare-earth

1) Particles-containing glass obtained by doping directly the glass with the nanoparticles
2) GC obtained by heat treating the glass leading to in-situ particles growth in glass

Schematic diagram of RE distribution in various glasses*



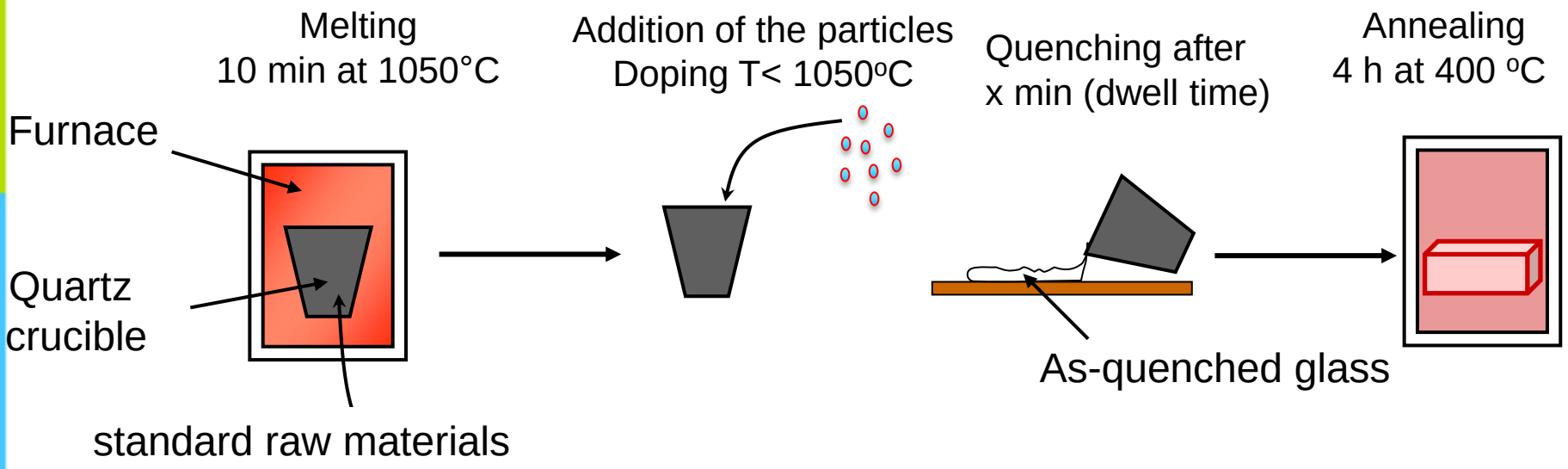



*J. Zhao et al, Adv. Optical Mater. 2016, doi: 10.1002/adom.201600296

# Direct particles doping method

**Glass system:** $50P_2O_5$-$10Na_2O$-40SrO (mol%)

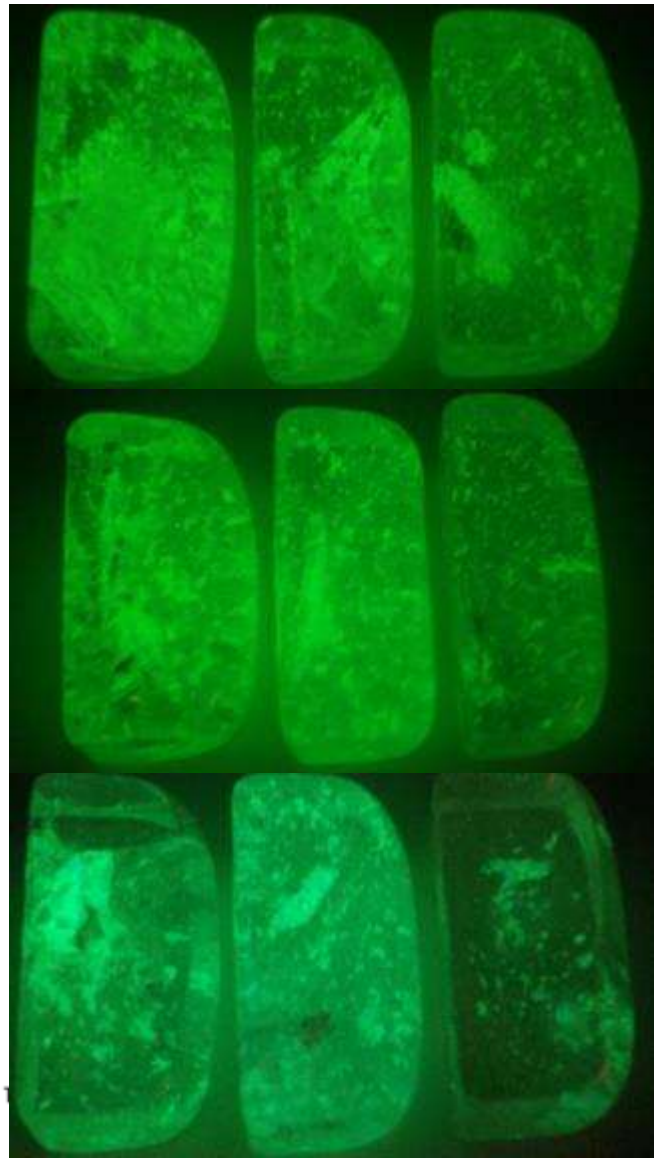
## Modified melting process




To balance the survival and dispersion of the particles, 2 parameters to optimize:

1) doping temperature
2) dwell time before quenching the glass

# Optimization of the direct doping process




Analysis of the images using ImageJ, Java-based image processing program

| Melting condition | | |
|---|---|---|
| **Dwell time** | **Temperature (°C)** | **SdtDev** |
| 3min | 975 | 10 |
| | 1000 | 11 |
| | 1025 | 9 |
| 5min | 975 | 10 |
| | 1000 | 8 |
| | 1025 | 6 |
| 10min | 975 | 20 |
| | 1000 | 12 |
| | 1025 | 11 |

*Glass with more uniform PL = SdtDev as small as possible*

Based on ImageJ analysis and on the luminescence properties of the glasses

Optimized doping temperature = 1000ºC
Optimized dwell time= 5min

# Particles containing glasses

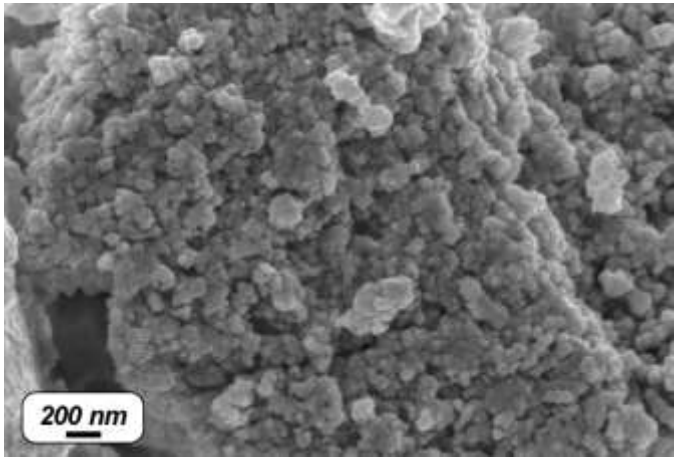
**Glass matrix:** $50P_2O_5$-$10Na_2O$-40SrO (mol%)

**Particles:** Er: $Al_2O_3$, Er:$TiO_2$ and Er,Yb:YAG ($Y_3Al_5O_{12}$)

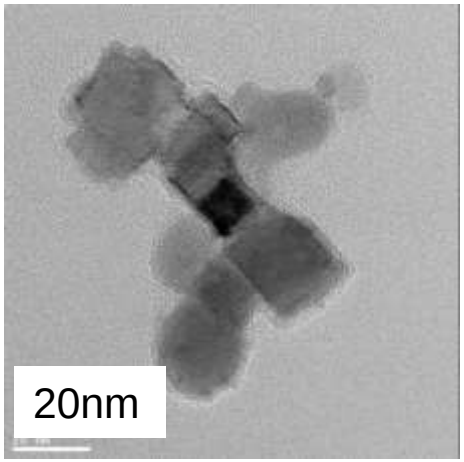
*YAG NPs also prepared with a layer of silica with a thickness of 5 (YAG5) and 25nm (YAG25)*

All particles are thermally stable at 1000$^o$C, the doping temperature

SEM image of Er:$TiO_2$

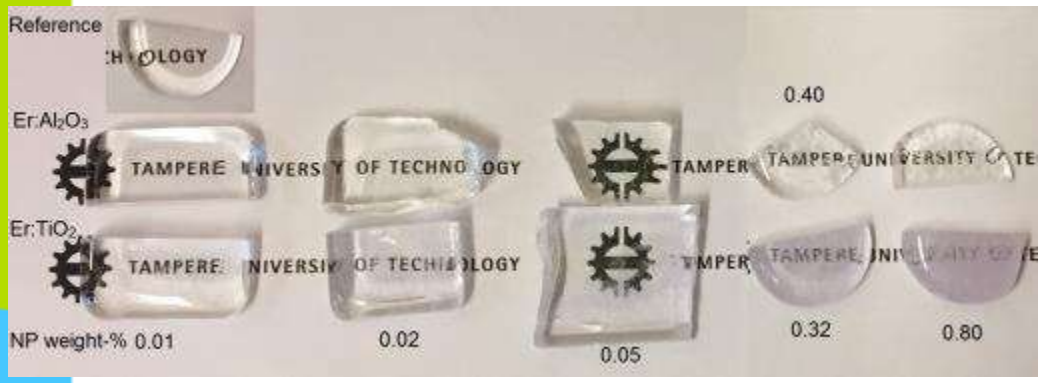



TEM image of YAG5

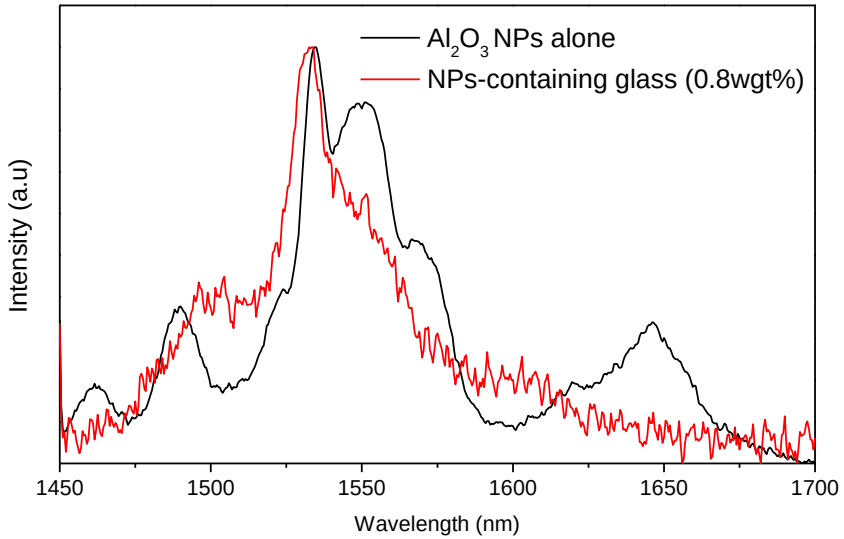


# Er: $Al_2O_3$ & Er:$TiO_2$ containing glasses

Picture of prepared glasses along with the weight-% of added NPs

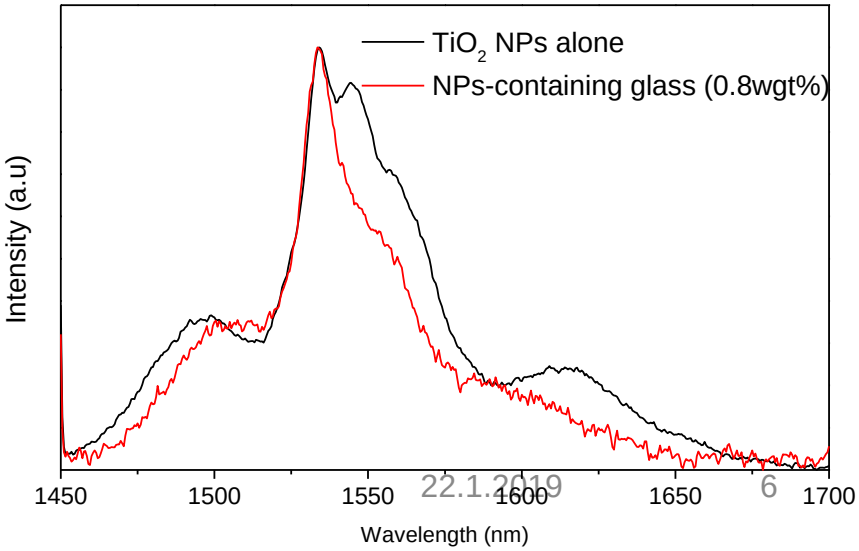



Normalized emission spectra ($\lambda_{exc}$=976nm)

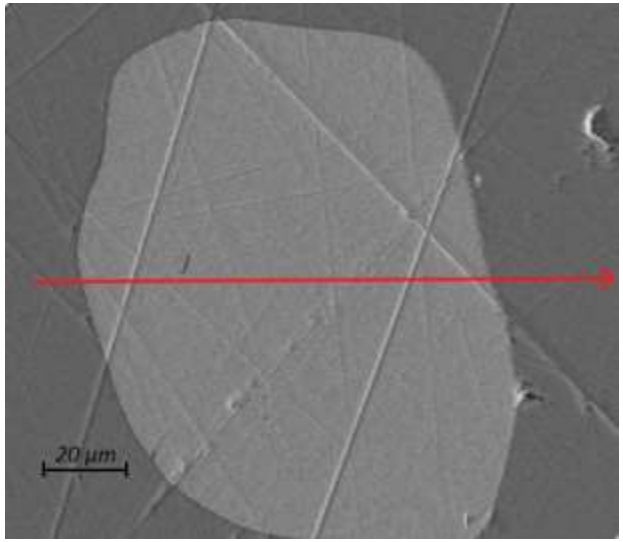



Emission band of the NPs is different after being added in the glass
→ $Er^{3+}$ in amorphous network

in agreement with the increase in the $Er^{3+}$:$^4I_{13/2}$ lifetime after adding the NPs in the glasses



# SEM/EDS

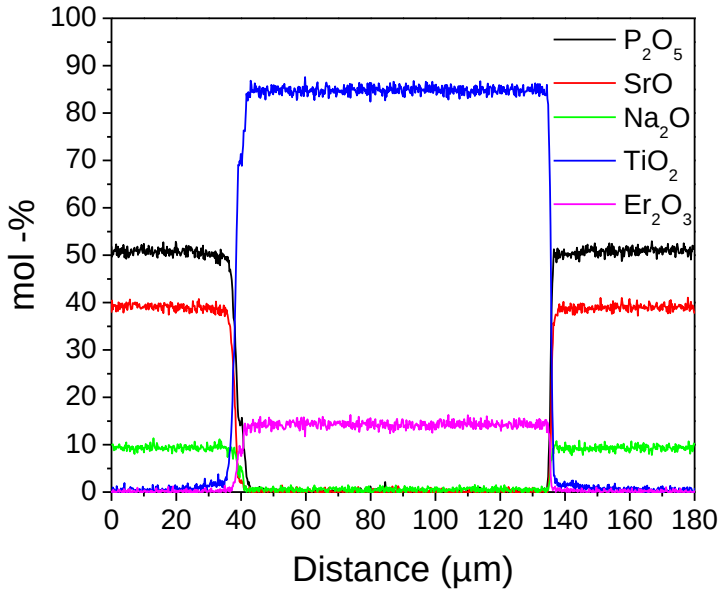



Er:$TiO_2$ –particles were found very easily with sizes up to ~100 µm.

Composition of the glass in agreement with the target composition of $50P_2O_5$–$40SrO$–$10Na_2O$ (mol%).

The particles were compositionally stable in the center

A small amount of NPs does survive during the glass preparation



# YAG-containing glasses

Picture of YAG-containing glasses
(1.25wgt% of YAG)


with 5nm silica layer  with 25nm silica layer

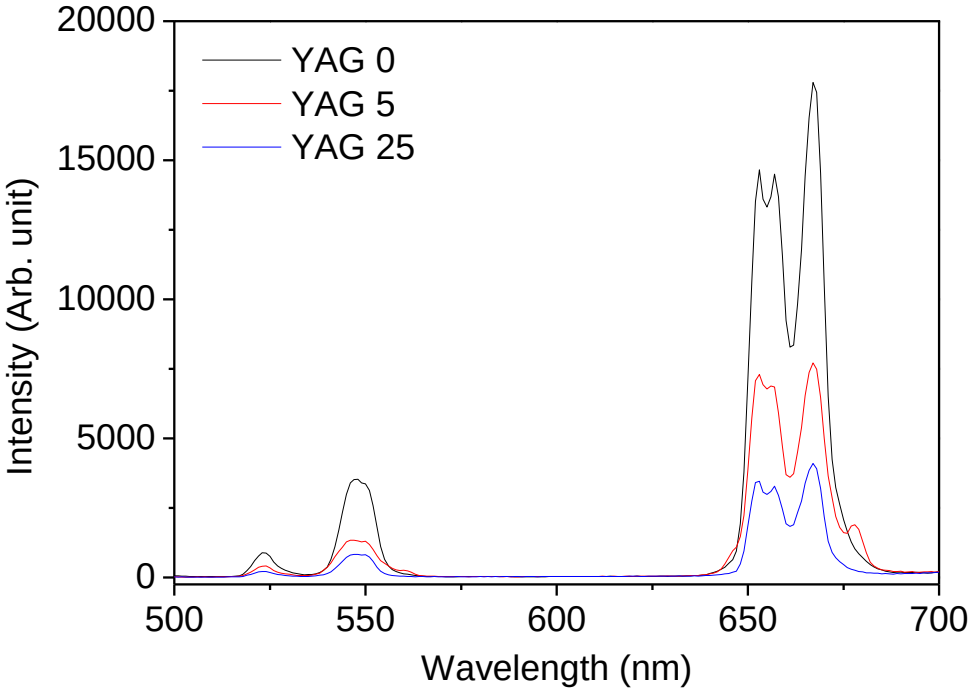
1.25w% of YAG
=
0.0038mol%$Er_2O_3$ –
0.035mol%$Yb_2O_3$

Agglomerates from the drying of the YAG-containing solutions.

Successful preparation of phosphate glasses with upconversion
while using small amount of RE

Stronger upconversion from YAG0-containing glasses

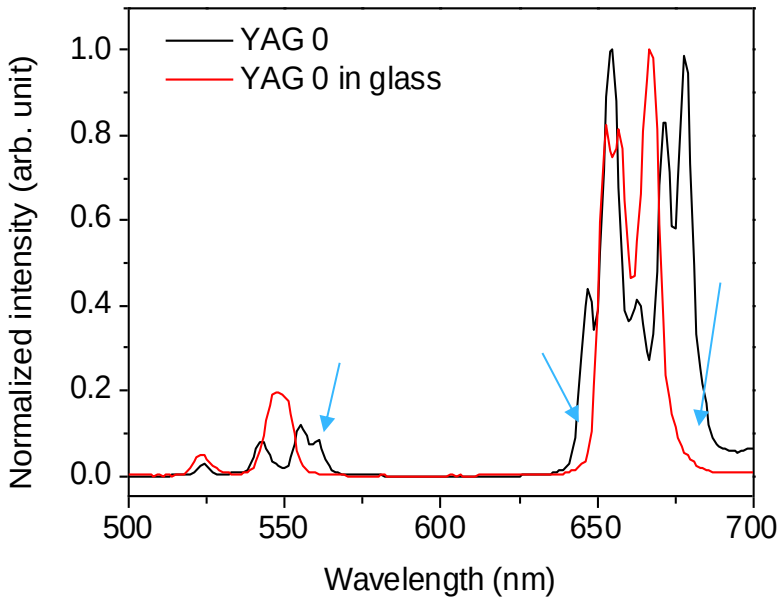
Upconversion spectra
($\lambda_{exc}$=980nm)



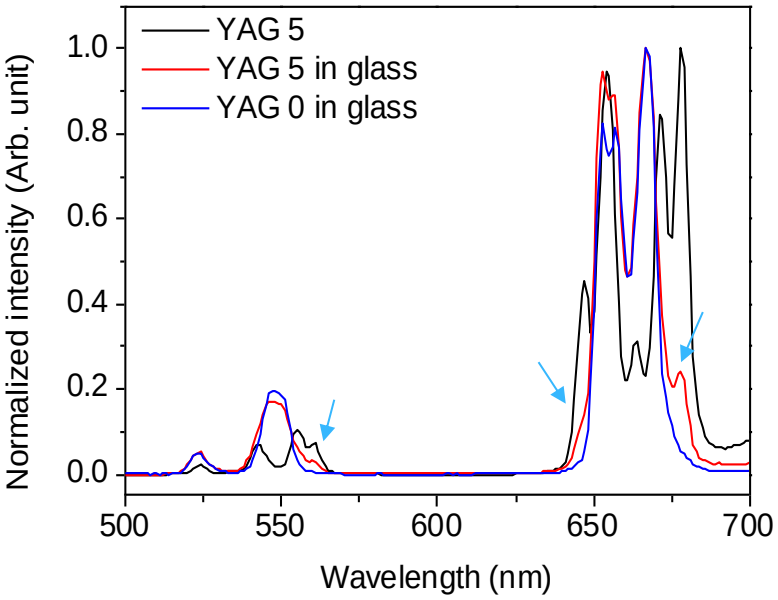
# YAG-containing glasses

Different emission shape when NPs are added in the glass
→ $Er^{3+}$ environment modified.

Normalized upconversion spectra ($\lambda_{exc}$ = 980nm)




Normalized upconversion spectra ($\lambda_{exc}$=980nm)

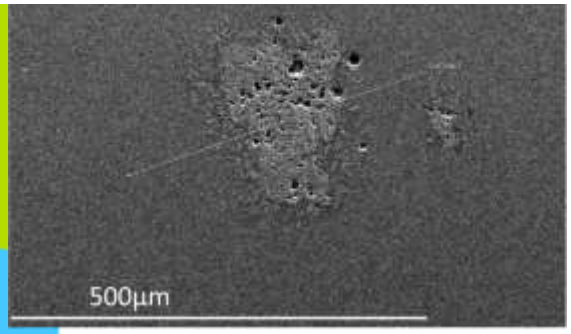



Residual peaks of YAG in YAG5-containing glass.

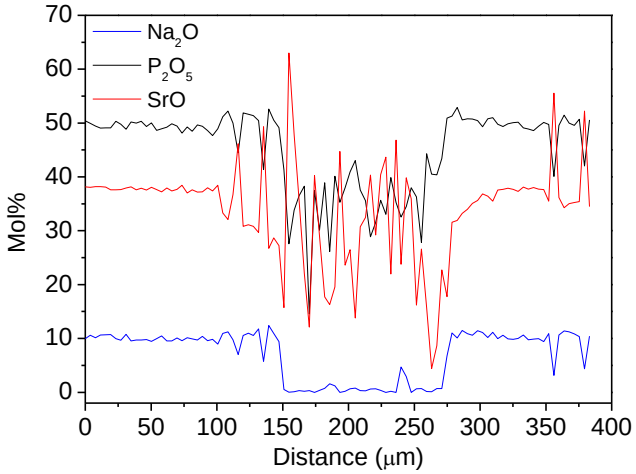
→ **Partial survival of YAG NP structure** in YAG 5
→ Thin layer of $SiO_2$ seems to have an impact on the survival of the particles.

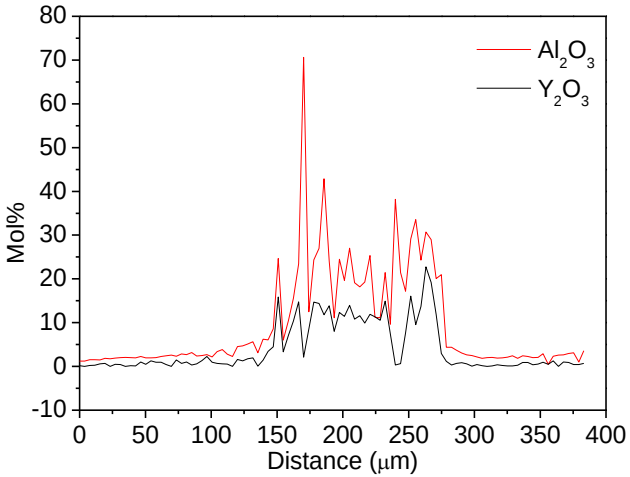
# YAG-containing glasses

SEM picture of an agglomerate found in YAG0-containing glass




Composition analysis along the line (mol% in oxide)




Composition of the glass in accordance with the theoretical one
Sr-rich crystals seen around the particles

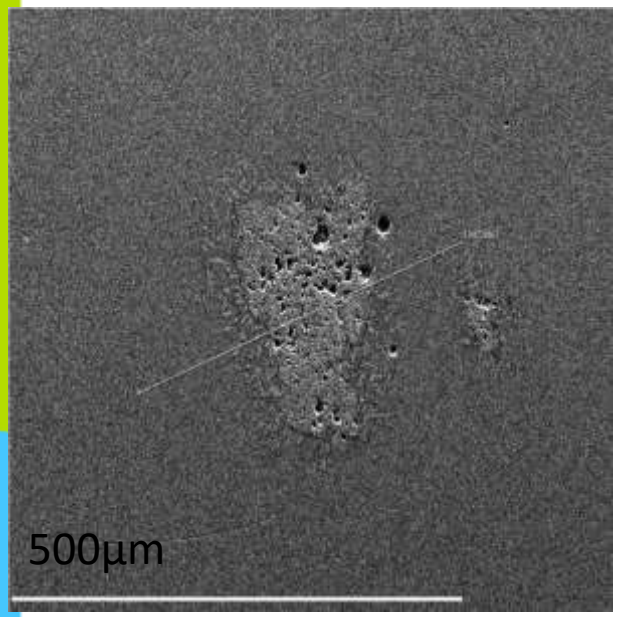
$Al_2O_3$ and $Y_2O_3$ detected ($SiO_2$ in the YAG5 and YAG25 containing glasses)

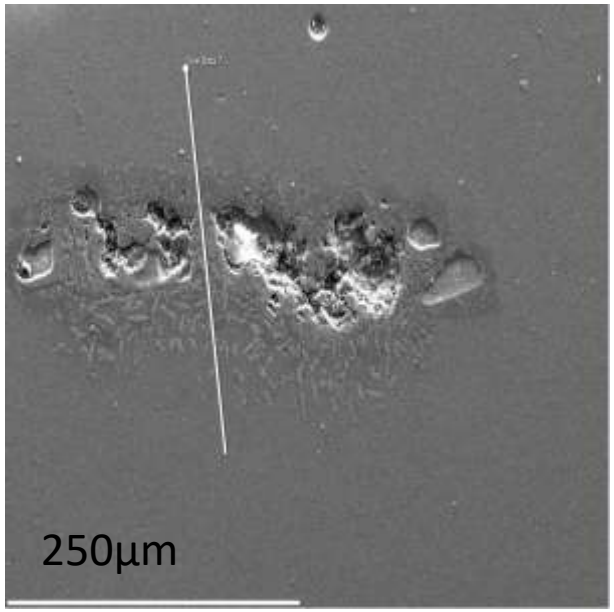
From the upconversion measurement and the composition analysis, no doubt about the survival of the YAG NPs BUT with a different crystalline phase.

# YAG-containing glasses

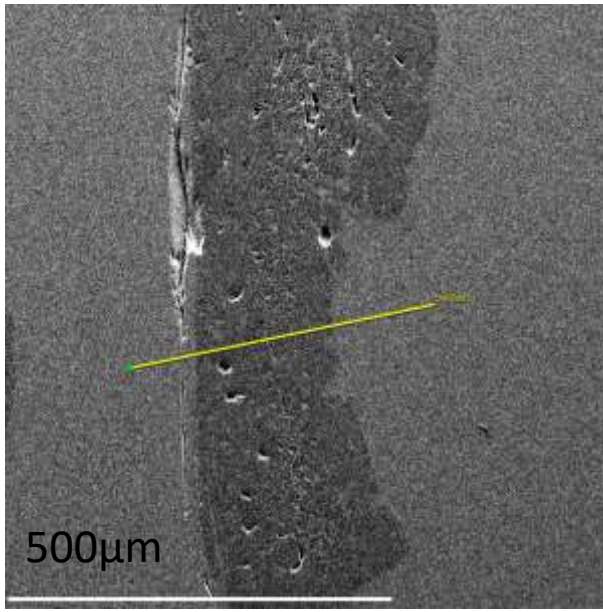
SEM picture of an agglomerate found in YAG5--containing glass

YAG0-containing glass




YAG25-containing glass

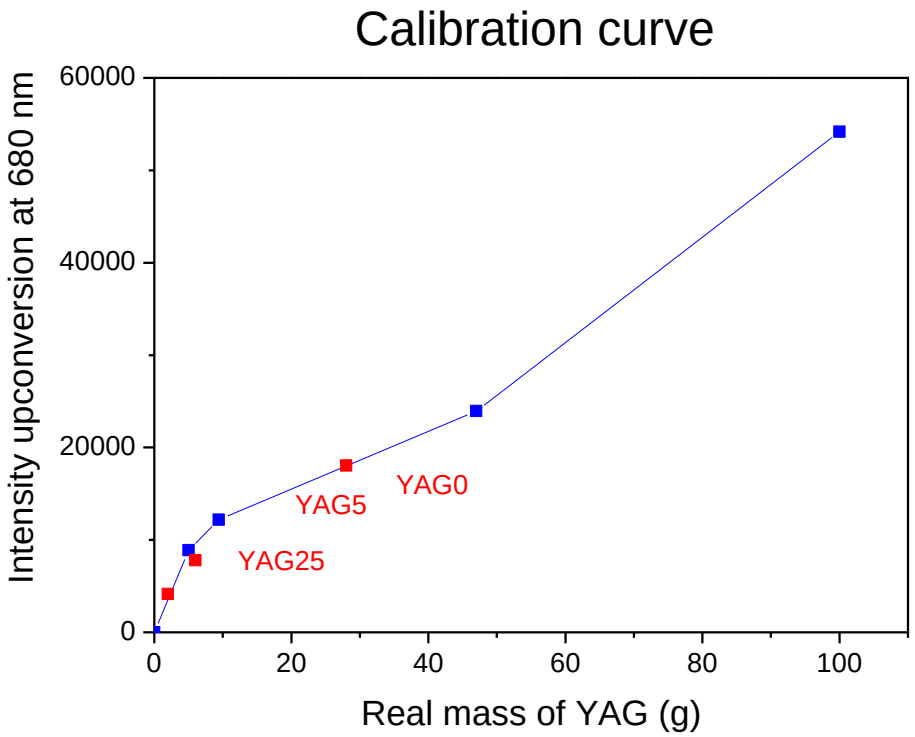



No crystals seen around the particles when the YAG are surrounded by a thick $SiO_2$ layer (25nm-YAG25)

Formation of crystals thought to be due to the diffusion of Al in the glass

# YAG-containing glasses

Samples with known amount of YAGs were used to estimate the % of YAGs survival in the glasses




30-35 wgt% of YAGs survive during the glass processing

$SiO_2$ layer seems to increase the % survival of the YAGs (To be confirmed)

# Conclusion

Possible to prepare particles containing glasses using direct doping method

- Upconversion can be obtained from a phosphate glass which contain 0.0038mol%$Er_2O_3$ – 0.035mol%$Yb_2O_3$ using YAGs. YAGs are supposed to survive but in different phases (to be identified)

- Thermal stability of the particles is not the only parameter to consider for the survival of the particles. The corrosion behavior of the glass melt is an important parameter to consider in order to engineer new NPs-containing glasses


7th International Workshop on

# PHOTOLUMINESCENCE IN RARE EARTHS: PHOTONIC MATERIALS AND DEVICES (PRE'17)

November 30 – December 2, 2017 | Rome, Italy

CENTRO FERMI
Museo Storico della Fisica e Centro Studi e Ricerche Enrico Fermi

ICG TC20
Glasses for Optoelectronics

fotonica.it

- ***Fundamental photoluminescence properties & spectroscopic measurements***
- ***Modeling, first-principles calculations***
- ***Photonic devices exploiting rare-earths characteristics***
- ***Rare-earth-doped crystalline materials***
- ***Transparent ceramics and glass-ceramic materials***
- ***Rare-earth complexes***
- ***Rare-earth optical amplifiers for telecommunication***
- ***Fiber lasers and micro-chip lasers***
- ***Phosphor materials for solid-state lighting***
- ***Persistent phosphors***
- ***Scintillators***
- ***Up- and down-conversion for PV applications***
- ***Rare-earth-doped materials for biological applications***

## *Call for Papers*

Plan to participate and submit one-page abstract by **15 September 2017**

**www.pre17.org**