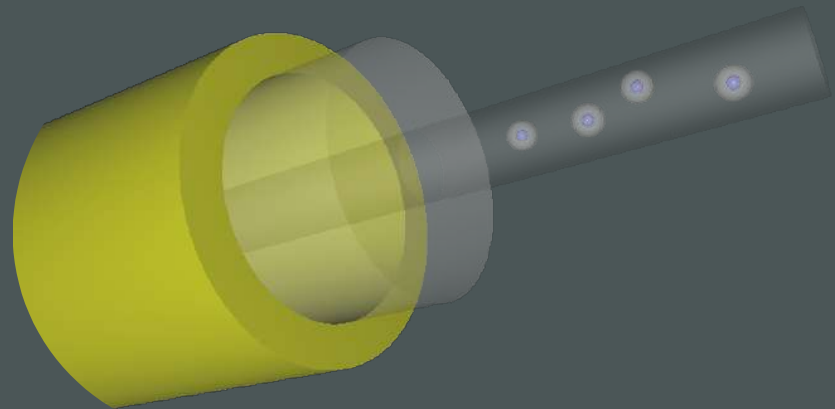


# FORMATION ET APPLICATIONS DES NANOPARTICULES DANS LES FIBRES OPTIQUES À BASE DE SILICE

WILFRIED BLANC, BERNARD DUSSARDIER  
LPMC – NICE

EKATERINA BUROV, ALAIN PASTOURET  
PRYSMIAN GROUP



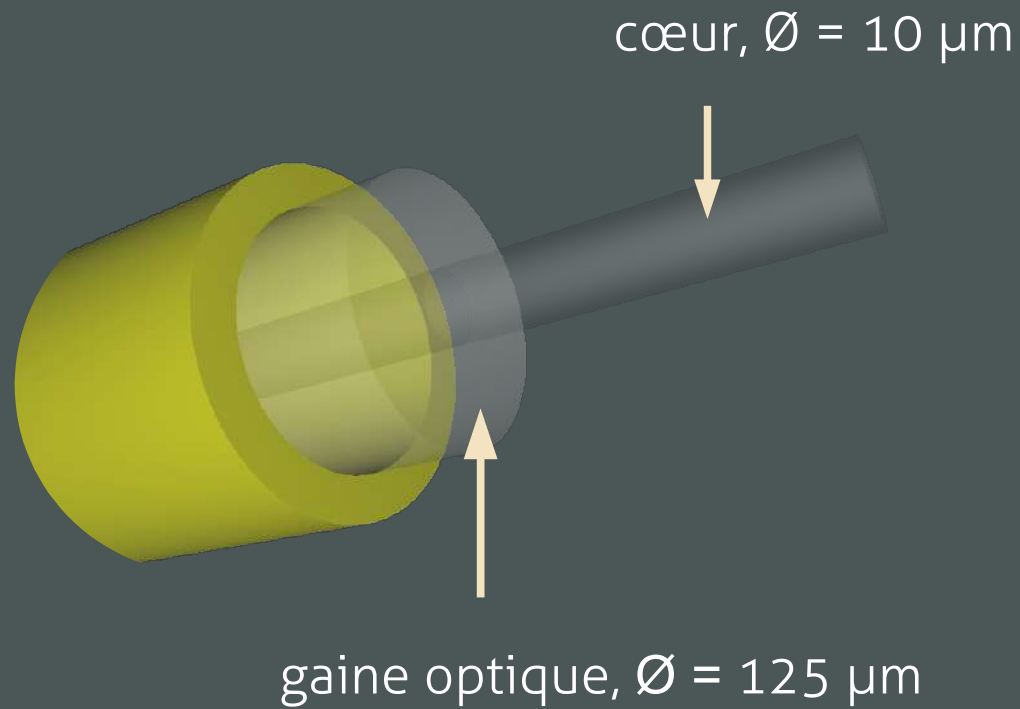
# PLAN

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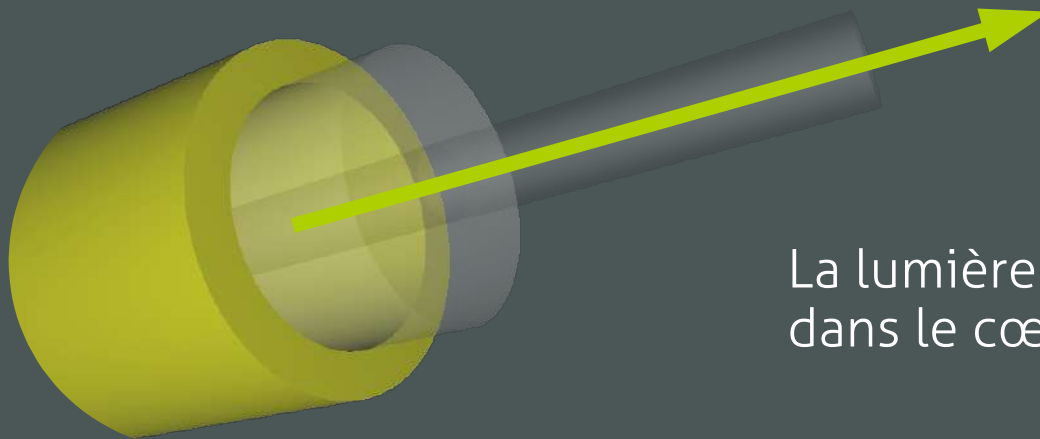
- Généralités sur les fibres optiques
- Silice: avantages / limitations
- Nanoparticules dans les fibres
  - Procédés de fabrication
  - Variétés des nanoparticules
  - Applications
- Conclusion

# FIBRE OPTIQUE À BASE DE SILICE

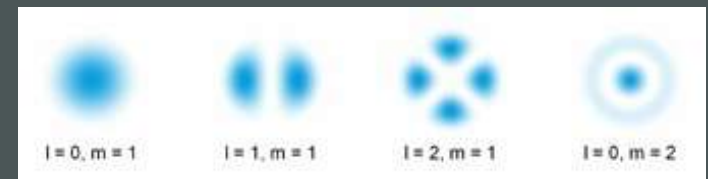
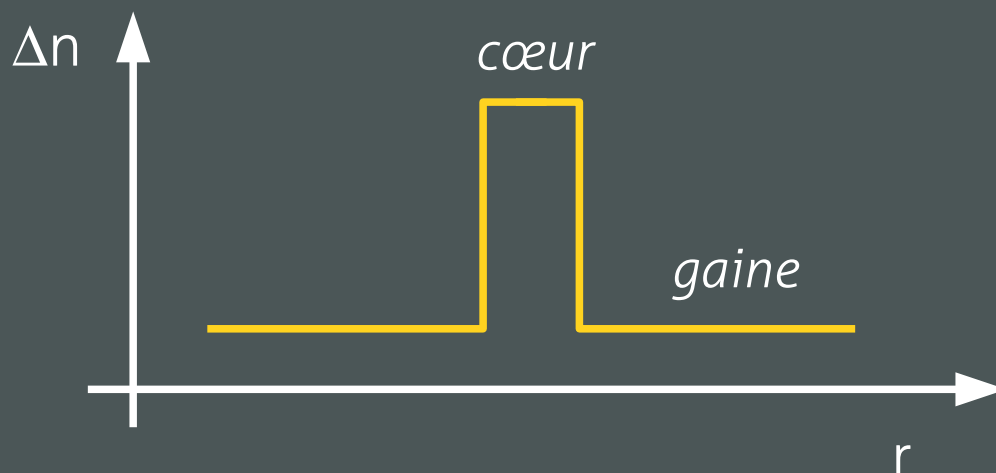
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# FIBRE OPTIQUE À BASE DE SILICE

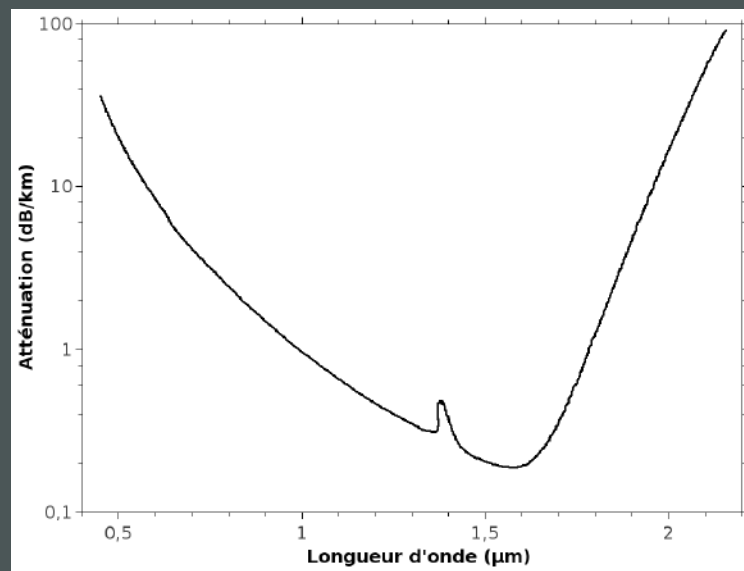


La lumière se propage dans le cœur



Modes de propagation

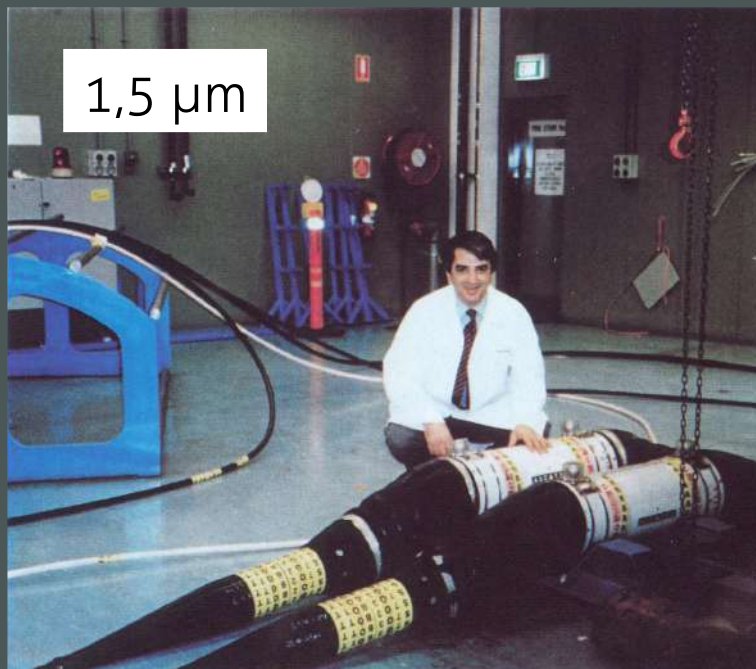
# TRANSPARENCE DE LA SILICE



	Pertes (dB/km)	1% du signal après
vitre	200 000	10 cm
optique	2 000	10 m
fibre	0,2	100 km

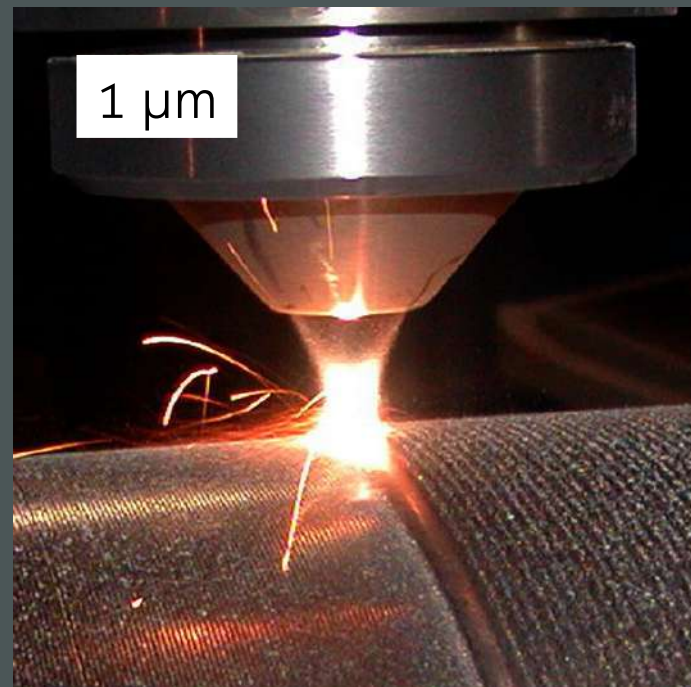
$$\alpha[\text{cm}^{-1}] = 0,23 \times \alpha[\text{dB/cm}]$$

# FIBRES AMPLIFICATRICES



1,5  $\mu\text{m}$

Fibres amplificatrices  
Télécoms



1  $\mu\text{m}$

Lasers à fibre de puissance  
Usinage, ...

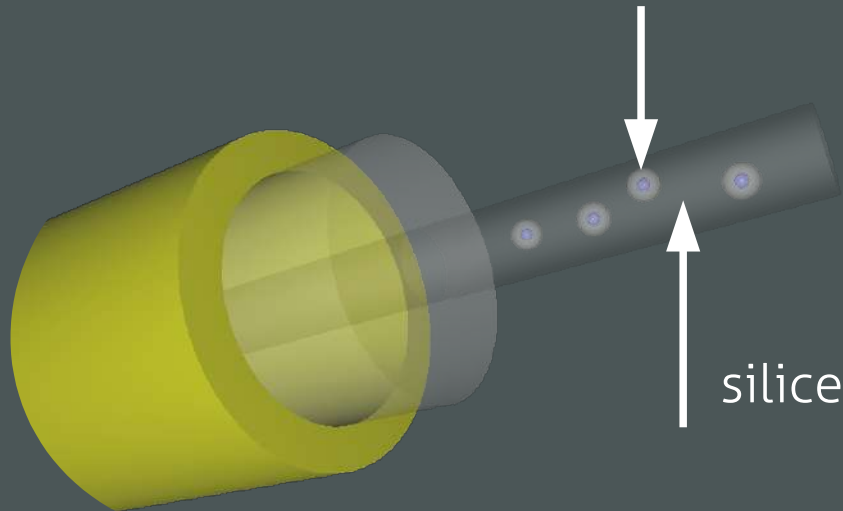
## LIMITATIONS DE LA SILICE

---

- Faible solubilité des ions luminescents
- Énergie de phonons élevée
- Environnement de silice
- Faibles effets non-linéaires
- Transmission limitée à 2  $\mu\text{m}$

# FIBRE OPTIQUE « AUGMENTÉE »

Ions luminescents dans les nanoparticules



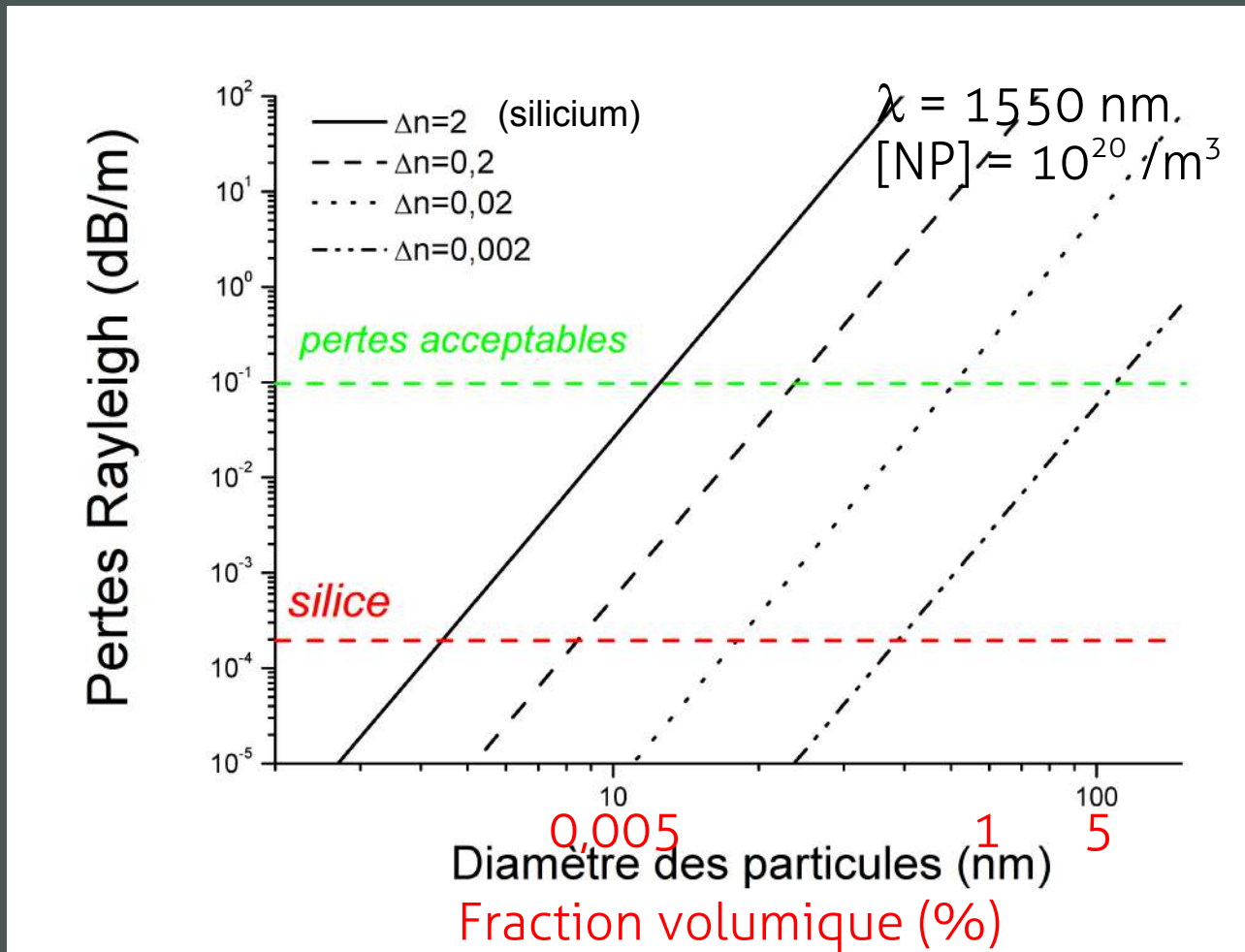
Nanoparticules :

- Spectroscopie (émission, temps de vie, gain, ...)
- Énergie de phonons (efficacité quantique, ...)
- Valence (métaux de transition)
- Défauts (photo-noircissement)

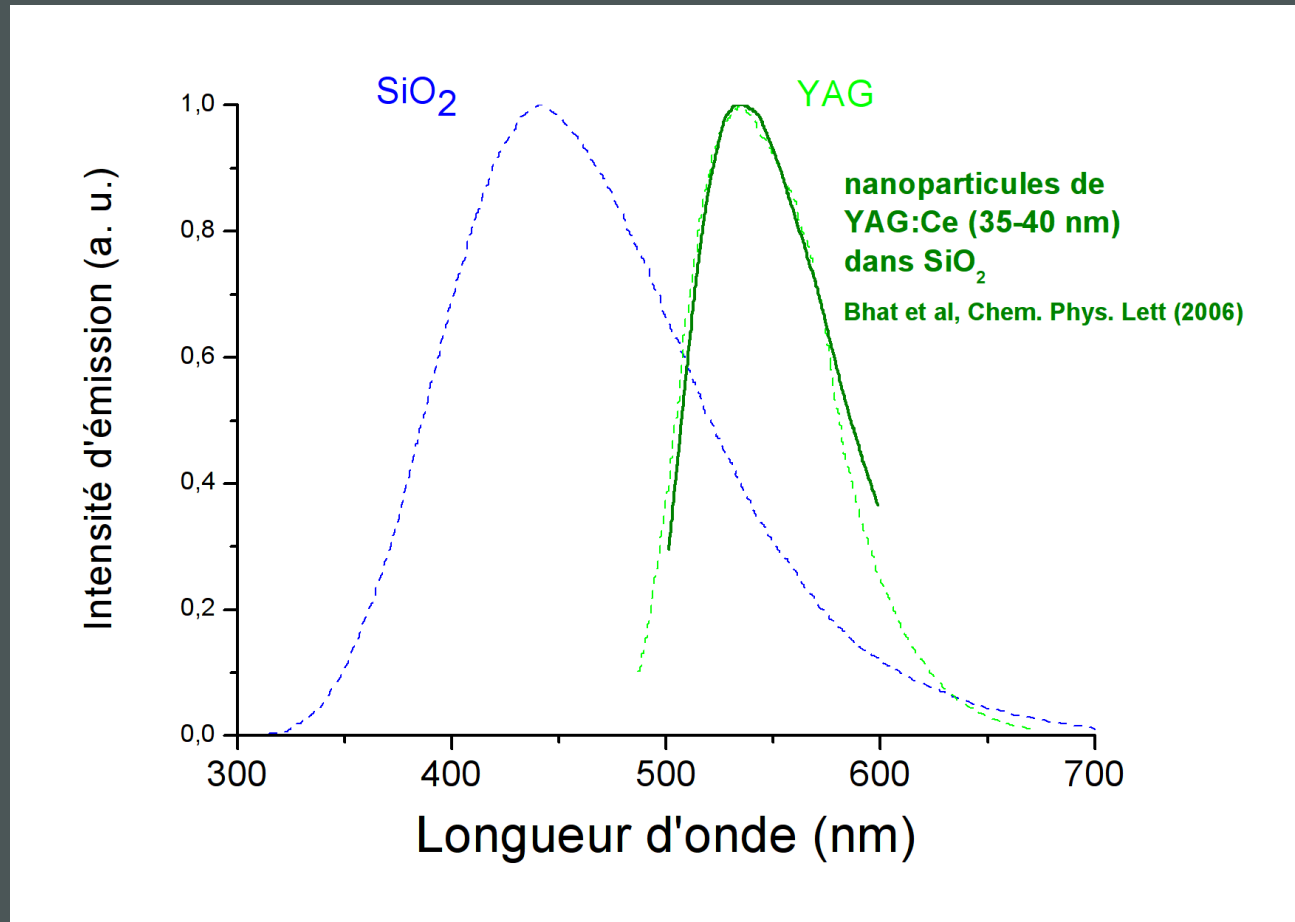


# DIFFUSION RAYLEIGH

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

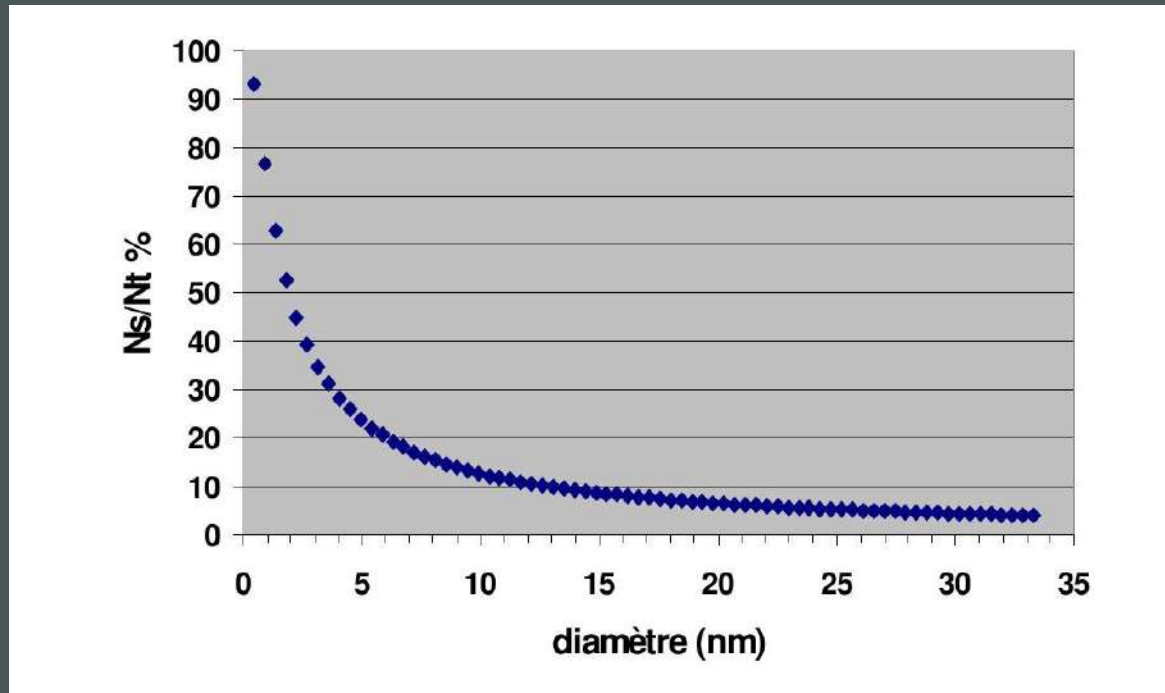


# FLUORESCENCE : NANO = MASSIF ?



Effets de surface très importants si particule < 10 nm

# RAPPORT ATOMES SURFACE/VOLUME



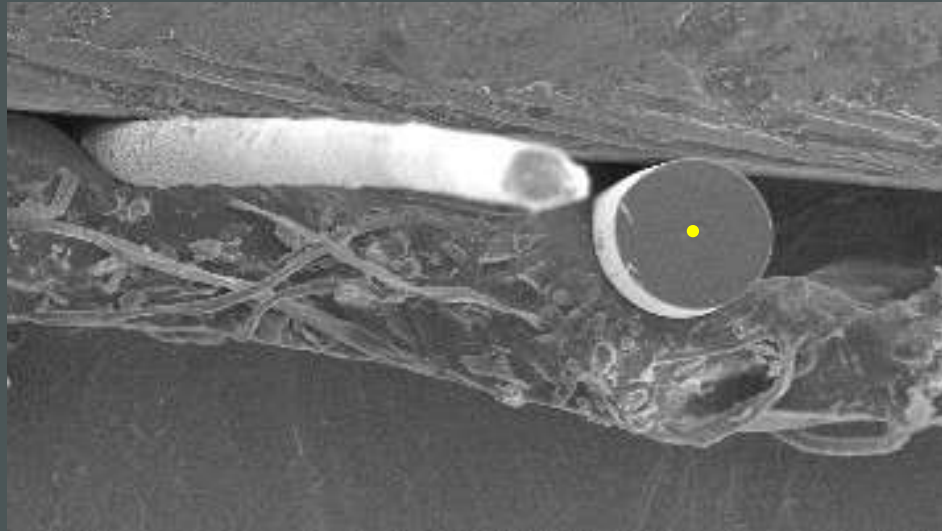
Pour une particule de 2 nm (~500 atomes dans le cas de Au), le rapport est de 50/50

*Thèse B. Mercier, LPCML, 2005*

# CARACTÉRISATIONS DANS LA FIBRE

Cheveu

Fibre optique



- Difficultés de caractérisation dans la fibre → résultats dans la préforme
- Pour les nanos cristallines → DRX (structure, composition, taille)
- Pour les nanos amorphes → MEB, MET, Nanosims
- Caract. indirectes: mesures «globales» (absorption, fluo, etc)

# HISTORIQUE FIBRES CÉRAMIQUES

---

1950's: 1ère vitrocéramique (Corning)

1970: 1ère fibre optique ultra-transparente (Corning)

1993: 1ère vitrocéramique optique transparente (Wang et Ohwaki)

1998: 1ère fibre optique vitrocéramique (Corning)

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

## **Are low-loss glass–ceramic optical waveguides possible?**

**P. A. Tick**

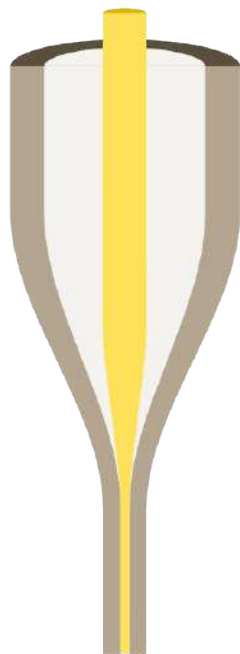
*Corning Incorporated, SP-AR-O2-1, Corning, New York 14831-0001*

Received September 24, 1998

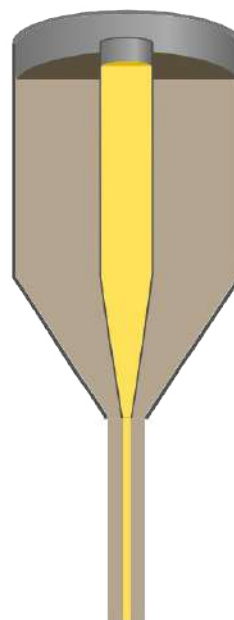
The results of a cutback measurement of a glass–ceramic optical waveguide with single-mode fiber geometry have demonstrated that sub decibels per kilometer losses can be achieved. Difference spectra show that the limit of intrinsic scattering in these two-phase structures ought to be tens of decibels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

© 1998 Optical Society of America

# MÉTHODES DE FABRICATION



Rod-in-tube



Double-creuset

+ Traitements thermiques de la fibre

# OXYFLUORÉS

Système étudié:  $30\text{SiO}_2 - 15\text{AlO}_{3/2} - 29\text{CdF}_2 - 17\text{PbF}_2 - 4\text{YF}_3 - 5\text{ZnF}_2 : \text{Tm}$

Technique de fabrication: double-creuset + chauffage de la fibre

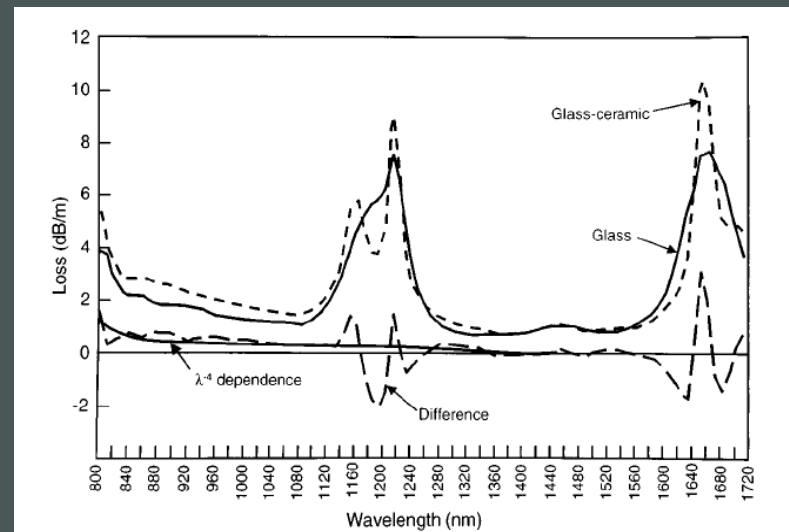
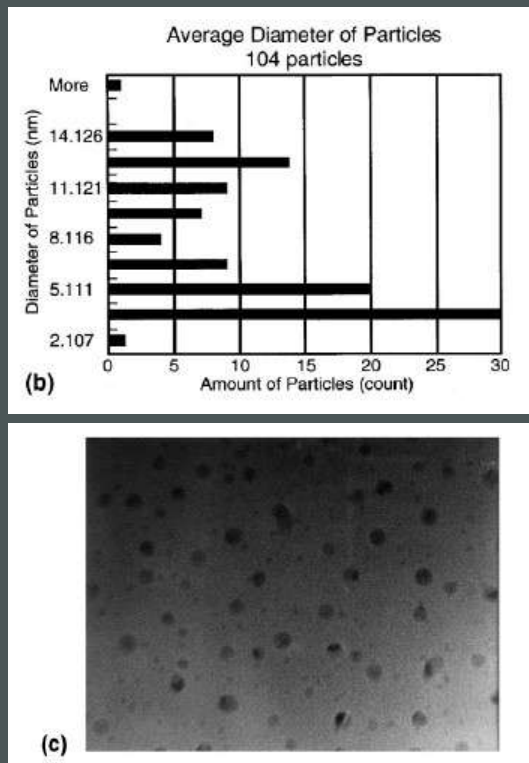


Fig. 2. Cutback spectral loss measurement of a Tm-doped effective medium glass-ceramic waveguide.

Particle size distribution (b), and TEM micrograph (c) for fiber cerammed at  $460^\circ\text{C}$  for 50 min.

$T_g \sim 400^\circ\text{C}$ ,  $T_x \sim 460^\circ\text{C}$

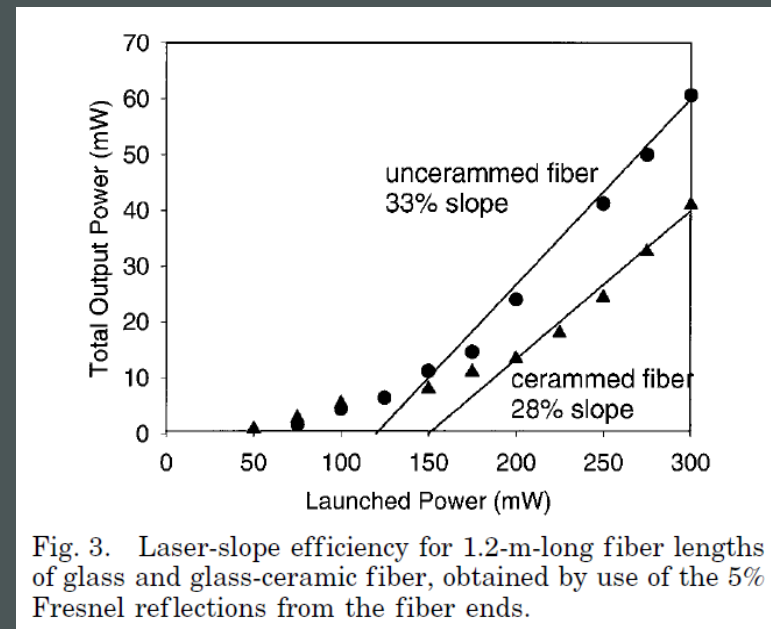
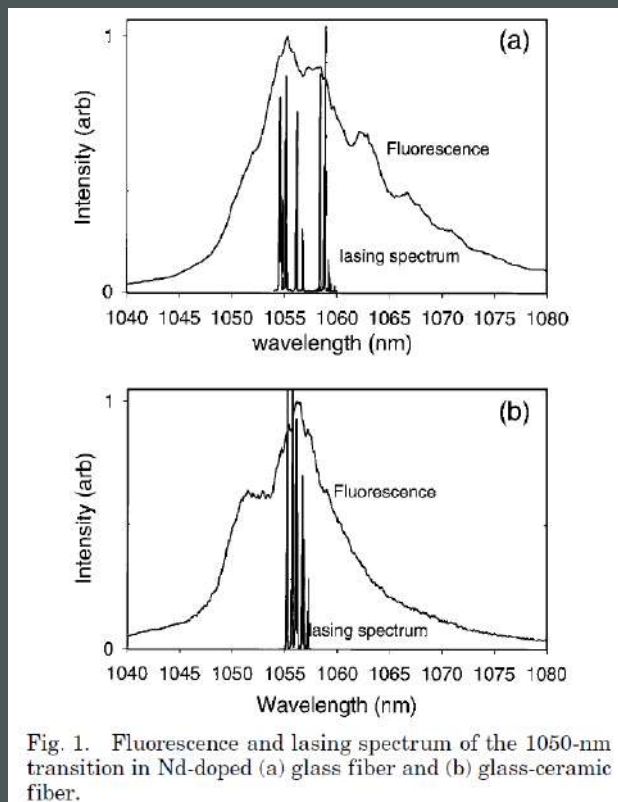
PA Tick, *Optics Letter* (1998)  
PA Tick et al., *Optical Materials* (2000)

# OXYFLUORÉS

Système étudié:  $30\text{SiO}_2 - 15\text{AlO}_{3/2} - 29\text{CdF}_2 - 17\text{PbF}_2 - 4\text{YF}_3 - 5\text{ZnF}_2 : \text{Nd}$

Technique de fabrication: double-creuset + chauffage de la fibre

450 °c – 30 min



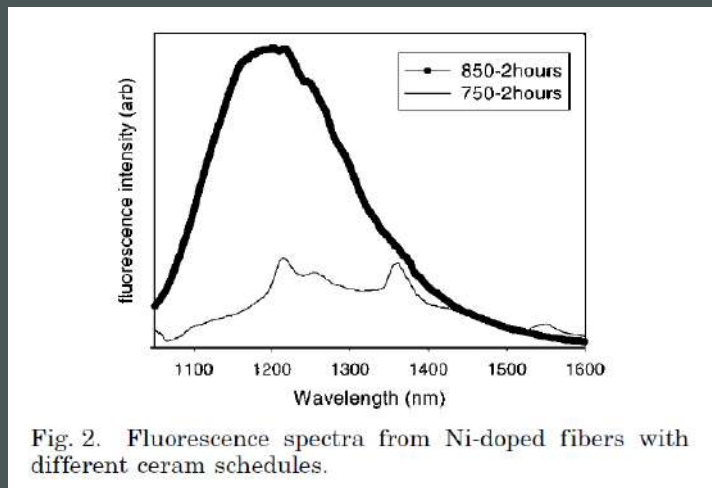
*BN Samson et al., Optics Letters (2001)*



# OXYDES

Système étudié:  $\text{SiO}_2$ - $\underline{\text{Ga}}_2\text{O}_3$ - $\underline{\text{Al}}_2\text{O}_3$ - $\text{K}_2\text{O}$ - $\text{Na}_2\text{O}$ - $\text{Li}_2\text{O}$ : NiO

Technique de fabrication: rod-in-tube + chauffage de la fibre



Efficacité quantique de Ni ~ 70%

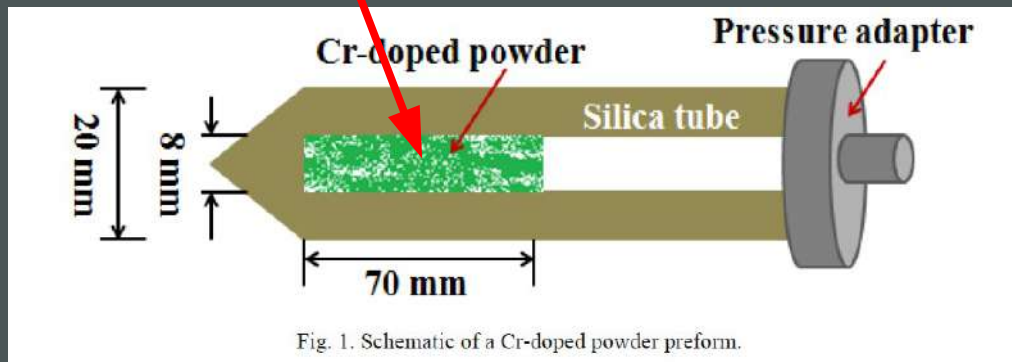
Atténuation à 1310 nm: ~15 dB/m

*« The strength and ease of handling of the cerammed fibers depend strongly on the details of the fiber drawing process and on the particular heat-treatment schedule used, and these particular fibers can be readily cleaved and spliced without too much difficulty. »*

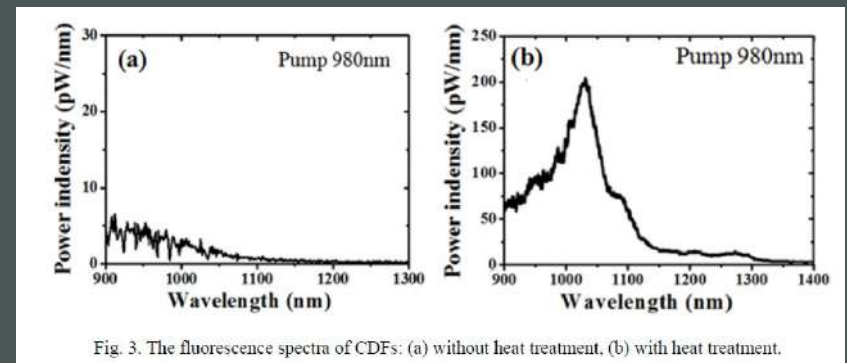
*BN Samson et al., Optics Letters (2002)*

## PROCÉDÉ « POUDRE »

Poudre:  $\text{Al}_2\text{O}_3$ - $\text{MgO}$ - $\text{K}_2\text{O}$ - $\text{TiO}_2$ - $\text{Cr}_2\text{O}_3$   
wt%: 30,5 – 32,1 – 28 – 9,4 – 0,25



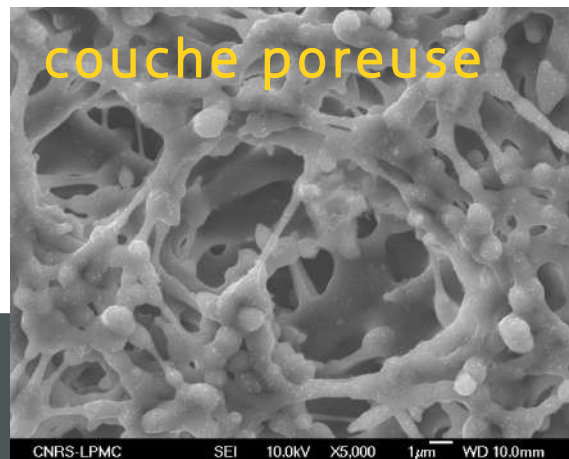
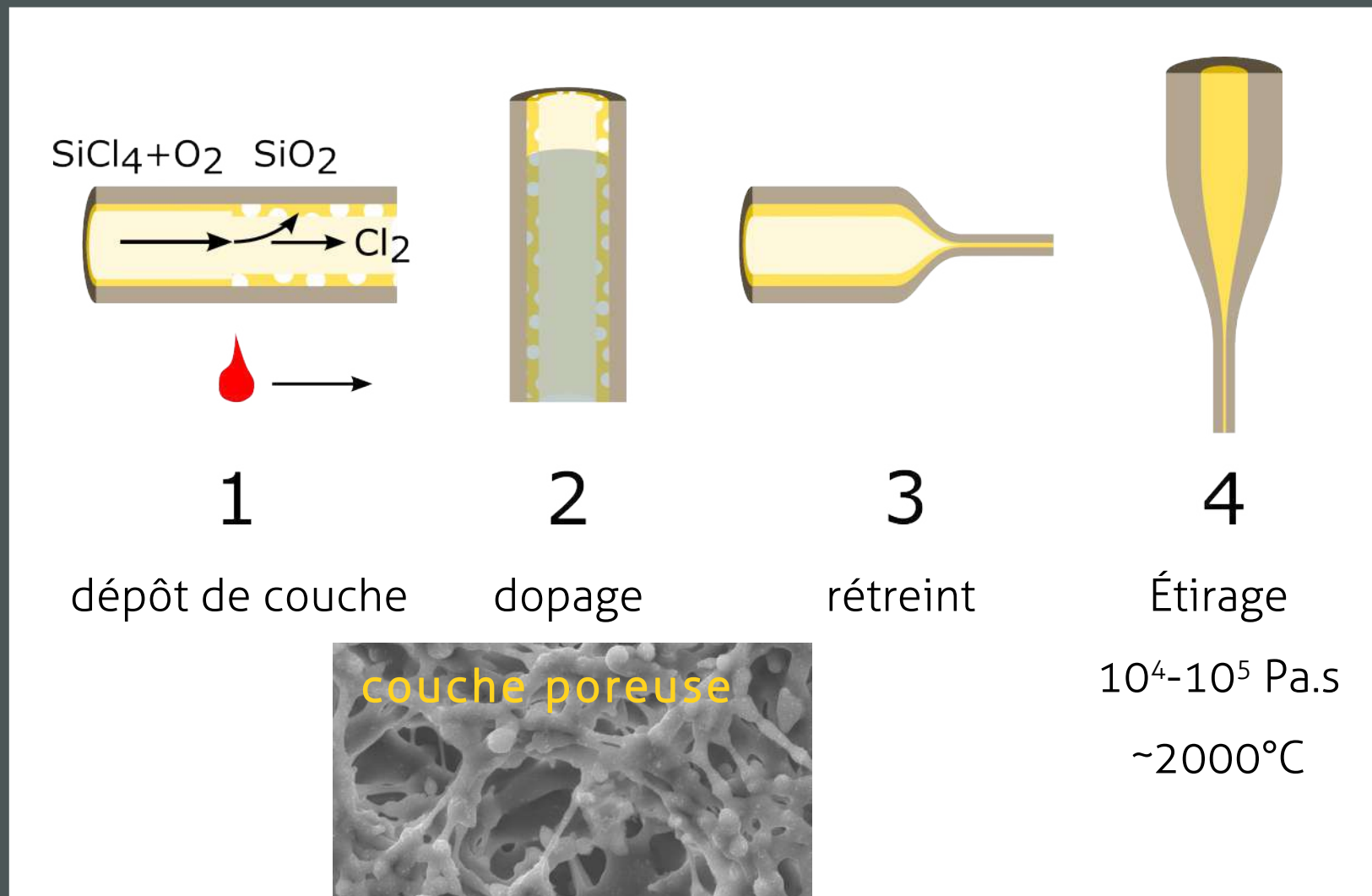
→ Nanocristaux de  $\text{Mg}_2\text{SiO}_4:\text{Cr}^{4+}$   
par chauffage de la fibre:  
4h à 525 °C + 4h à 900 °C



↗ Fluorescence de  $\text{Cr}^{4+}$

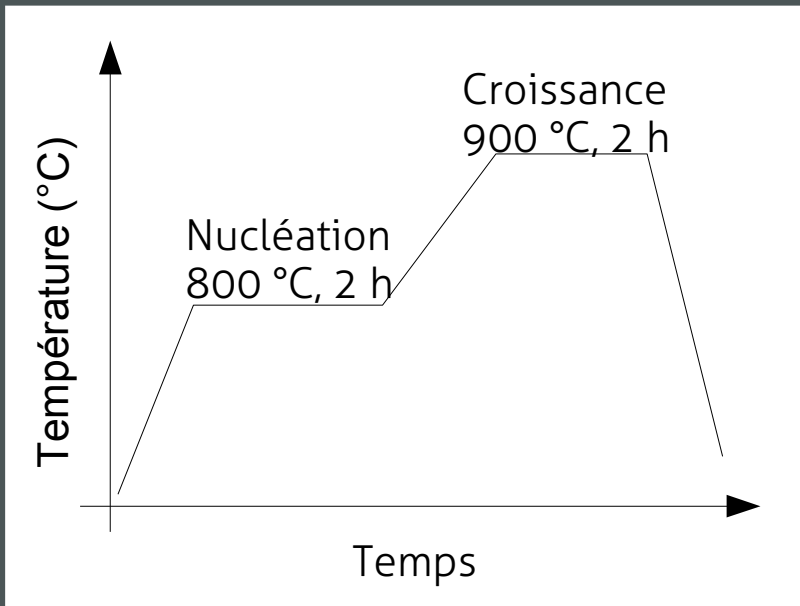
YC Huang et al., *Optics Express* (2013)

# MODIFIED CHEMICAL VAPOR DEPOSITION (MCVD)

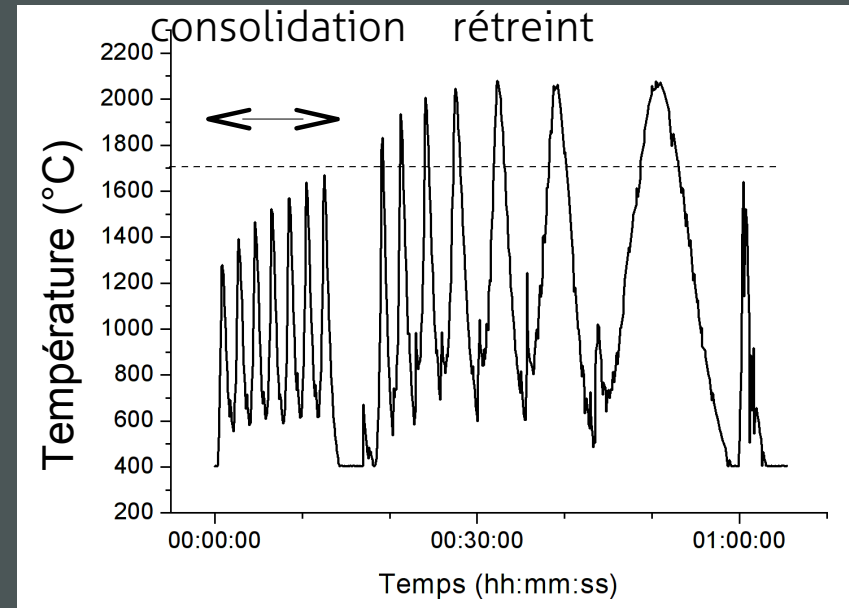


# TRAITEMENTS THERMIQUES

## Vitro-céramique



## MCVD

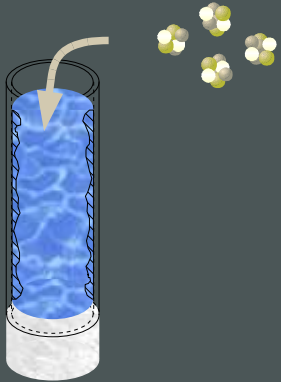


+ phase étirage

«It should be noted that the fluoride nanoparticles are expected to convert to oxides at the elevated temperatures used to process the subsequent silica preform.»

C. Kucera et al., Optics Letters (2009)

## « SLURRY METHOD »



Poudre de verre de  $\text{ZnO-Al}_2\text{O}_3\text{-SiO}_2\text{:Co}^{2+}$   
+  
poudre de silice  
+  
eau

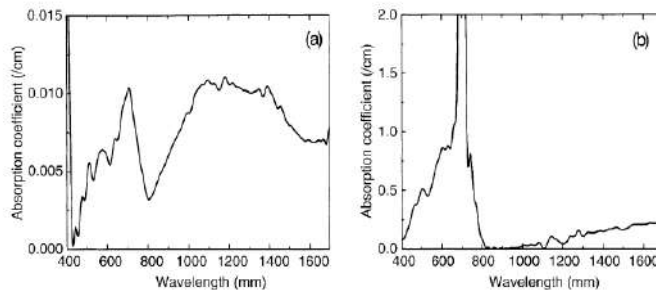


Fig. 5. Absorption spectra of the optical fiber containing the  $\text{Co}^{2+}$  doped ZAS glass prepared by the silica slurry method (a) and of the  $\text{Co}^{2+}$  doped optical fiber by the solution doping method (b).

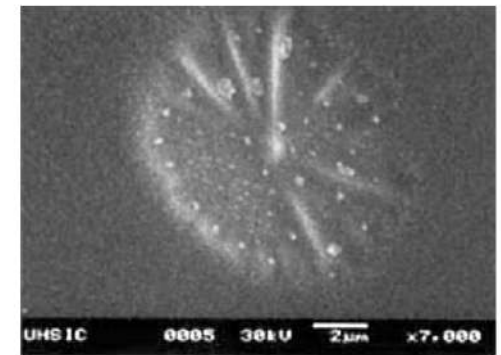
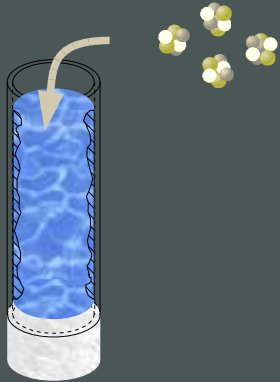


Fig. 6. SEM micrograph of the core region of the optical fiber containing the  $\text{Co}^{2+}$  doped ZAS glass-ceramics particles.

→ après étirage ( $2100\text{ }^\circ\text{C}$ ): nanocristaux de  $\text{ZnAl}_2\text{O}_4\text{:Co}^{2+}$   
(ZAS:  $T_g = 750\text{ }^\circ\text{C}$ ,  $T_x = 900\text{ }^\circ\text{C}$ ,  $T_m = 1370\text{ }^\circ\text{C}$ )

*S. Yoo et al., Journal of Non-Cryst. Solids (2003)*

# NANOPARTICULES PRÉ-FORMÉES



Nanos de  $\text{SiO}_2$  dopée Er, avec ou sans Al

Table 1. EDFs and Associated EDFA Parameters

Fiber Name	Al-NB	Al-LB	NP-Al	NP-Si	NP-Si+
Erbium absorption (dB/m@1530nm)	4.7	12.3	23	2	3.2
Aluminum (wt%)	<1	6-8	4-6	0	0
Pump power (dBm)	23	23	21	23	21
Optimal Length (m)	25	6	2.5	45	22
Output signal (dBm)	17	18	16	17	15

Fibers "NP-Al" and "NP-Si+" exhibit lower output power because of lower pump power. For 23 dBm pump power, "NP-Al" would exhibit output power close to "Al-LB", while "NP-Si+" would exhibit output power similar to "Al-NB" or "NP-Si".

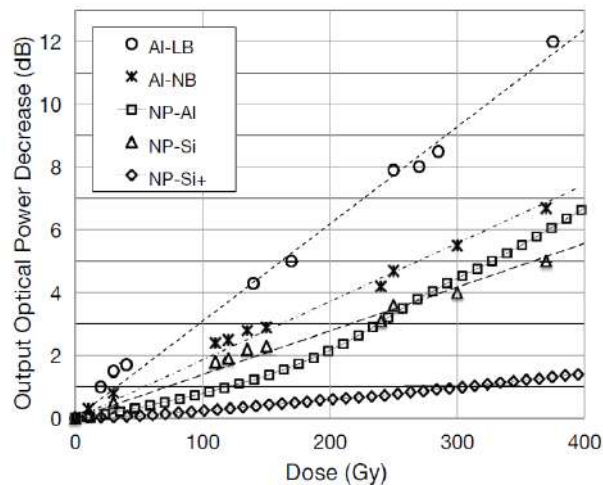


Fig. 4. Optical Power decrease for each EDFA configuration.

→ Diminution du photo-noircissement

*J. Thomas et al., Optics Express (2012)*

# DÉMIXION DES TERRES ALCALINES

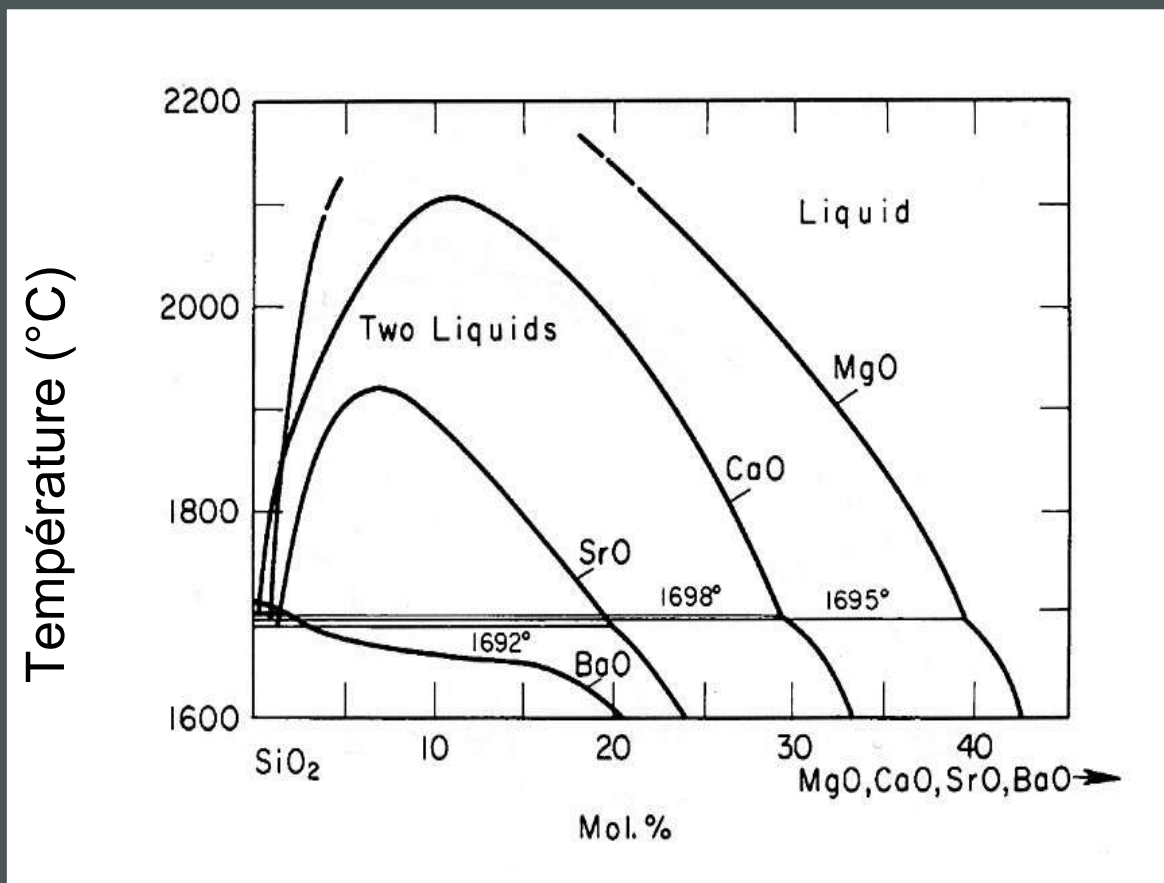
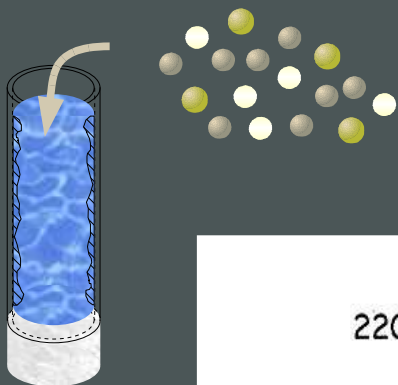
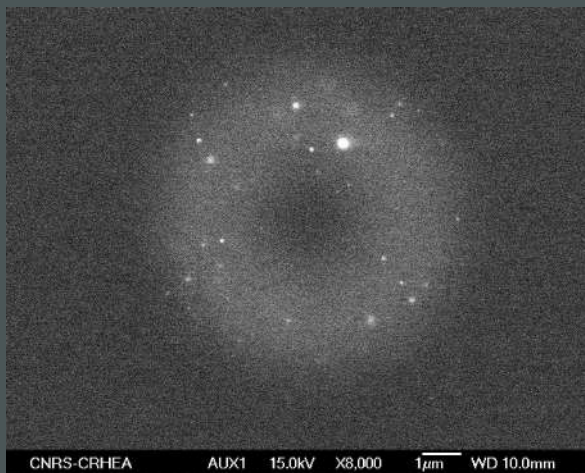


Diagramme de phase de  $\text{SiO}_2$  -  $\text{MO}$  ( $\text{M}=\text{Mg}, \text{Ca}, \text{Sr}$ )



# IMAGES MEB DE FIBRES OPTIQUES



Sr



Ca



Mg



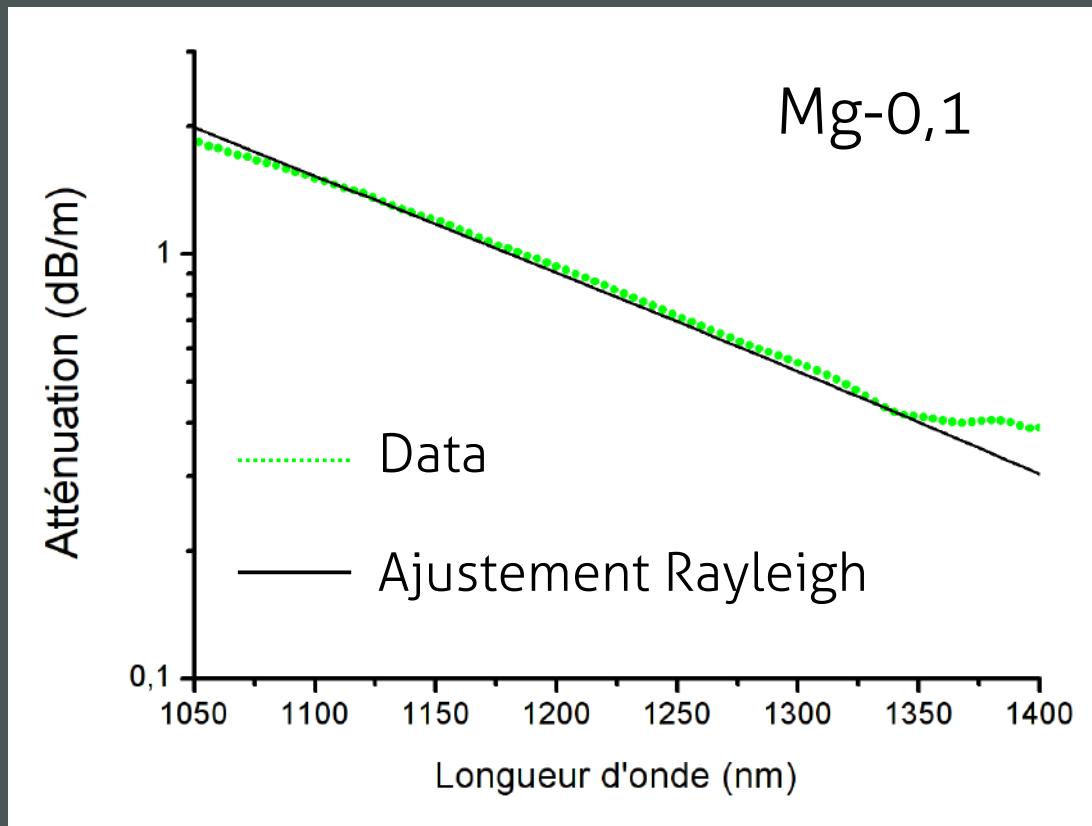
$[\text{Terre alcaline}]_{\text{solution}} = 0.1 \text{ mol/l}$

*W. Blanc et al., International J. of Nanotech. (2012)*



# PERTES OPTIQUES

$$\text{Rayleigh scattering} = [NP] \times \frac{d^6}{\lambda^4} \times n_m^2 \left( \frac{n_n^2 - n_m^2}{n_n^2 + 2n_m^2} \right)^2 \times \Gamma$$

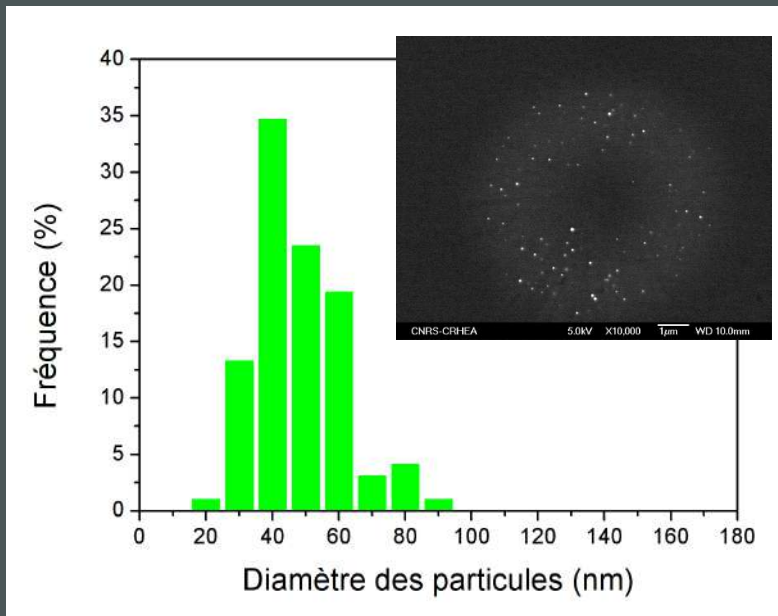


Paramètres fixés :  
 $n_d = 1,65$   
 $d = 50 \text{ nm}$

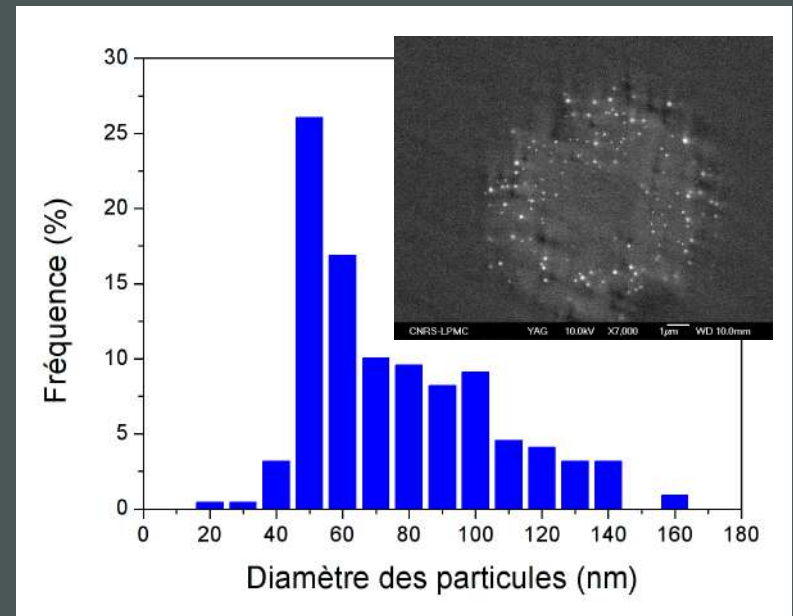
$\rightarrow N = 0,4 \cdot 10^{20} \text{ m}^3$   
 $L_{\text{part-part}} \approx 300 \text{ nm}$

*W. Blanc et al., J. of the Amer. Ceram. Soc. (2011)*

# EFFET DE LA CONCENTRATION EN MG



$[Mg]_{sol} = 0,1 \text{ mol/l}$   
 $\emptyset_{moyen} : 50 \text{ nm}$

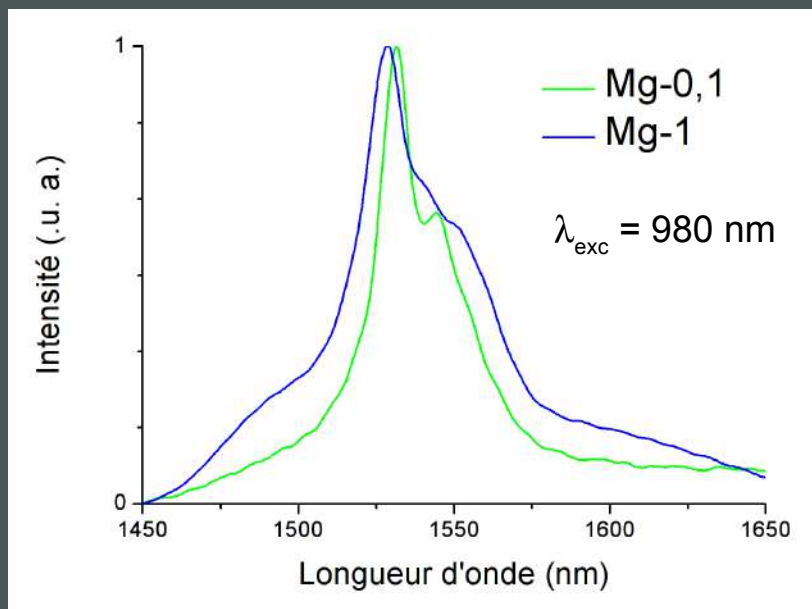


$[Mg]_{sol} = 1 \text{ mol/l}$   
 $\emptyset_{moyen} : 80 \text{ nm}$

*W. Blanc et al., J. of the Amer. Ceram. Soc. (2011)*

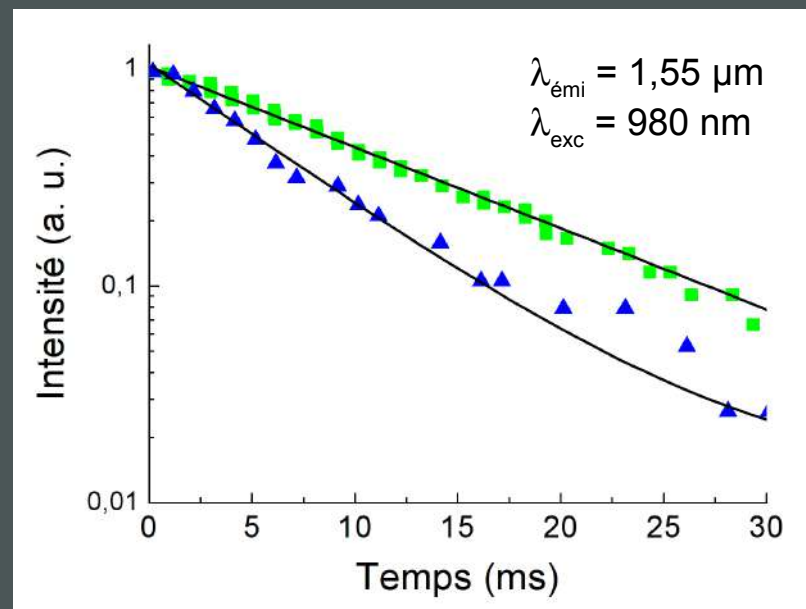
# SPECTROSCOPIE DE ER<sup>3+</sup>

## Spectres d'émission



FWHM : +60%

## Durées de vie de fluorescence



■  $\tau(\text{Mg-0,1}) = 11,7 \text{ ms}$

▲  $\tau(\text{Mg-1}) = 6,7 \text{ ms}$

*W. Blanc et al., J. of the Amer. Ceram. Soc. (2011)*

# COMPOSITION À L'ECHELLE NANOMÉTRIQUE PAR NANOSIMS

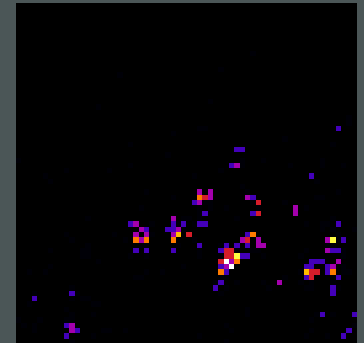
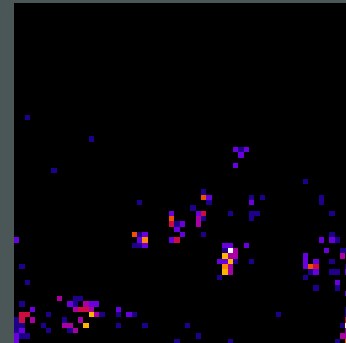
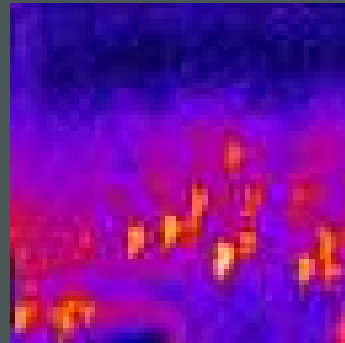
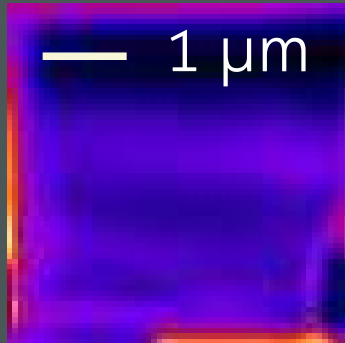
Si

P

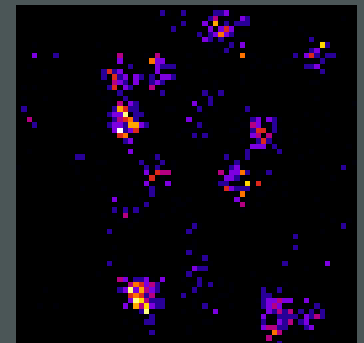
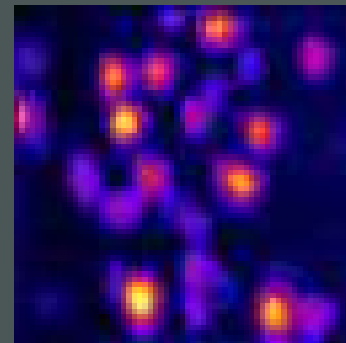
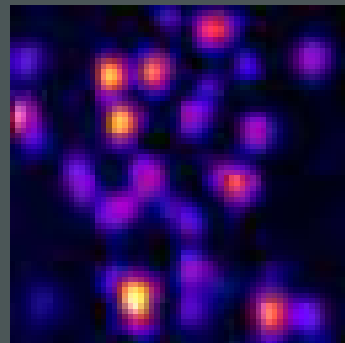
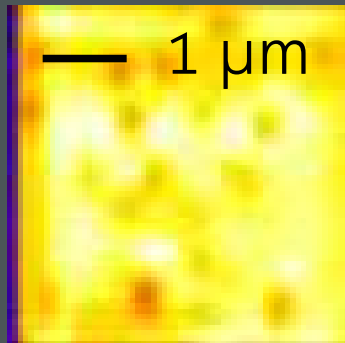
Mg

Er

Mg-0,1

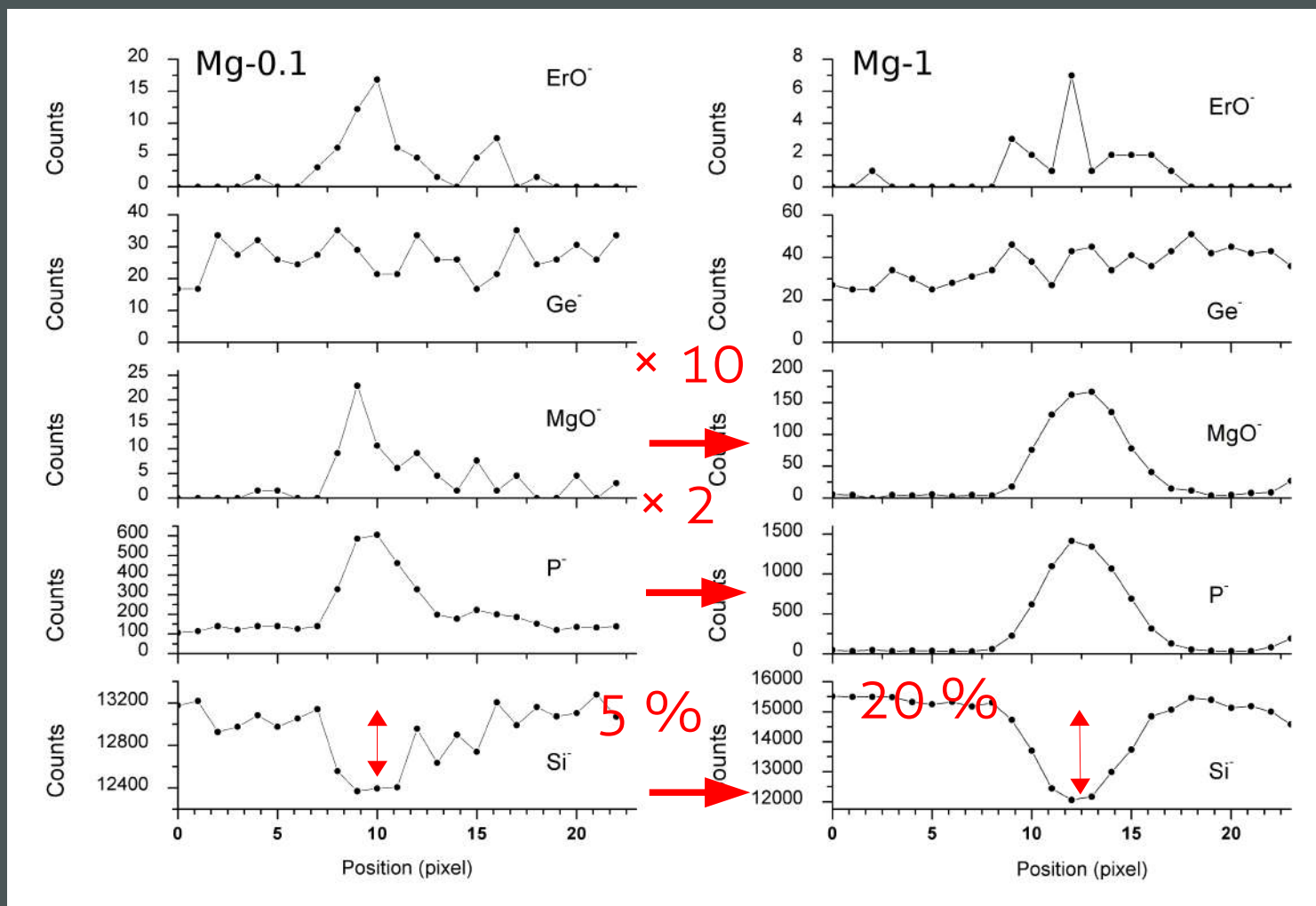


Mg-1



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

# COMPOSITION À L'ECHELLE NANOMÉTRIQUE PAR NANOSIMS

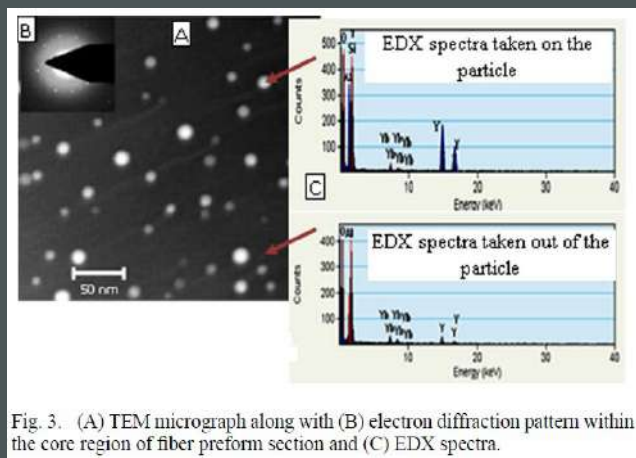


W. Blanc et al., *Optical Materials Express* (2012)

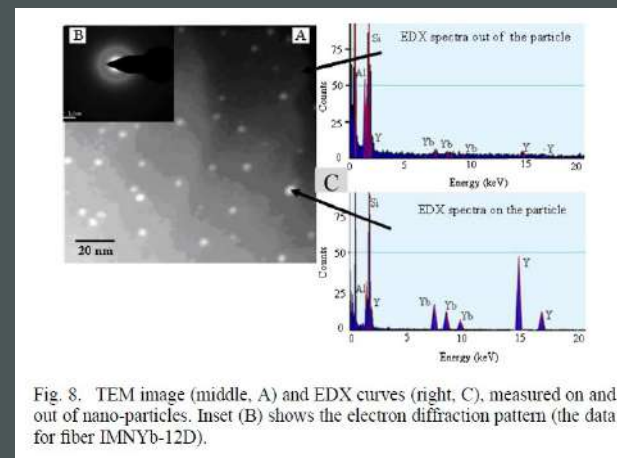
# NANOCRISTAUX DE YAG:Yb

## Composition du cœur hors SiO<sub>2</sub> (EPMA)

	P <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	Yb <sub>2</sub> O <sub>3</sub>	F	Li <sub>2</sub> O	(BaO)
wt%	1	0,9	0,6	0,4	0,2	?	
mol%	0,4	0,5	0,2	0,06	0,3		



Préforme  
chauffée à 1450 °C, 3h  
→ Nanocristaux de YAG:Yb



Fibre  
→ nanoparticules amorphes  
dopées Yb, moins d'Al

MC Paul et al., *Journal of Lightwave Technology* (2012)

# NANOCRISTAUX DE YAG:YB : APPLICATIONS

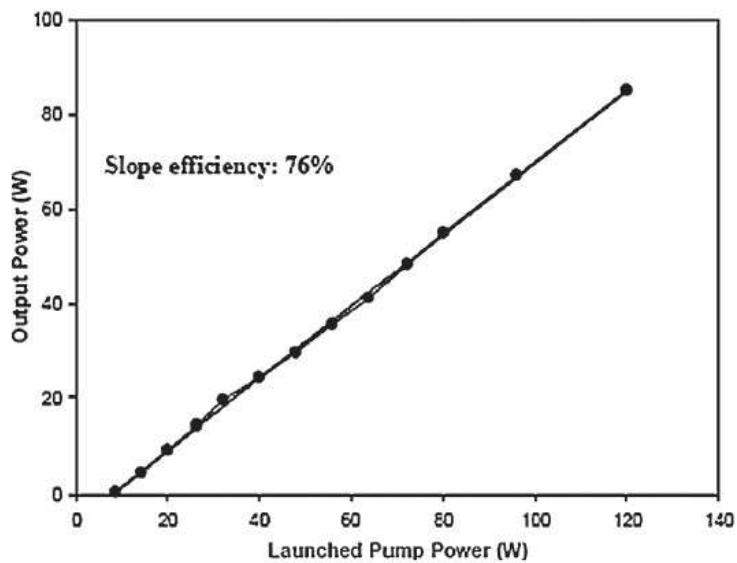


Fig. 42. Laser performance of 4 meter length of nano-engineering fiber (NYb-7).

→ laser

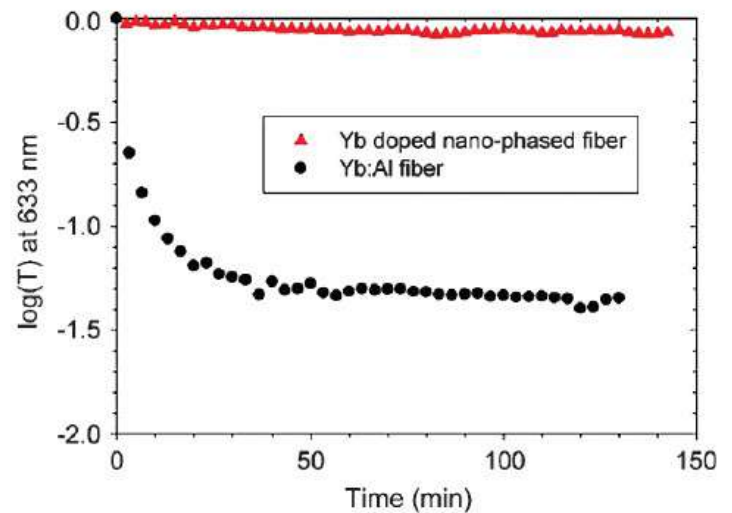


Fig. 47. Temporal characteristics of transmitted power at 633 nm for Yb-doped nanoparticle fiber and Yb:Al fiber. Reproduced from Ref. [65], S. Yoo et al., *J. Optics Communications* 283, 3423 (2010). © 2010, Elsevier Science.

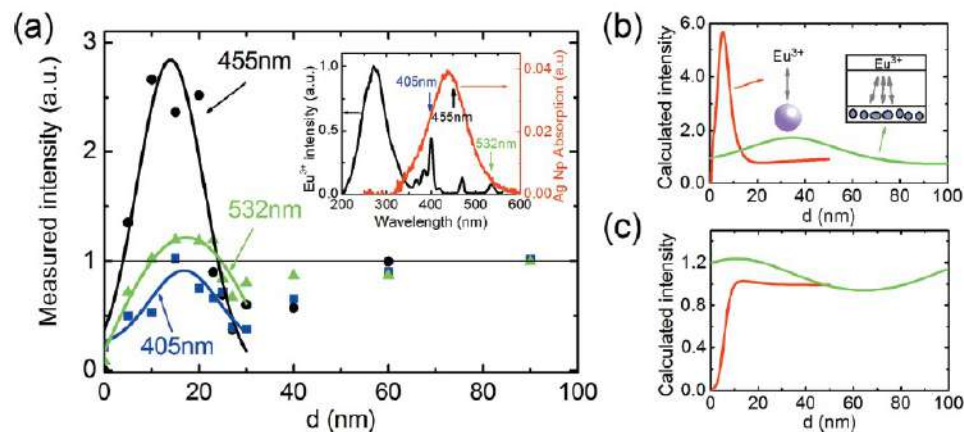
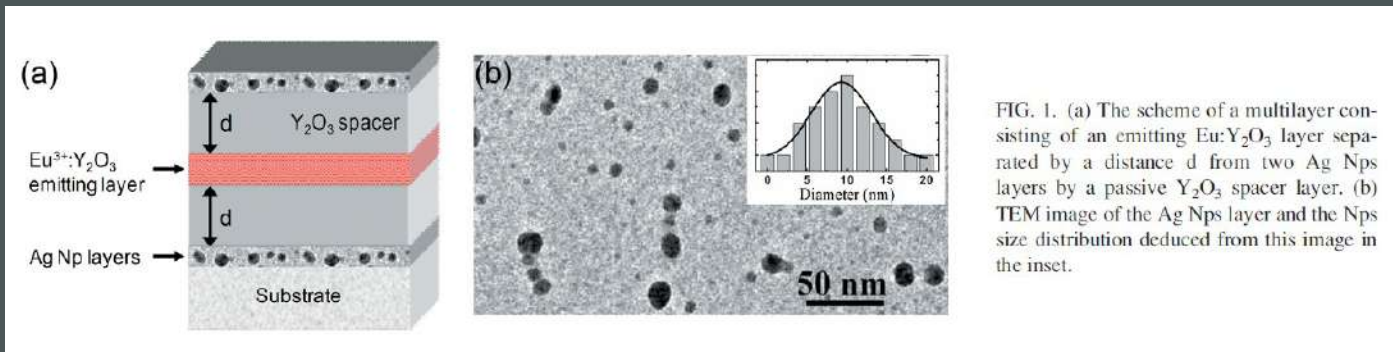
→ photo-noircissement

MC Paul et al., *Science of Advanced Materials* (2012)



# NANOPARTICULES MÉTALLIQUES

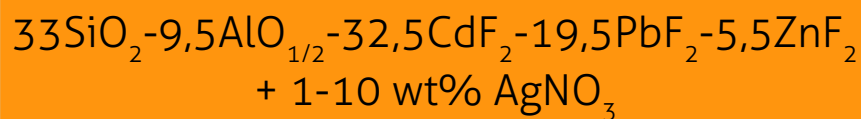
Exaltation de la fluorescence de Eu démontrée dans le massif mais très dépendant de la distance Er-NPM



A. Pillonnet et al., Applied Phys. Letters (2012)

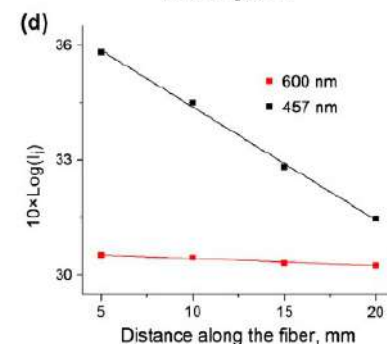
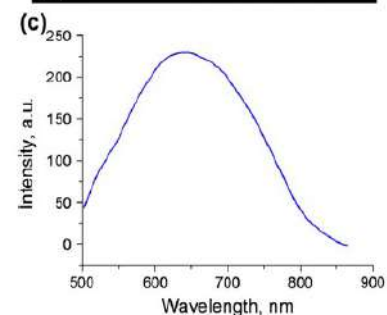
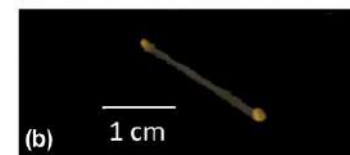
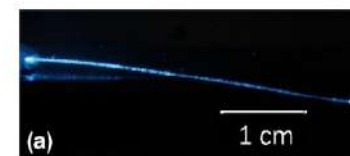


# FLUORESCENCE DE NANOPARTICULES D'ARGENT



$T = 850 \text{ }^\circ\text{C}$

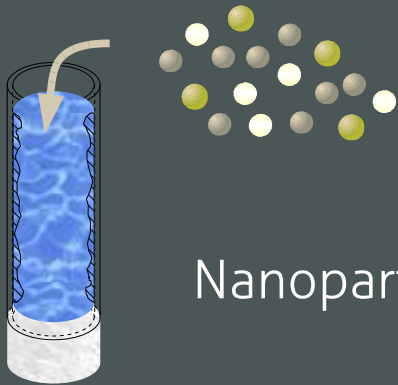
→ Formation de  $\text{Ag}_4^{2+}$   
dans le réseau  $\text{CdF}_2\text{-PbF}_2$



**Fig. 7.** (a) 457 nm propagating light launched in the fiber at the left end; (b) luminescent fiber excited from above by invisible light of UV lamp at 366 nm; (c) luminescence spectrum taken from the middle point of the fiber (d) optical loss of the fiber at 457 and 600 nm. The fiber was pulled from the viscous melt and no extra heat treatment steps of the fiber were undertaken.

*AS Kuztnetsov et al., Optical Materials (2012)*

# FLUORESCENCE DE NANOPARTICULES D'OR



$\text{Au}(\text{OH})_3$  dissout dans  $\text{HNO}_3$

Nanoparticules d'or obtenues directement dans la fibre

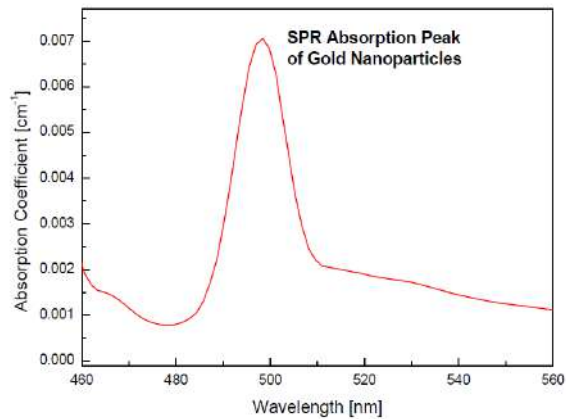


Fig. 2. Experimental absorption spectrum of the germano-silicate fiber incorporated with gold nanoparticles.

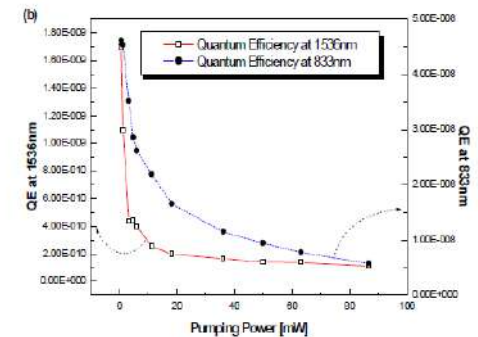
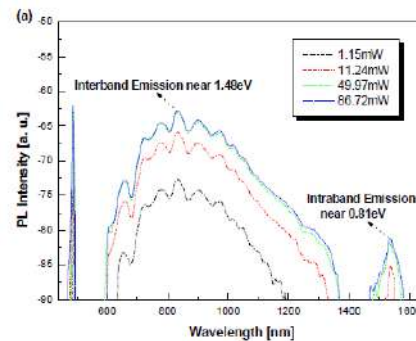
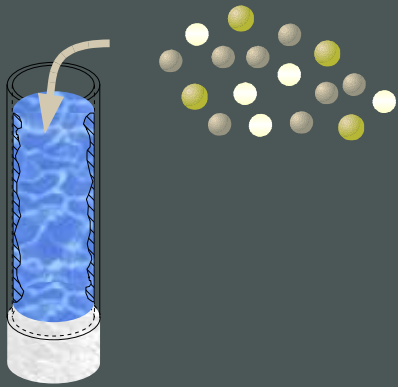


Fig. 3. Broadband visible to narrowband infrared photoluminescence (a) and the quantum efficiencies at 833nm and 1536nm (b) of the 30m-long germano-silicate glass fiber incorporated with gold nanoparticles pumping with 488nm

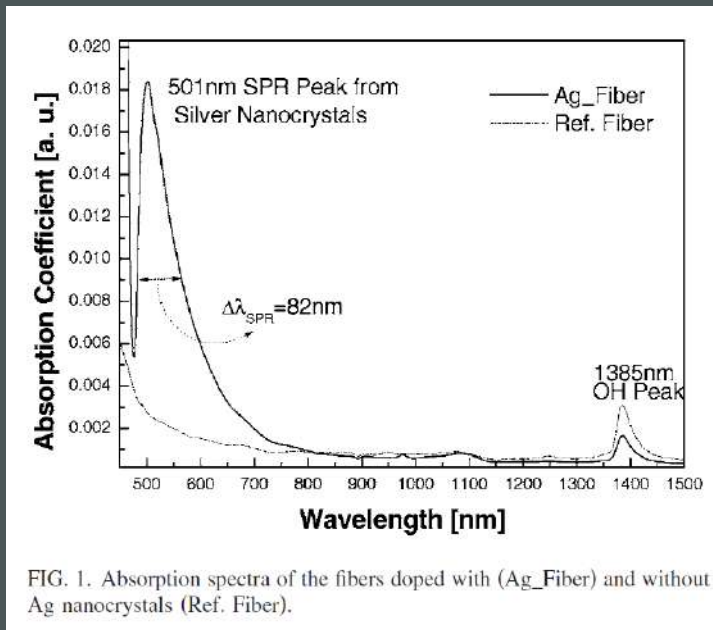
A. Lin et al., *Optics Express* (2007)

# EXACERBATION DES NON-LINÉARITÉS D'ORDRE 3



Ag (+ Ce pour réduire Ag)

Nanoparticules d'Ag de ~3 nm



	$n_2$ $10^{-16} \text{ m}^2/\text{W}$
Ag_Fiber	5,4
Au_Fiber	5
Ref. Fiber	0,4

A. Lin et al., Applied Phys. Letters (2008)

## EXACERBATION DES NON-LINÉARITÉS D'ORDRE 2

$30\text{BaO}-15\text{TiO}_2-30\text{GeO}_2-25\text{SiO}_2$

→ étirer en fibre «massive»

+ 1 heure à 826 °C

→ phase fresnoite ( $\text{Ba}_2\text{TiSi}_2\text{O}_8$ )  
en surface

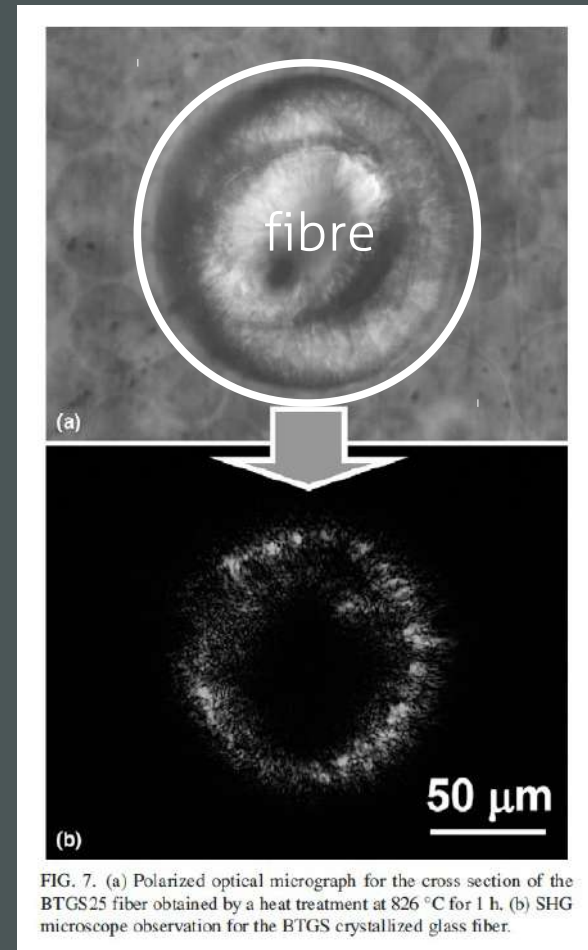


FIG. 7. (a) Polarized optical micrograph for the cross section of the BTGS25 fiber obtained by a heat treatment at 826 °C for 1 h. (b) SHG microscope observation for the BTGS crystallized glass fiber.

*H. Masai et al., Journal of Materials Research (2009)*

## CRISTALLISATION DE LA PHASE FRESNOITE PAR LASER

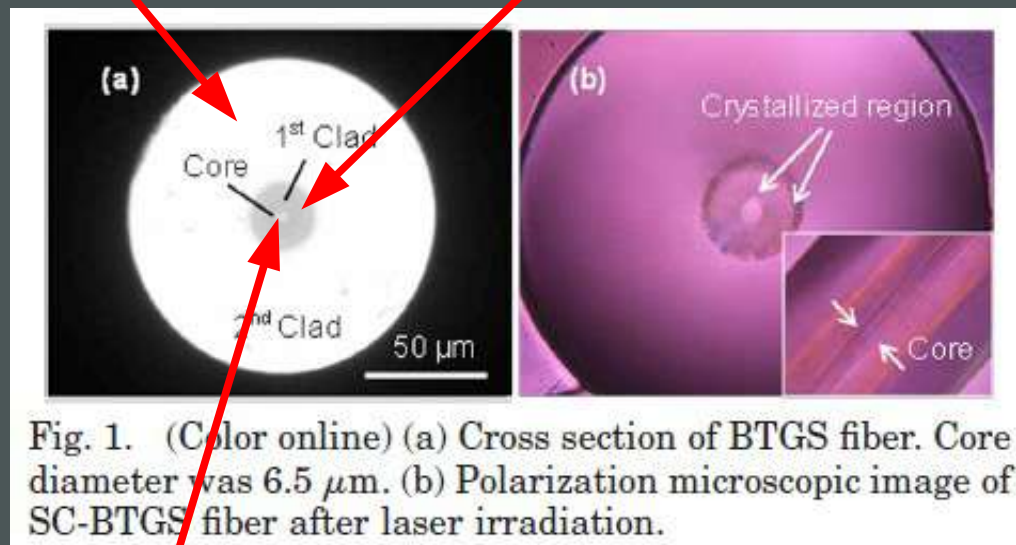
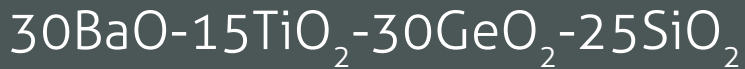


Fig. 1. (Color online) (a) Cross section of BTGS fiber. Core diameter was  $6.5 \mu\text{m}$ . (b) Polarization microscopic image of SC-BTGS fiber after laser irradiation.



- Assemblage par rod-in-tube
- Irradiation par laser à  $1,09 \mu\text{m}$  de la fibre chauffée à  $700 \text{ }^\circ\text{C}$

*S. Ohara et al., Optics Letters (2009)*

*S. Ohara et al., Journal of the Ceramic Society of Japan (2008)*

# NANOPARTICULES DE SN PAR IRRADIATION LASER

Table 2  
Fiber core composition

Sample #	[SnO <sub>2</sub> ] mol%	[P <sub>2</sub> O <sub>5</sub> ] mol%	[GeO <sub>2</sub> ] mol%	[SiO <sub>2</sub> ] mol%
A	6.5 ± 0.1	–	30 ± 0.5	63.5 ± 0.5
B	6 ± 0.1	6.5 ± 0.1	–	87.5 ± 0.1
C	1 ± 0.1	–	–	99 ± 0.1

[SnO<sub>2</sub>], [P<sub>2</sub>O<sub>5</sub>], [GeO<sub>2</sub>] and [SiO<sub>2</sub>] represent SnO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, GeO<sub>2</sub> and SiO<sub>2</sub> concentrations in the fiber core.

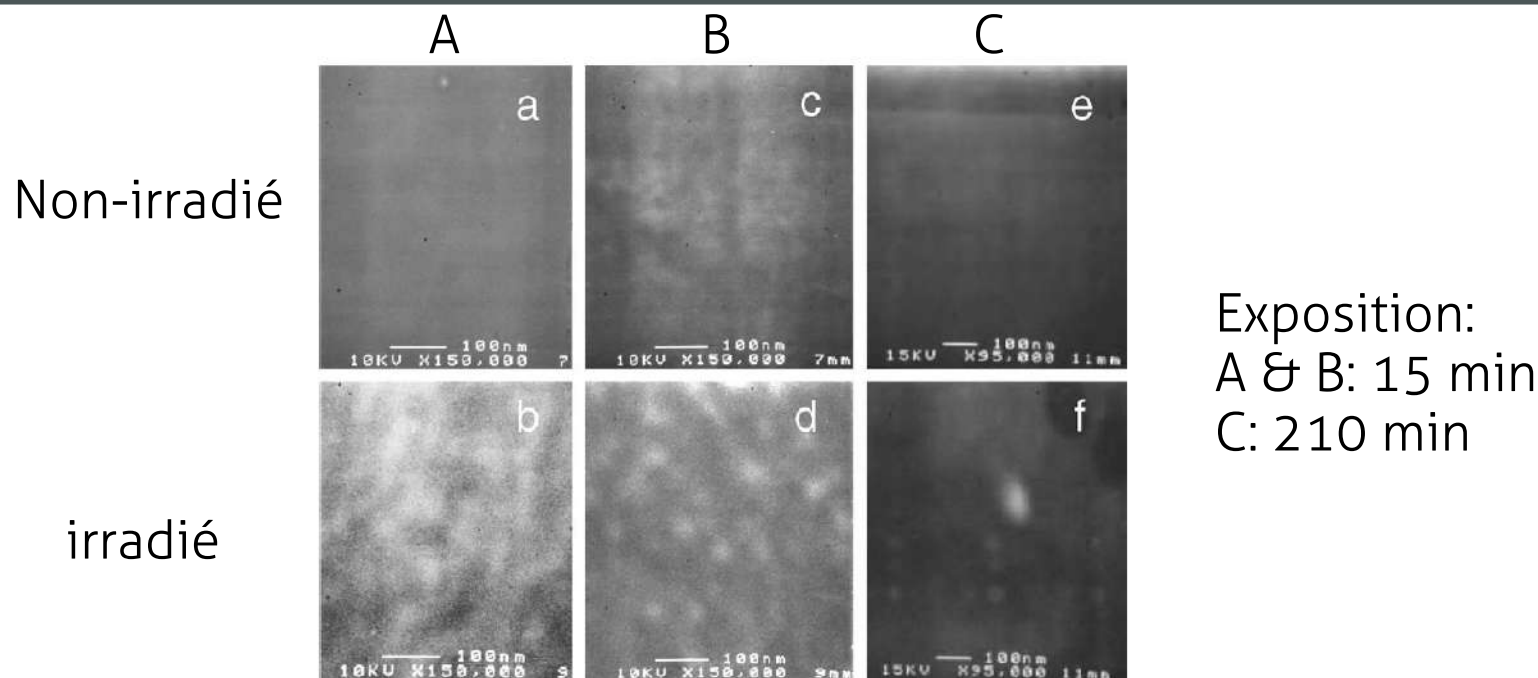


Fig. 1. SEM pictures of sample A ((a) and (b)), B ((c) and (d)) and C ((e) and (f)) unexposed (top row) and exposed (bottom row) to UV laser radiation (248 nm) at 20 Hz and  $0.1 \pm 0.01 \text{ J/cm}^2$ . While samples A and B show phase separation after UV exposure, sample C maintains the uniformity observed before the exposure.

*G. Brambilla et al., Journal of Non-cryst. Solids (2006)*

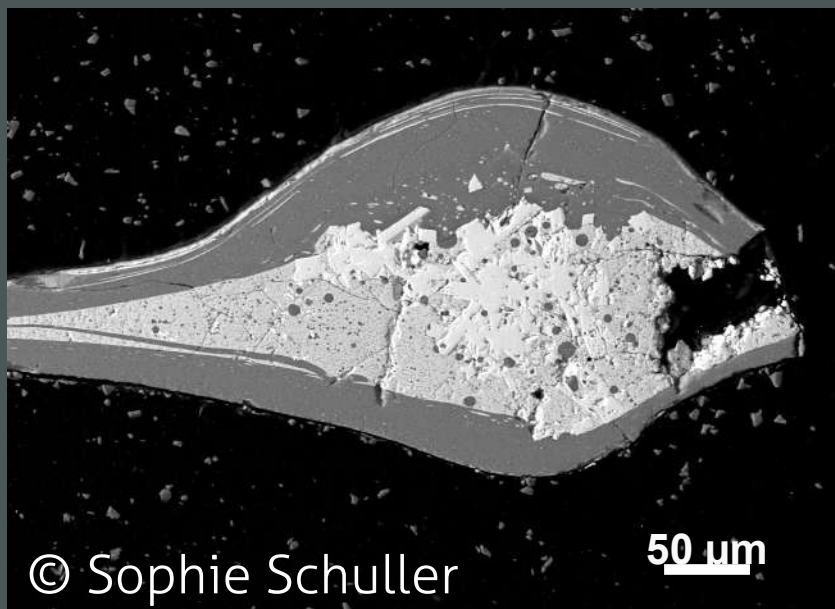
## CONCLUSION

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- Développement récent des fibres optiques contenant des nanoparticules
- Variété des procédés de fabrication
  - *Double-creuset / Rod-in-tube / MCVD / massif étiré*
  - *Nanoparticules dans la préforme / chauffage (laser) de la fibre*
- Variété des types de nanoparticules
  - *fluorées / oxydes / métalliques*
  - *amorphes / cristallines*
- Quelques applications
  - *Luminescence : laser, amplificateur, photo-noircissement, source de lumière ...*
  - *Non-linéarités : d'ordre 2, d'ordre 3*



# DE L'ART OU DU POISSON





# DE L'ART OU DU POISSON

