Chalcogenide-glass-based mid-infrared sources

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Outline

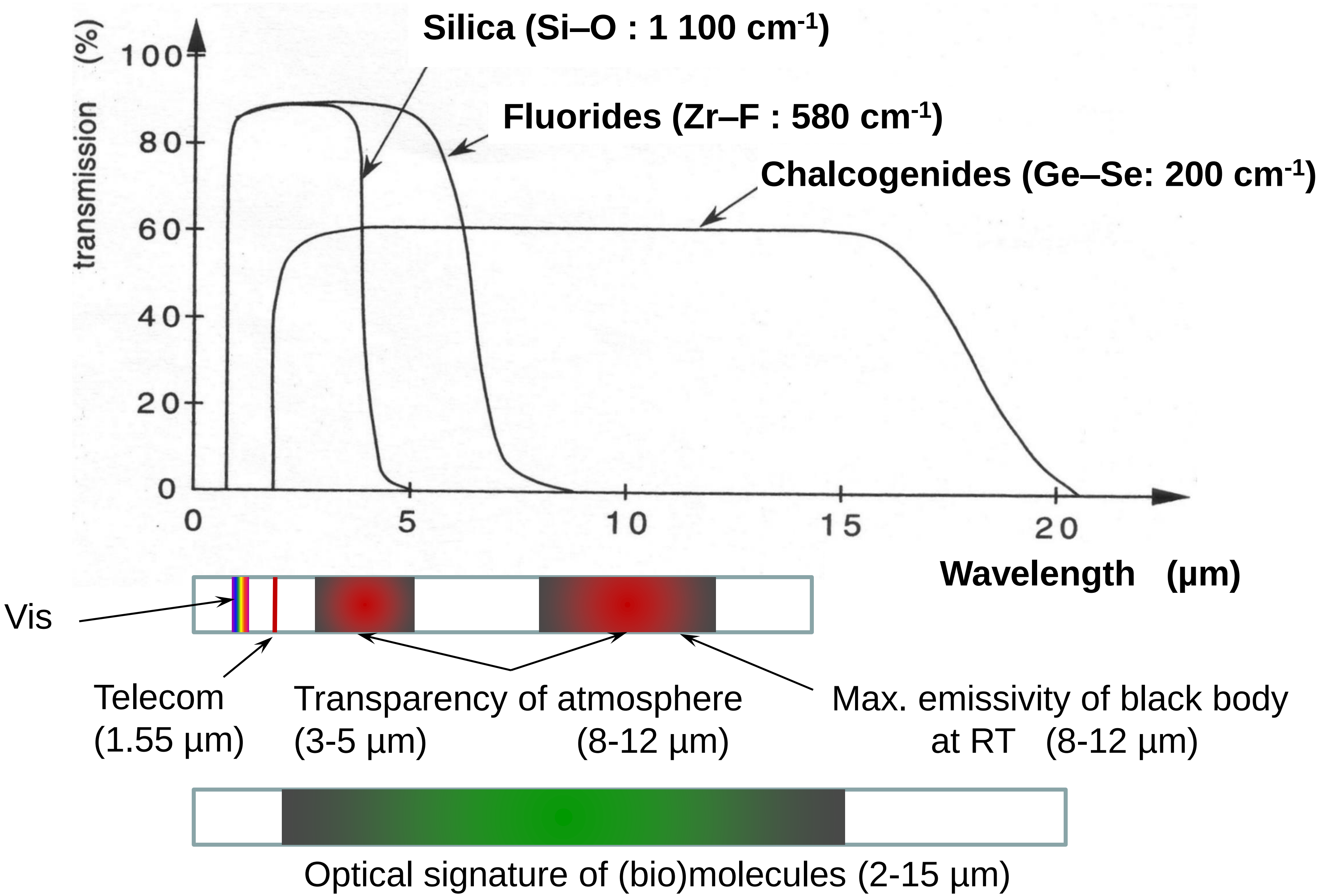
- Compositions and properties of some chalcogenide glasses
- Mid-IR emissions from rare-earth-doped chalcogenide glasses for sensing application
  - Dy^{3+} - doped fibers
  - Dy^{3+}, Pr^{3+} - co-doped fibers
- Microstructured chalcogenide optical fibers for IR laser light delivery

Chalcogenide Glasses → Infrared Glasses

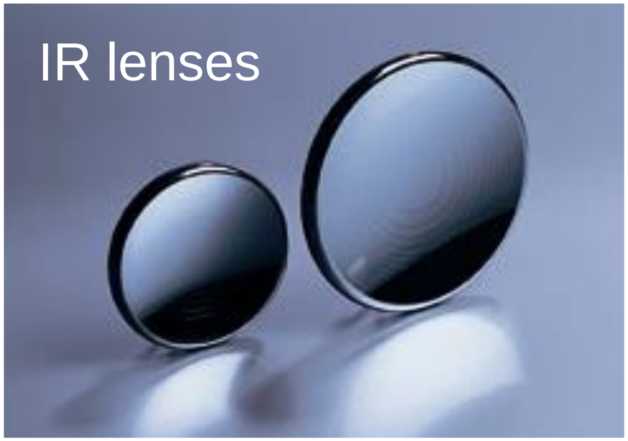
Composition	T_g
$S_{65}Sb_{10}Ge_{20}Ga_5$ (2S2G)	305°C
$As_{40}Se_{60}$ (As_2Se_3)	180°C
$Te_{20}As_{30}Se_{50}$ (TAS)	135°C

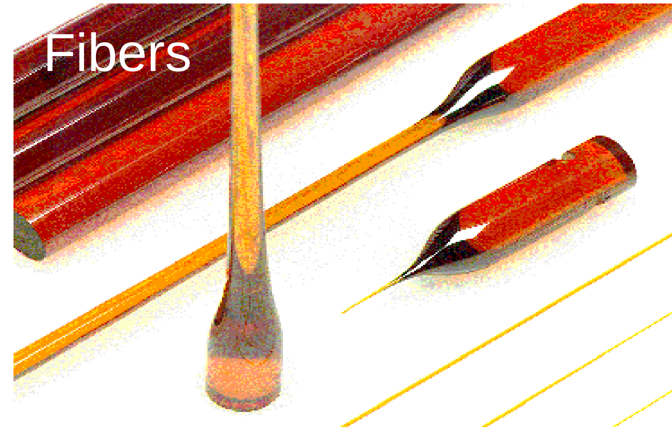
- Stable against crystallization
- Broad optical transmission window ($\lambda > 10$ µm)
- Low phonon energies (Ge – S : 340 cm^{-1}; Ge – Se : 200 cm^{-1})
- High non-linear refractive index : $n_2 \gg n_2$ silica (2-3 orders of magnitude)
- Viscoplastic properties : molding, drawing, pressing, …
- Applications : transmission of IR signal, lenses for IR camera, sensors, light sources, light conversion, supercontinuum, …
  - ✓ Luminescence: substitution of active Ln for Ga in 2S2G glass

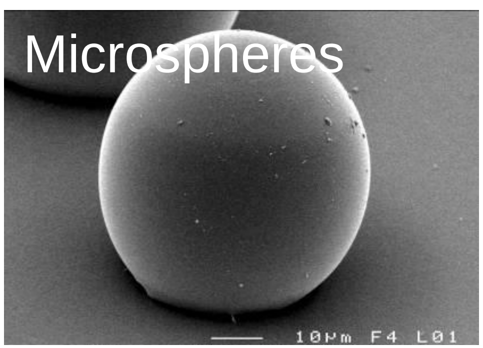
Optical transmission of glasses

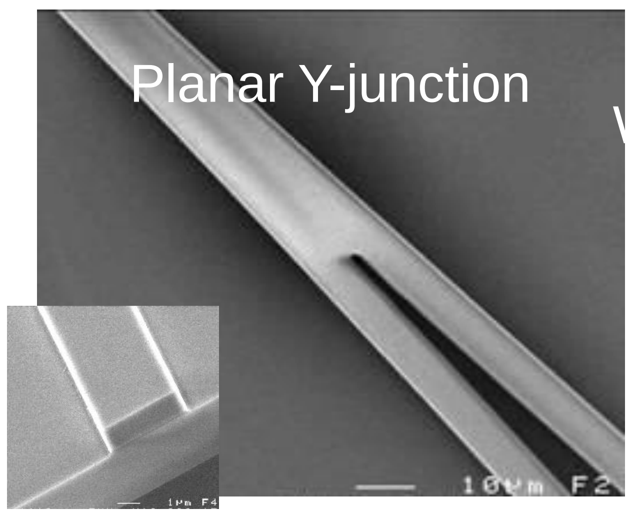


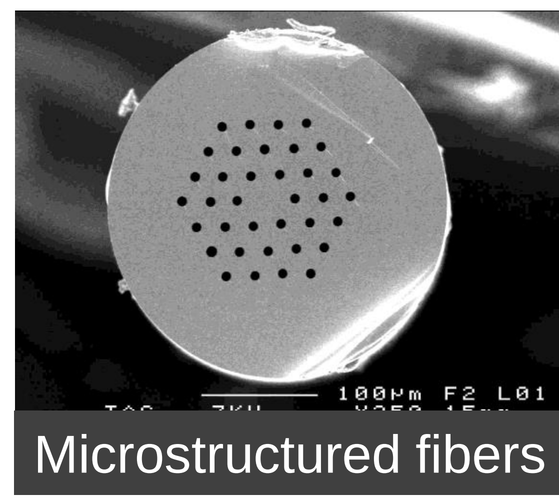
Chalcogenide Glasses are suitable for Molding, Drawing or Deposition
- Bulk optics , Optical fibers & Waveguides for the IR -



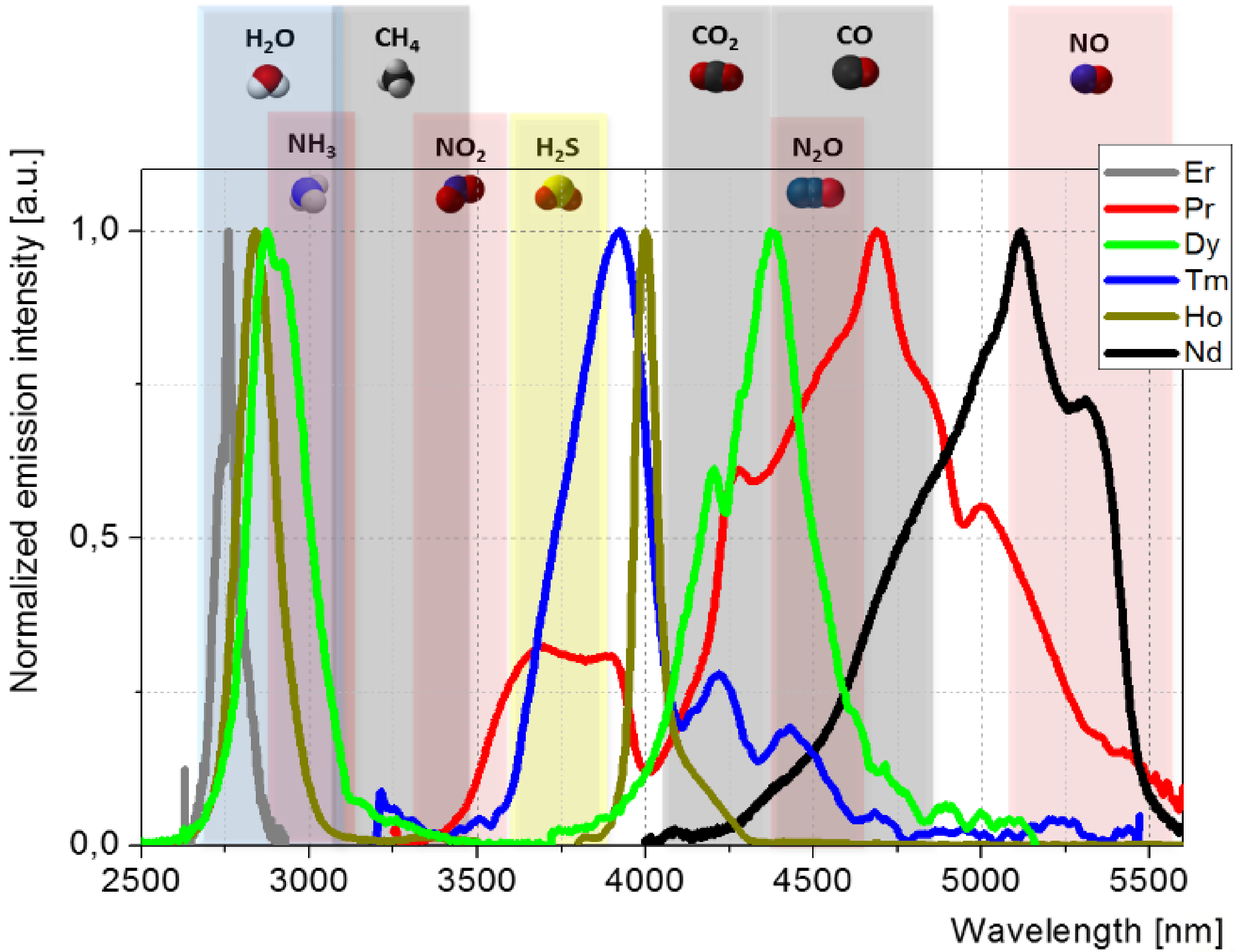








Interest of rare-earth doped chalcogenide glasses for sensing molecules



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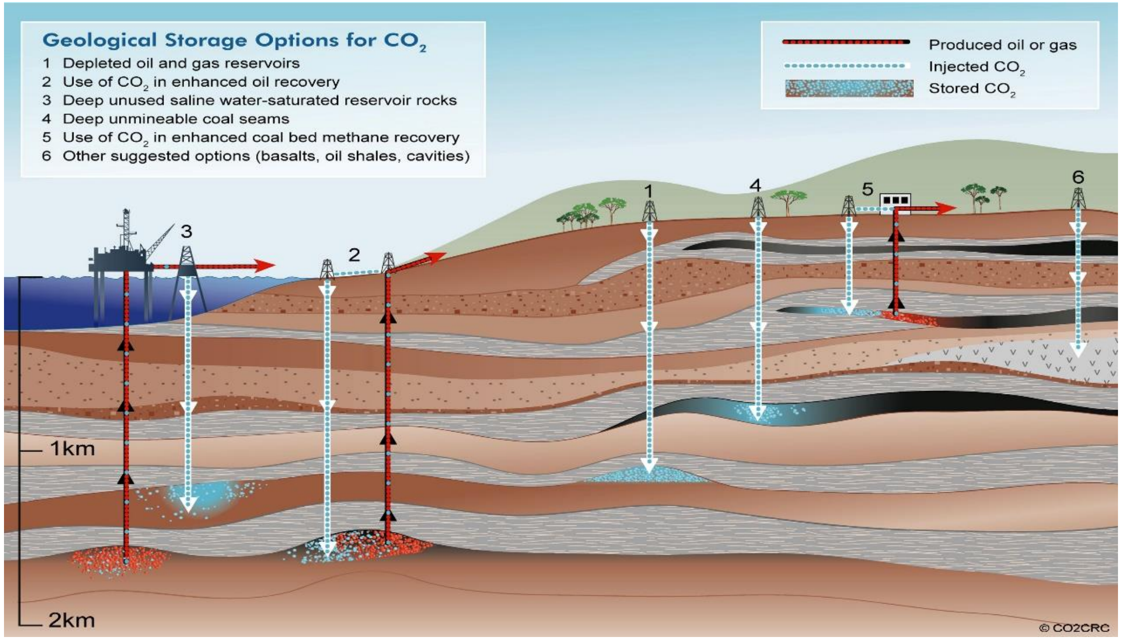
CONTEXT : environmental monitoring

Global warming related to increase of *Greenhouse gas*

like CO_2 emissions

31 Billion tons of CO_2 per year in 2010

50 Billion tons of CO_2 per year in 2050



Capturing and safely storing the CO_2 in suitable deep underground geological formations :

Deep saline aquifers – everywhere in the world, large storage capacity

Depleted oil and gas reservoirs – CO_2 used in enhanced oil recovery

Deep unmineable coal seams – enhanced methane recovery

Geoscience for a sustainable Earth brgm

Monitoring of CO_2 storage sites

Development of remote optical sensor

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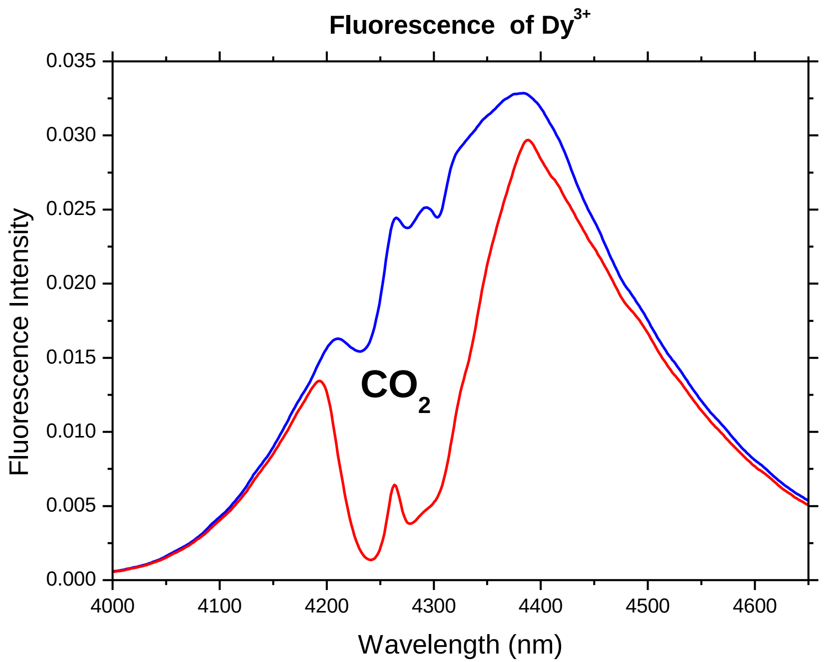
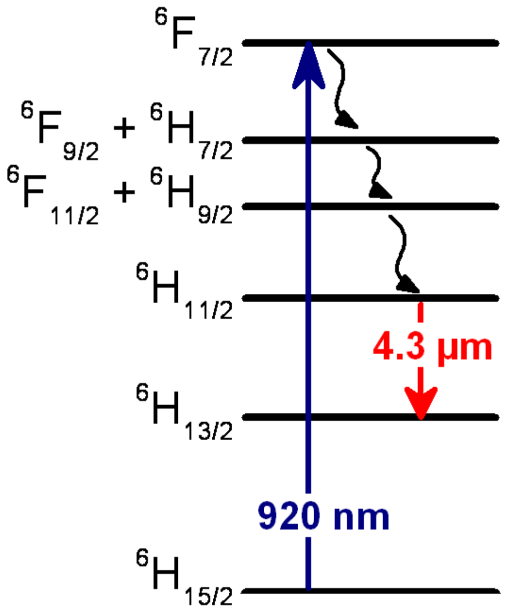
Chalcogenide glasses - 2S2G:Dy^{3+} : an IR source for the detection of CO_2





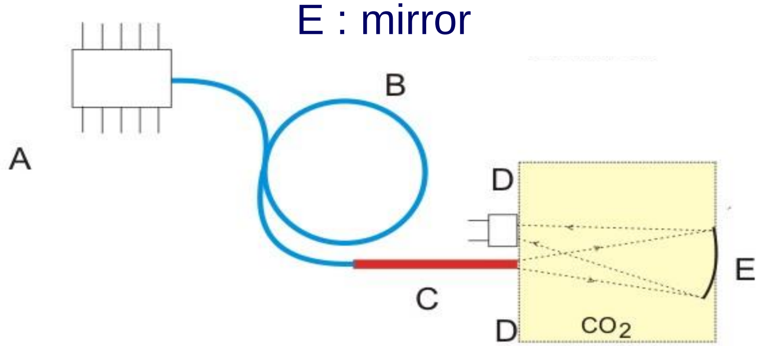
$^6H_{11/2} \rightarrow {}^6H_{13/2}$ transition observed in low-phonon energy materials

➔ Very sensitive to the presence of CO_2

Infrared optical sensor for CO_2 detection with 2S2G: Dy^{3+} glass

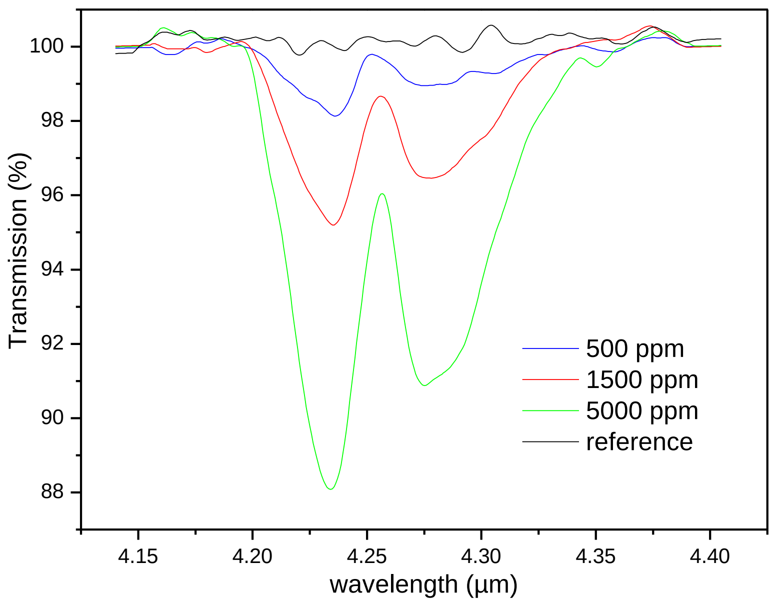
➢ <u>Studied concentrations :</u> 500, 1500 et 5000 ppm CO_2 (reference gas bottles)

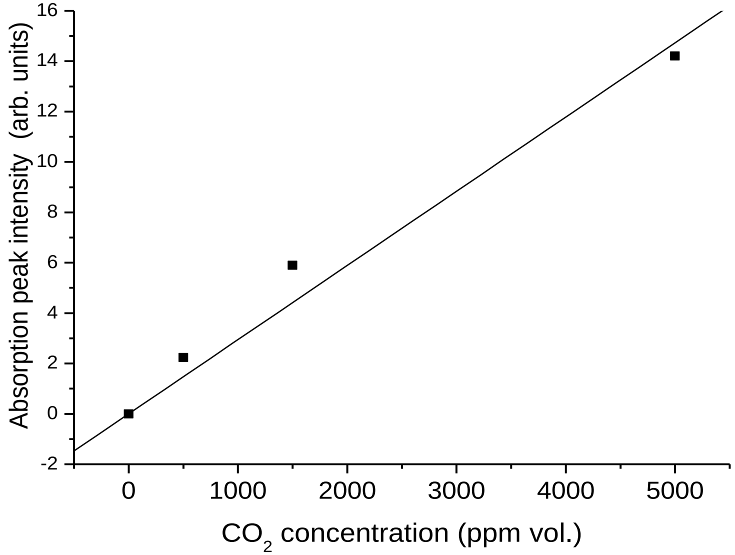
A : Laser diode 920 nm
B : Silica fiber
C : Dy^{3+} Chalcogenide fiber
D : InSb detector
E : mirror



Scheme of gas optical sensor *(not on scale)*

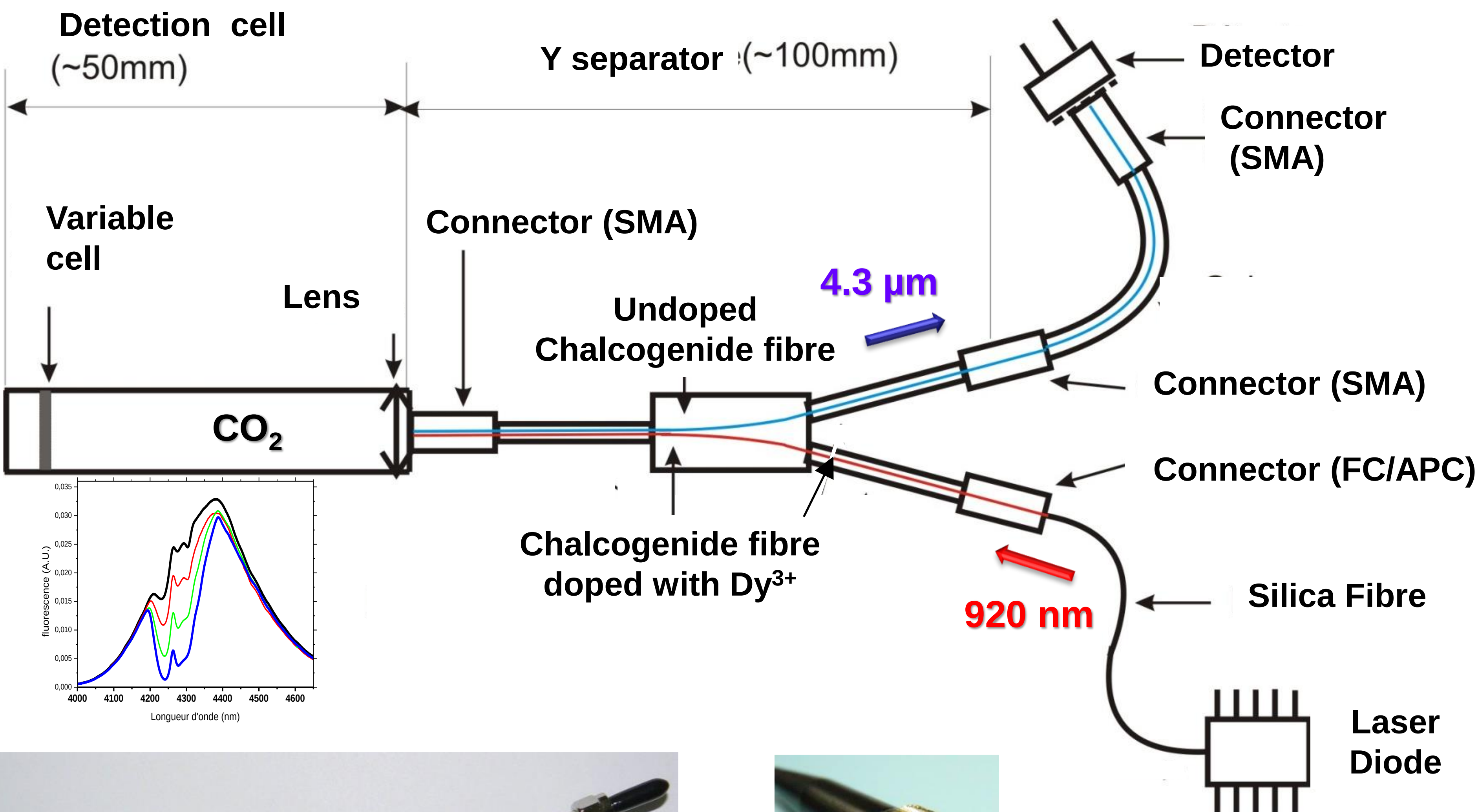
- Sensitivity threshold is about 500 ppm for cell of 4mm length filled with CO_2
- System is fully reversible





CiMap UNIVERSITÉ DE RENNES 1 ueb brgm Géosciences pour une Terre durable

Infrared optical sensor for CO_2 detection with 2S2G: Dy^{3+} glass



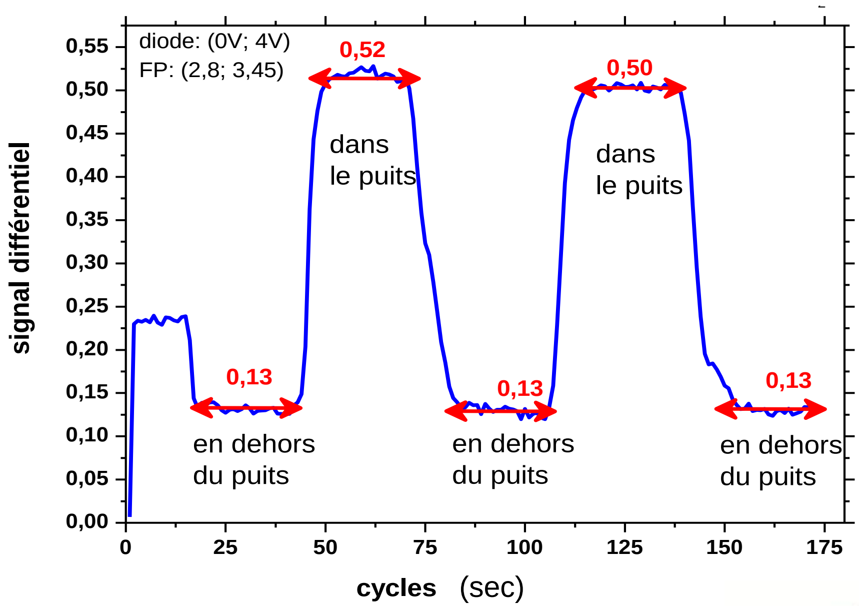
Standard connectors

Infrared optical sensor for CO_2 detection with 2S2G: Dy^{3+} chalcogenide glass fiber

On-site experiment

Best achievements to date:

- Detection by using mid-IR fluorescence of Dy^{3+} at depth > 350 m
- Detection threshold of 400 ppm with accuracy of 15 ppm
- Reversibility demonstrated



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F. Starecki et al., Sensors Actuators 207 (2015) 518

Towards all-optical CO_2 gas sensor

- Limitation to all-optical: high attenuation of chalcogenide fibers (vs silica)

- Solution: use of silica fiber for the « exit signal », as well

Back-conversion
of IR (4.4 µm) to silica-compatible wavelength

Advantages:
Low propagation losses of silica fibers
High sensitivity of detectors in the Vis-NIR range

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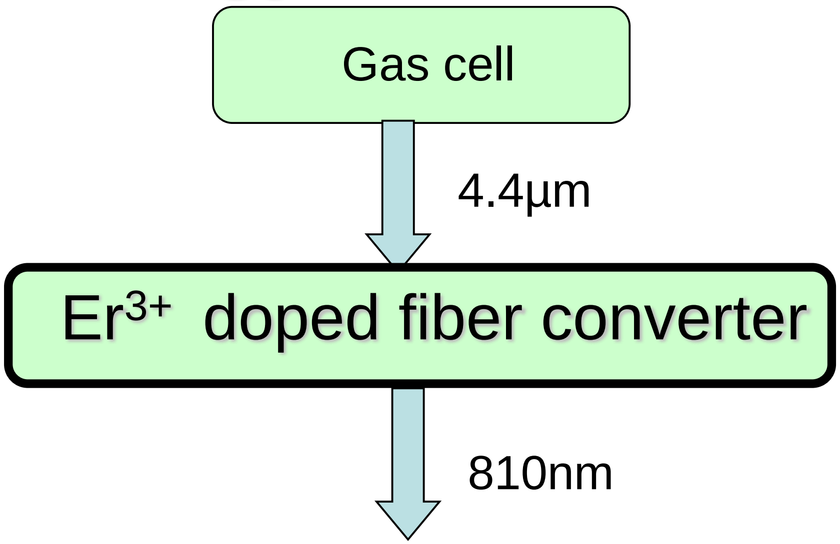
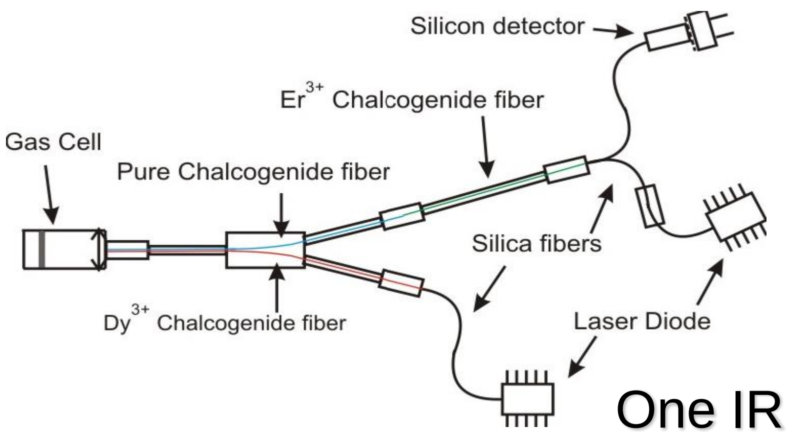
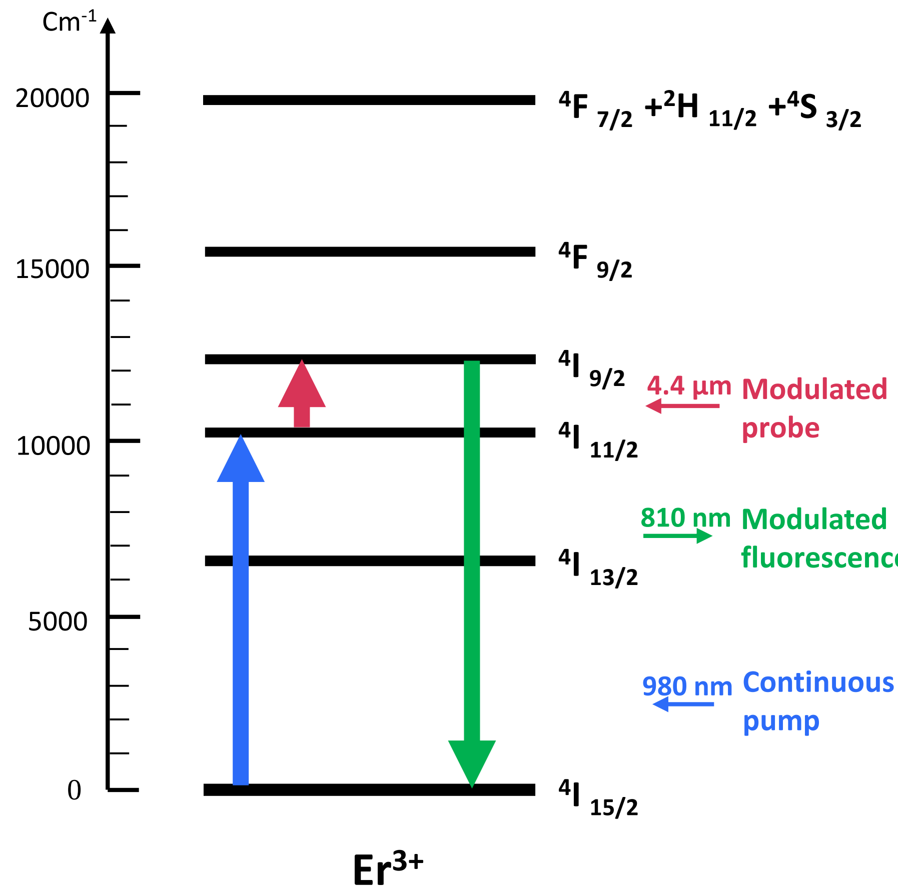
Energy conversion from 4.4µm to 810 nm







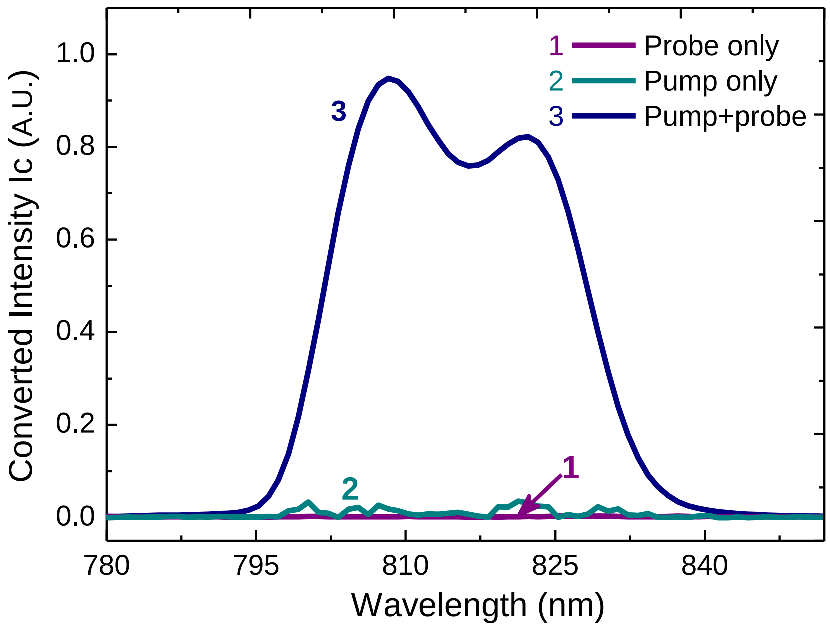
One IR photon gives one visible photon following Excited State Absorption (ESA)

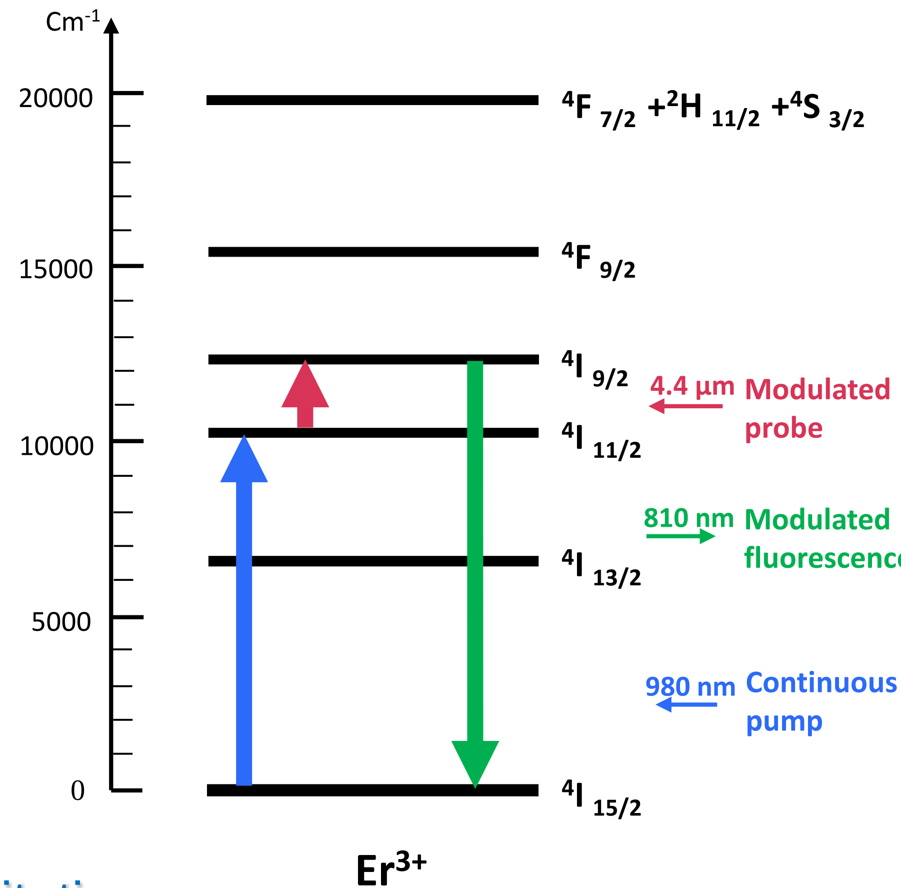
A.L. Pelé et al. Optics Express 23 (2015) 4163

Energy conversion from 4.4µm to 810 nm

Demonstration of the 4.4µm to 810nm conversion

in Er^{3+} doped 2S2G bulk and fibers





Converted signal only exists
with simultaneous pump-probe excitation

A.L. Pelé et al. "Wavelength conversion in Er^{3+} doped chalcogenide fibers for optical gas sensors", Optics Express 23 (2015) 4163

Pr^{3+}–Dy^{3+} codoped GaGeSbS fibers for emission between 3-5µm

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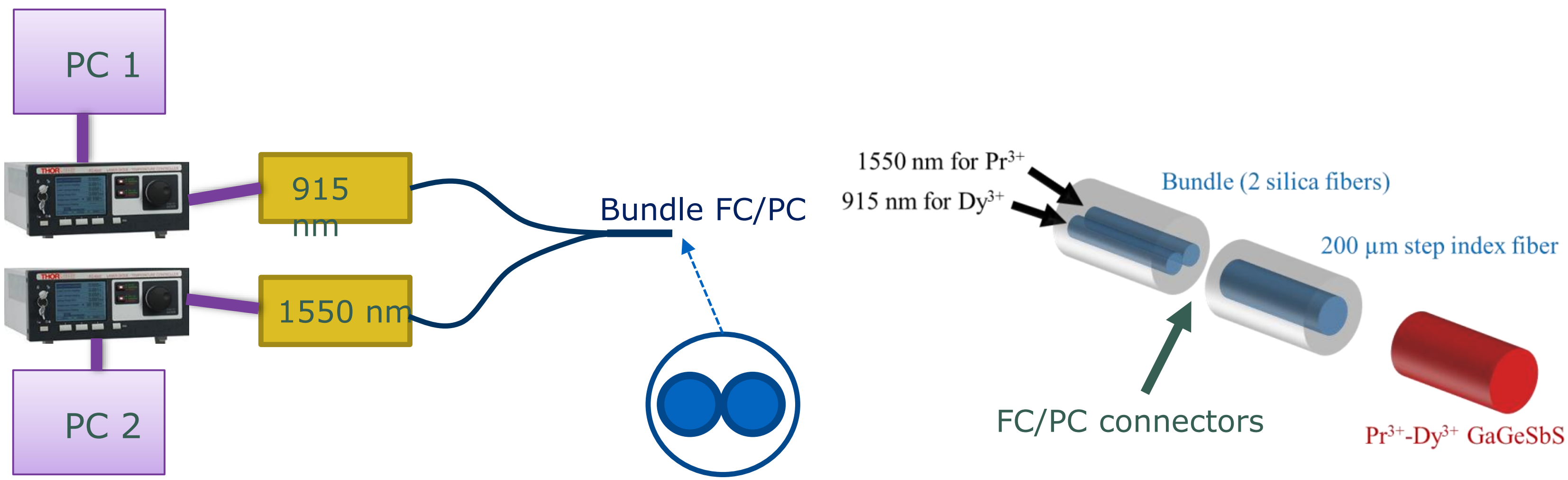
Co-pumping system for Pr^{3+}-Dy^{3+} couple

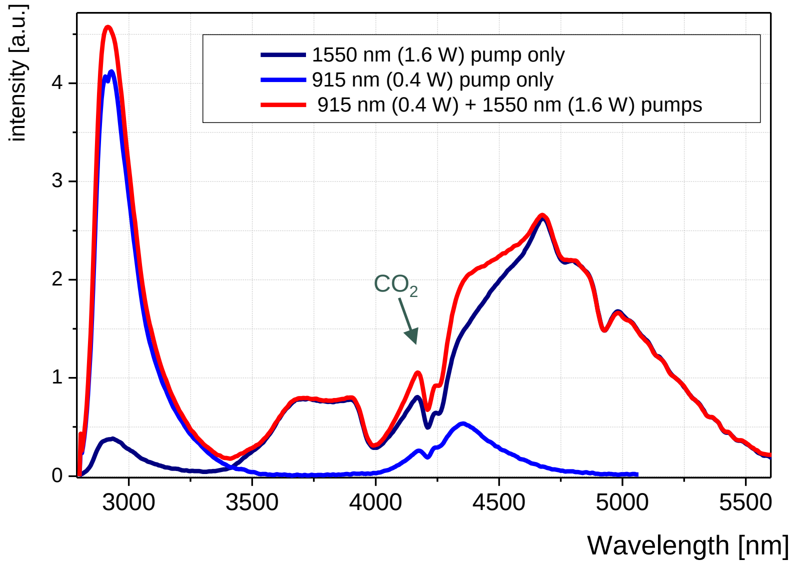


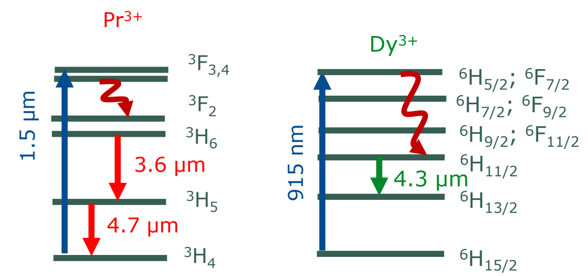
➡ Co-injection synchronized in a single silica multimode fiber

Pr^{3+}-Dy^{3+} codoped GaGeSbS fibers

Mid-IR signal generation

1000 ppm Pr^{3+} – 200 ppm Dy^{3+}
$Ga_5Ge_{20}Sb_{10}S_{65}$



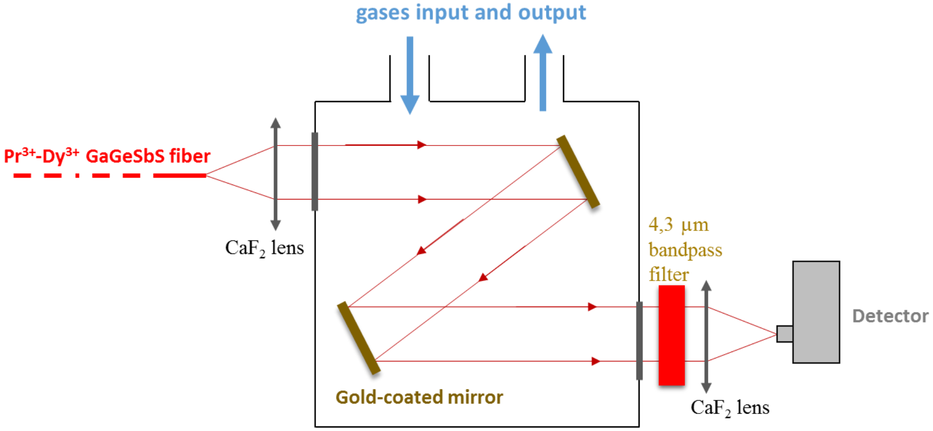


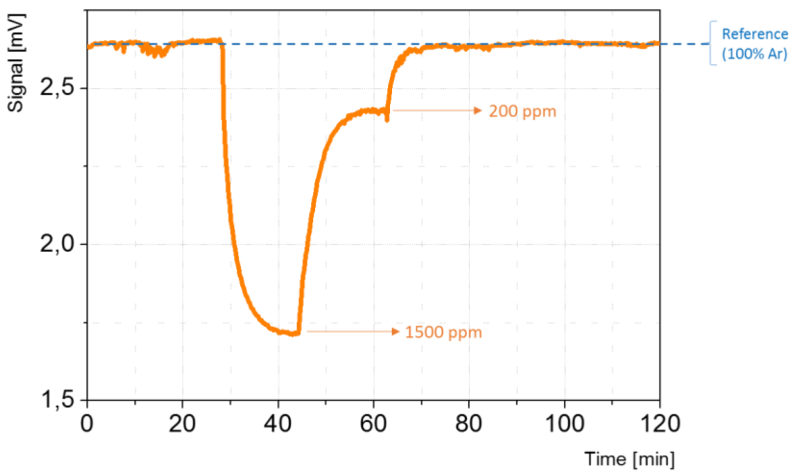
- Negligible interactions between Dy^{3+} and Pr^{3+} ions
- "Addition" of both single luminescence spectrum

RE content [ppm]		Pr^{3+} [µs]		Dy^{3+} [ms]	
Pr^{3+} content	Dy^{3+} content	$^3H_6$	$^3H_5$	$^6H_{11/2}$	$^6H_{13/2}$
1000	200	220	270	1.13	5.21
1000	500	170	220	1.08	5.18
1000	1000	180	200	0.86	4.30

CO_2 demonstrator based on the Pr^{3+}-Dy^{3+} couple

CO_2 detection: Results





- Two gold-coated mirrors who form a 45 cm Z configuration optical path

CO_2 sensitivity = 15 ppmv

Microstructured optical fibers

for IR laser delivery

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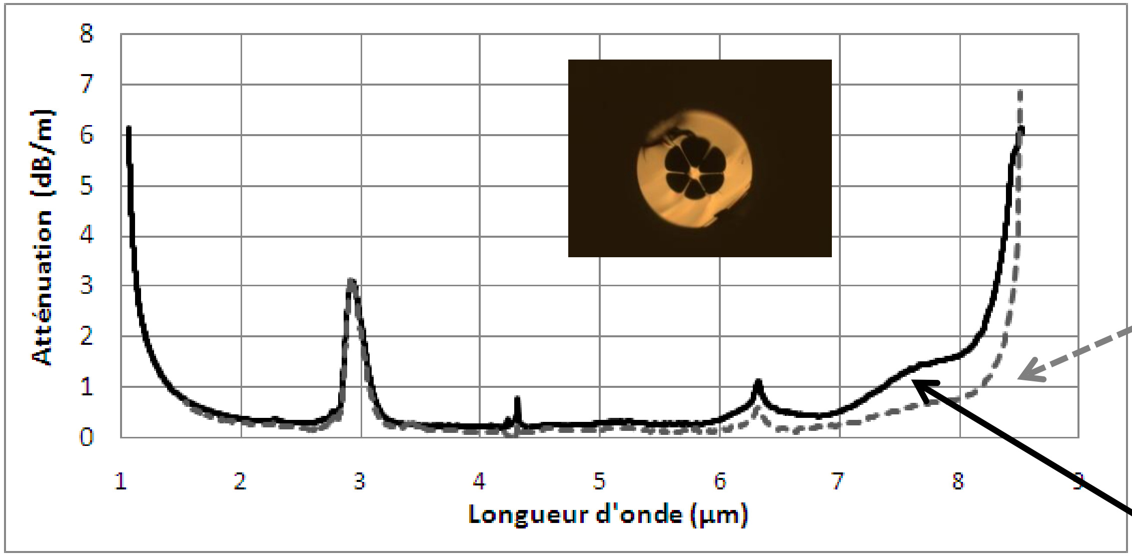
Optical losses in chalcogenide glass microstructured fibers

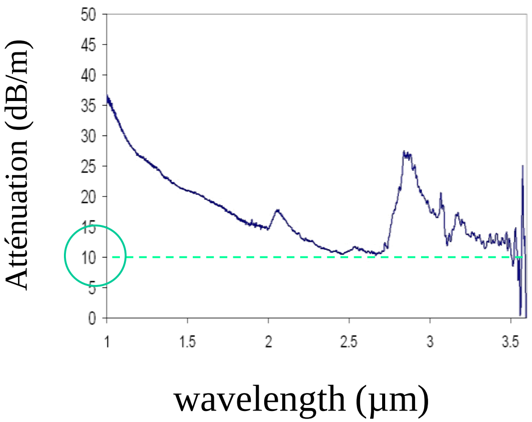


Wire Fiber from As-Se single-index glass preform

As-Se suspended-core Microstructured Optical Fiber

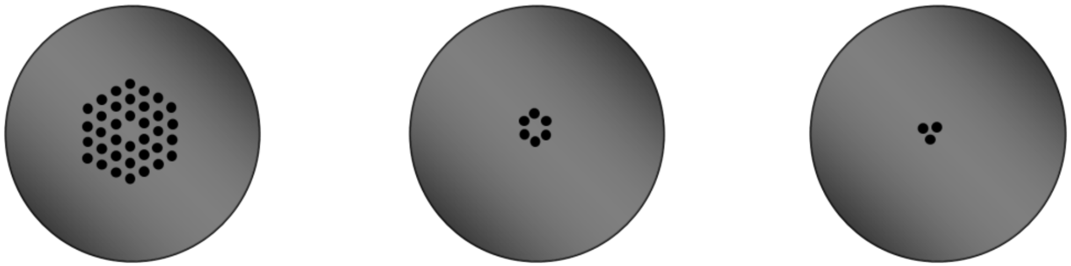
Preform prepared by molding : losses < 0.1 dB/m

Fibers from "stack and draw" preform ➔



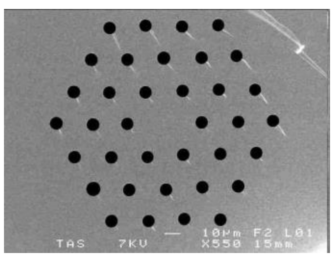
Microstructured Chalcogenide IR fibers

Preforms (Ø= 16 or 20 mm)

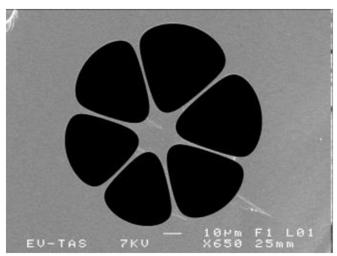


MOFs:

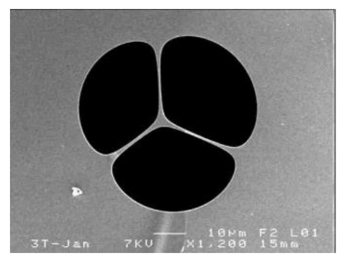
3-ring | **Suspended-core**



Singlemode
3 µm < $Ø_c$ < 30 µm

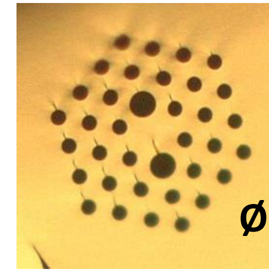


Multimode
20 µm < $Ø_c$ < 30 µm

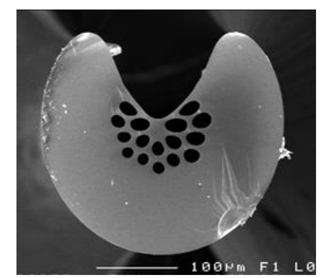


Singlemode
3 µm < $Ø_c$ < 4 µm

- **Reliability of the casting method**
- **Various MOF designs can be realized**



Single-mode Polarization maintaining between 3-8 µm
C. Caillaud et al., Opt. Express 24 (2016) 7977



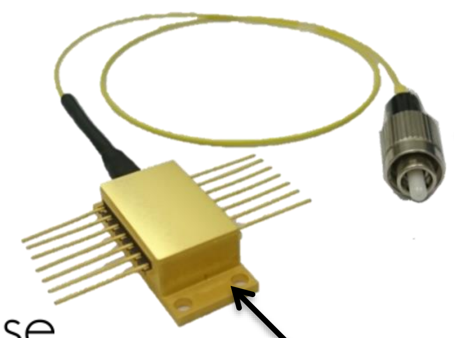
Exposed-core MOF for optical sensing
P. Toupin et al., J. Non-Cryst. Solids 377 (2013) 217

Chalcogenide MOF connected to a 7.4 µm QCL

→ Delivering infrared laser beam for spectrocopy applications:

The first chalcogenide MOF connnected to a QCL

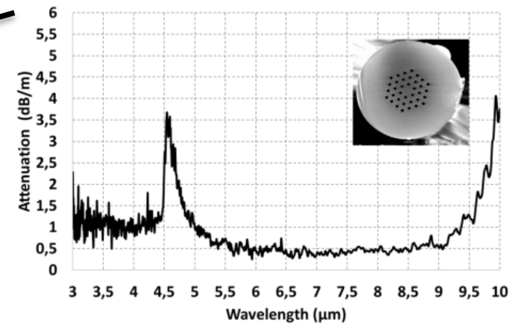
SelenOptics



mir sense

Quantum Cascade Laser
λ=7.4 µm,
200 mW output

Single Mode AsSe MOF



Fiber output power
> 1mw

- High quality of the beam exiting the single mode fiber
- Standard connectors → easy combination with other optical components

Summary

- Chalcogenide glass fibers doped with Dy^{3+}
  - Broad emission centered at 4.4 µm
  - CO_2 sensor demonstrated
  - On the way to develop an all-optical sensor
  - Better sensitivity with Pr^{3+} co-doping
- Low-loss chalcogenide microstructured optical fibers
  - Connection to QCL for IR laser beam delivery at 7.4 µm

Acknowledgements

- Karine Michel
- Lionel Quetel

INSTITUTE of CHEMICAL SCIENCES

at University of Rennes

Thank you for your attention

The city of Rennes

15th International Conference on The Physics of Non-Crystalline Solids & 14th European Symposium on Glass conference

Important Dates

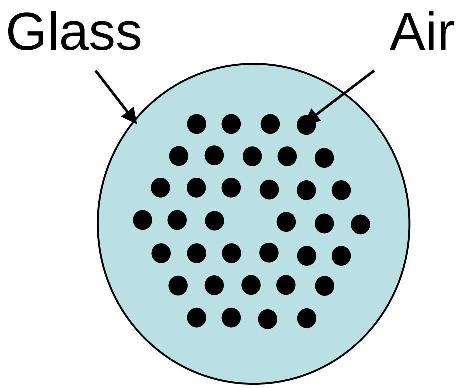
Abstract submission deadline: December 31st, 2017

Notification of abstract acceptance: February 15th, 2018

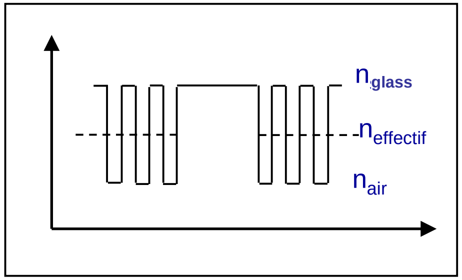
Early bird registration: Mai 1st, 2018

1-Photonic Crystal Fibers (microstructured fibers) for IR

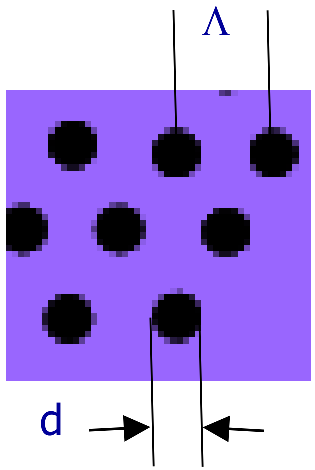
- Lower average refractive index around the core ($n_{air} < n_{glass}$ (= 2.3-2.8))



- Properties depend on d, Λ



- Endlessly single mode for $d/\Lambda < 0.40$
- Broad tunability of dispersion



- 1000 μm^2 > Effective mode area > 1 μm^2

Potential applications of IR Photonic Crystal Fibers

Single-mode fibers + 1000 µm² > Effective mode areas > 1 µm²

Passive optical functions

- Power transmission of gaussian beams (CO_2 laser)
- Broad-band single-mode transmission of IR light
- Optical gas sensing (CH_4, CO_2 …)
- Spatial filtering of infrared light, infrared interferometry

Active optical functions

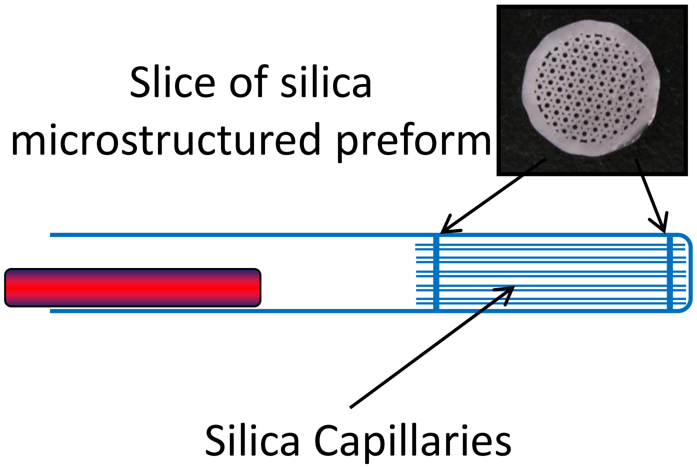
Glass	n_2 (10^{-18} m^2/W)
Silica	0.027
As_2S_3	5
As_2Se_3	19
$Ge_5As_{30}Se_{65}$	24

High non-linearity : $\gamma = 2\pi n_2 / \lambda A_{eff}$

- Generation of supercontinuum in the IR
- Wavelength conversion

Preform and Microstructured IR fibers

Casting Method for chalcogenide preform fabrication



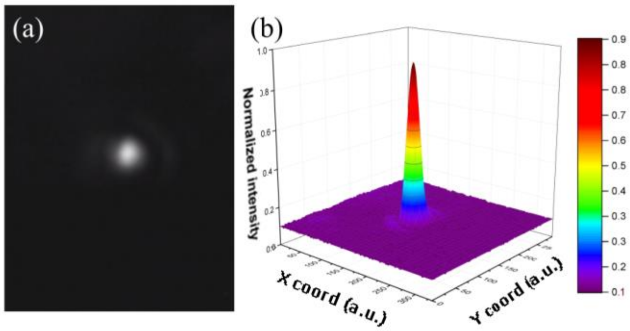
1st step: Silica mould fabrication

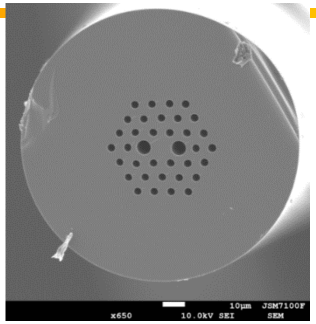
-Q. Coulombier & al, Optics Express 18(8) 9107-9112 (2010)
-P. Toupin & al, Opt. Mater. Express, vol 2, 1359-1366 (2012)

Microstructured Chalcogenide IR fibers

3—8-μm polarization maintaining fibers

- **Single-mode transmission demonstrated at 3.39 μm**
- **Optical losses below 1 dB/m from 2 to 8 μm (0.3 dB/m @ 6 μm)**



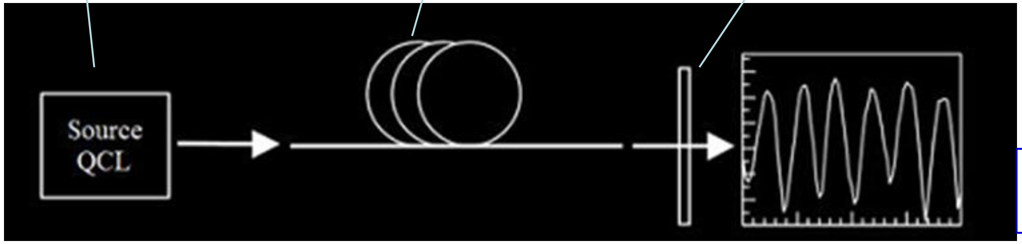


- **High birefringence in the Mid-IR**

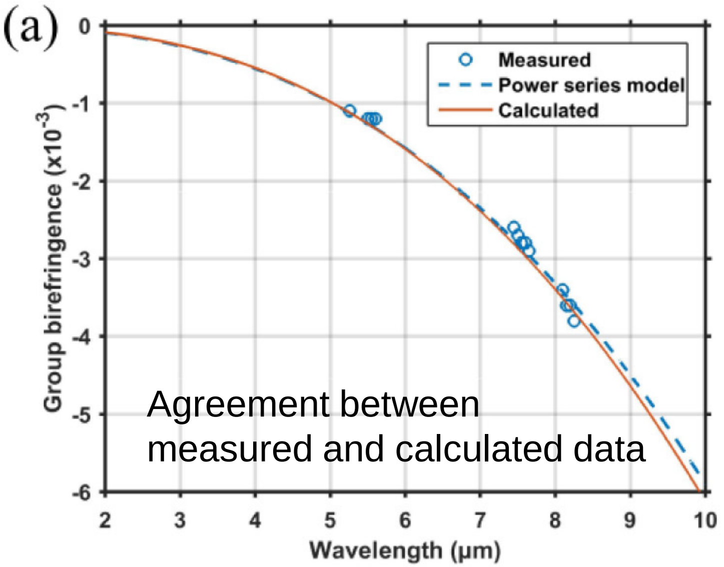
Light from QCL's (5.25 ; 5.55 ; 7.55 ; 8.2 μm), 45° - polarized

Microstructured fiber (L = 2.6 m)

45° polarizer

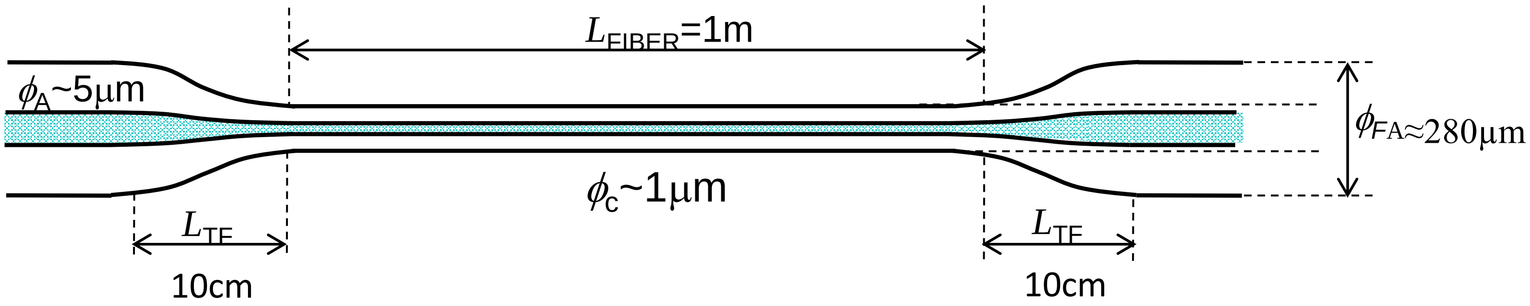


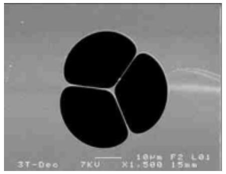
Output spectrum

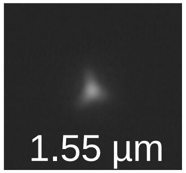


Highly nonlinear AsSe suspended-core fiber

Tapered, As-Se, suspended core fiber







A_{eff} ≈ 1 µm²

n_2 ≈ 500 n_2 (silica)

Non-linear parameter: $\gamma = 2\pi n_2 / \lambda A_{eff}$

γ = 46 000 km^{-1} W^{-1}

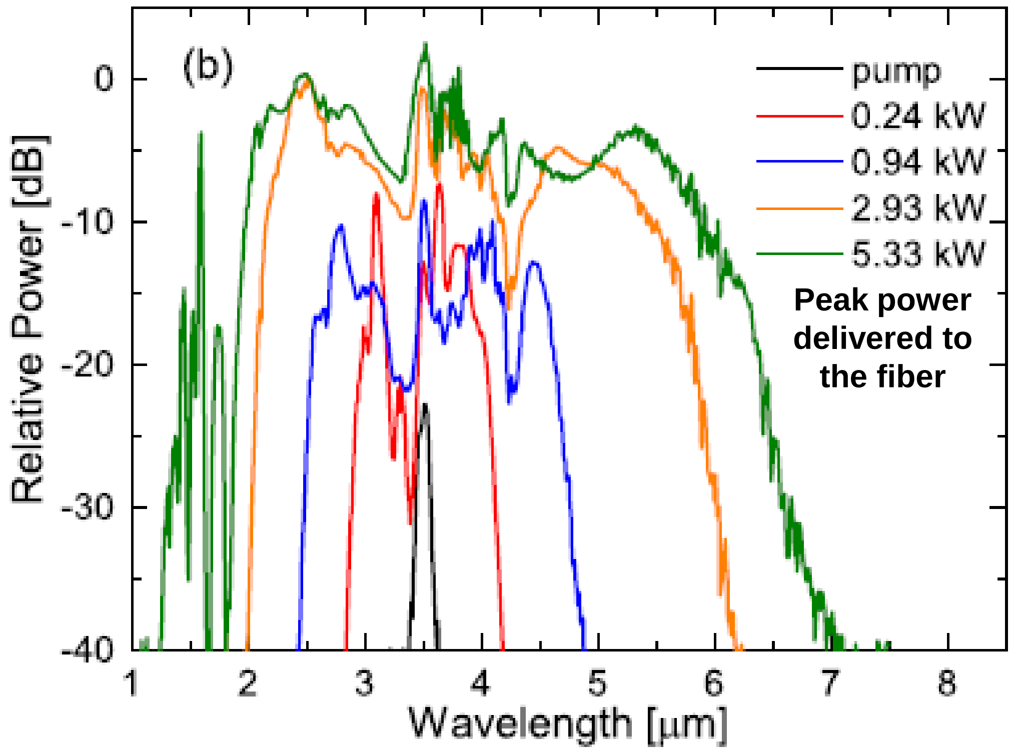
High γ enables enhanced non-linear effect at low power or short fiber length

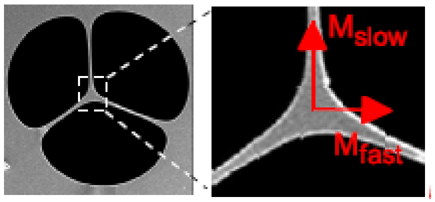
γ ≈ **2** km^{-1} W^{-1} for standard silica fiber

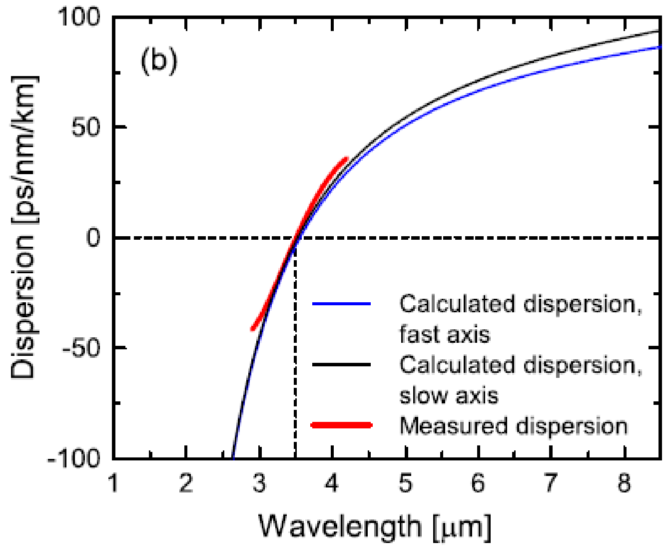
γ ≈ **70** km^{-1} W^{-1} for high-NL silica PCF

Generation of supercontinuum in the mid-IR

suspended core As-Se fiber (Ø=4.5 µm ; L=18 cm)







Zero-dispersion at 3.5 µm

- **Source: OPA (320 fs pulses), with max peak power of 14.8 KW**
- **Supercontinuum from 1.8 to 7 µm, with pump at 3.5 µm**
- **Average output power: 15.6 mW (pump at 4.4 µm, SC up to 7.5 µm)**

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