Laboratoire
Physique de la Matière Condensée

DESIGNING NANOPARTICLES DURING THE DRAWING STEP

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CRHEA

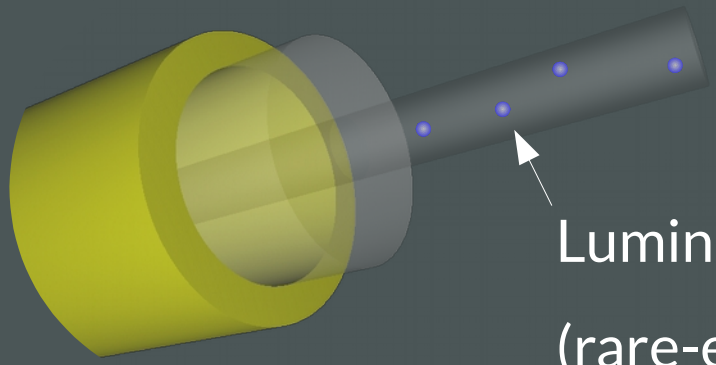
Centre Pluridisciplinaire de Microscopie électronique et de Microanalyse

CLEMSON UNIVERSITY

COMSET

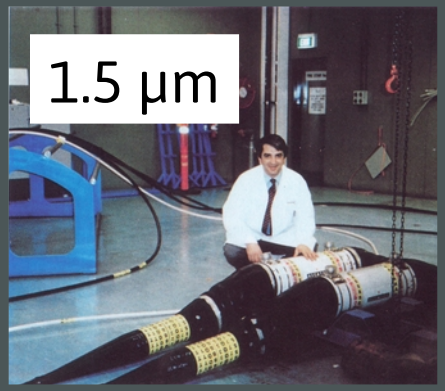
PROJET FINANCÉ PAR L'ANR - PROJECT FUNDED BY THE ANR

Fibre lasers and amplifiers



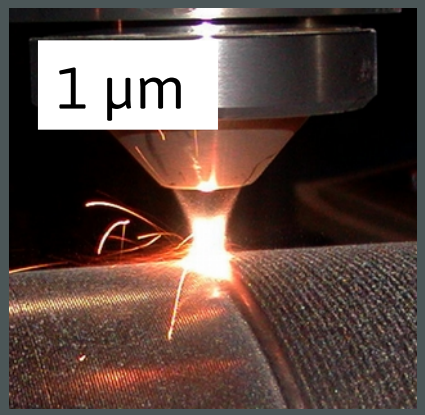
Luminescent ions

(rare-earth ions)



Fiber Amplifiers

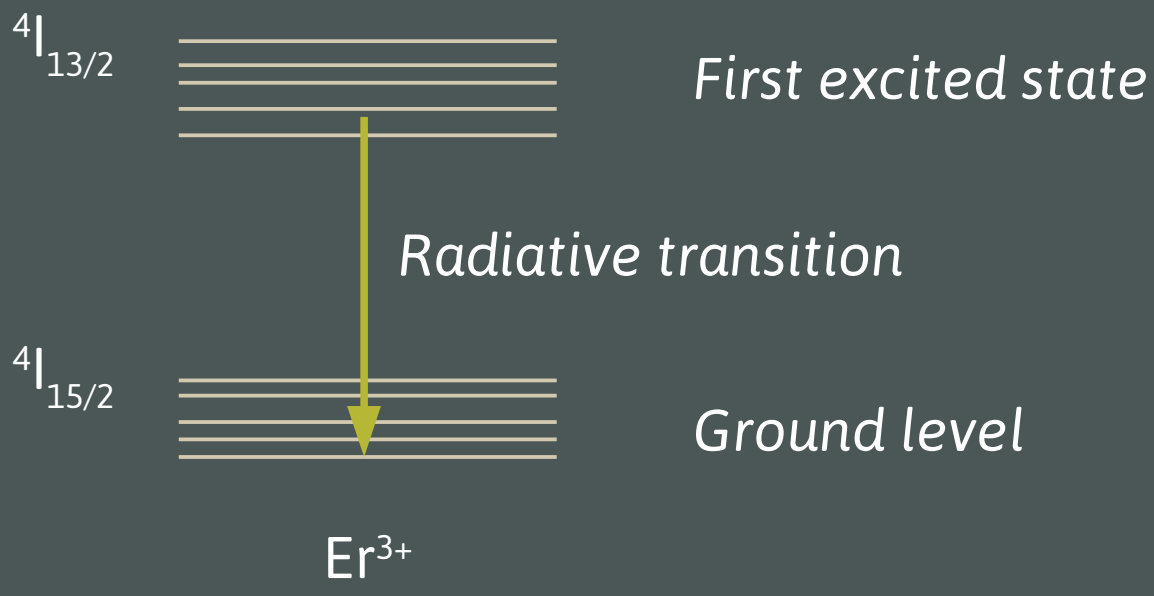
Telecoms



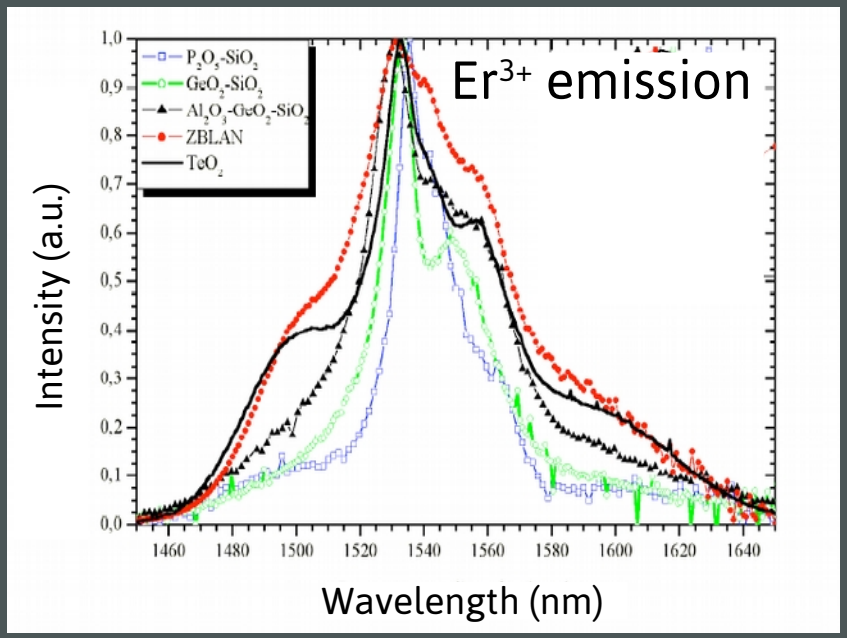
High power Fiber Lasers

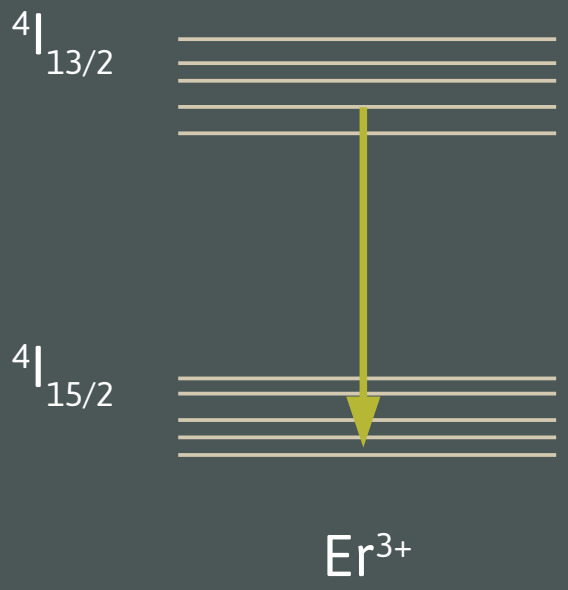
Machining, ...

Er^{3+} fluorescence



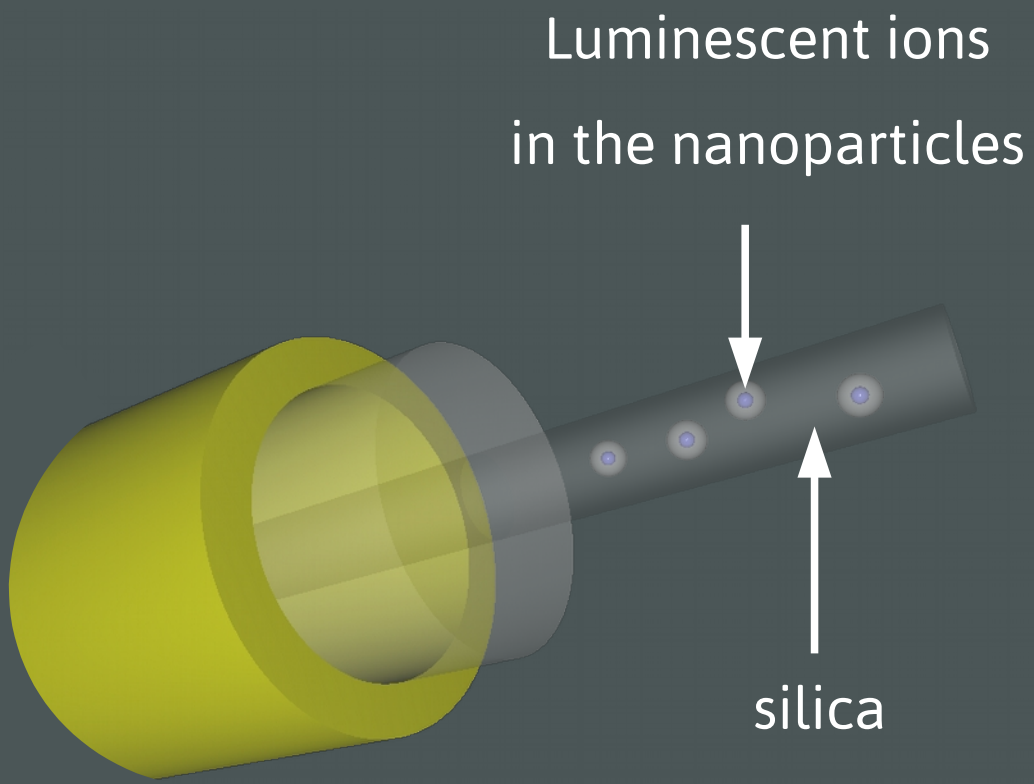
Er^{3+} fluorescence



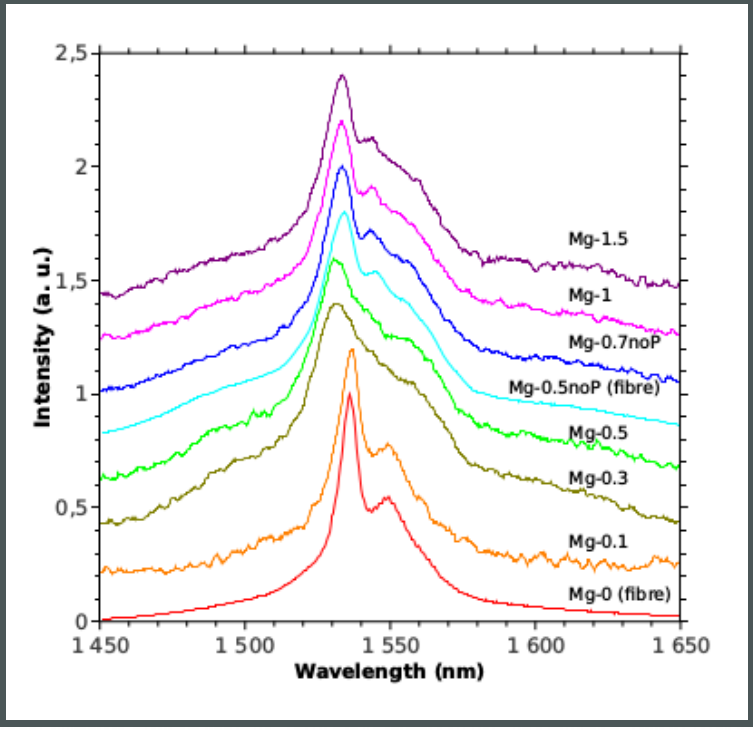


« *Spectroscopic properties of rare earths in optical materials* », *Liu & Jacquier (2005)*

Nanostructured optical fibres

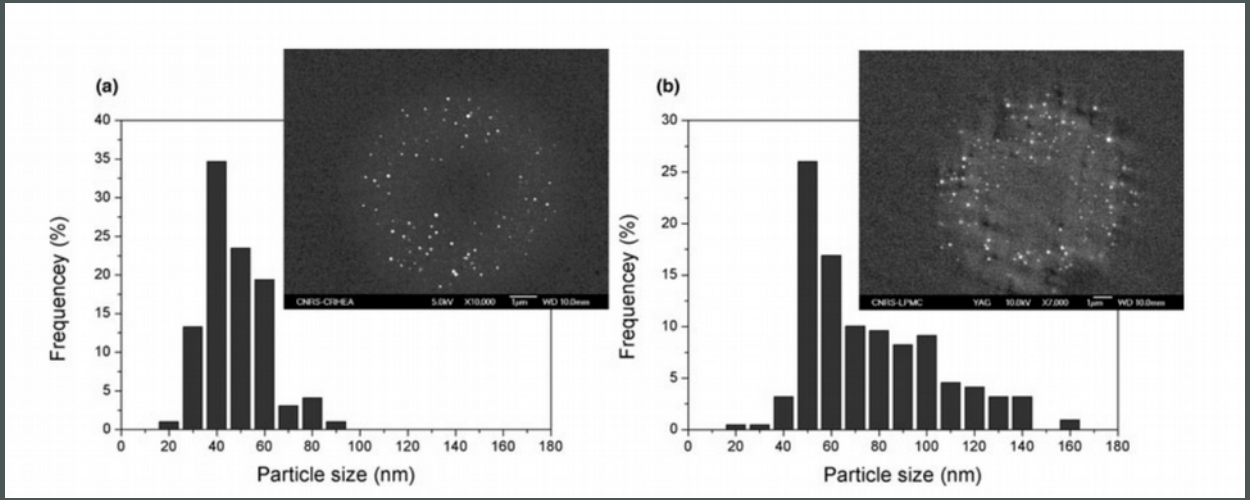


Modification of luminescence properties



F. d'Acapito et al.,

J. Non-Cryst. Sol. (2014)

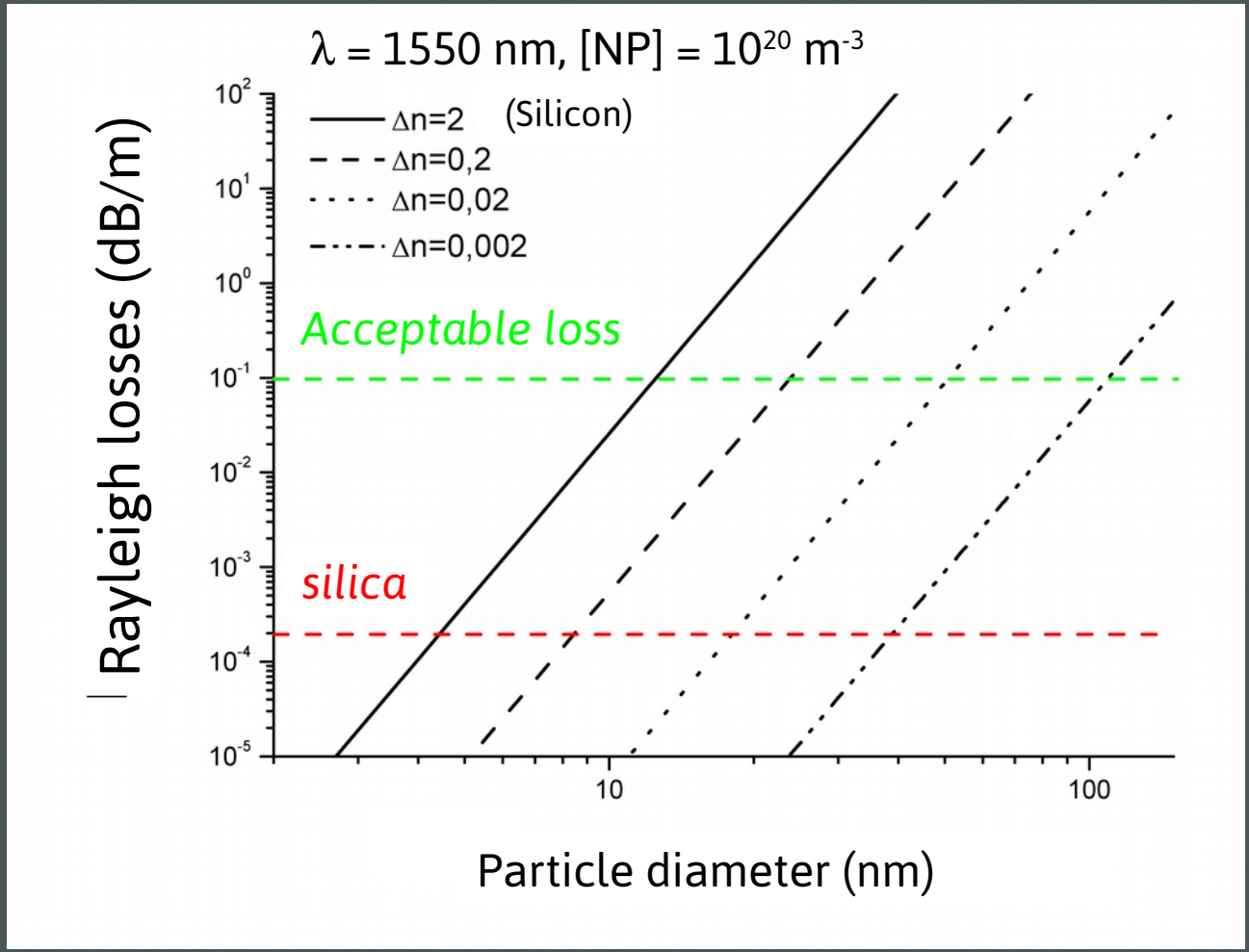


W. Blanc et al., J. Am. Ceram. Soc. (2011)

Rayleigh scattering

$$Rayleigh\ losses \propto [NP] \times L \times \frac{d^6}{\lambda^4} \times n_m^2 \left(\frac{n_n^2 - n_m^2}{n_n^2 + 2n_m^2} \right)^2$$

d×2 → RL×64 !



Influence of the volume fraction

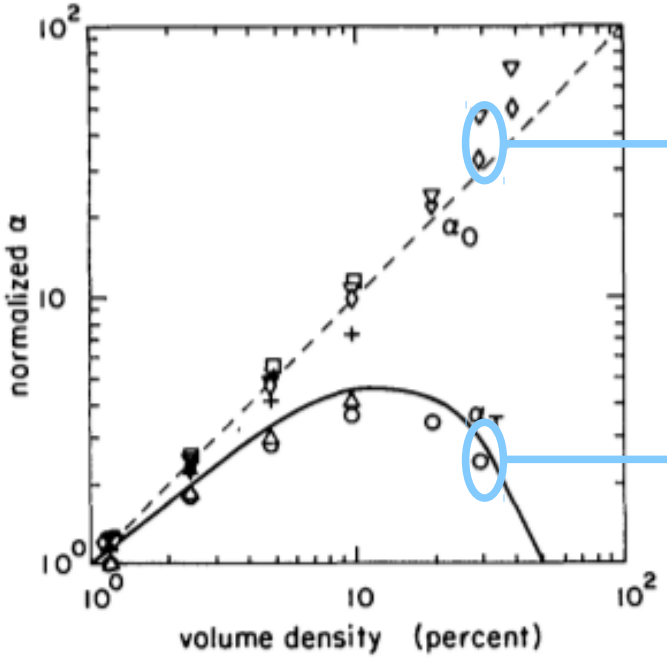


Fig. 4. Normalized α, α_o, and α_T: ○, 0.091 μm; △, 0.109 μm; +, 0.481 μm; X, 1.101 μm; □, 2.02 μm; ▽, 5.7 μm; and ◇, 11.9 μm.

Nanoparticles > λ

λ = 475 nm

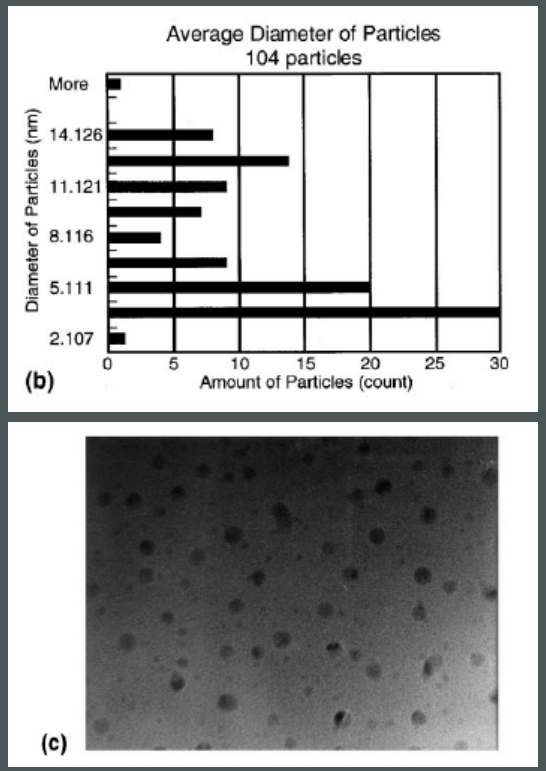
Nanoparticles < λ

But high volume fraction may induce Ostwald ripening...

A. Ishimaru, Y. Kuga, J. Opt. Soc. Am. (1982)

Heat-treatment of the fibre

Core composition: $30SiO_2$-$15AlO_{3/2}$-$29\underline{Cd}F_2$-$17\underline{Pb}F_2$-$4\underline{YF}_3$-$5ZnF_2$: Tm



Particle size distribution (b), and TEM micrograph (c) for fiber cerammed at 460°C for 50 min.

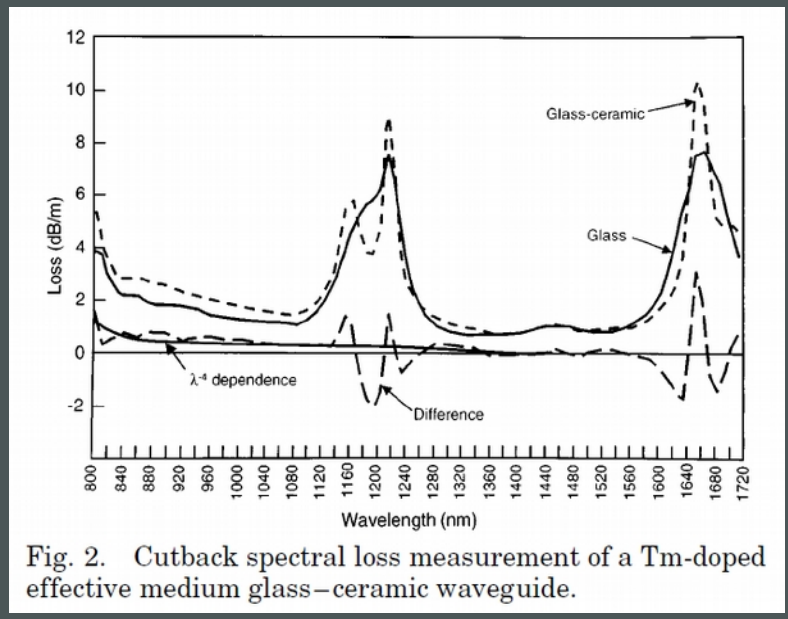


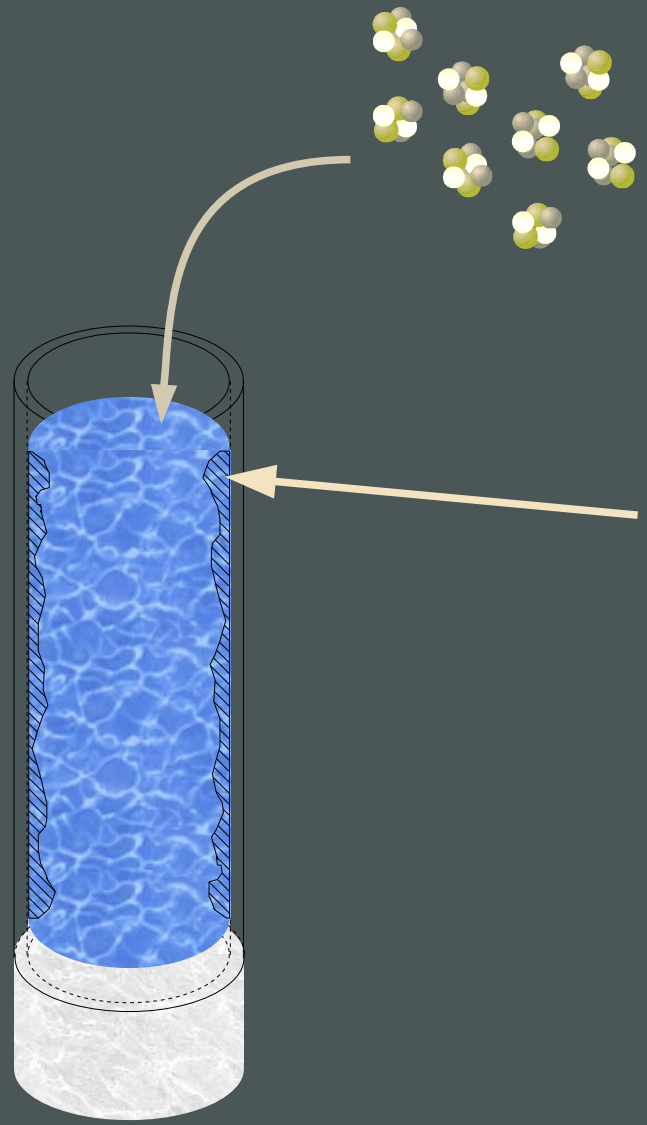
Fig. 2. Cutback spectral loss measurement of a Tm-doped effective medium glass–ceramic waveguide.

T_g ~400 °C, T_x~460°C

P.A. Tick, Opt. Lett. (1998)

P.A. Tick et al., Opt. Mater. (2000)

Solution doping step



- 10 nm-LaF_3:Tm^{3+}
- Porous layer :

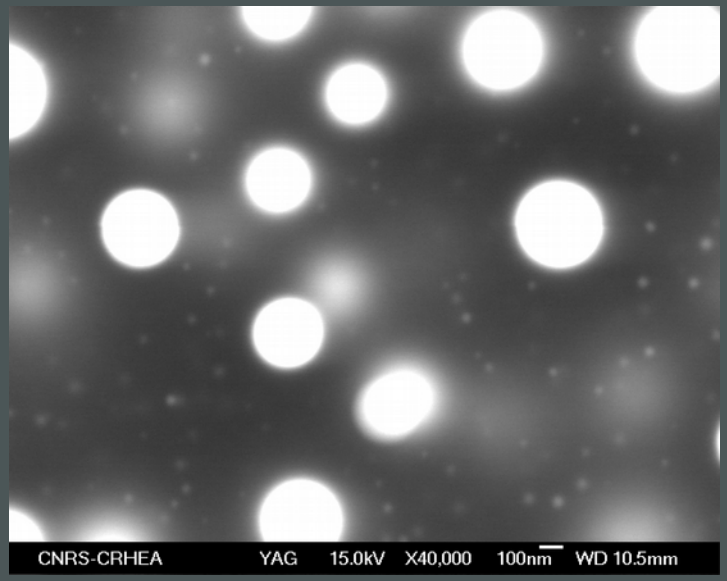
  $SiO_2 + GeO_2$

Average composition :

[Ge] = 0.4 – 0.8 at %

[La] = 0.4 – 2 at %

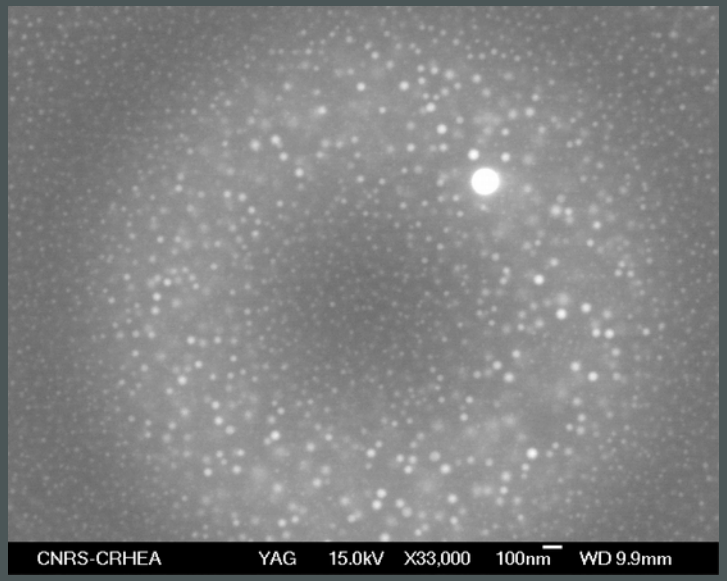
SEM images



preform

~ bimodal size distribution

>> 100 nm & 50 nm

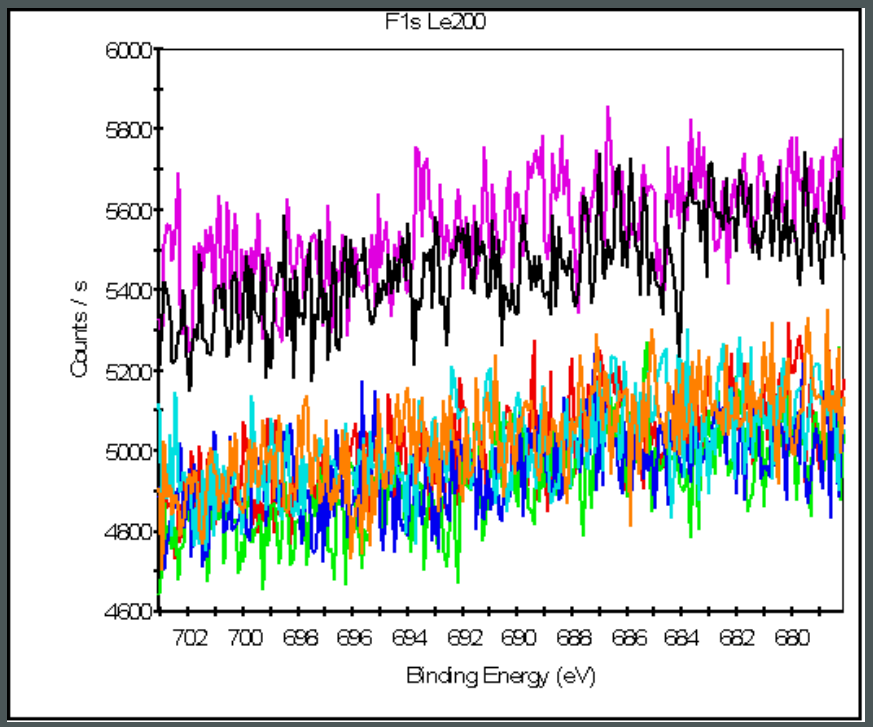


fiber

More uniform size distribution

Evaporation of F

XPS measurements

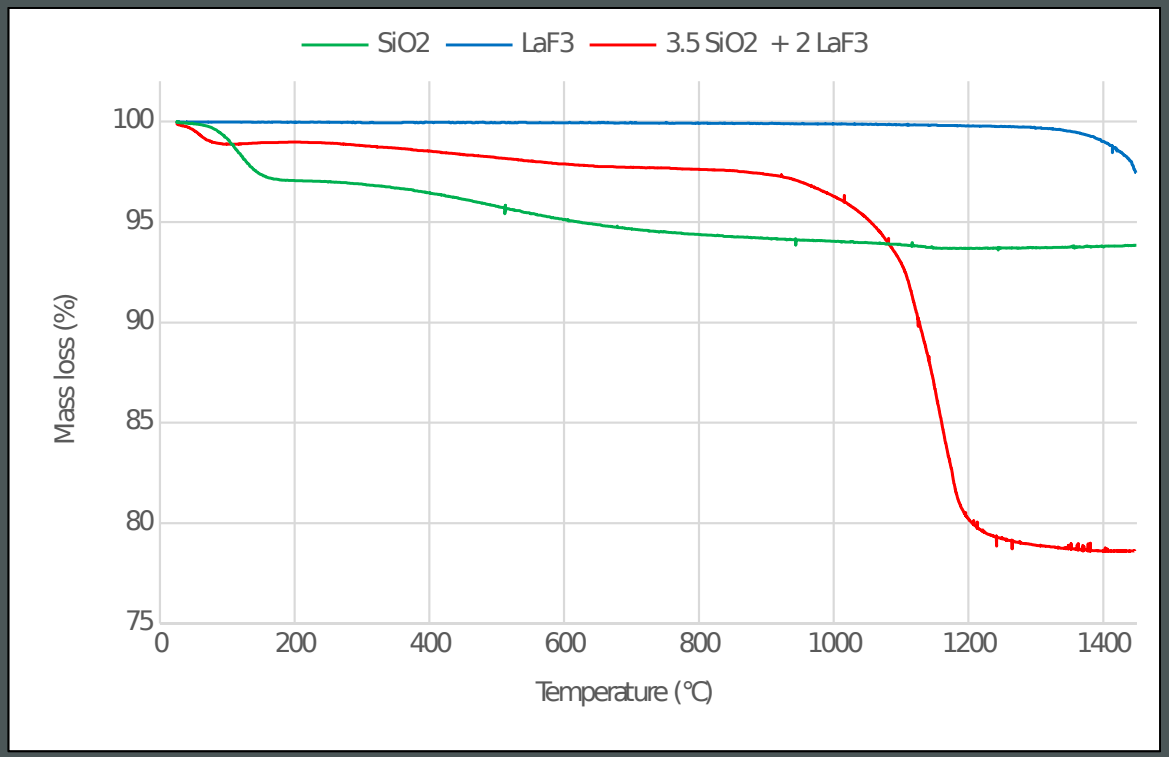


F1s binding energy : ~687 eV

MINES ParisTech Cemef

F. Giorgi

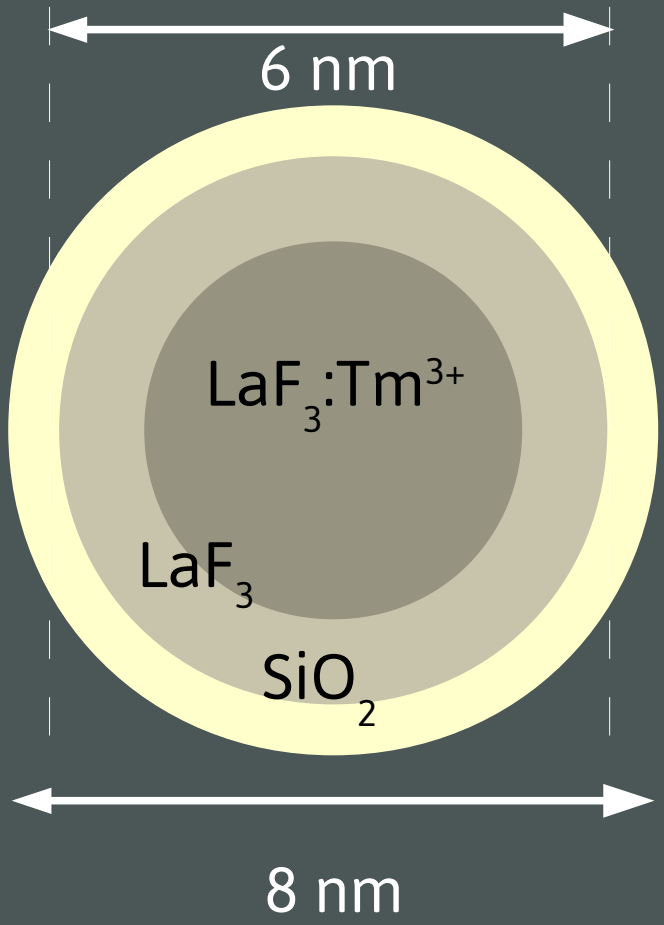
Thermogravimetric analyses (TGA)



ICG Montpellier

Coll. Hussein Fneich, Ahmad Mehdi

$LaF_3 \rightarrow La_2Si_2O_7$



900°C

12 h

$La_2Si_2O_7$ (59.5%)

α-cristobalite (40%)

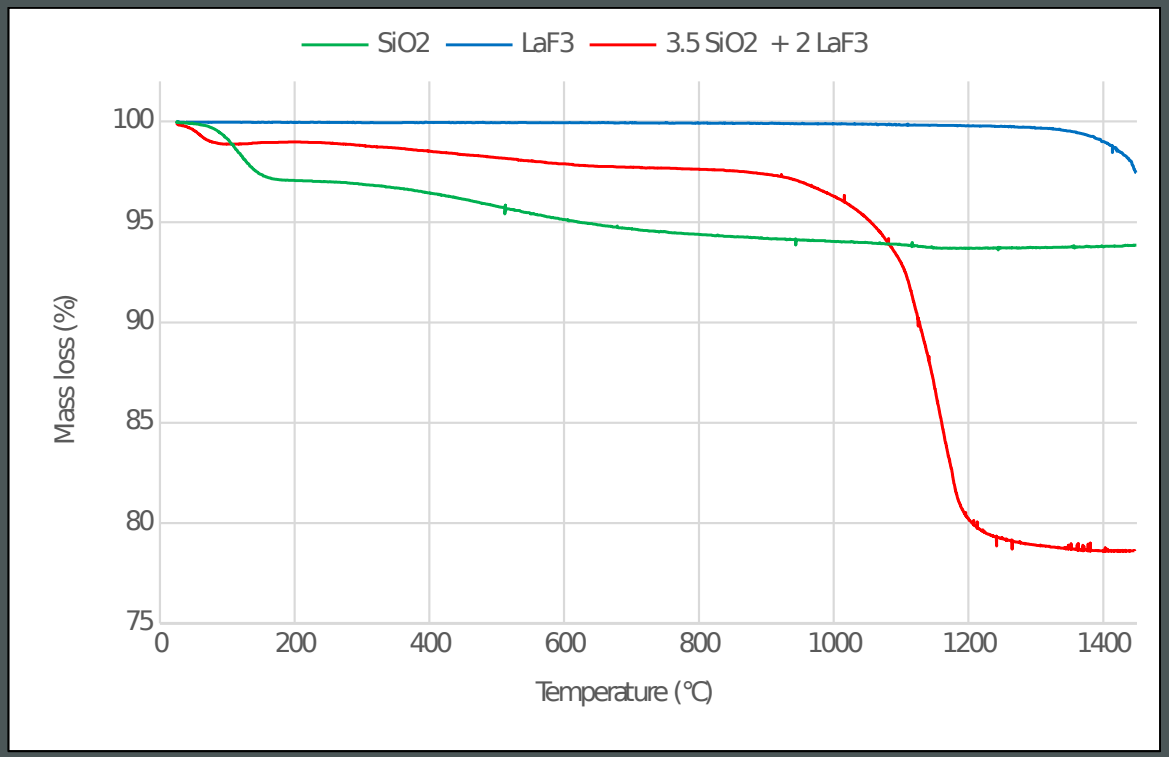
$La_{9.31}O_{6.24}Si_{26}$ (0.5%)

~~F~~

$\tau_{1/e}(^3H_4) = 56 \pm 11$ µs

P. R. Diamente et al., Adv. Funct. Mater. (2007)

Thermogravimetric analyses (TGA)



$$3.5\ SiO_2 + 2\ LaF_3 \rightarrow 1.5\ SiF_4\uparrow + La_2Si_2O_7$$

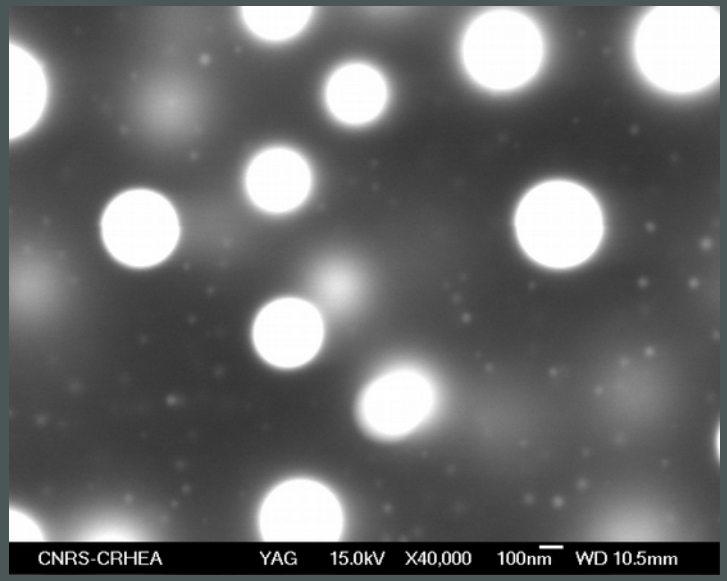
Theoretical mass loss: 26 %

Measured mass loss: 22 %

ICG Montpellier

M. Vermillac et al., Opt. Materials (submitted)

SEM images



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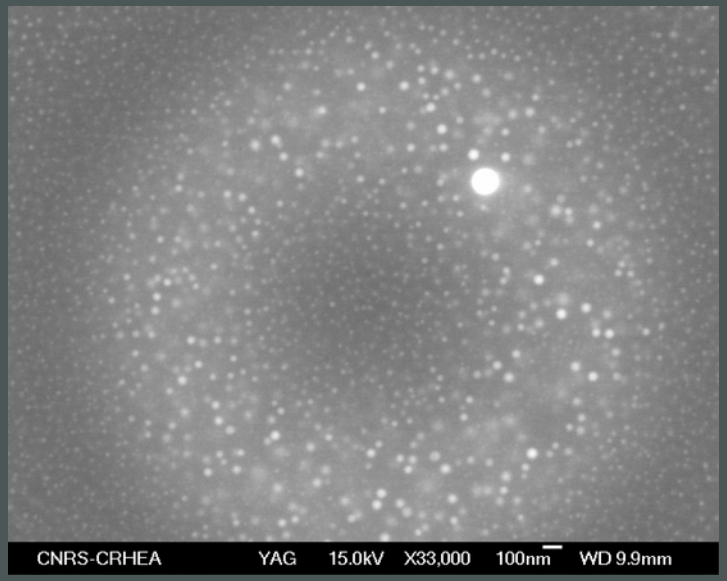
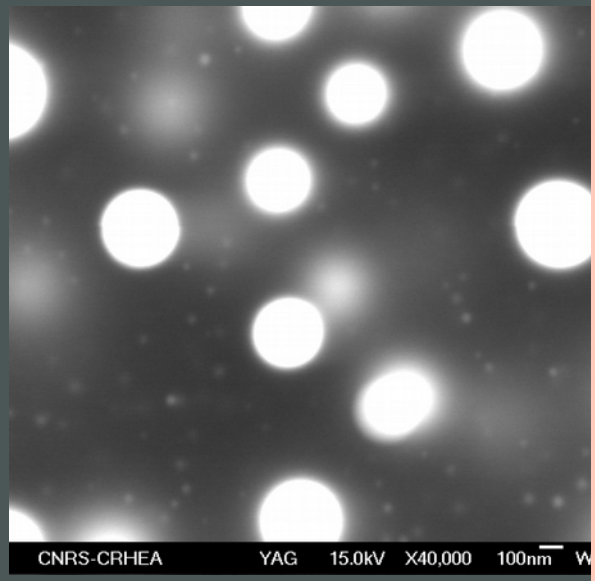


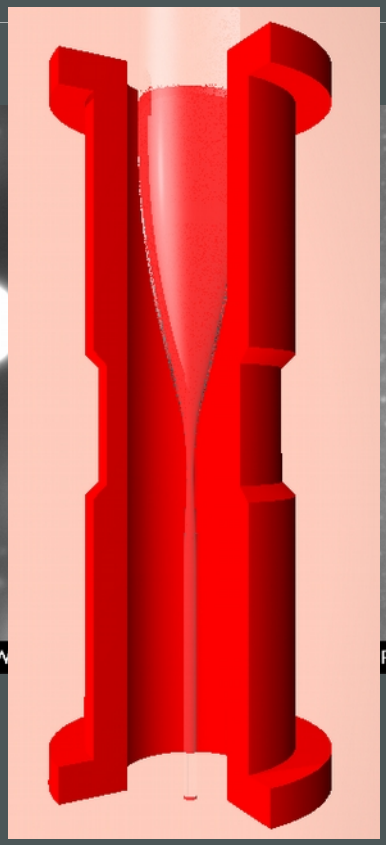
fibre

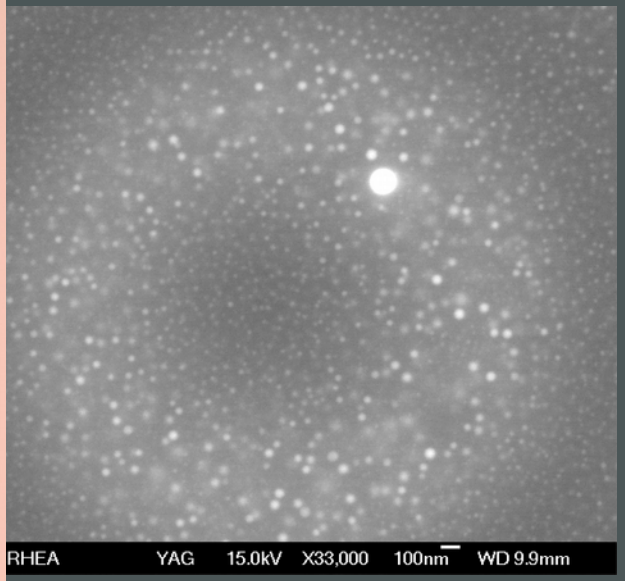
More uniform size distribution

Nanoparticles are La-rich silicate phase - F evaporates

SEM images







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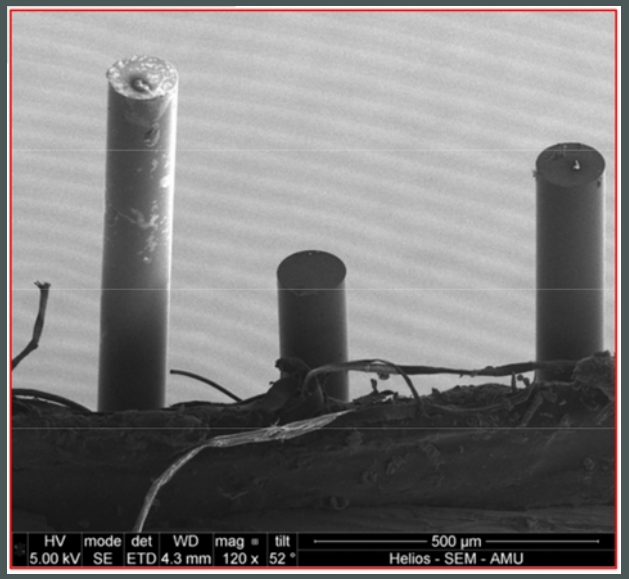
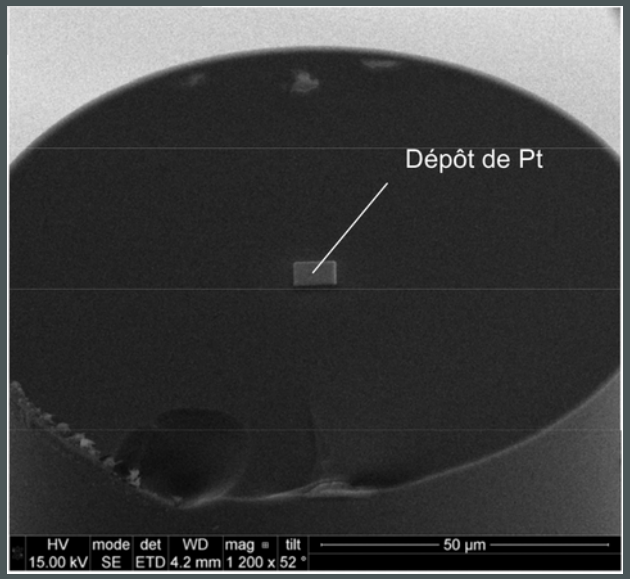
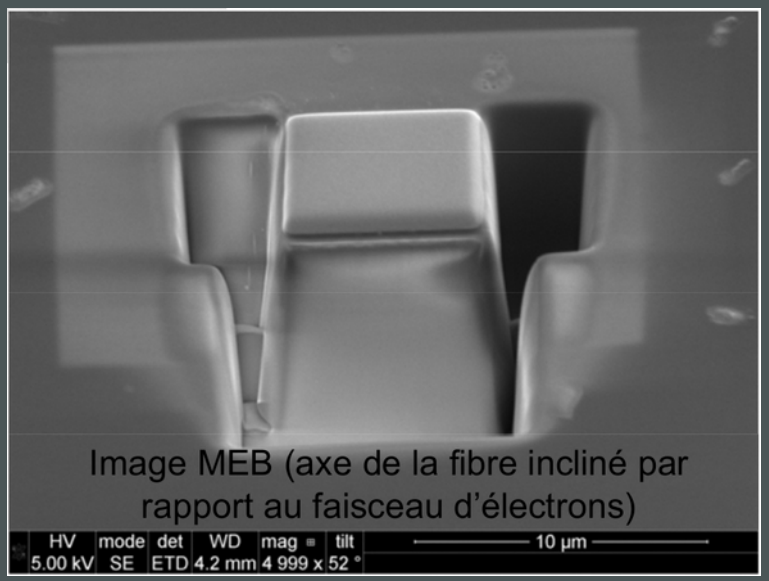
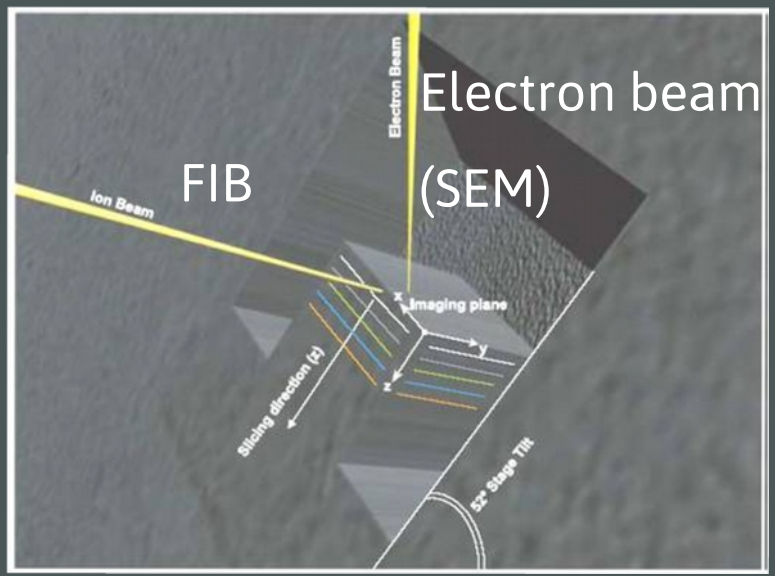
FIB/SEM tomography analyses

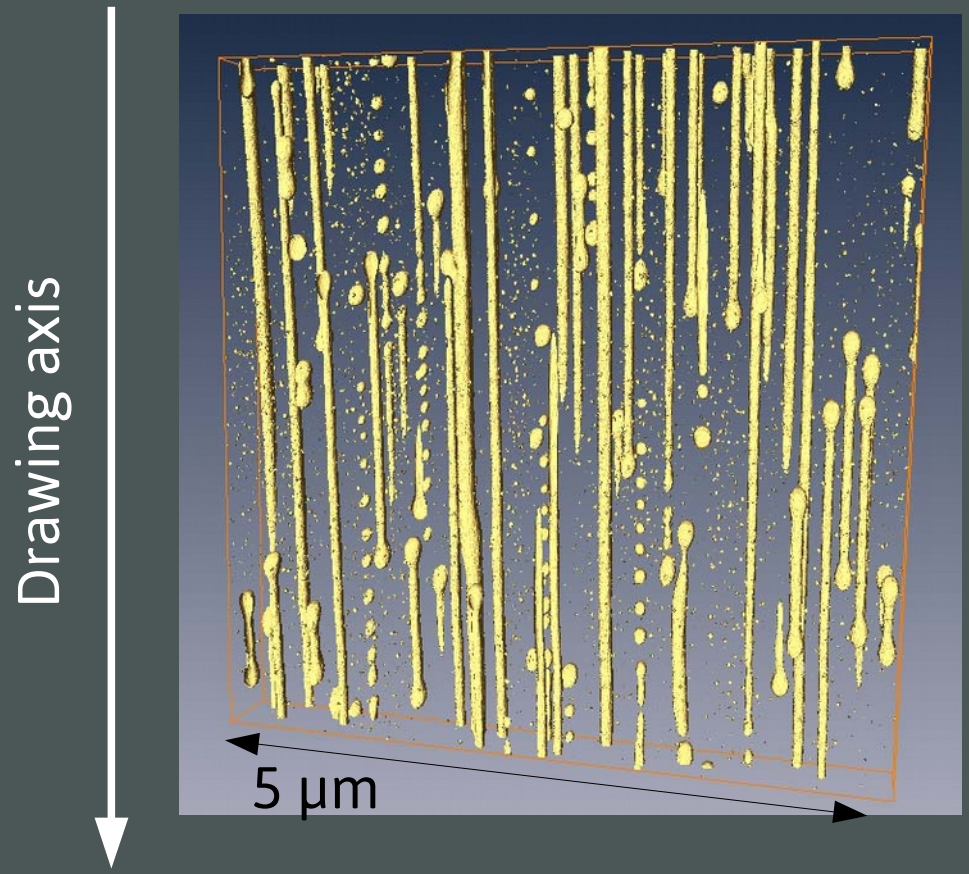


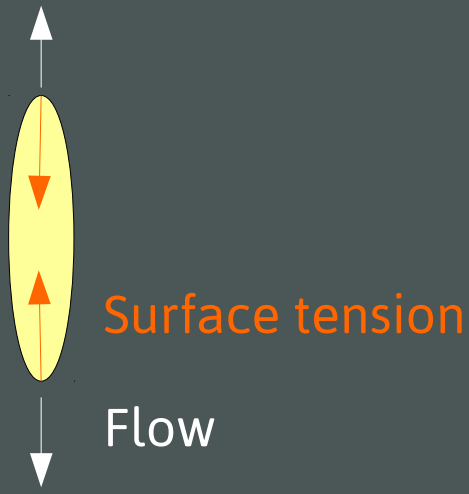






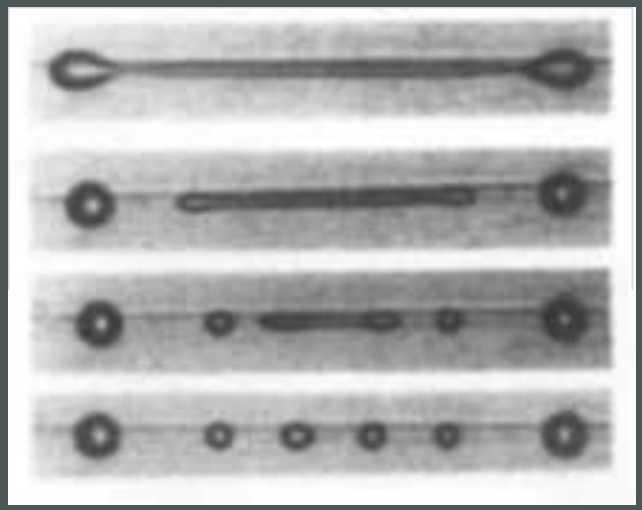
FIB/SEM tomography of fibre core



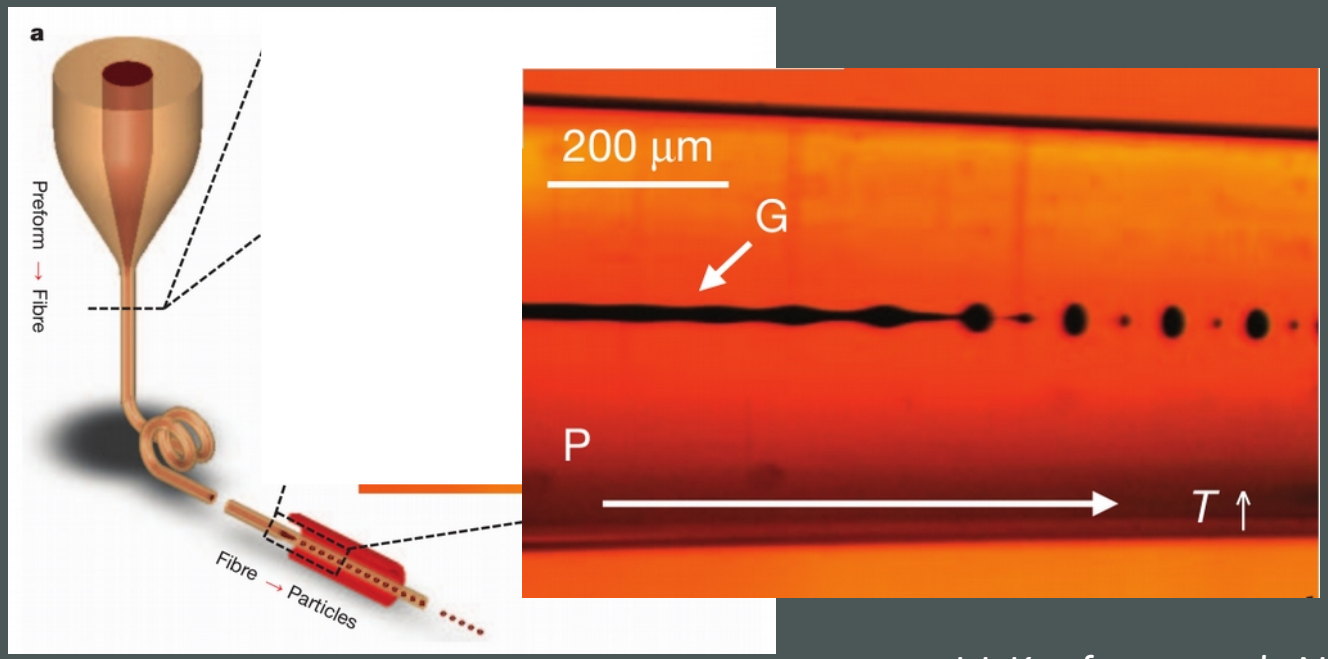


$$Ca = \frac{viscous\ forces}{surface\ tension} = \frac{\eta R \dot{\epsilon}}{\gamma}$$

Breakup of particles in viscous fluids

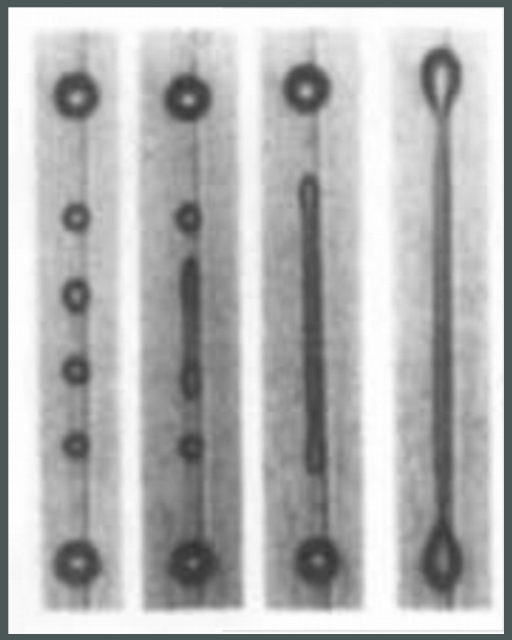


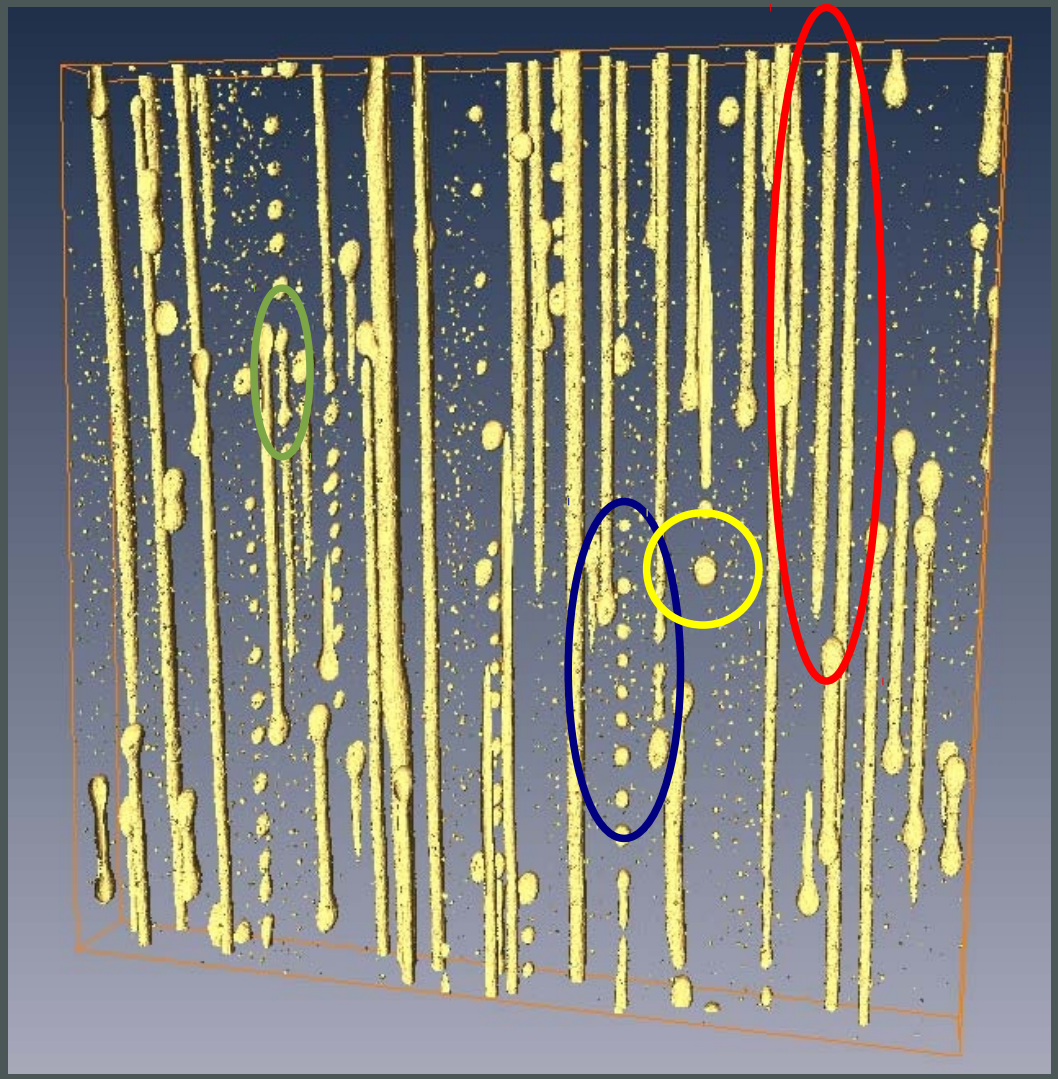
H.A. Stone, Annu. Rev. Fluid Mech. (1994)



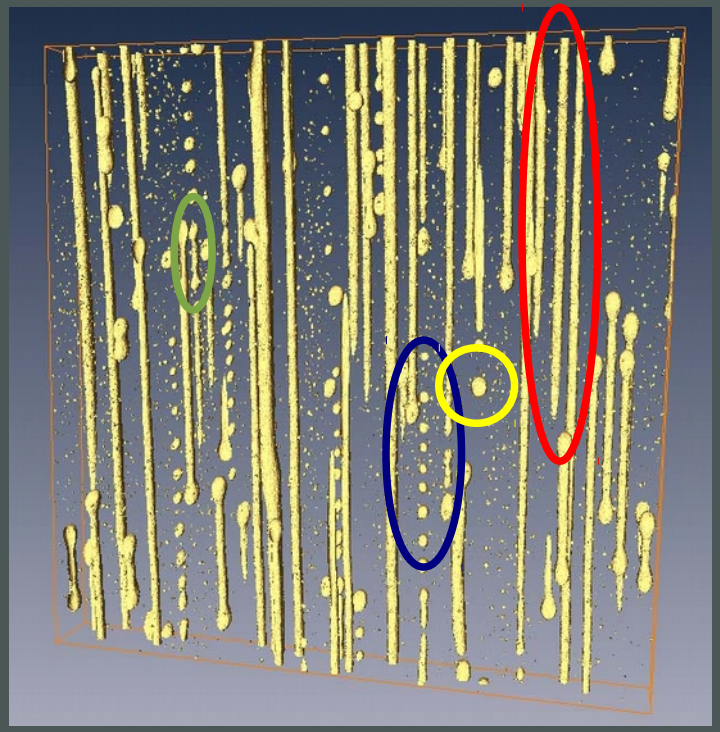
J.J. Kaufman et al., Nature (2012)

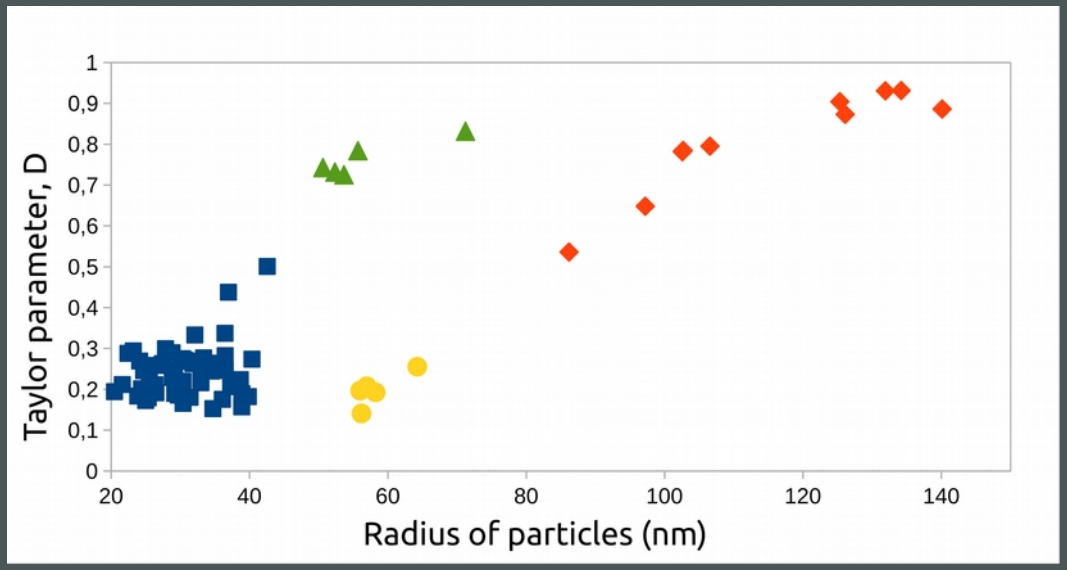
Deformation of particles



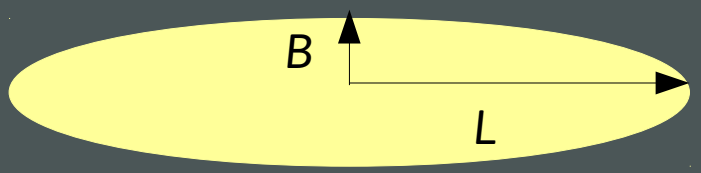


Deformation vs radius of particles

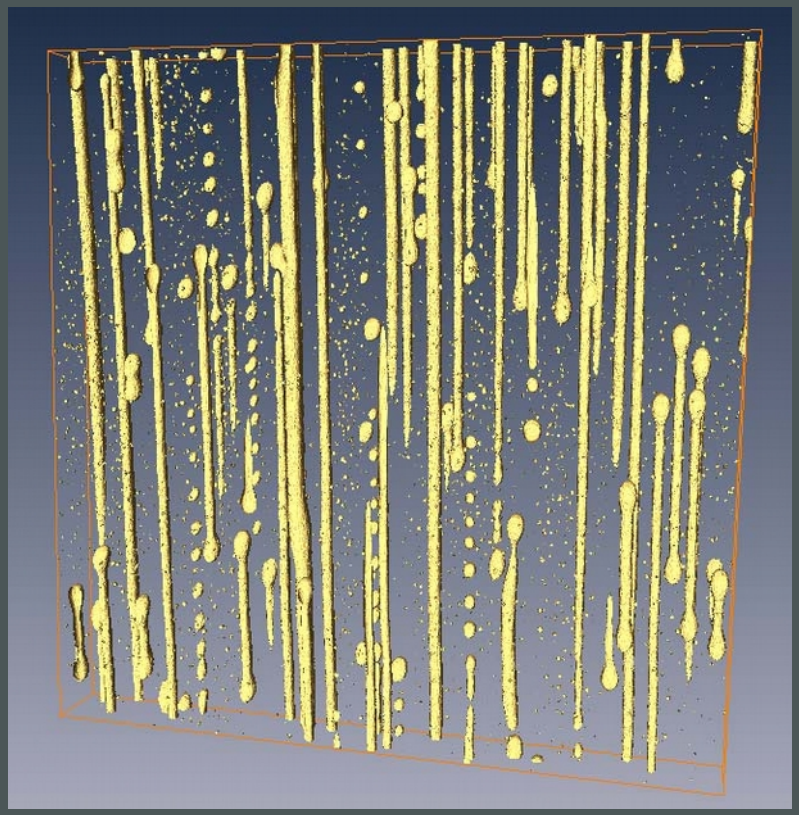




$$D = \frac{L - B}{L + B}$$



Control size of particles : transfer function of fibre drawing



Designing size distribution ?

- Break-up in evolving flow
- Knowing surface tension, viscosity ratio

→ Rheological phenomena *vs* Effect of dissolution/growth

Conclusion & perspectives

- Nanoparticles allow to get new luminescent properties
- Light scattering is the main limitation
- Rheological phenomena allow to reduce size of nanoparticles

- Modelisation of fibre drawing
- Modelisation of drop deformations