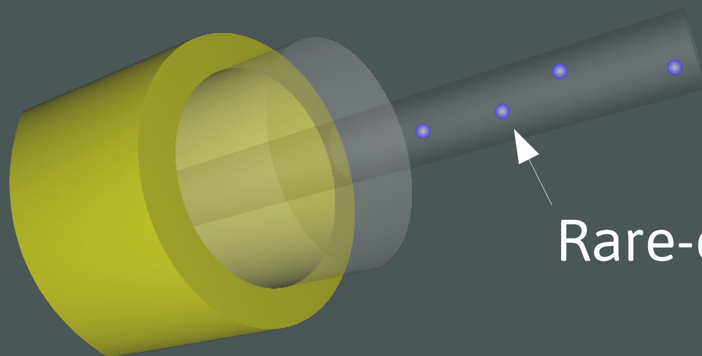
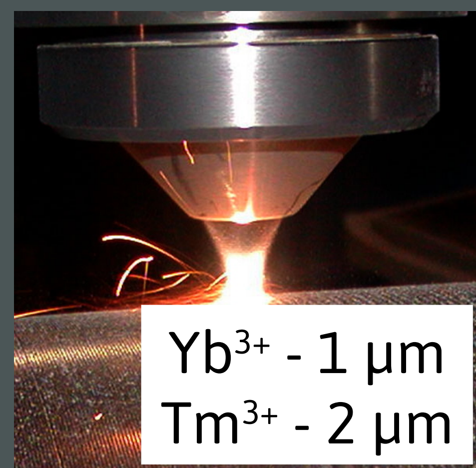
Caractérisation de la séparation de phase et de la cristallisation à petite échelle

Wilfried Blanc

Université Côte d'Azur, CNRS, InPhyNi, Nice, France

Fiber lasers and amplifiers





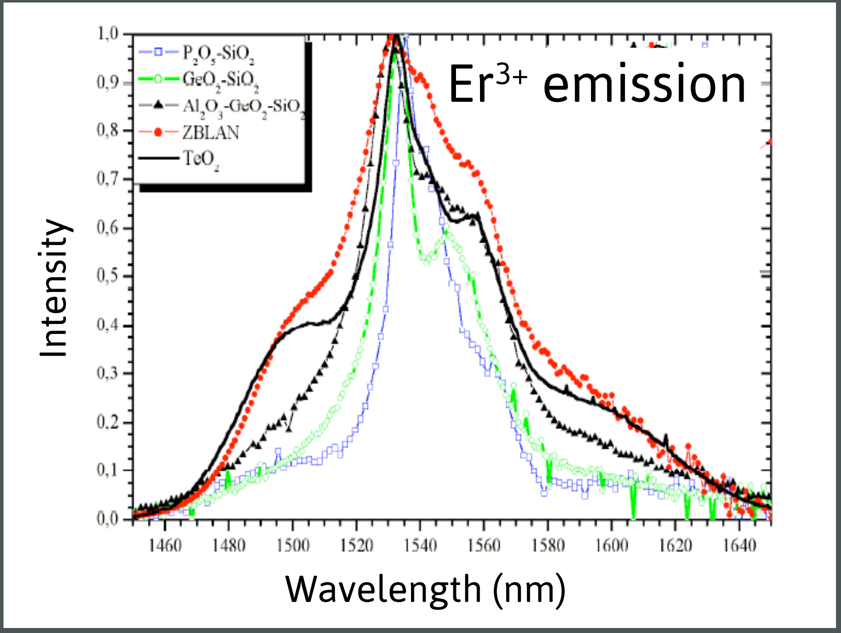
Fiber Amplifiers

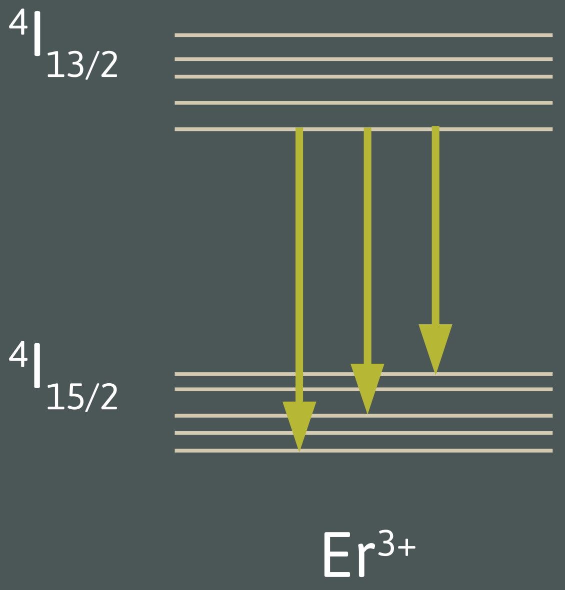
Telecoms

High power Fiber Lasers

Material processing, …

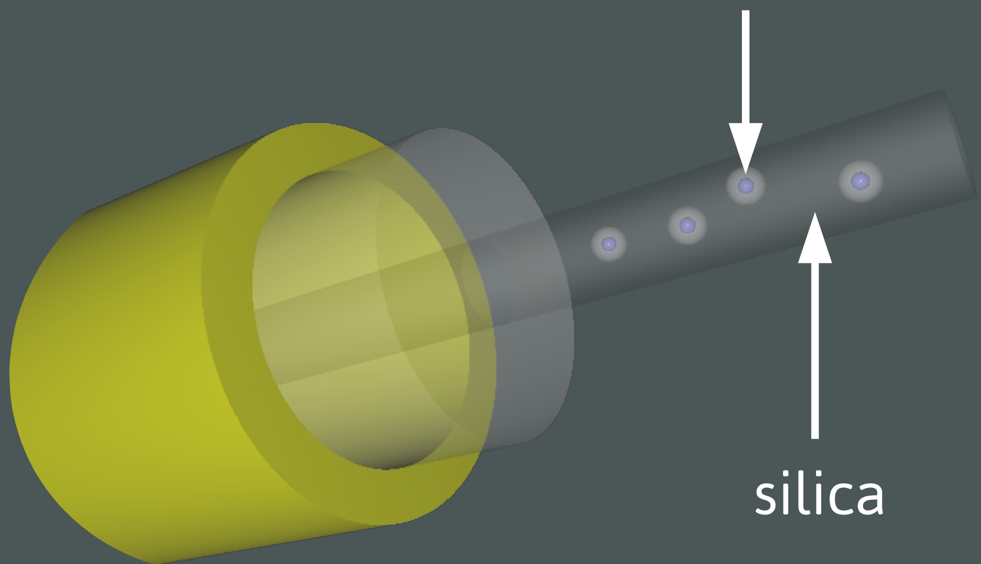
Er^{3+} fluorescence





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

Nanostructured optical fibers



1904 OPTICS LETTERS / Vol. 23, No. 24 / December 15, 1998

Are low-loss glass–ceramic optical waveguides possible?

P. A. Tick

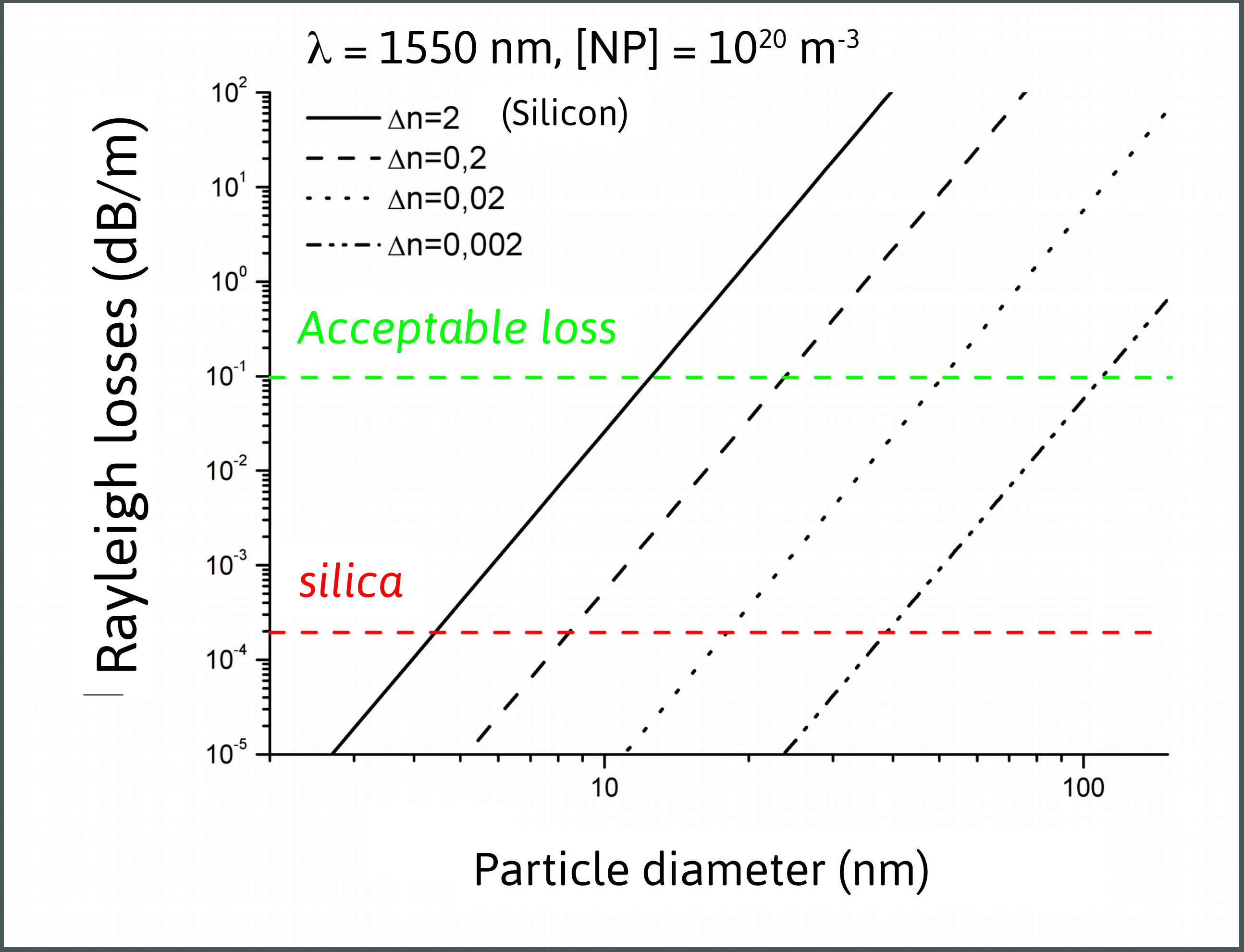
Corning Incorporated, SP-AR-O2-1, Corning, New York 14831-0001

Received September 24, 1998

The results of a cutback measurement of a glass–ceramic optical waveguide with single-mode fiber geometry have demonstrated that sub decibels per kilometer losses can be achieved. Difference spectra show that the limit of intrinsic scattering in these two-phase structures ought to be tens of decibels per kilometer.

Rayleigh scattering

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



Rayleigh scattering

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

Four requirements:

i) the particle size must be less than ~15 nm

ii) the distance between particles must be comparable to the particle size

iii) the size distribution must be narrow

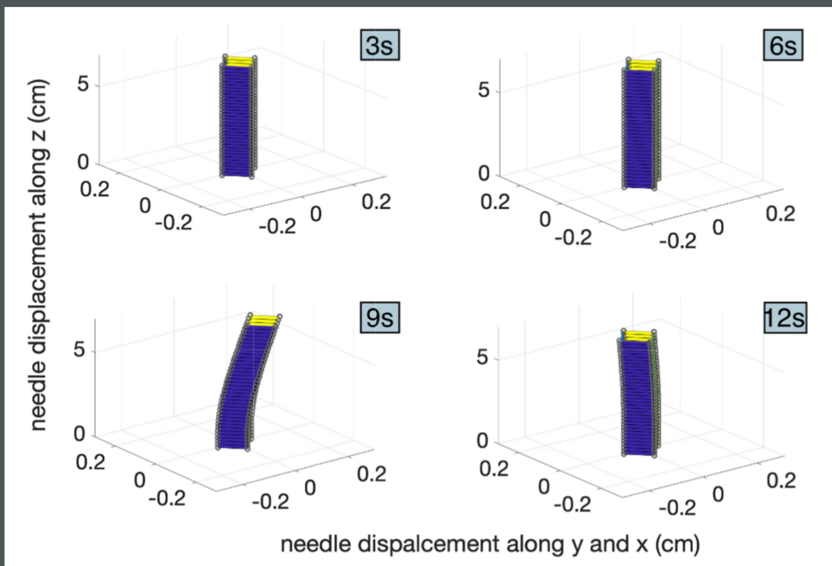
iv) the particles must not cluster together

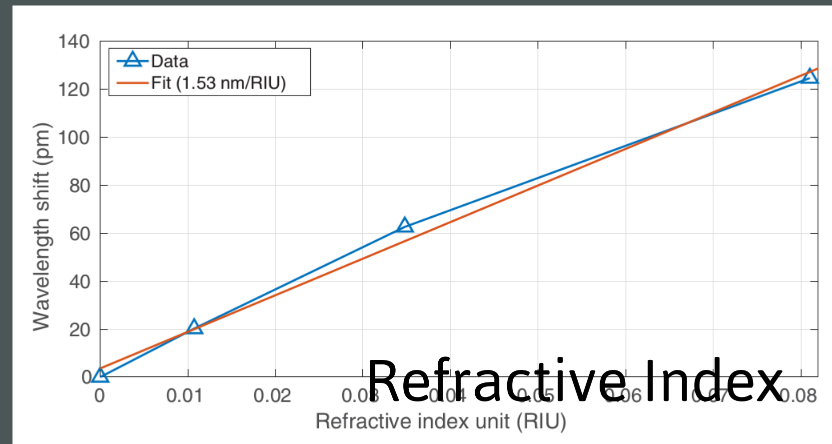
And lower refractive index difference

P. Tick, Opt. Lett. (1998)

Nanoparticles-doped fibers used as sensors

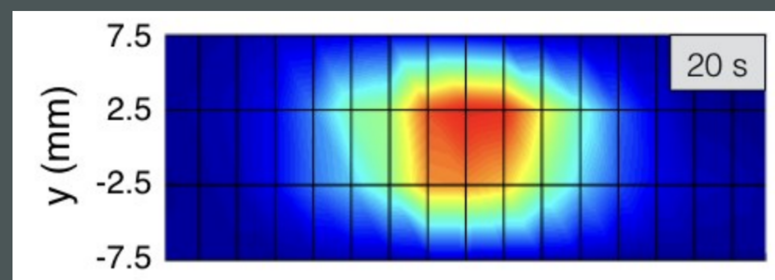
Strain → 3D-shape





Refractive Index

Temperature



NAZARBAYEV UNIVERSITY

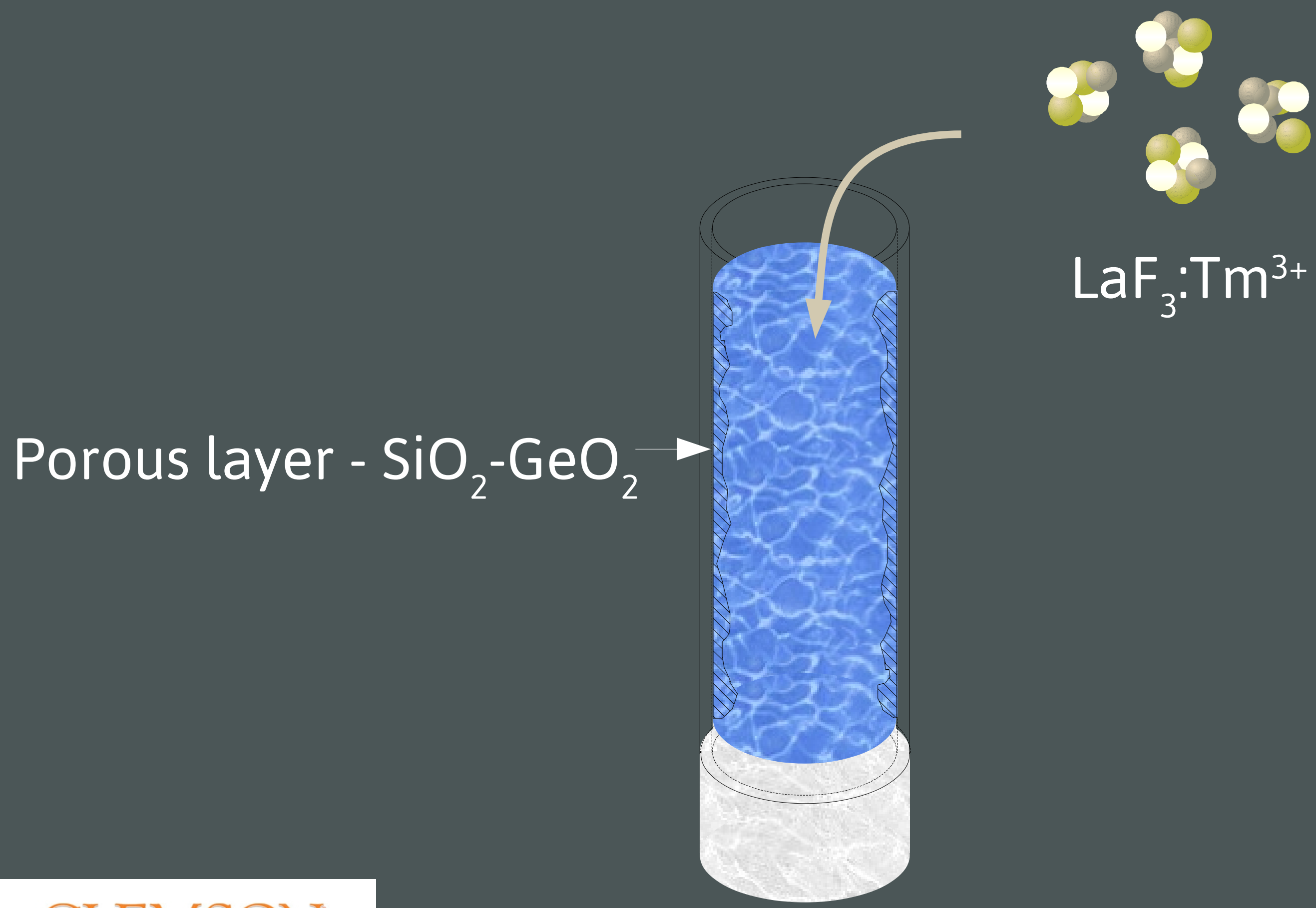
Daniele Tosi, Carlo Molardi

Opt. Lett. (2018), BioMed. Opt. Express (2019), Opt. Express (2019), J. Lightwave Technol. (2019)

Outline

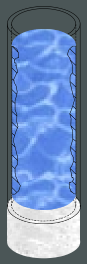
- Preparation of nanoparticles-doped fibers
- LaF_3:Tm^{3+} doped fiber
- Mg^{2+} and Er^{3+} doped fiber

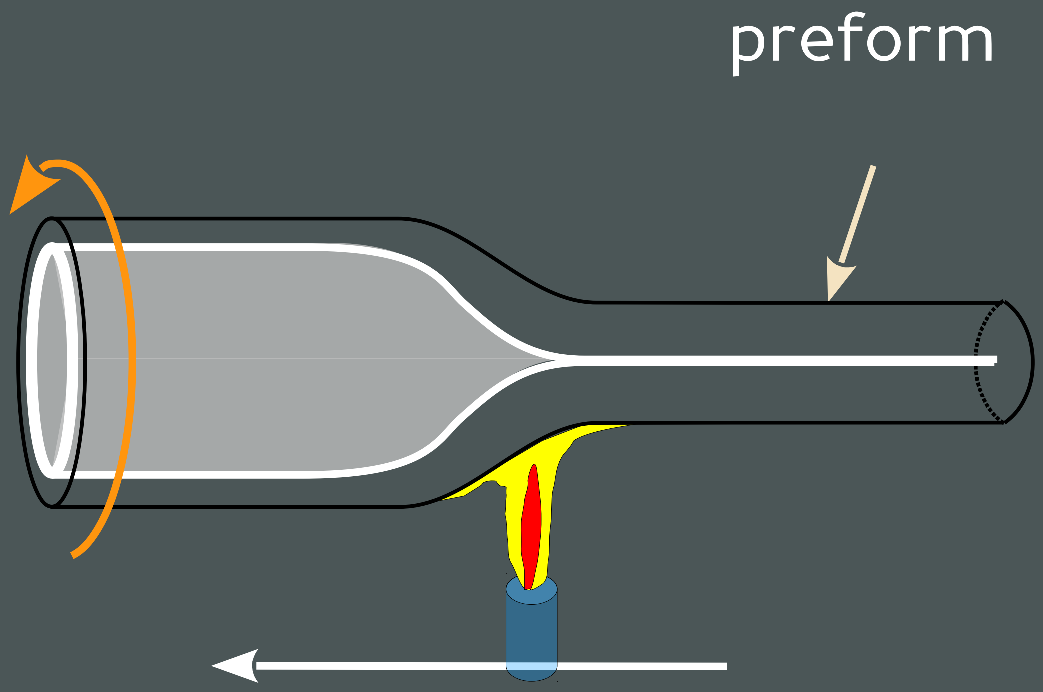
MCVD – solution doping step



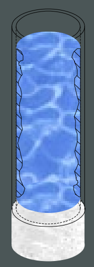
M. Vermillac et al., Opt. Mat. (2017)

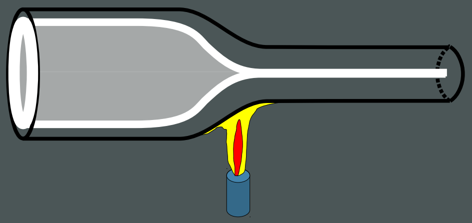
Collapsing stage

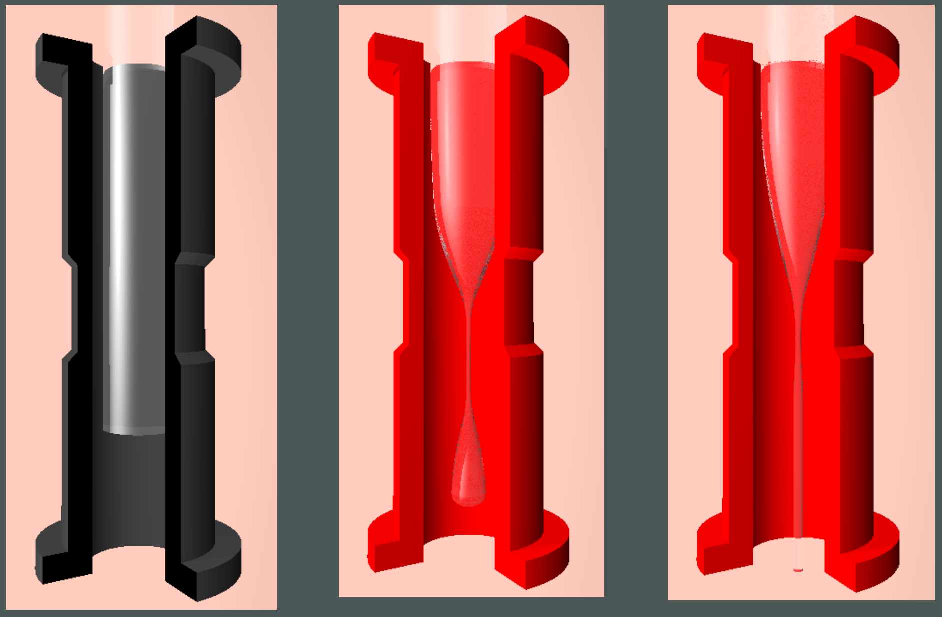




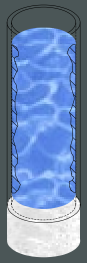
Drawing stage

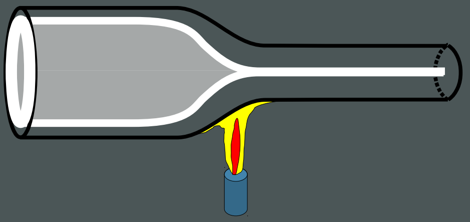


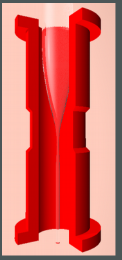


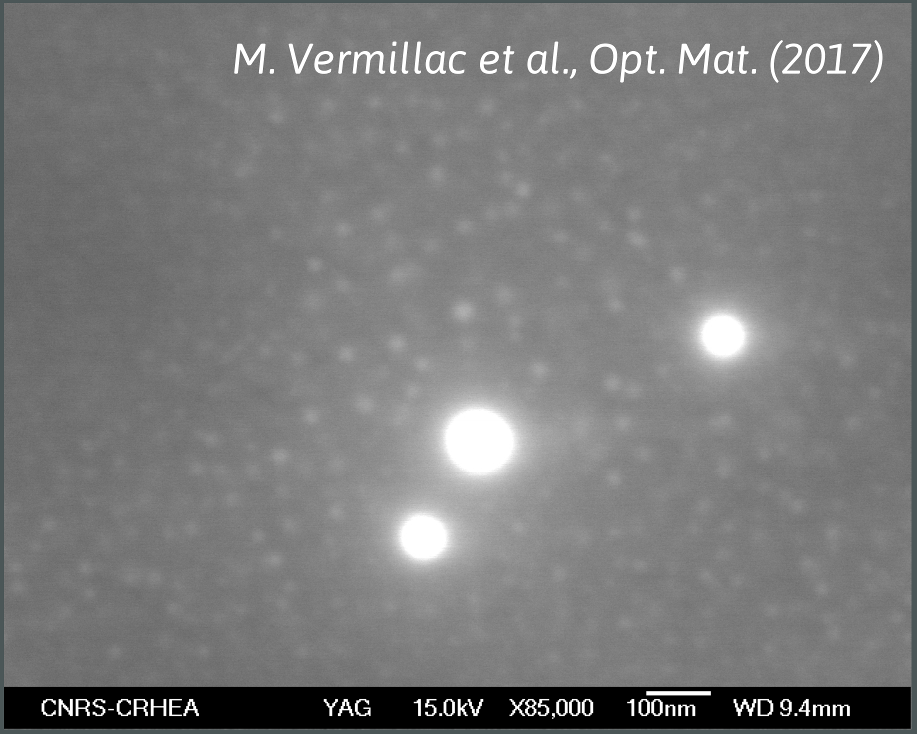


Nanoparticles in optical fiber

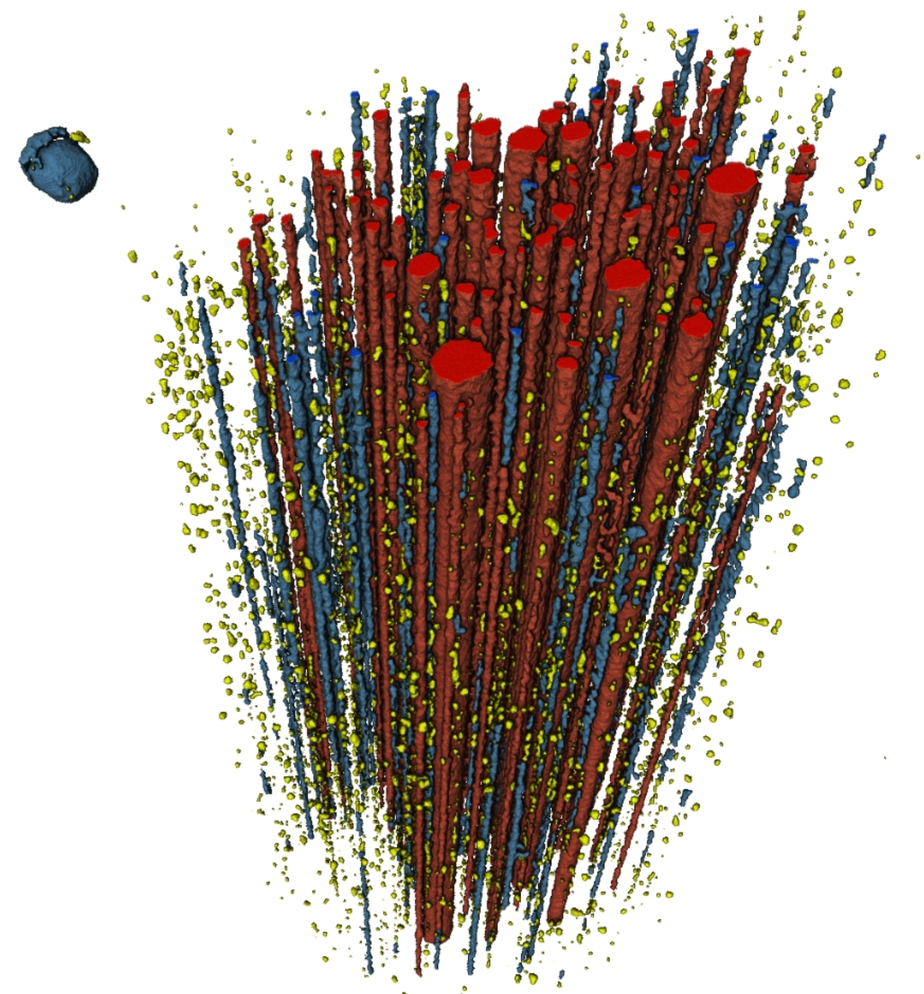








X-ray nanotomography

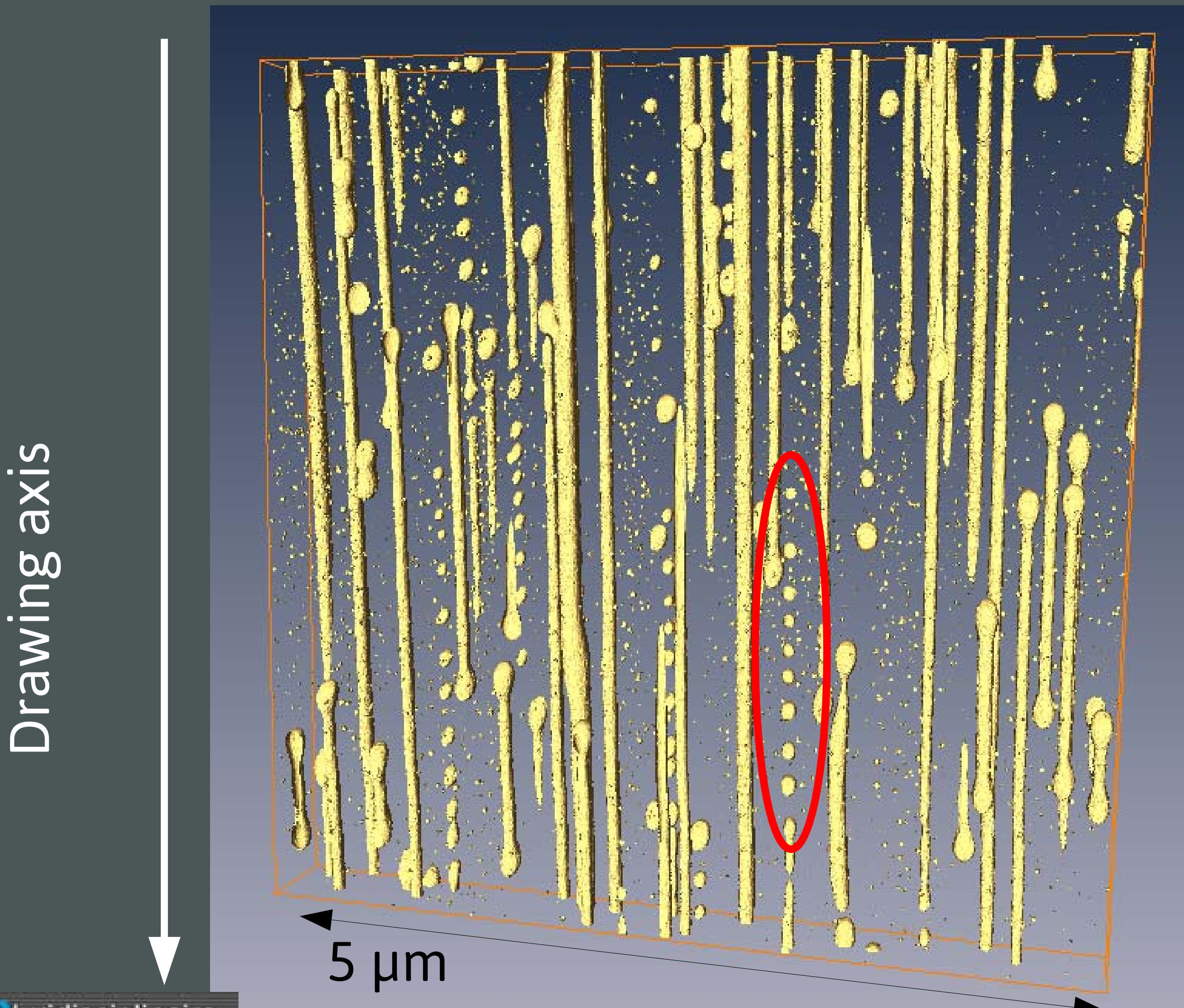


Core of a LaF_3:Tm-based fiber

Daniel Borschneck

M. Vermillac et al., Opt. Mat. (2018)

FIB/SEM tomography of fiber core

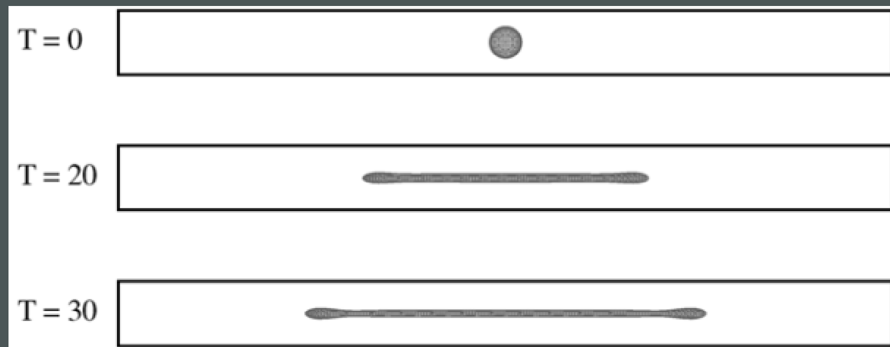


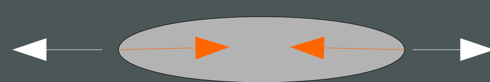
Centre Pluridisciplinaire de Microscopie électronique et de Microanalyse

Martiane Cabie

M. Vermillac et al., J. Am. Ceram. Soc. (2017)

Deformation of a drop under shear flow



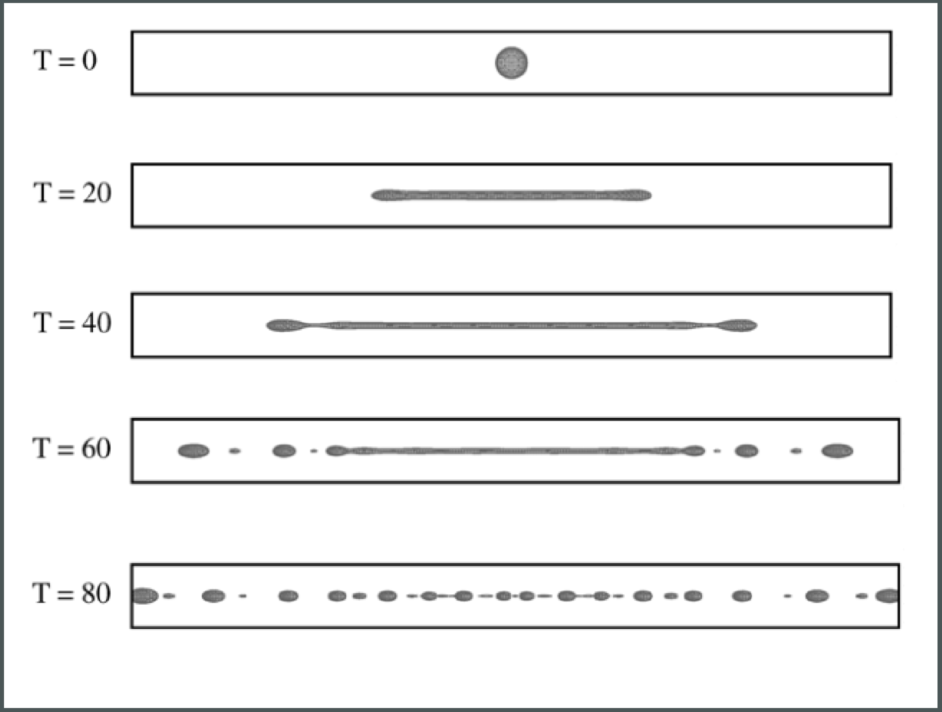


Flow Surface tension

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

J. Li & Y. Renardy, SIAM Rev. (2000)

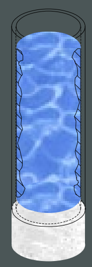
Deformation of a drop under shear flow

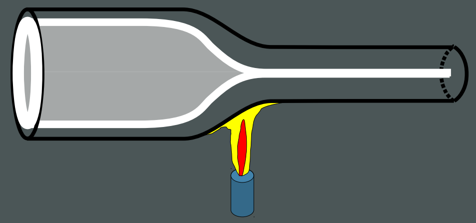


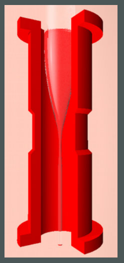
$Ca > Ca_C$ → Breakup of the drop

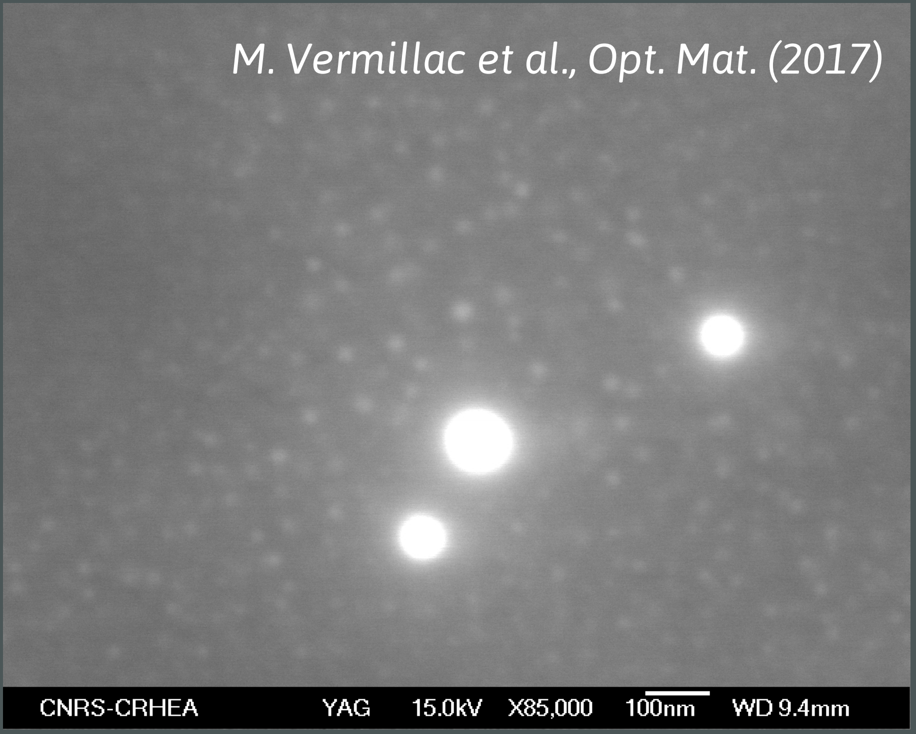
J. Li & Y. Renardy, SIAM Rev. (2000)

Nanoparticles in optical fiber



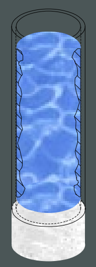


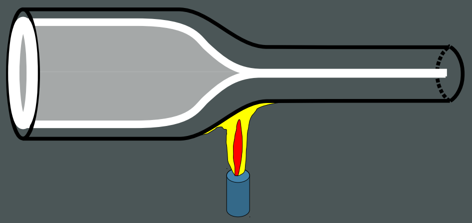


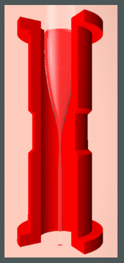


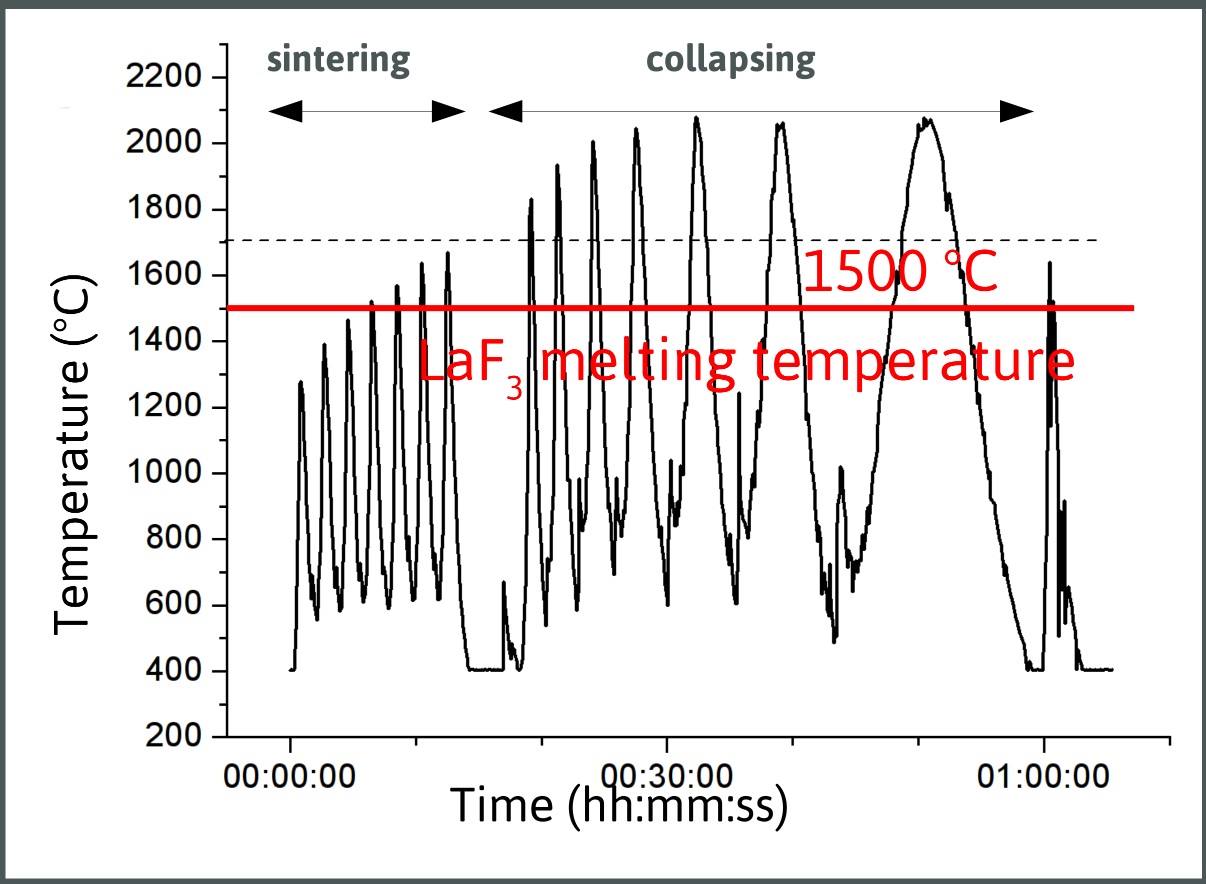
M. Vermillac et al., Opt. Mat. (2017)

Thermal treatments







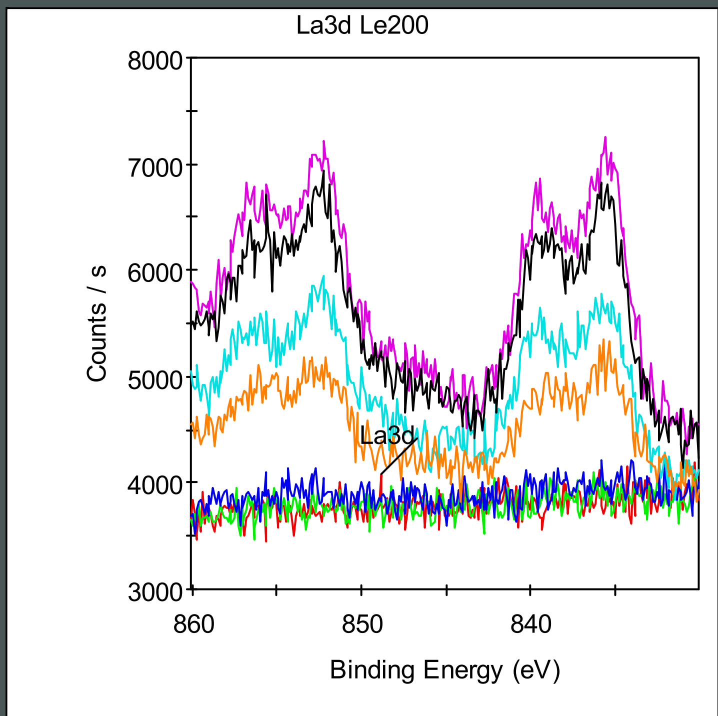


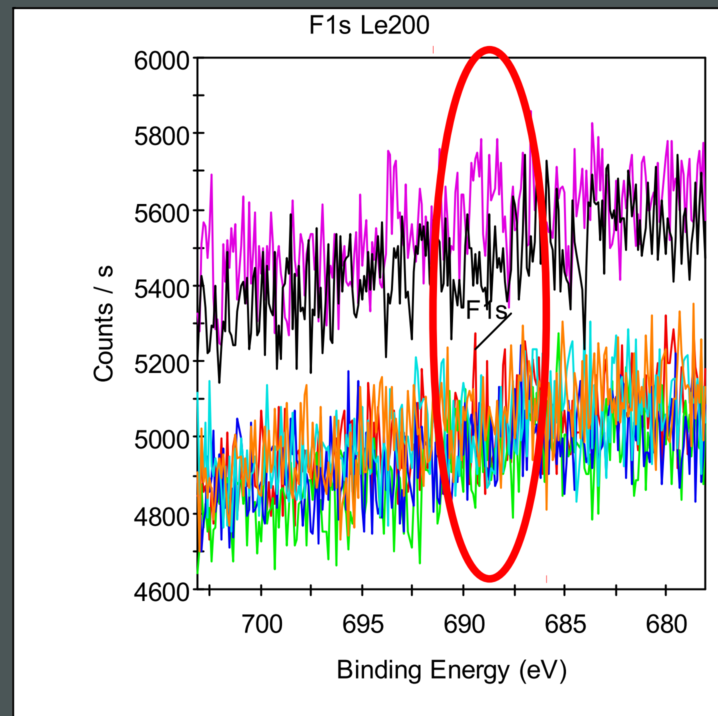
+

2000 °C

Evaporation of F

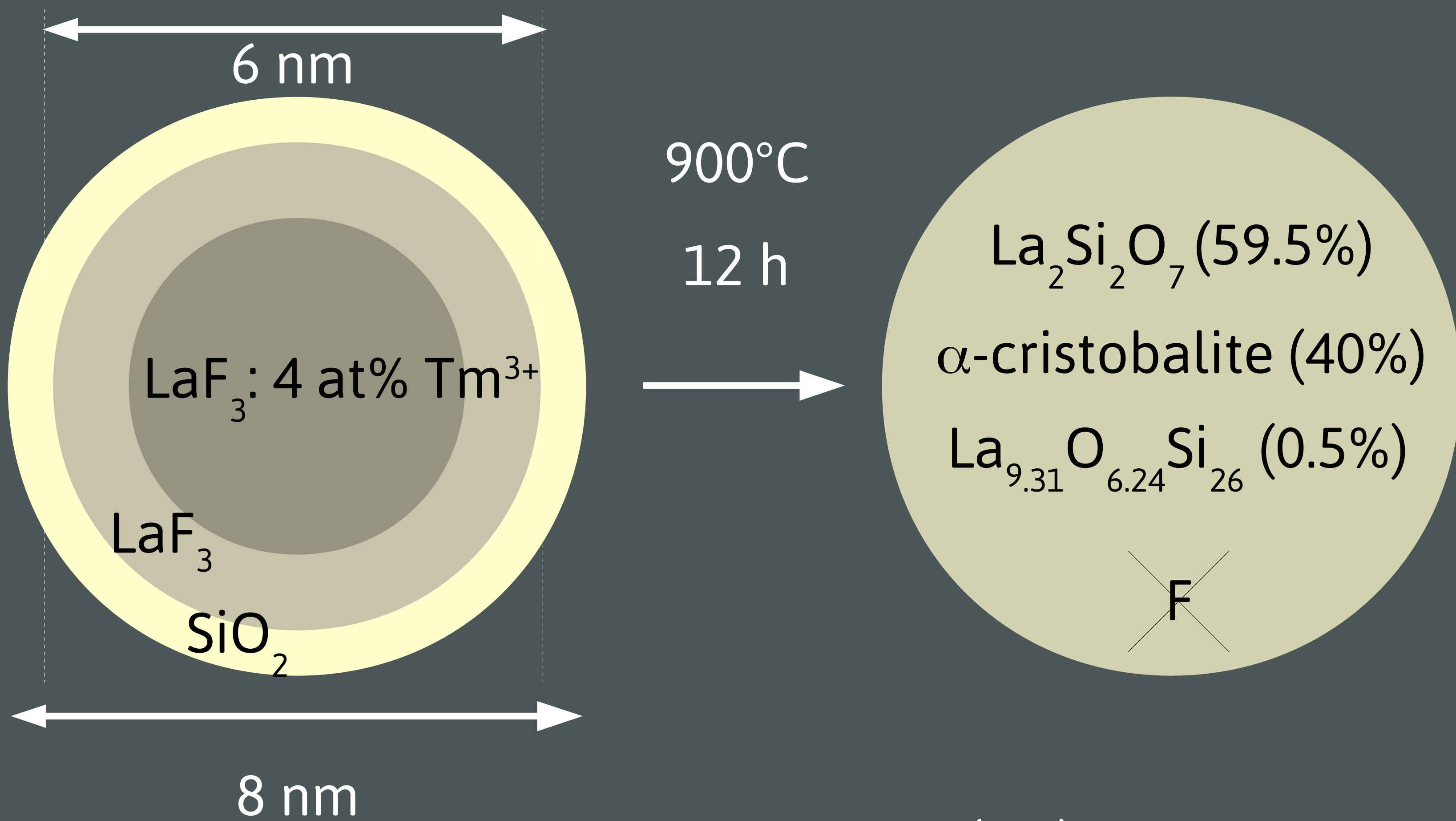
$$[La]_{measured} = 1 \text{ at.\%} \rightarrow [F]_{expected} = 3 \text{ at.\%}$$





F. Georgi

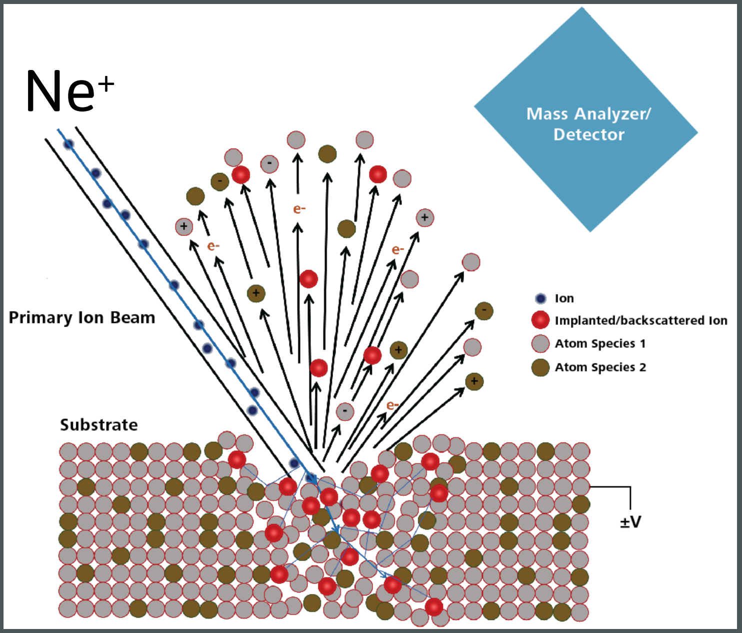
$LaF_3 \rightarrow La_2Si_2O_7$



$\tau_{1/e}(^3H_4) = 56 \pm 11\ \mu s$

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

Zeiss NanoFab – Secondary Ion Mass Spectrometer (SIMS)

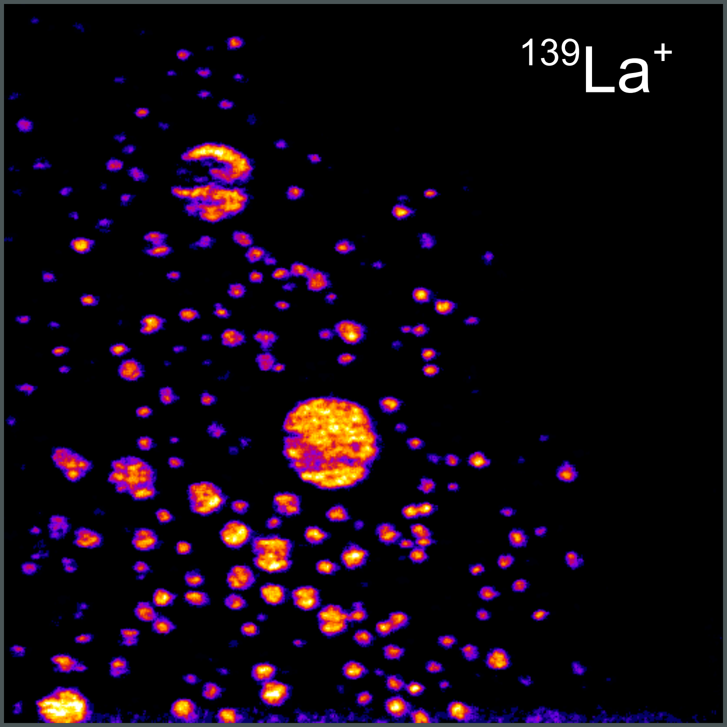


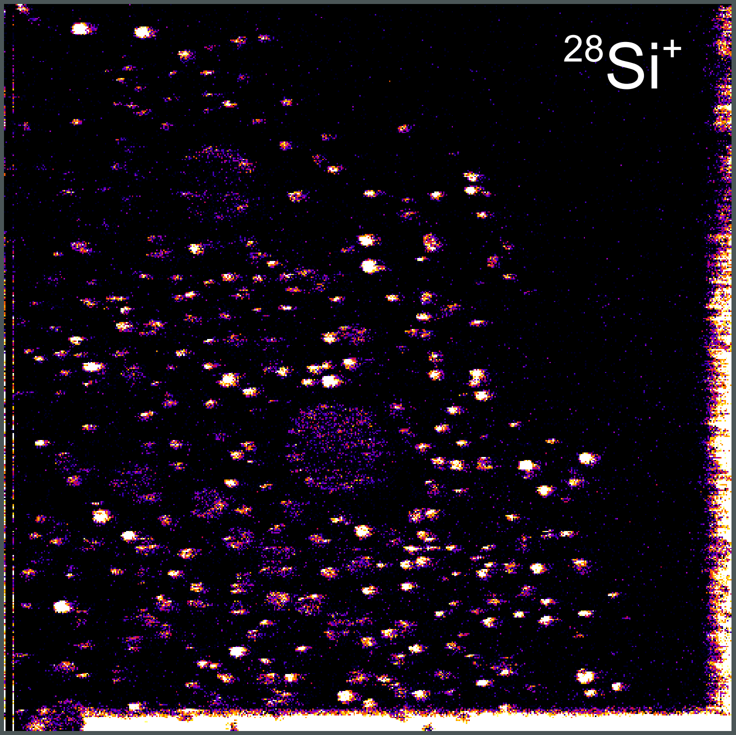
Chemical composition:
Spatial resolution < 15 nm with a 20 keV Neon beam

Particles ejected:

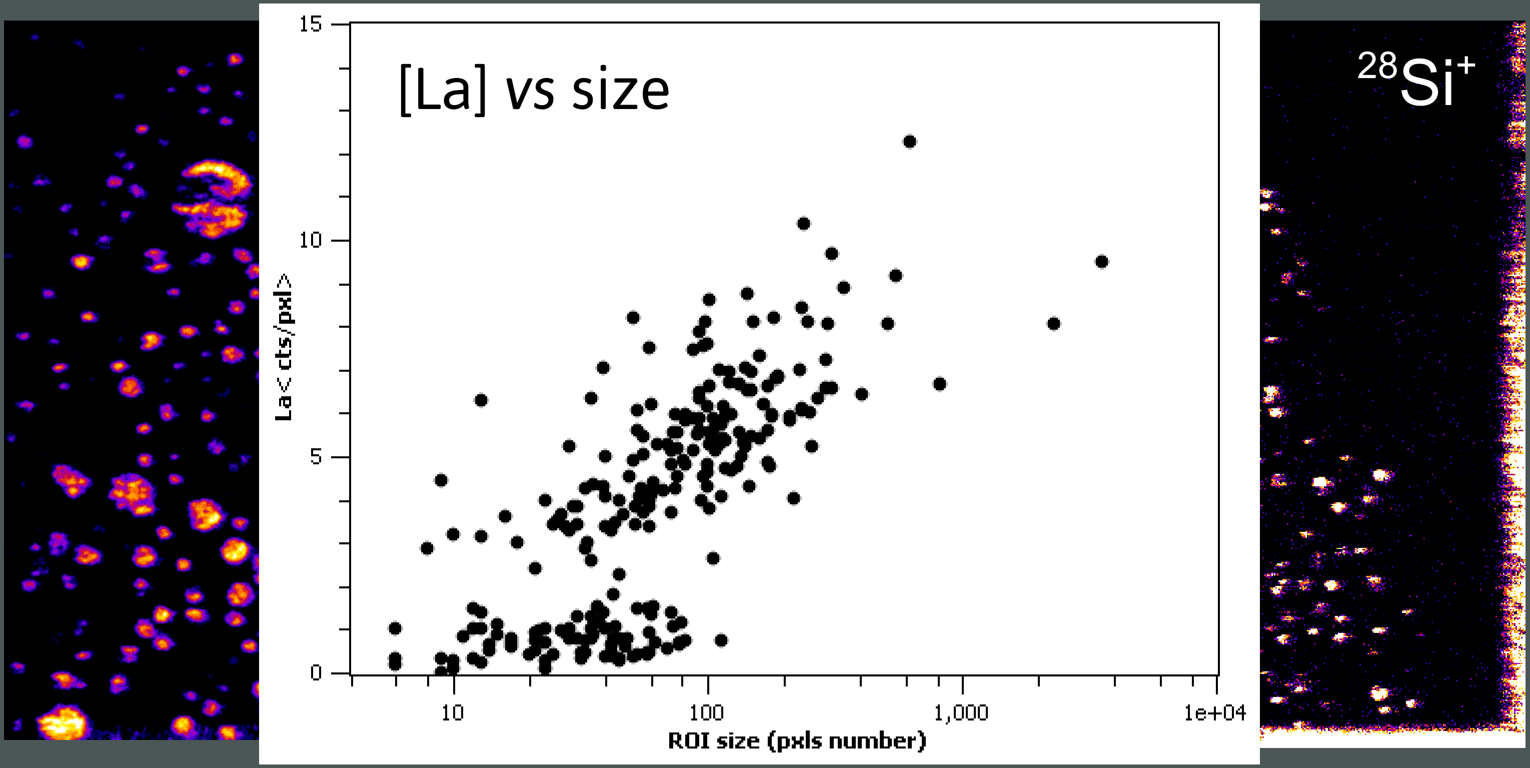
- Electrons
- Positive and negative secondary ions (SIs)
- Small molecular fragments and clusters
- Neutral species

Chemical composition of nanoparticles

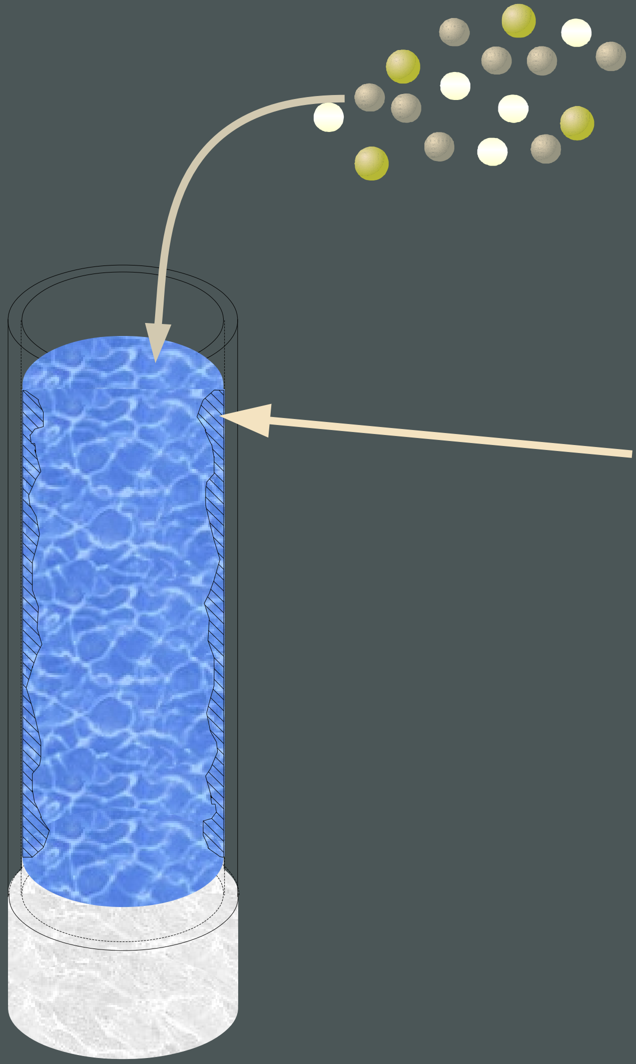




Chemical composition of nanoparticles



Er, Mg-doped optical fiber

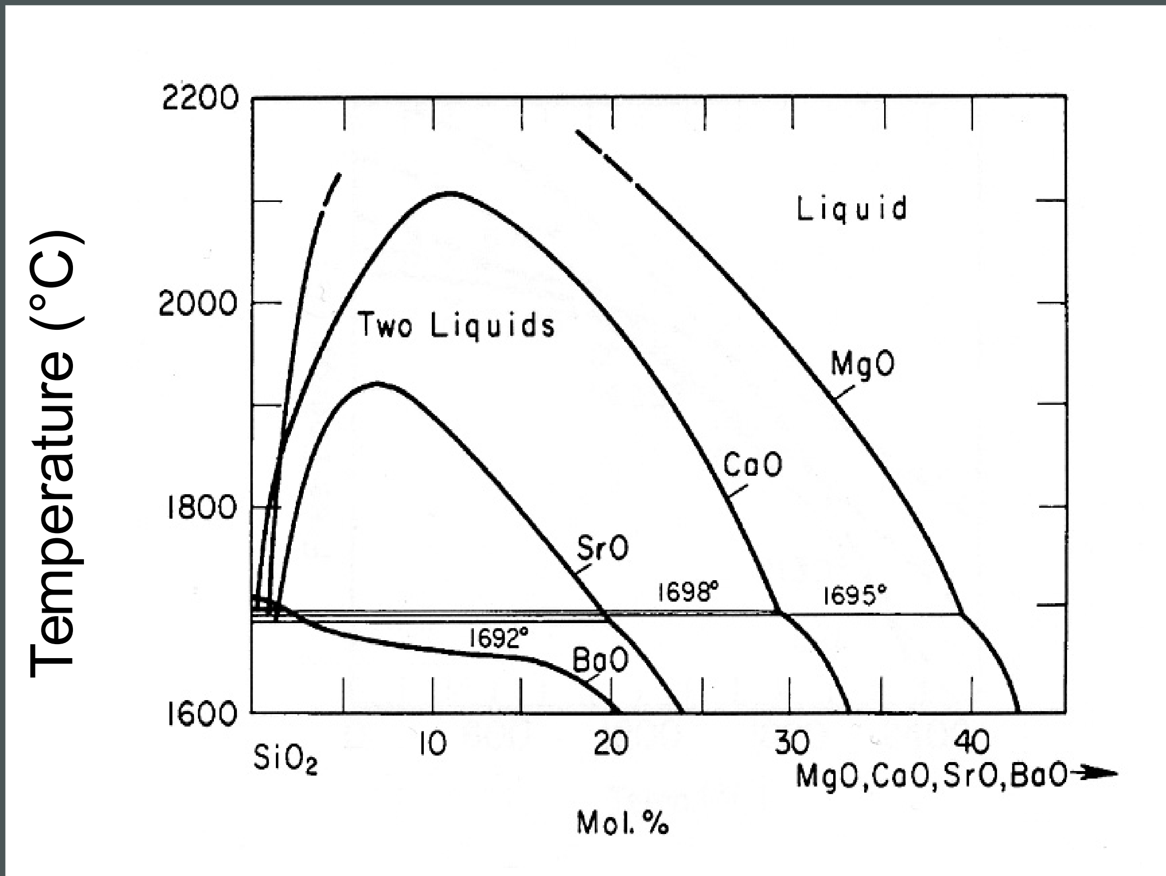


- $MgCl_2$ + $ErCl_3$ (ethanol)

- Porous layer :

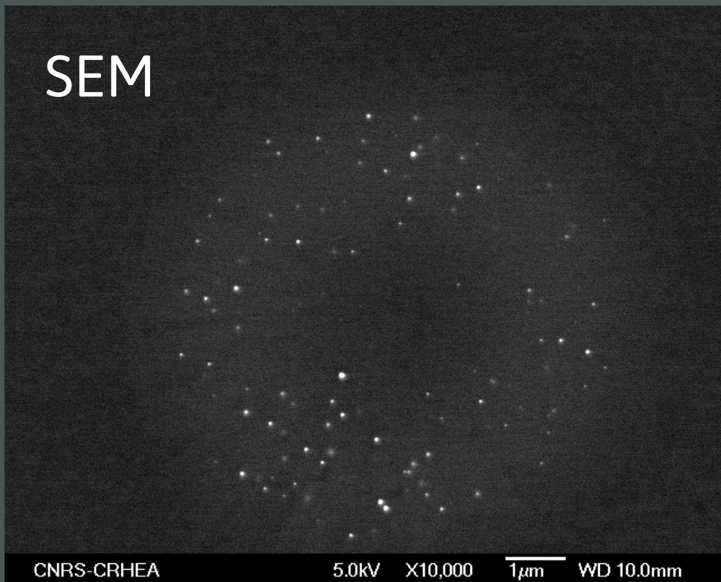
$SiO_2 + P_2O_5 + GeO_2$

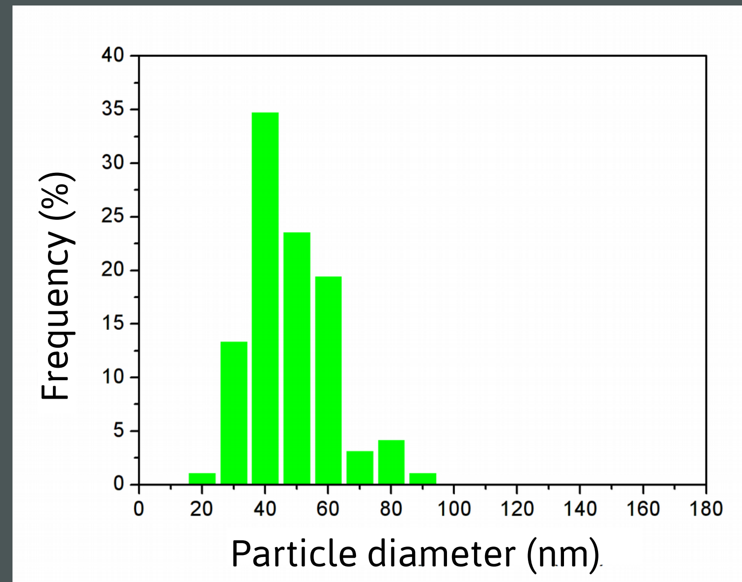
Alkaline earth ions phase separation



SiO_2 – MO (M=Mg, Ca, Sr) phase diagram

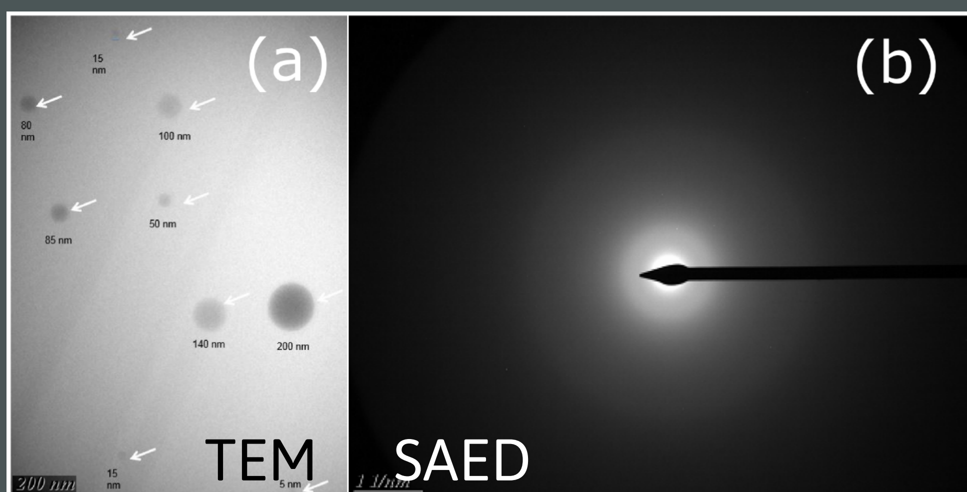
Nanoparticles in optical fiber





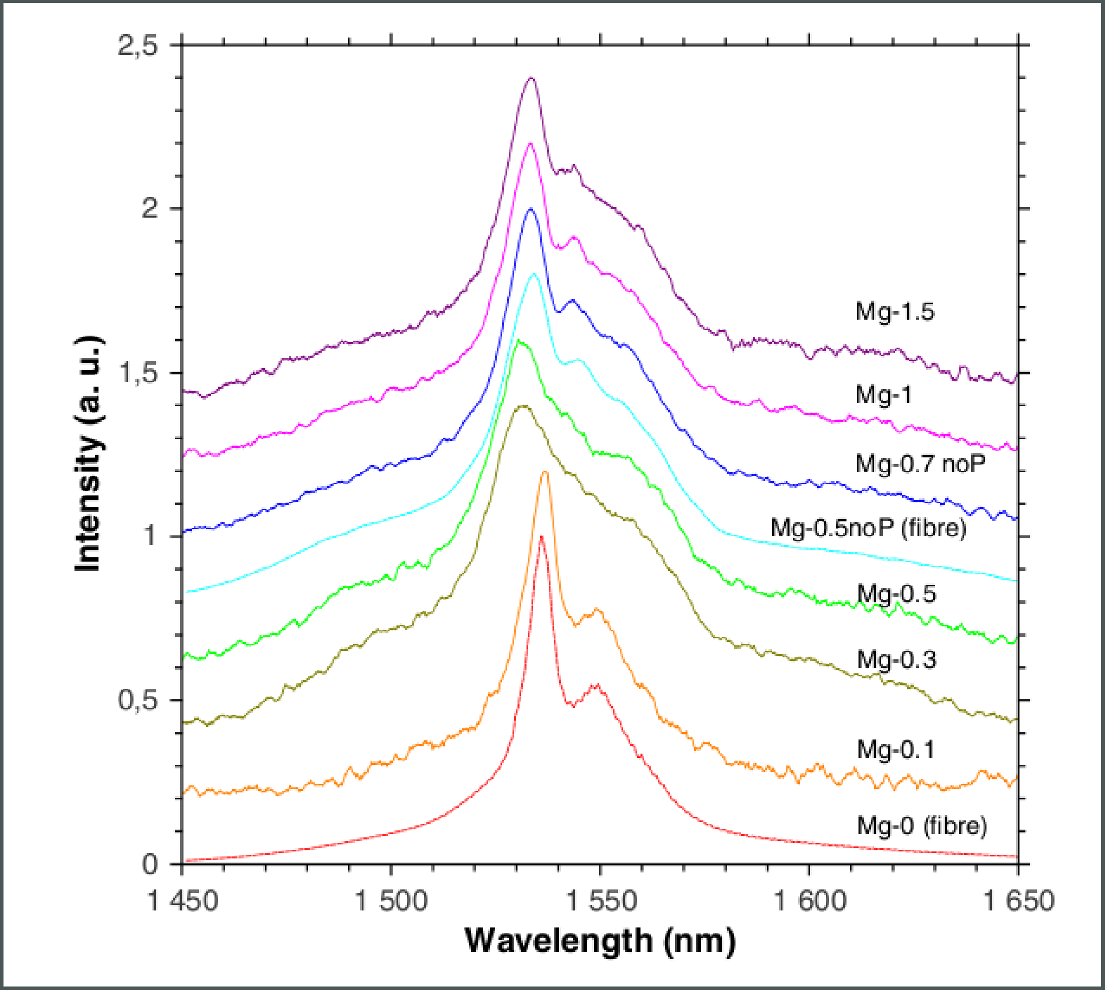
$[Mg]_{sol.}$ = 0.1 mol/l

$Ø_{mean}$: 50 nm



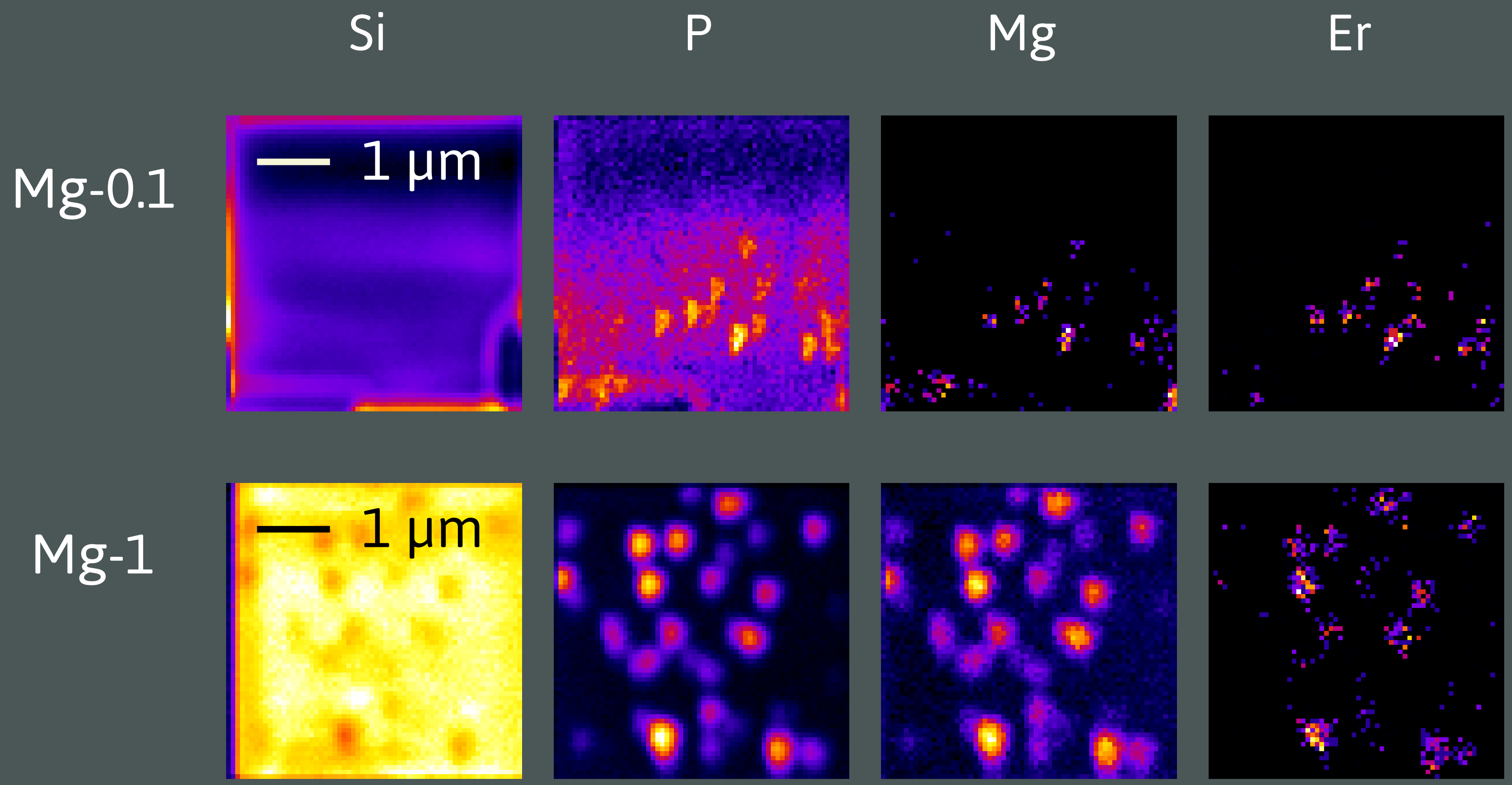
W. Blanc et al., J. Am. Ceram. Soc. (2011)

Er^{3+} fluorescence vs Mg concentration



F. D'Acapito et al., J. of Non-Cryst. Solids (2014)

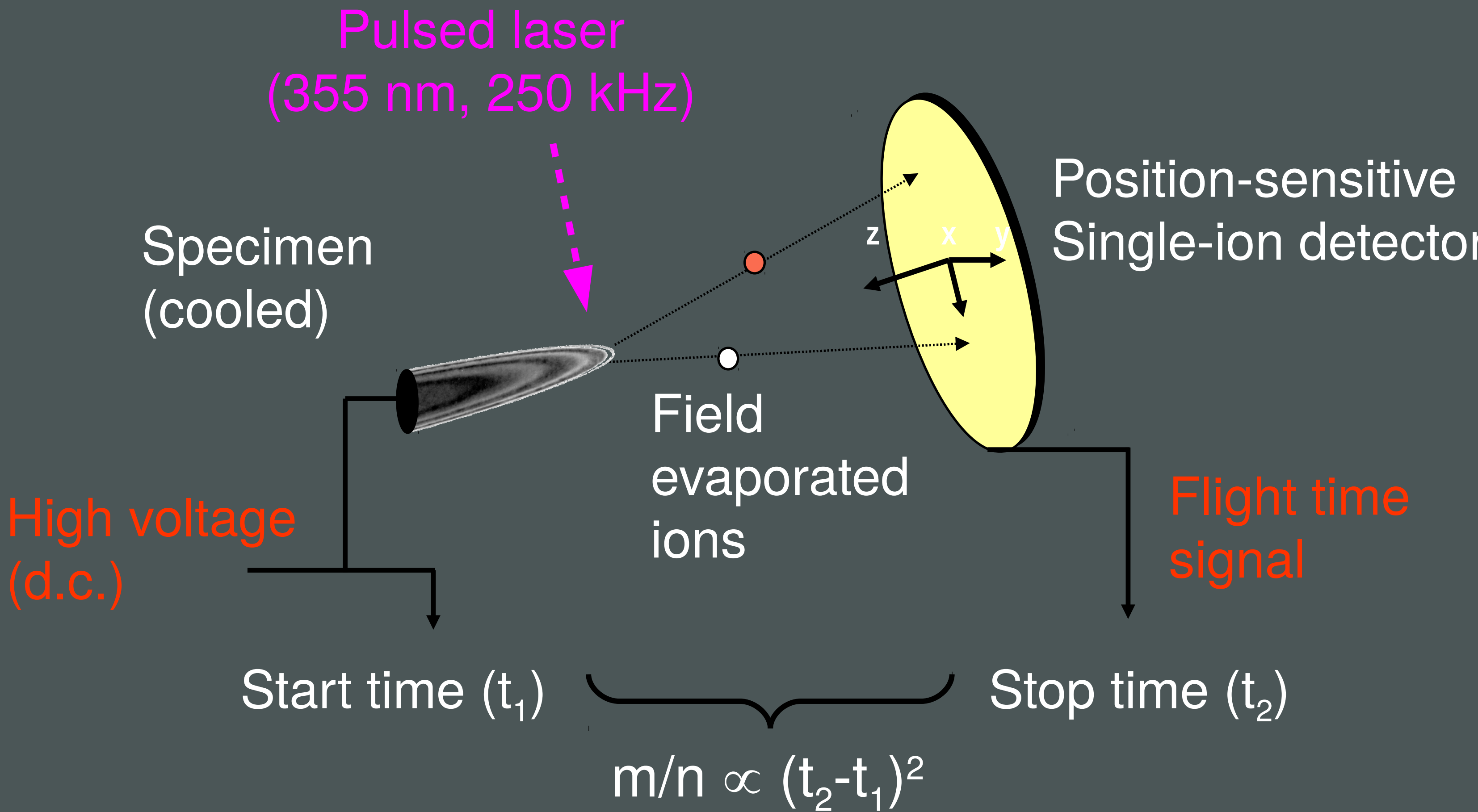
Particles composition by nanosims 50



- Spatial resolution: 60 nm
- Exact composition unknown

W. Blanc et al., Optical Materials Express (2012)

Atom Probe Tomography (APT)



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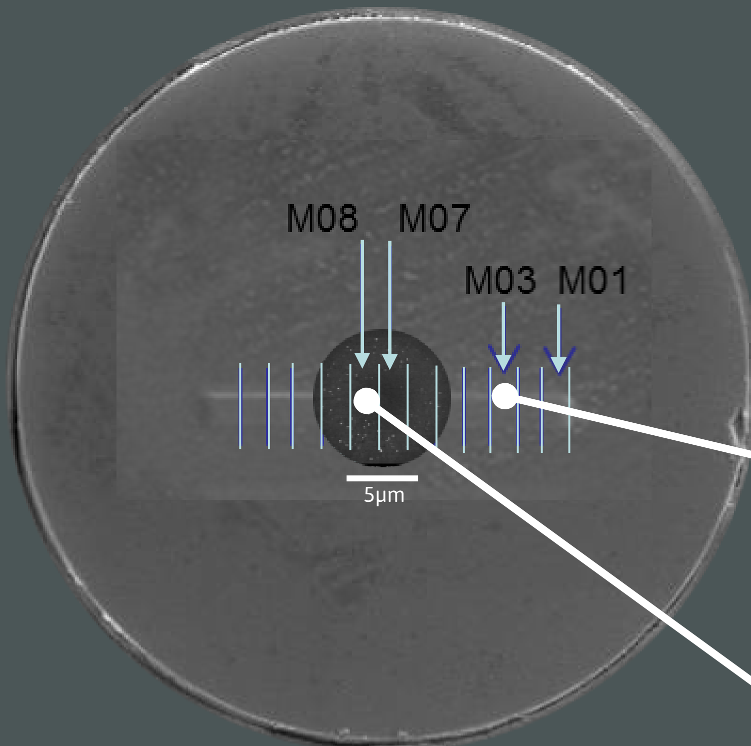
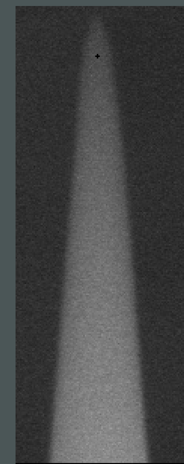
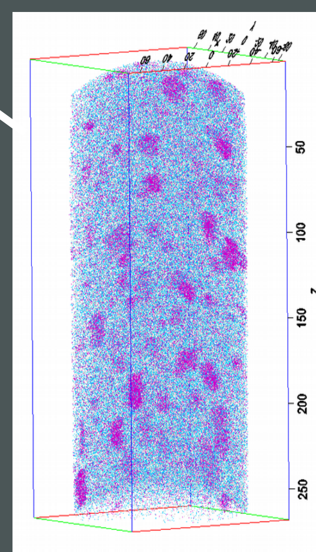
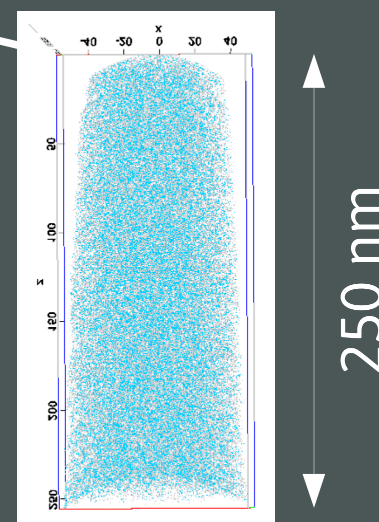
Atom Probe Tomography





Tip prepared by FIB

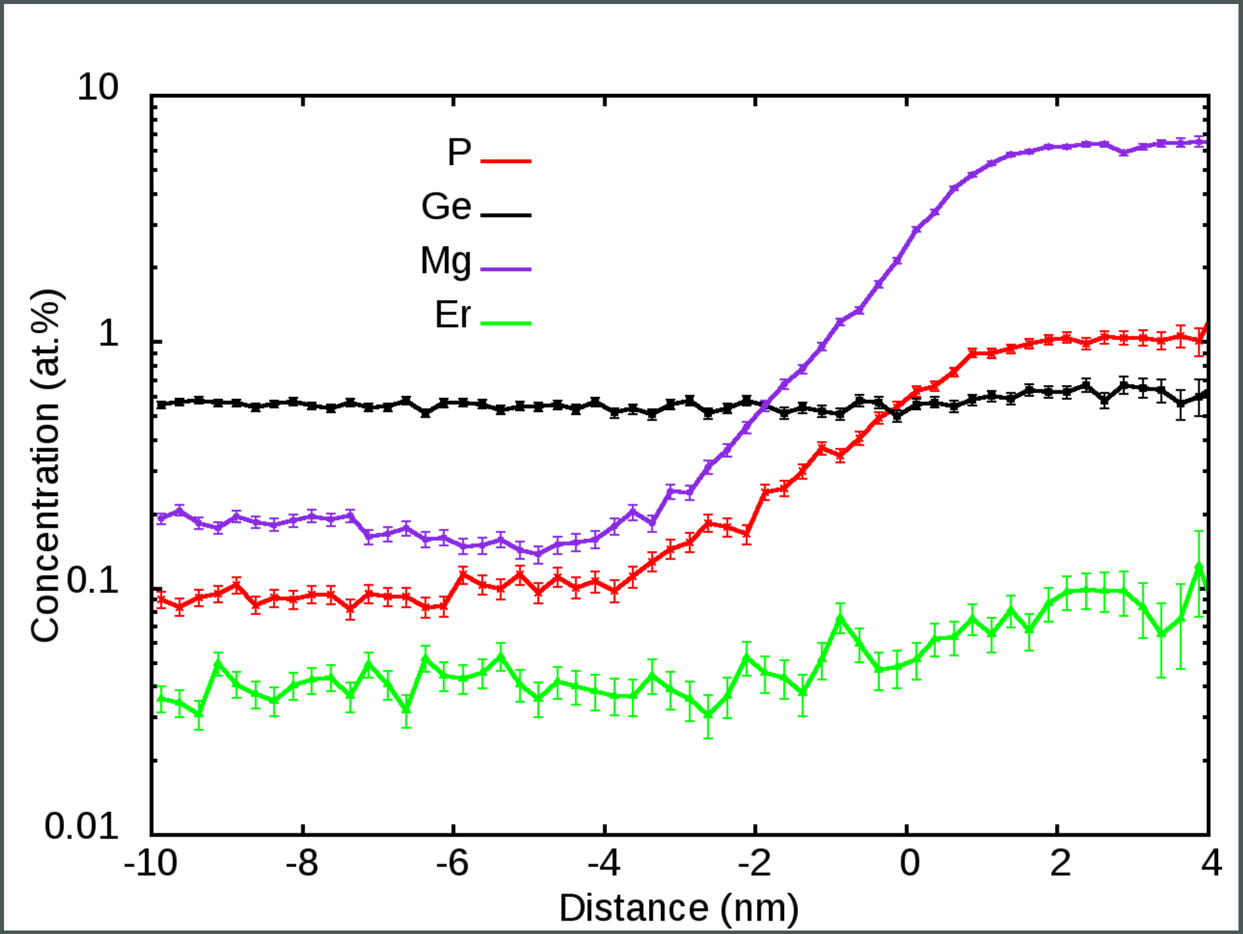




Si O Mg

W. Blanc et al., J. Phys. Chem. C (accepted)

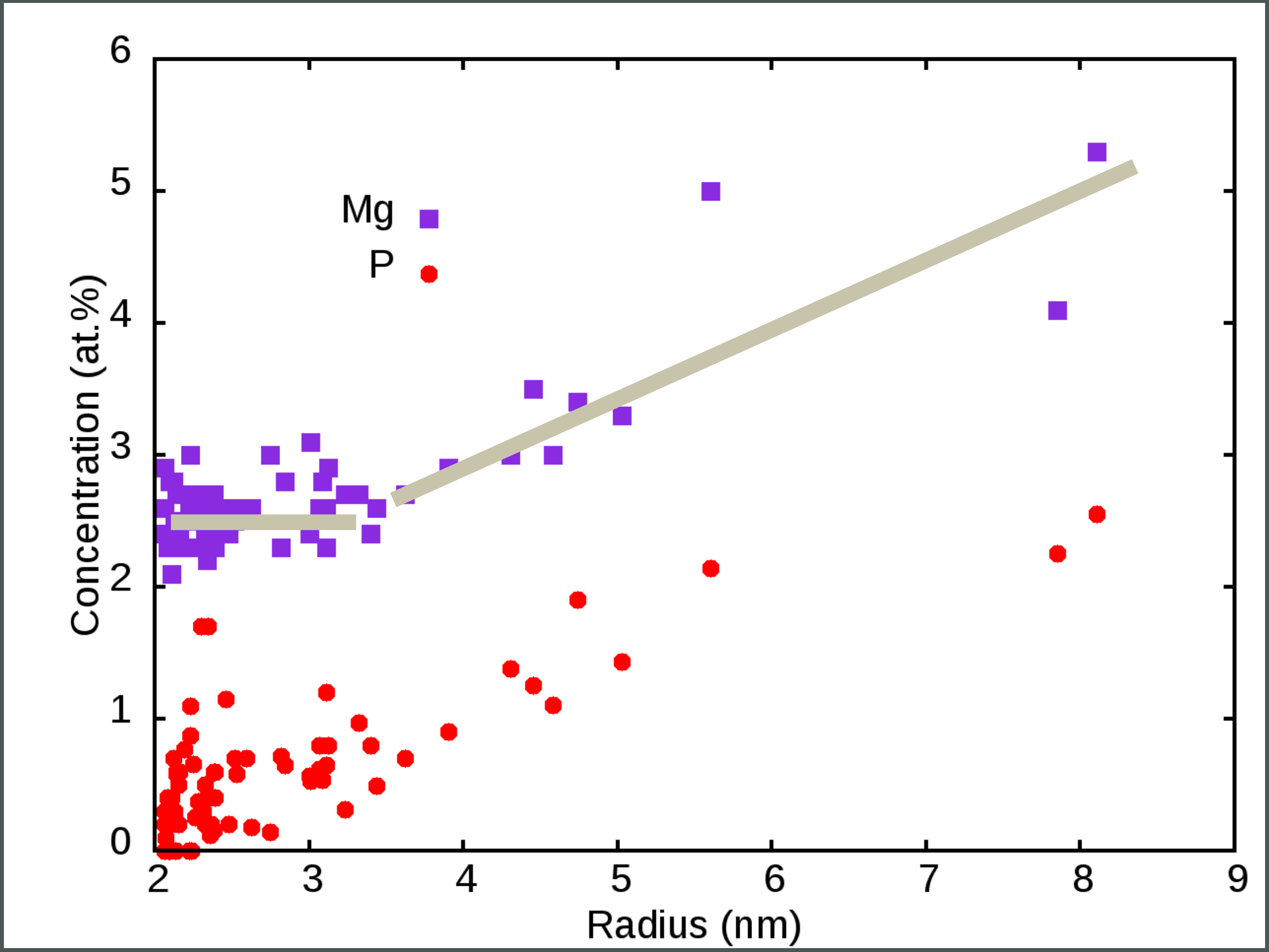
Transverse profile of nanoparticles



- Enrichment for P and Mg
- Clear uptake in Er

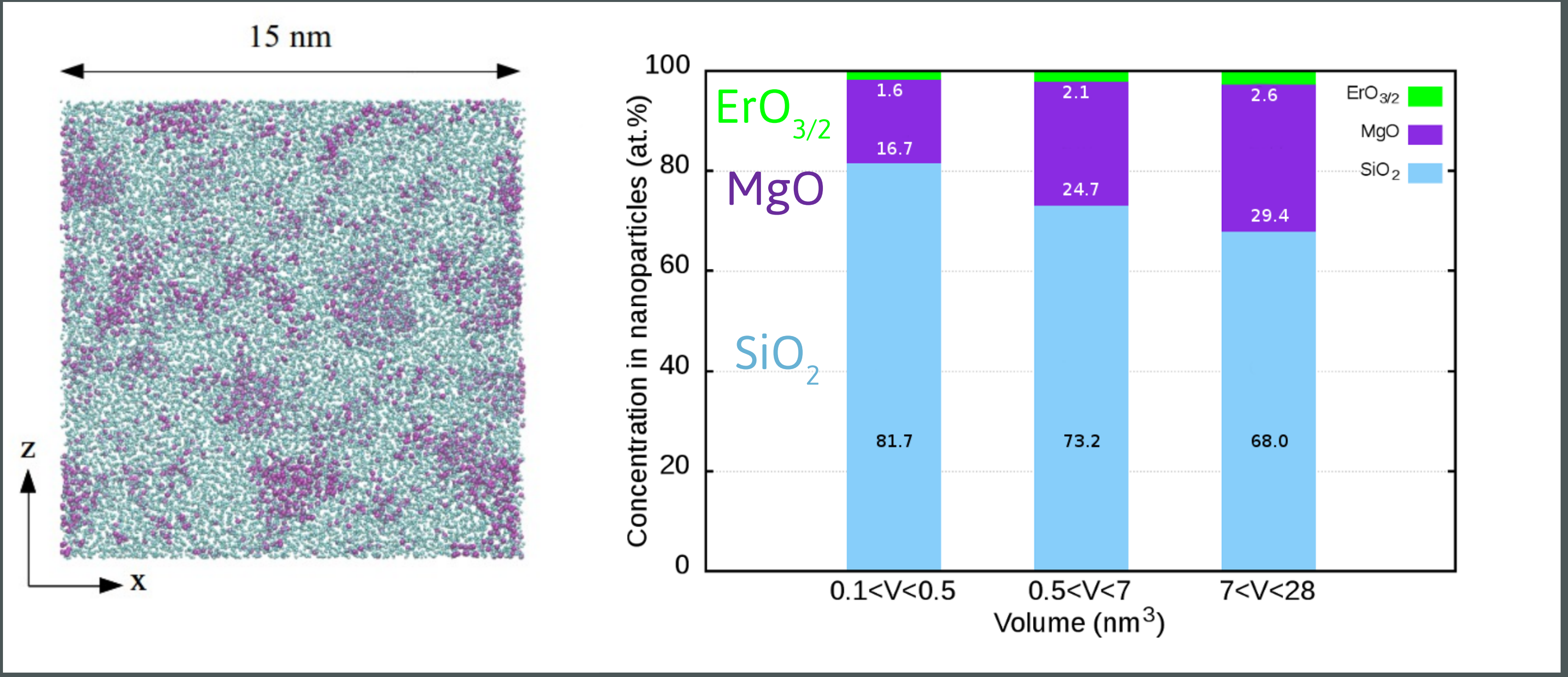
W. Blanc et al., J. Phys. Chem. C (accepted)

Composition *vs* Radius



W. Blanc et al., J. Phys. Chem. C (accepted)

Molecular dynamics simulations



$0.89SiO_2$-$0.10MgO$-$0.01ErO_{3/2}$

Stéphane Chaussedent

W. Blanc et al., J. Phys. Chem. C (accepted)

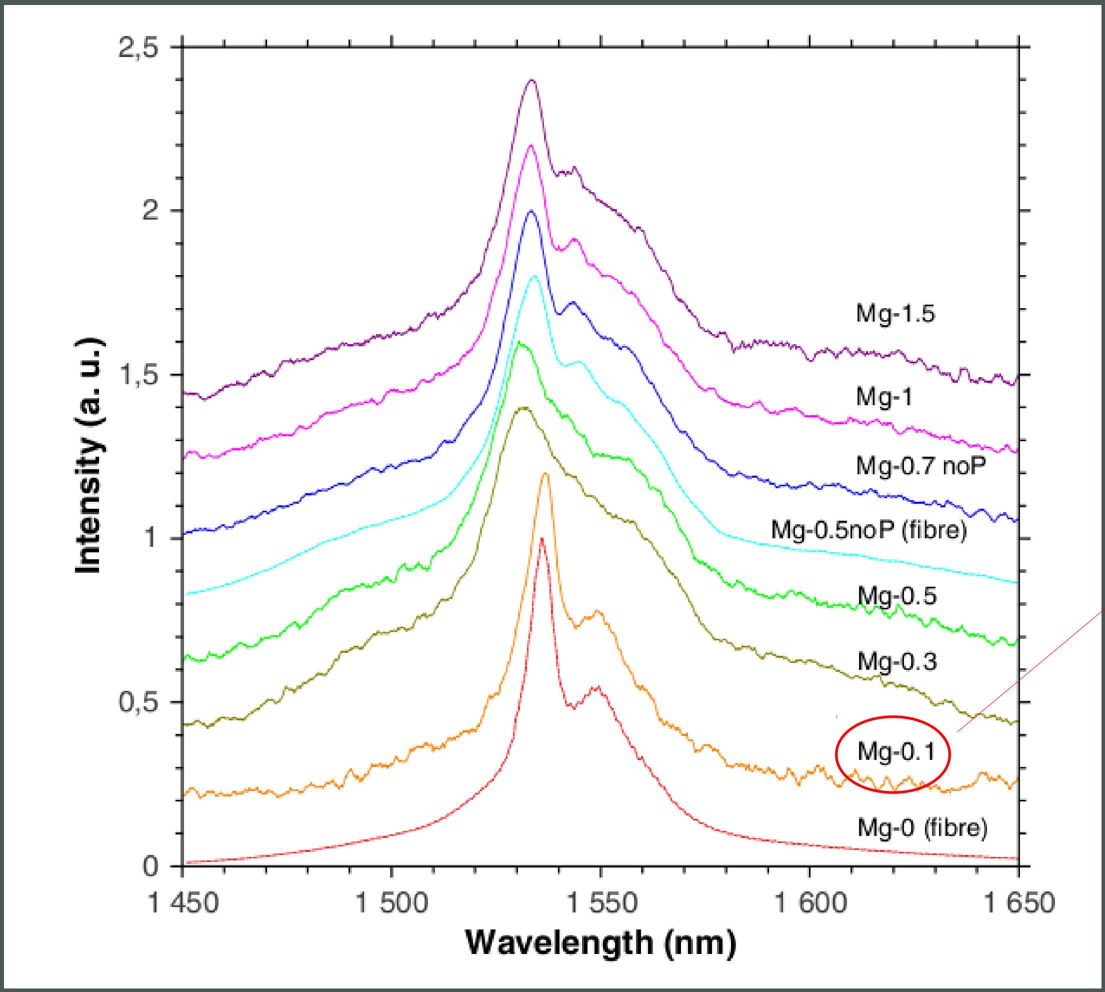
Er^{3+} environment

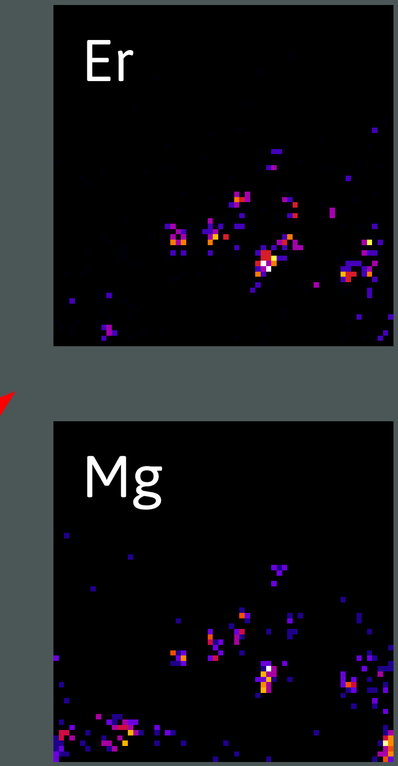
NP volume V (nm^3)	Er^{3+} coordination: O	Si	Mg	Er
0.1<V<0.5	6.3	6.9	1.9	0.2
0.5<V<7	6.6	6.7	3.3	0.3
7<V<28	6.7	6.5	4.2	0.5

First shell (O) — Second shell (Si, Mg, Er)

W. Blanc et al., J. Phys. Chem. C (accepted)

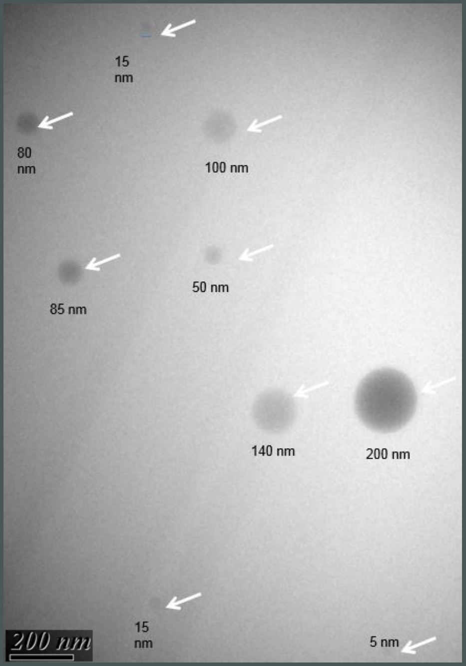
Er^{3+} fluorescence vs Mg concentration

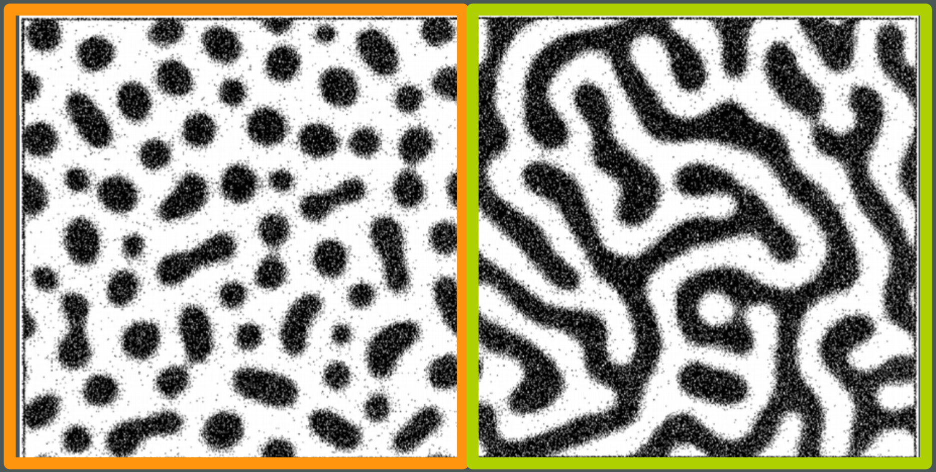


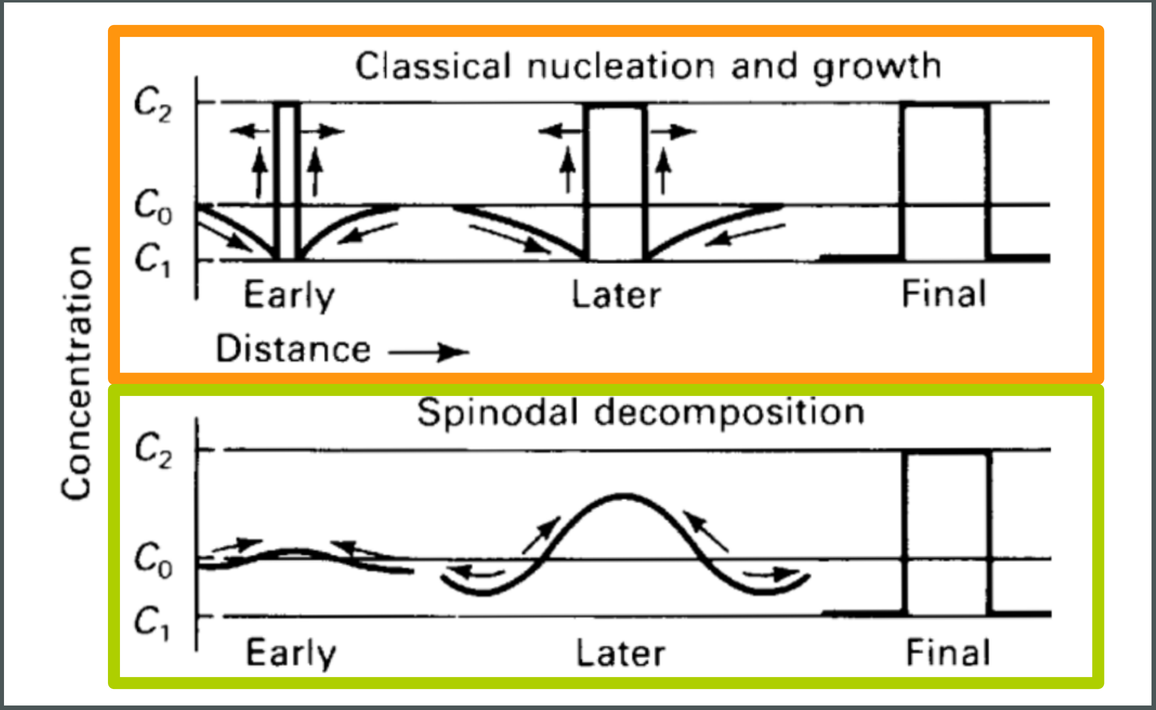


F. D'Acapito et al., J. of Non-Cryst. Solids (2014)

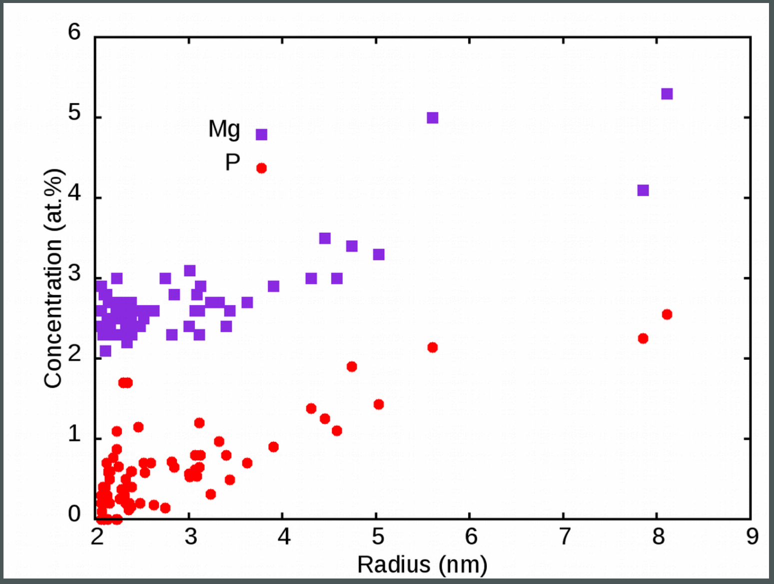
Classical Nucleation Theory (CNT) *vs.* Spinodal decomposition

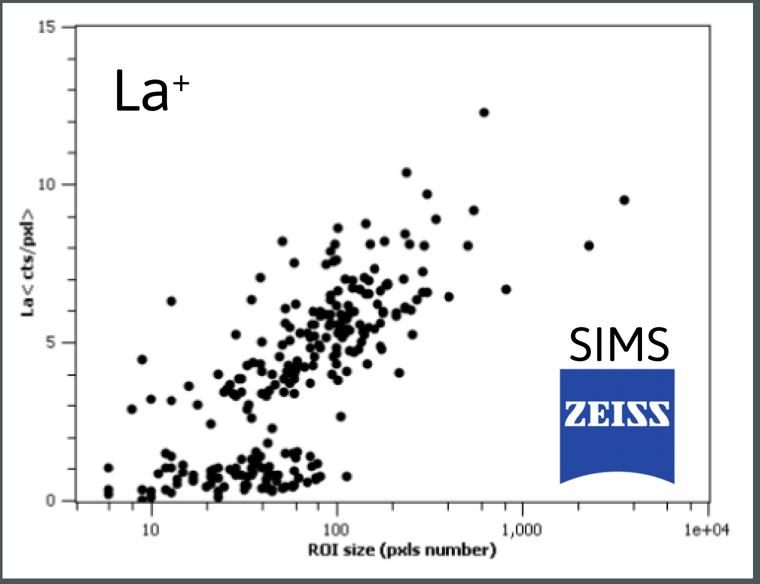


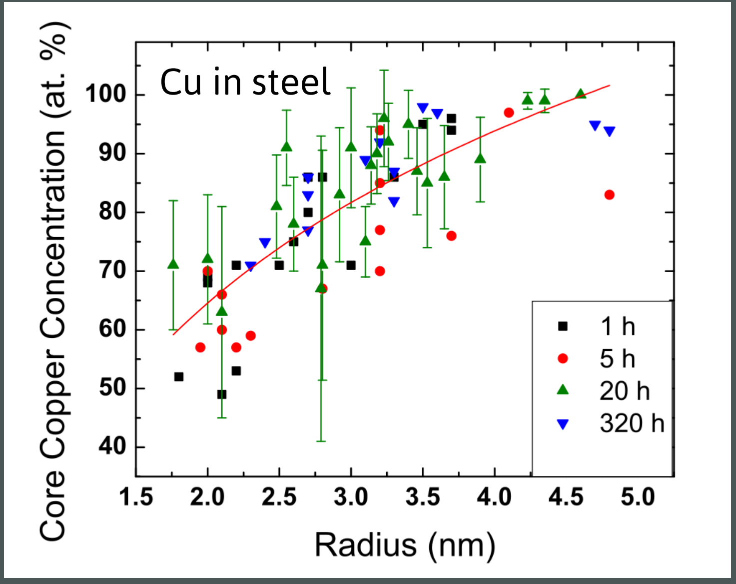


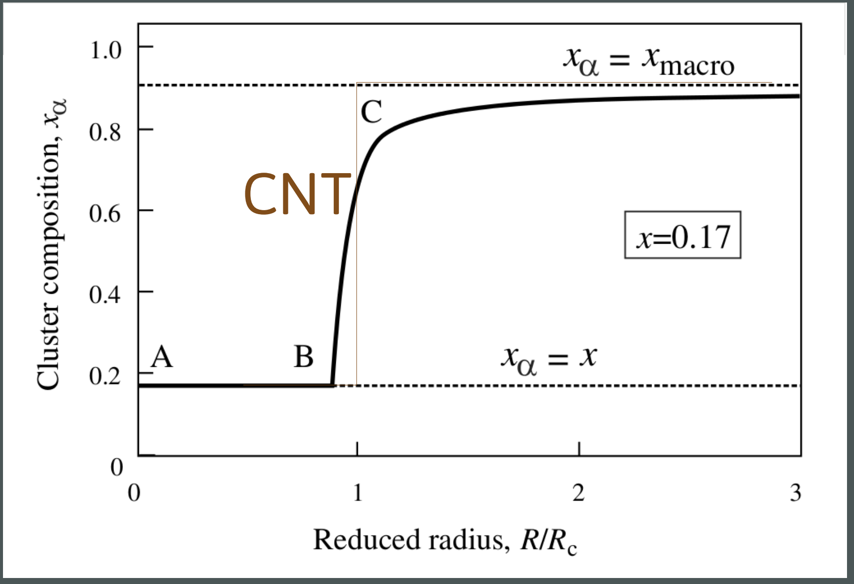


Composition *vs* Radius









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Conclusion

- Nanoparticles method allows to taylor RE luminescent properties
- APT and NanoSIMS allow to measure composition at nm-scale
- Nanoparticles composition depends on their sizes

→ Luminescence refractive index *vs.* size ?

→ Growth path: from amorphous to crystal