VERRES EXOTIQUES

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Verres et Céramiques
Université de Rennes

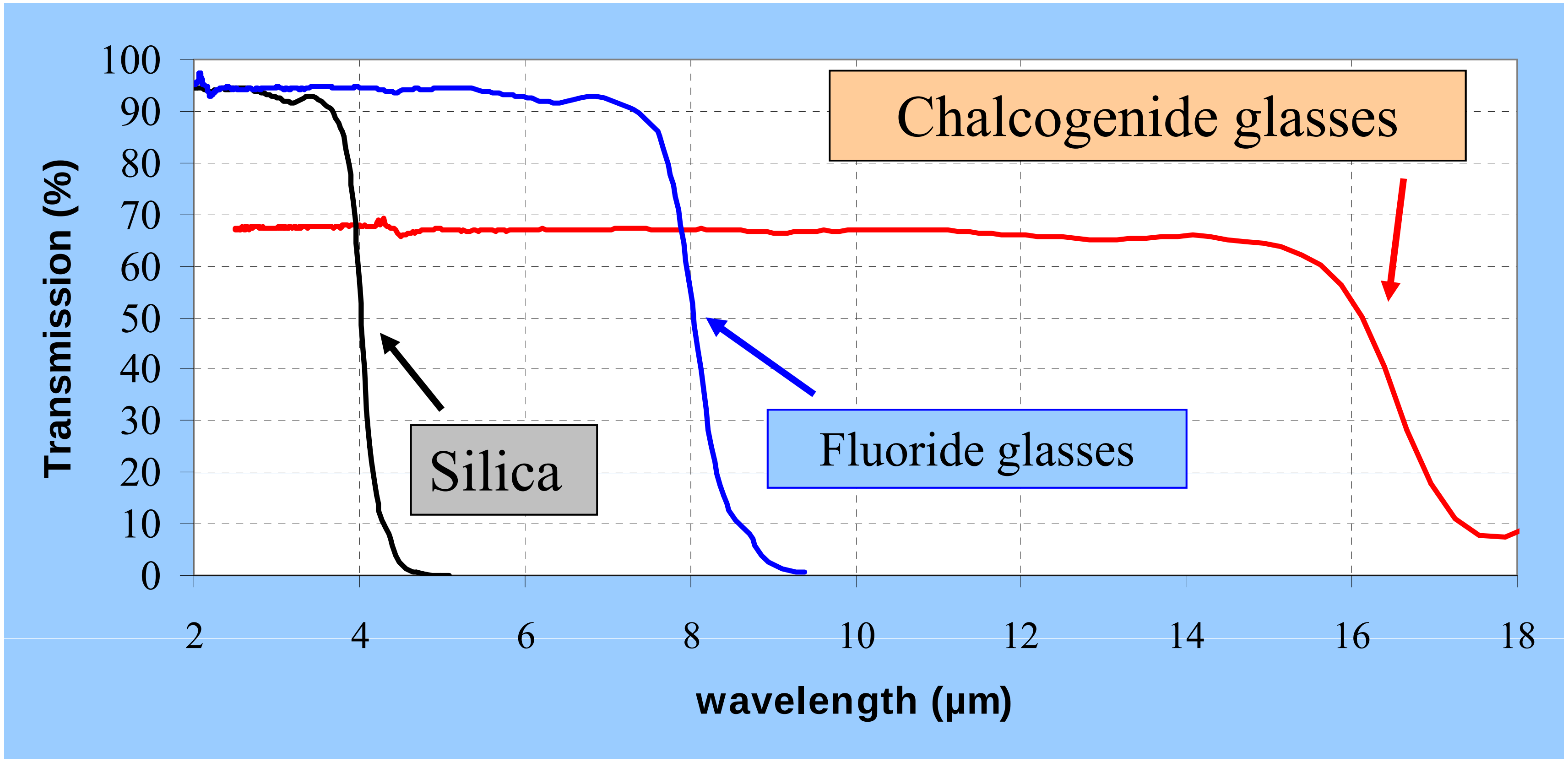
Verres base oxydes →
Énergies de phonon élevées
W_p=1100cm^{-1} pour SiO_2
opaque dans le moyen Infrarouge

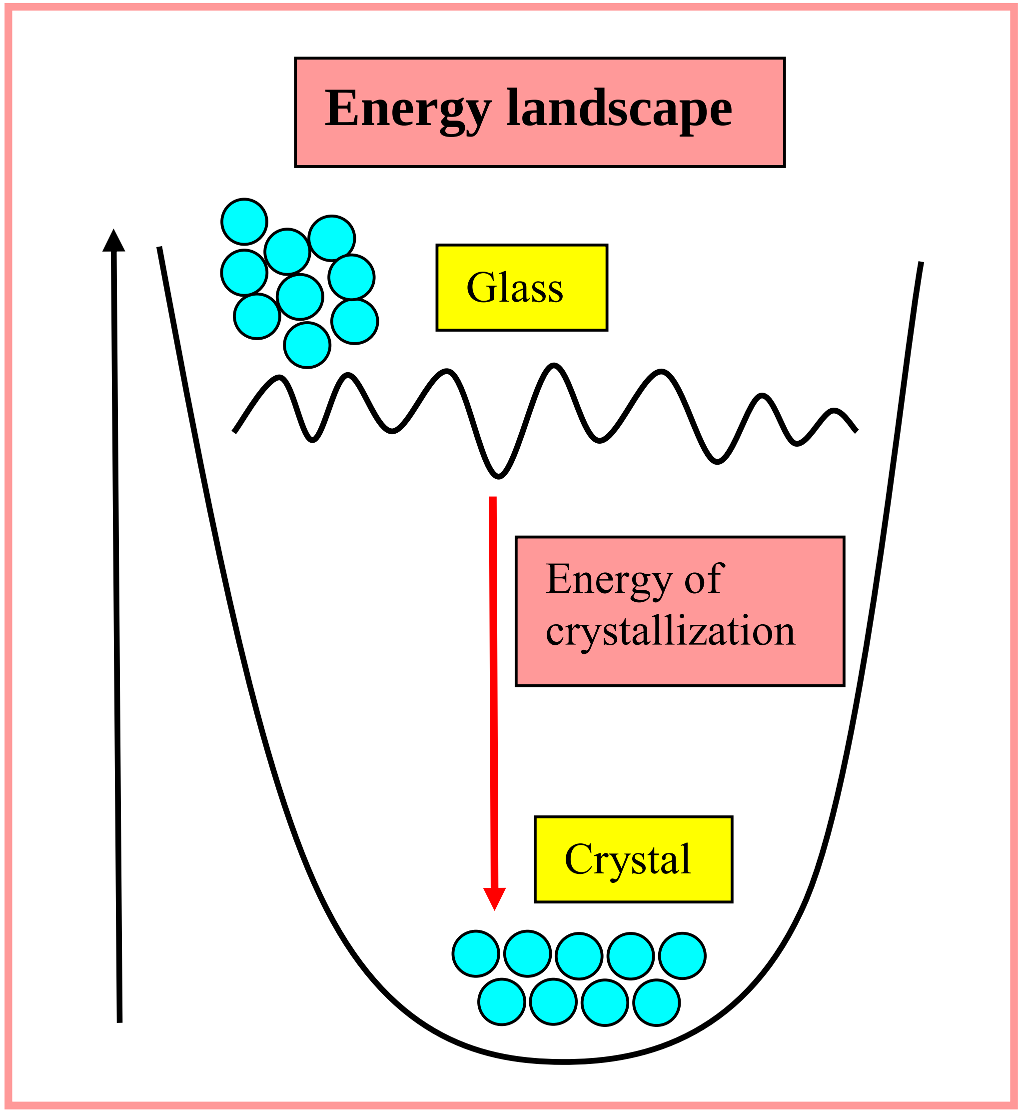
Chimie d’atomes lourds nécessaire →

HALOGENURES surtout fluorures

CHALCOGENURES: S,Se, Te

Transmission of different glasses



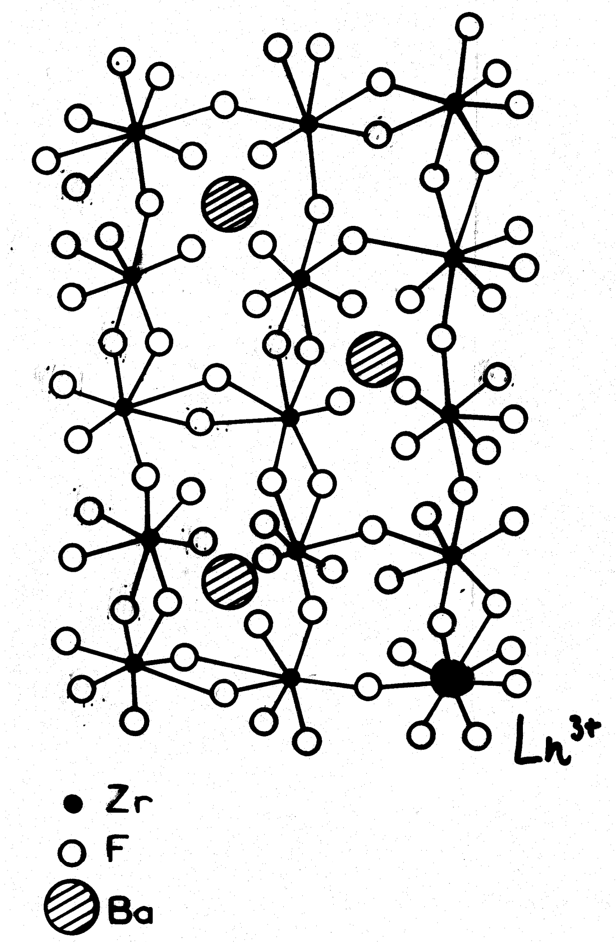

Energy landscape
Glass
Energy of crystallization
Crystal

Fluoride Glass Families

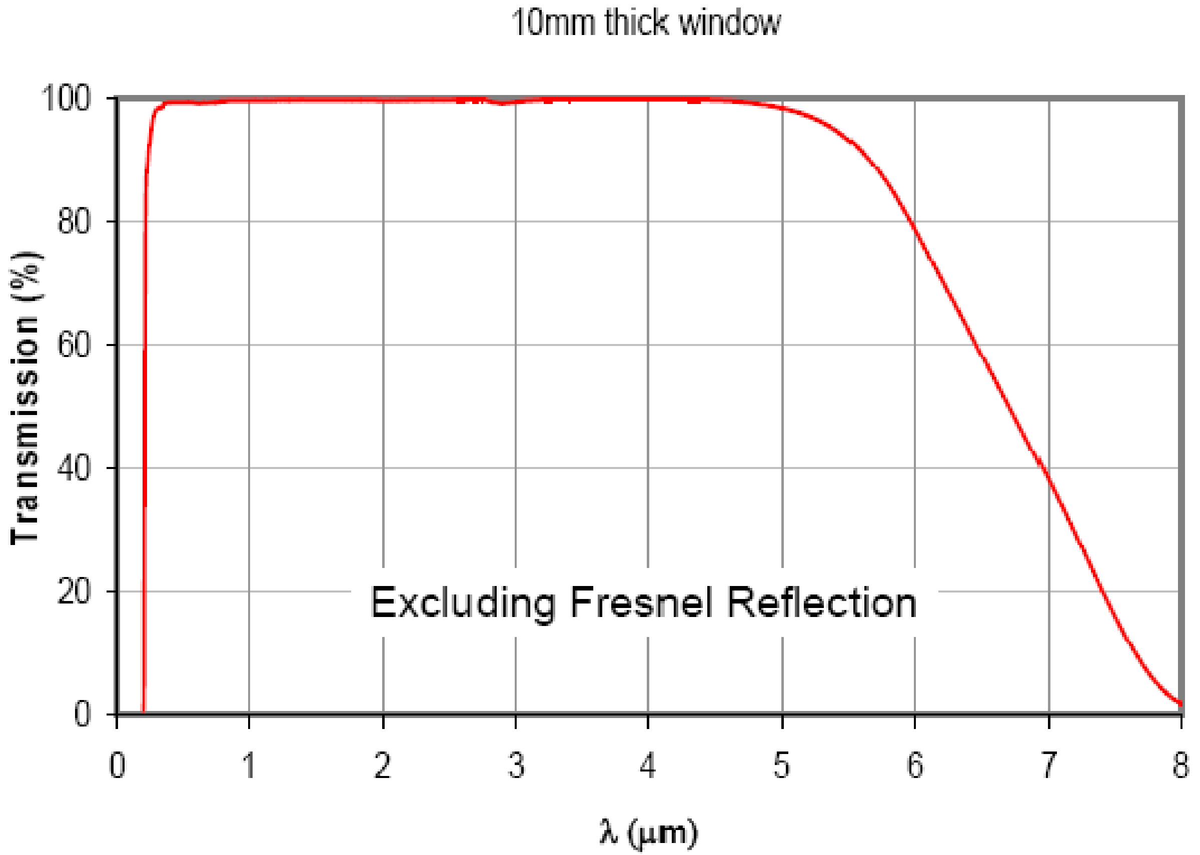
- Fluorozirconate ZrF_4
  - Lowest attenuation
  - High Strength up to 100 kpsi
  - Transmission from 0.3 to 4.3 um
- Fluoroindate InF_3
  - Fiber Transmission from 0.3 to 5,5 um
- Fluoroaluminate AlF_3
  - Less stable, but high resistance to liquid H_2O
- Fluorogallate GaF_3; Fluorozincate ZnF_2; Others

Hundreds of compositions but only few can be drawn into commercial fibers

Structure des Verres de Fluorures



ZBLAN Fluoride Glass Transmission



ZBLAN fibers

SM fiber 9 um core

D-shaped Fiber

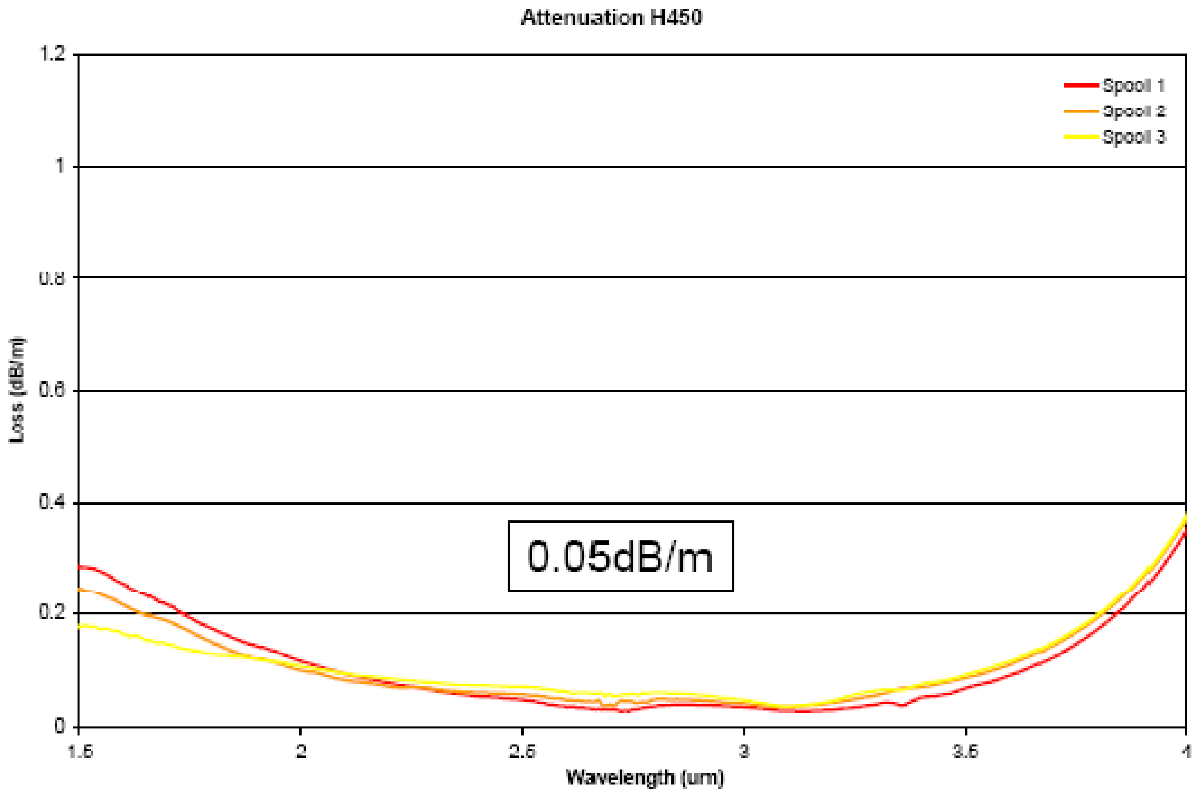
Multimode

Type of fluoride fibers

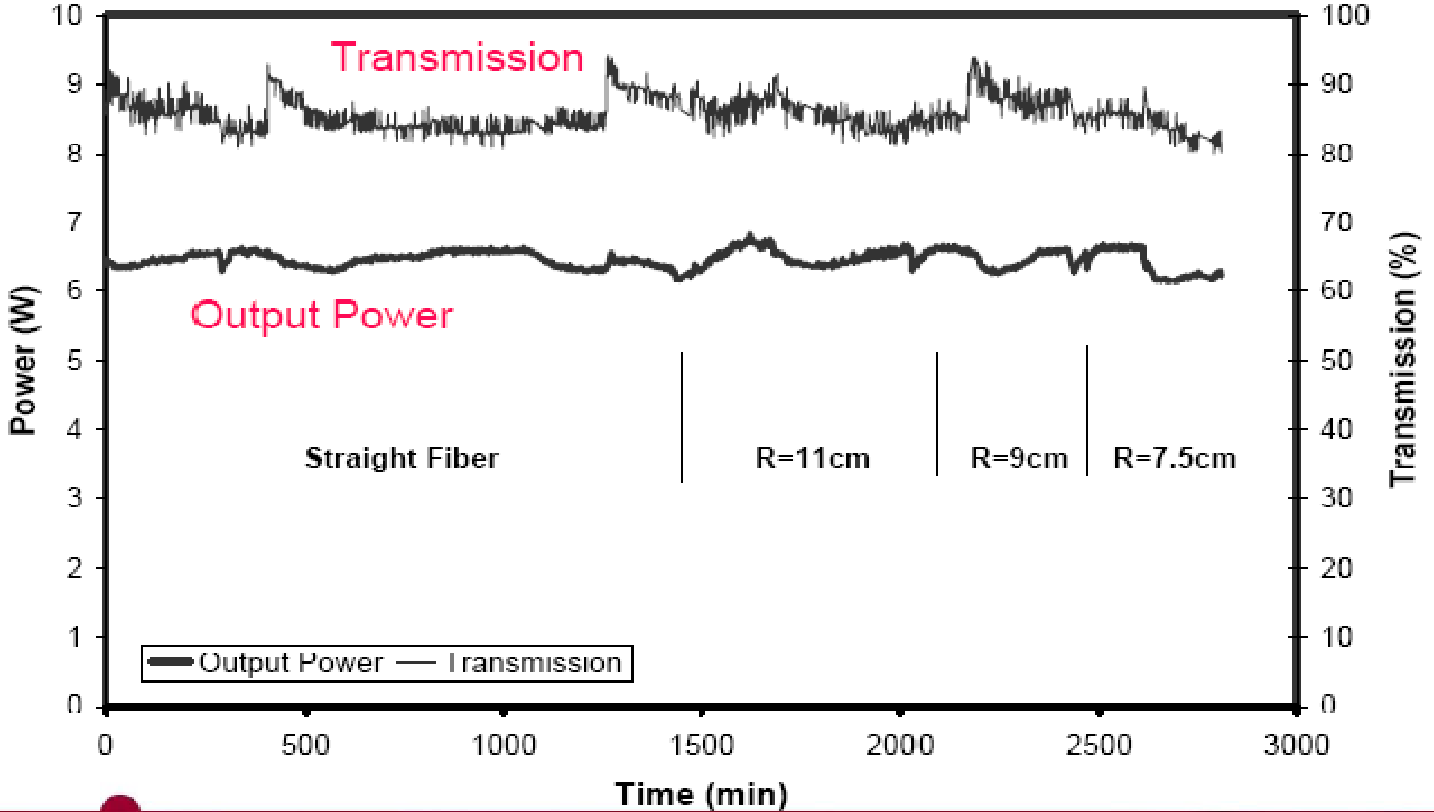
- Multimode (20 to 800 um core)
- Single mode (2 to 20 um core)
- Exotics fibers (D, square ….)
- Micro-structured fiber
- Bragg Grating

- Na from 0.05 to 0.3 (0.45)

Typical ZBLAN Fiber attenuation From IRphotonics



ZBLAN High Power Laser 2.78um Transmission 2.240000 shots



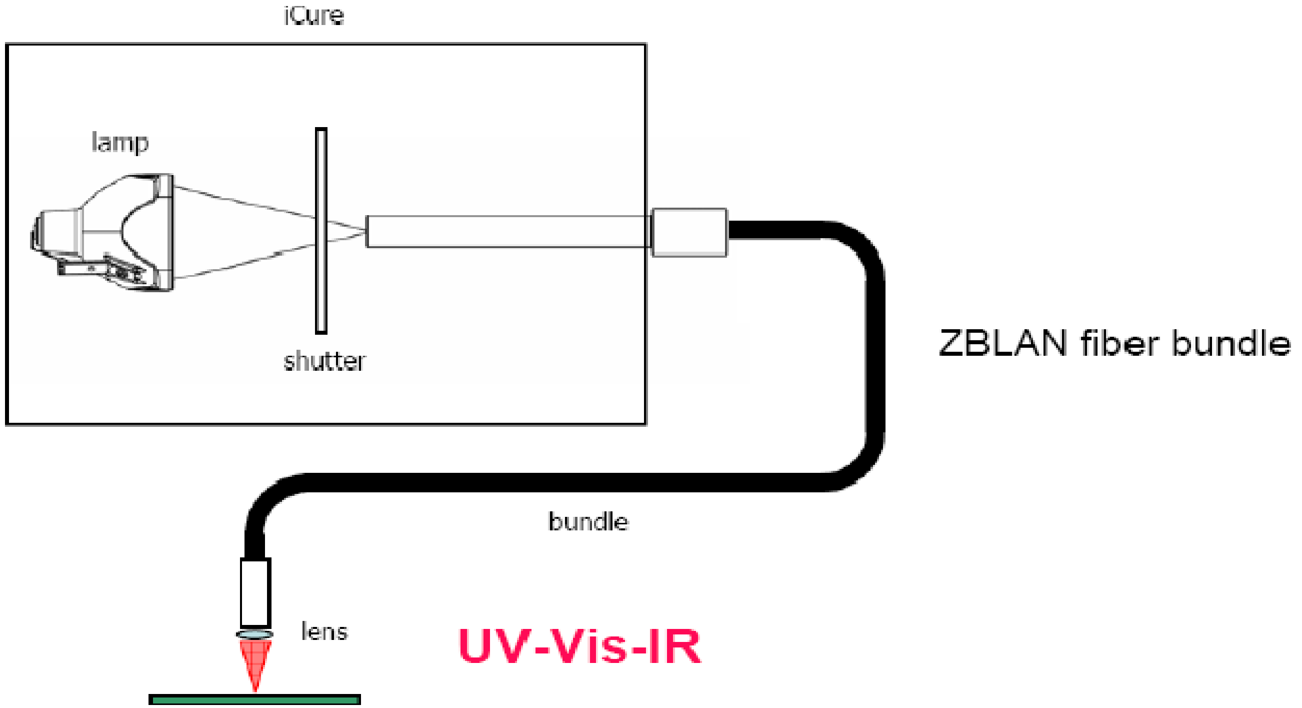
iCure System From IRphotonics

Spot curing system
Using Uv-Vis-Ir energy

Bundle ZBLAN Fibers

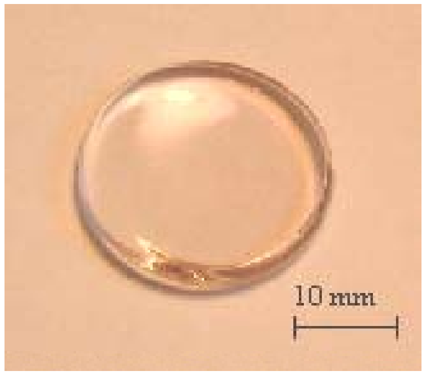
Curing time for most epoxies
5 to 15 s

Thermal Spot Curing: Basics



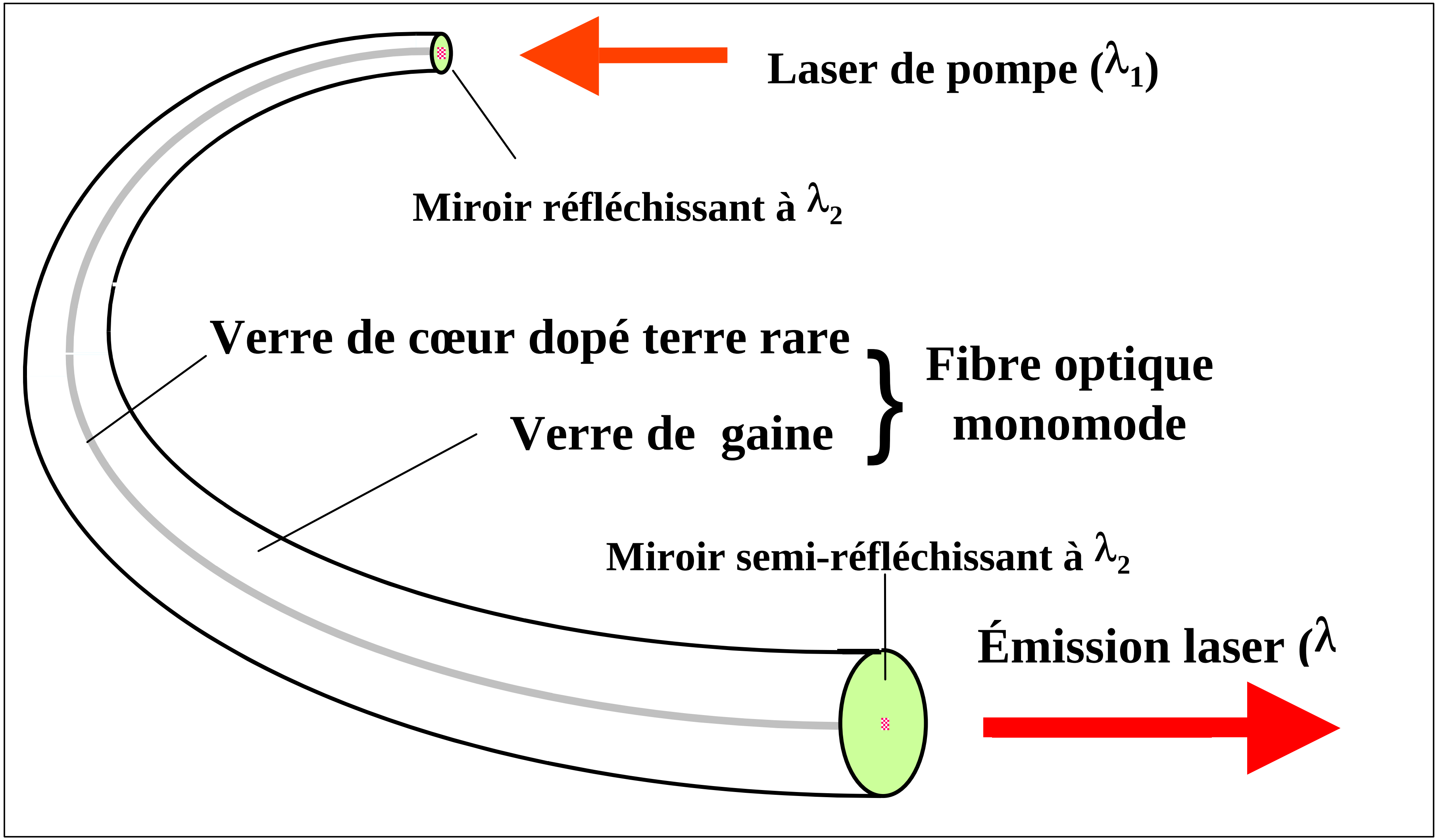
VERRES DE FLUORURES POUR L'OPTIQUE GUIDÉE

Glass	Composition	T_g (°C)	T_x (°C)	T_m (°C)	n_d	
ZBLAN	$ZrF_4 - BaF_2 - LaF_3 - AlF_3 -$ NaF	262	352	455	1.498	Optical fibers
ZBLA	without NaF	307	392	548	1.516	Channel waveguides
PZG	39 PbF_2 - 29 ZnF_2 - 32 GaF_3	266	304	543	1.574	

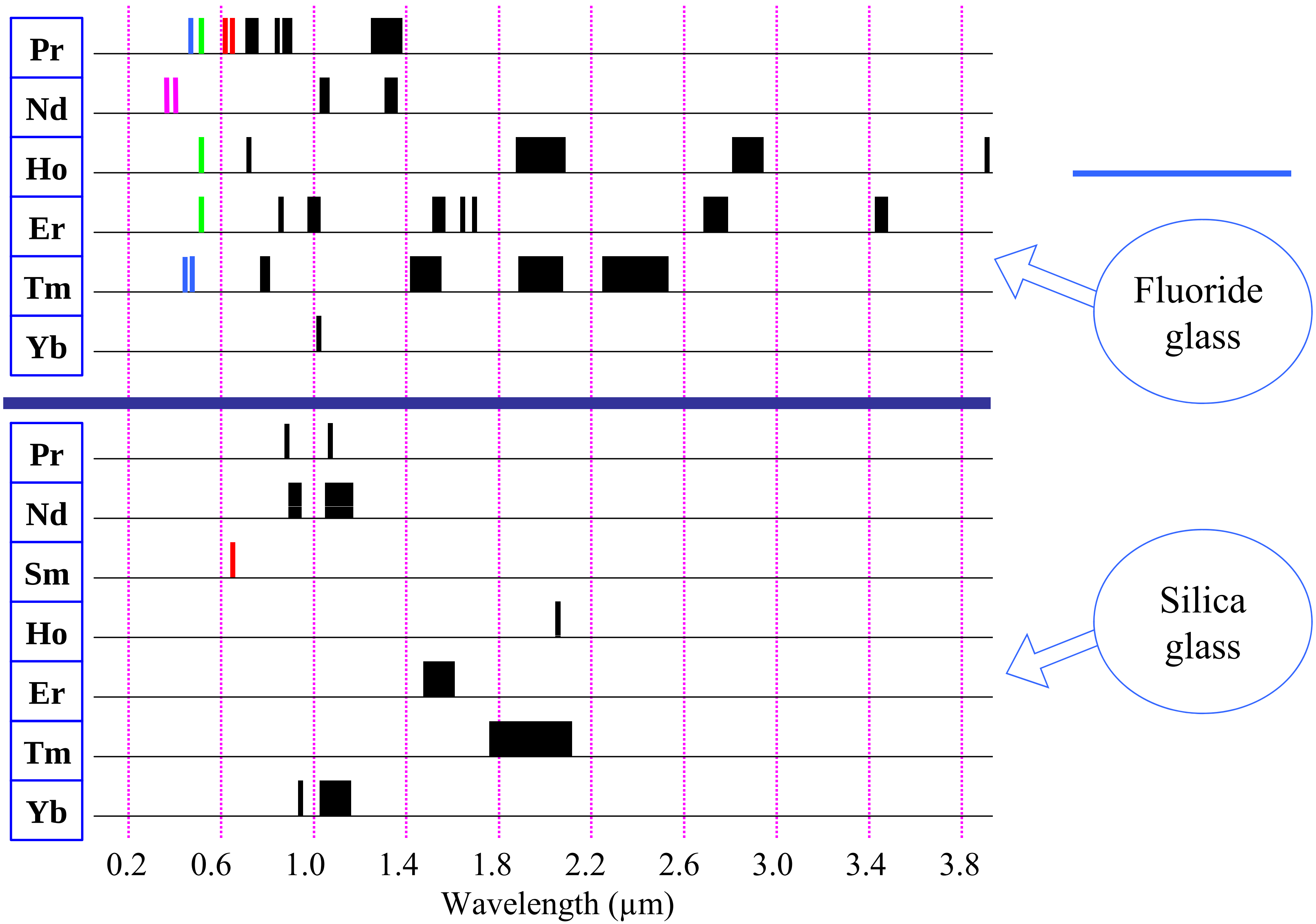


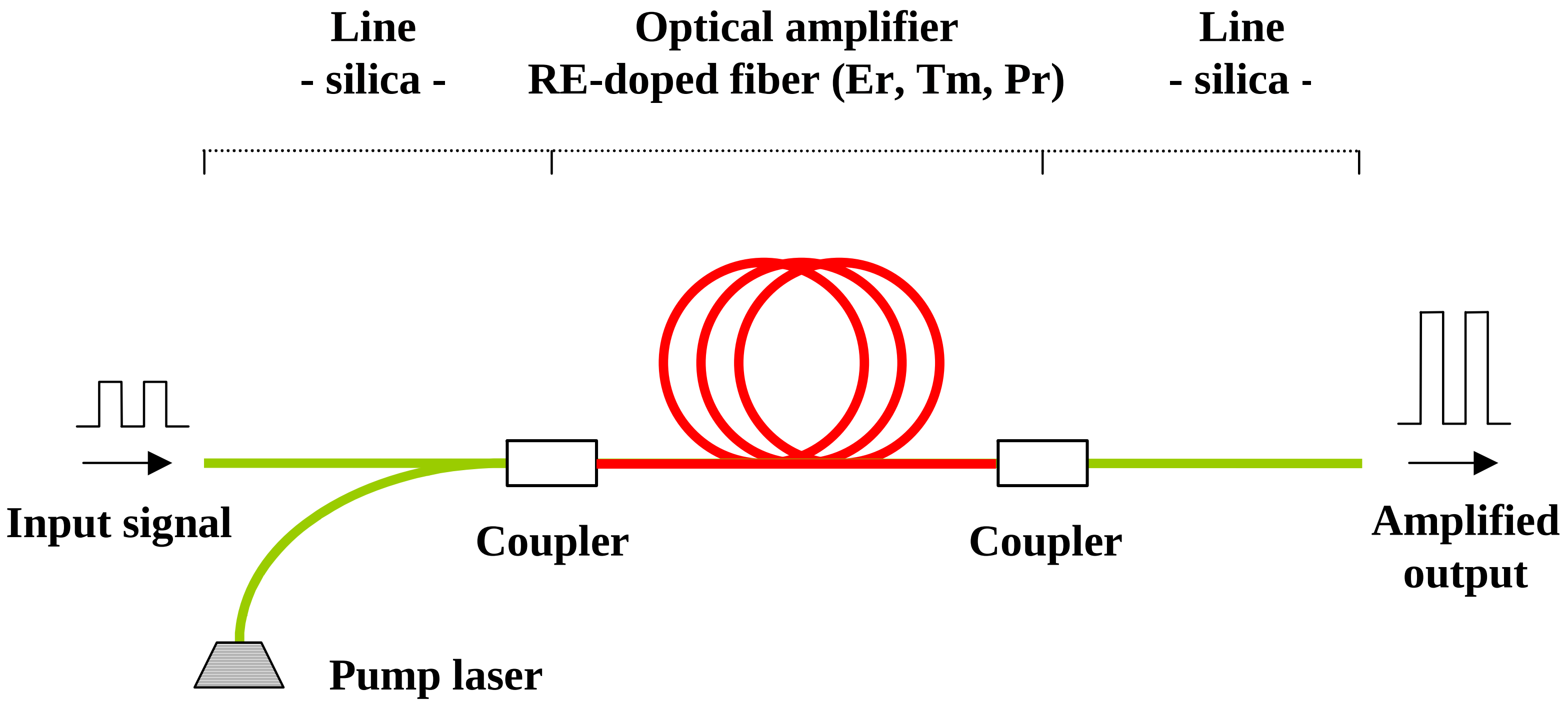
Fonction active

→ Dopage terre rare Ln^{3+}:
(Nd^{3+}, Pr^{3+}, Tm^{3+}, Er^{3+})

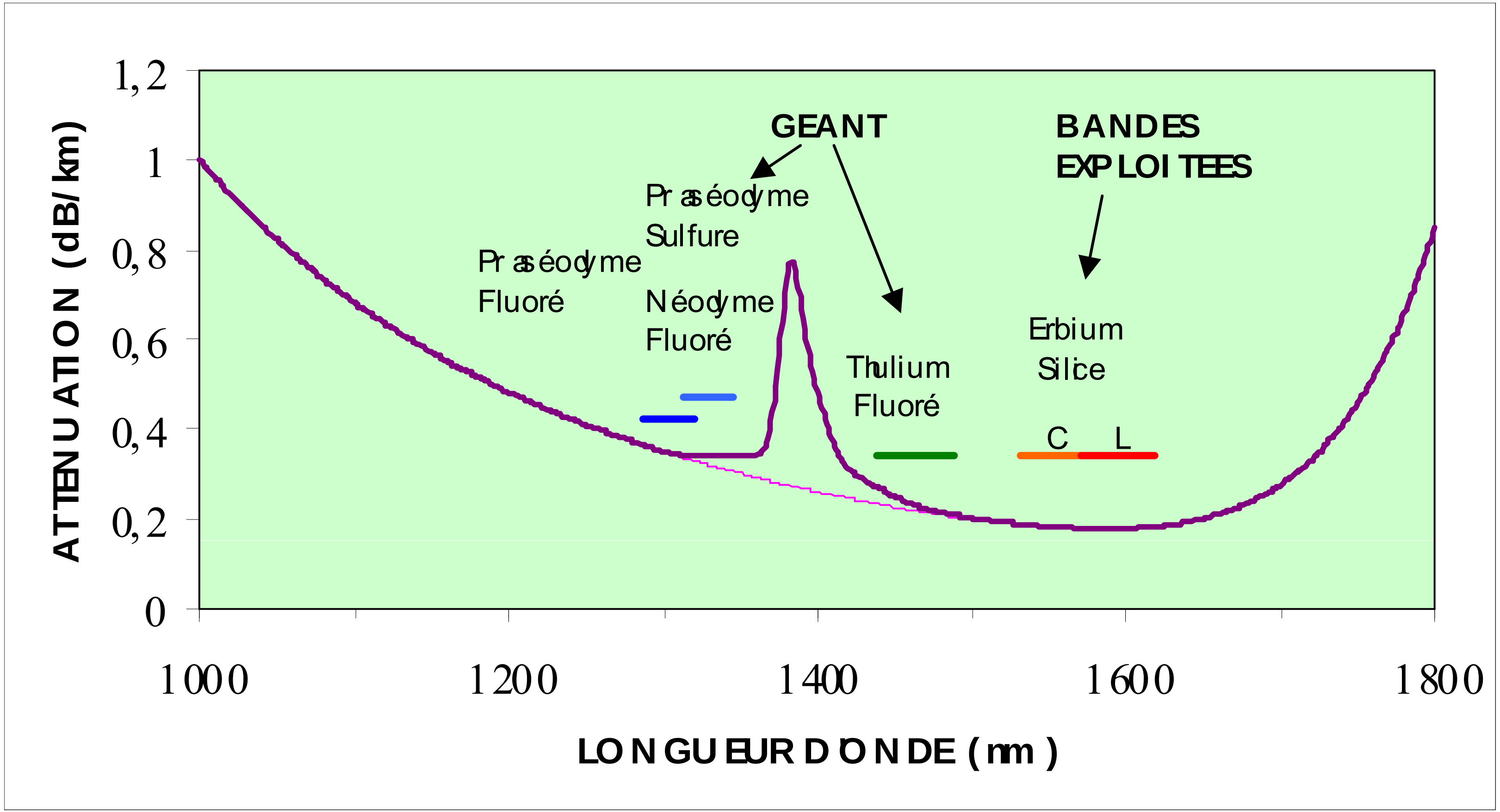


Laser de pompe (λ1)
Miroir réfléchissant à λ2
Verre de cœur dopé terre rare
Verre de gaine
Fibre optique monomode
Miroir semi-réfléchissant à λ2
Émission laser (λ


Pr
Nd
Ho
Er
Tm
Yb
Pr
Nd
Sm
Ho
Er
Tm
Yb
0.2
0.6
1.0
1.4
1.8
2.2
2.6
3.0
3.4
3.8
Wavelength (μm)
Fluoride glass
Silica glass



Line
- silica -
Optical amplifier
RE-doped fiber (Er, Tm, Pr)
Line
- silica -
Input signal
Coupler
Coupler
Amplified
output
Pump laser

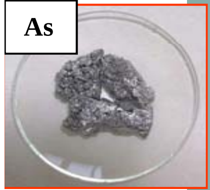


1,2
1
0,8
0,6
0,4
0,2
0
ATTENUATION (dB/km)
GEANT
BANDES EXPLOITEES
Praséodyme Sulfure
Praséodyme Fluoré
Néodyme Fluoré
Thulium Fluoré
Erbium Silice
C
L
1000
1200
1400
1600
1800
LONGUEUR D'ONDE (nm)

Chalcogenide glasses

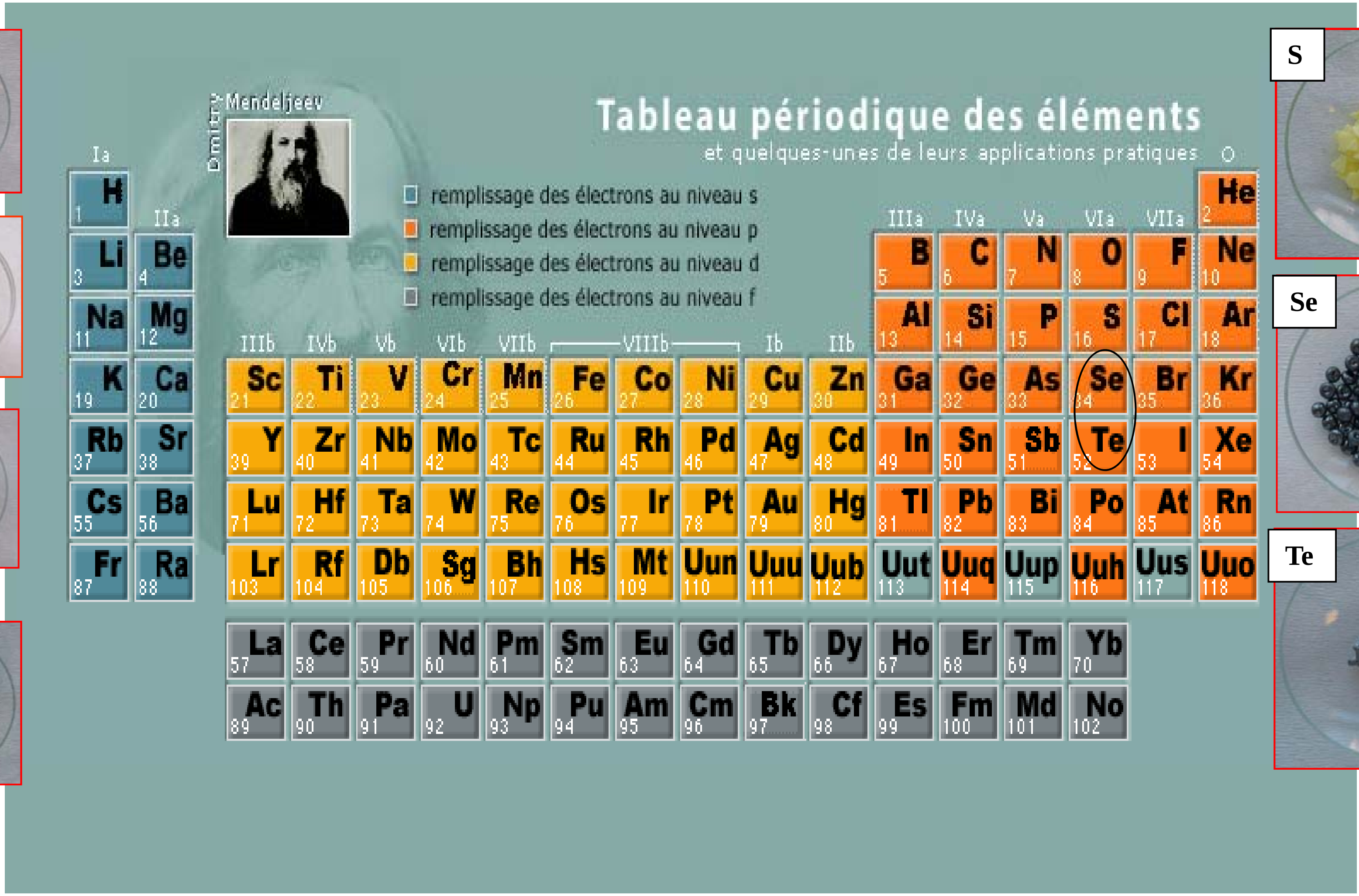
Sb

As



Ge

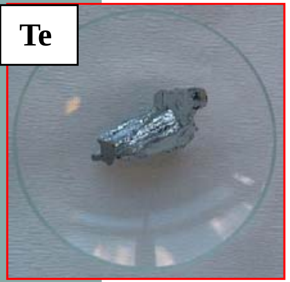
Ga



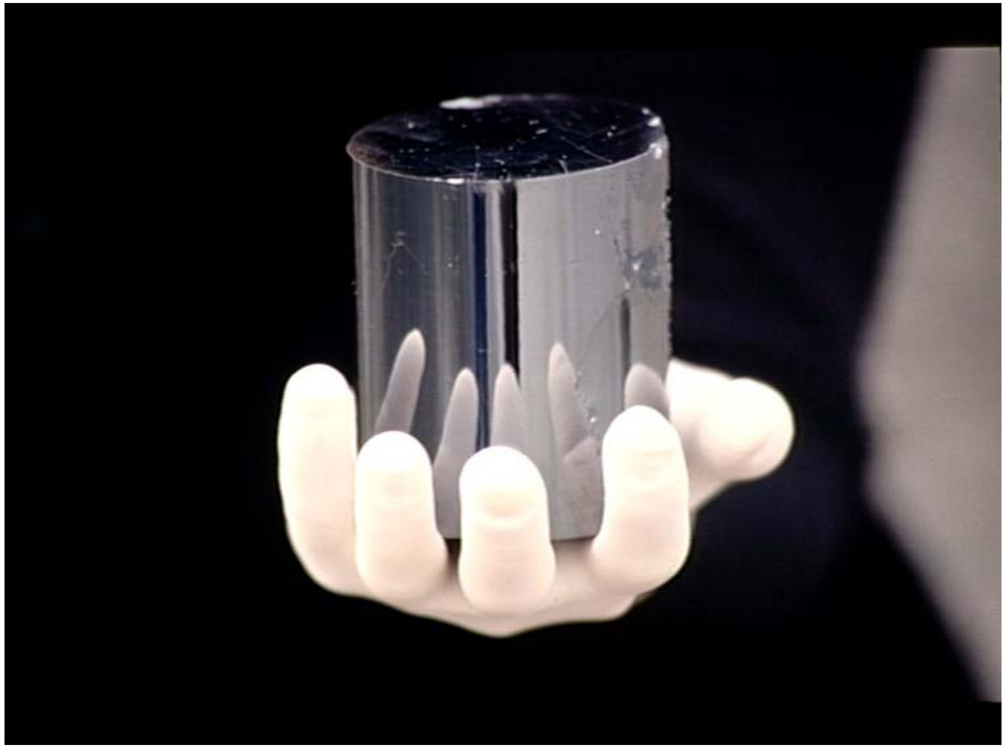
S

Se

Te



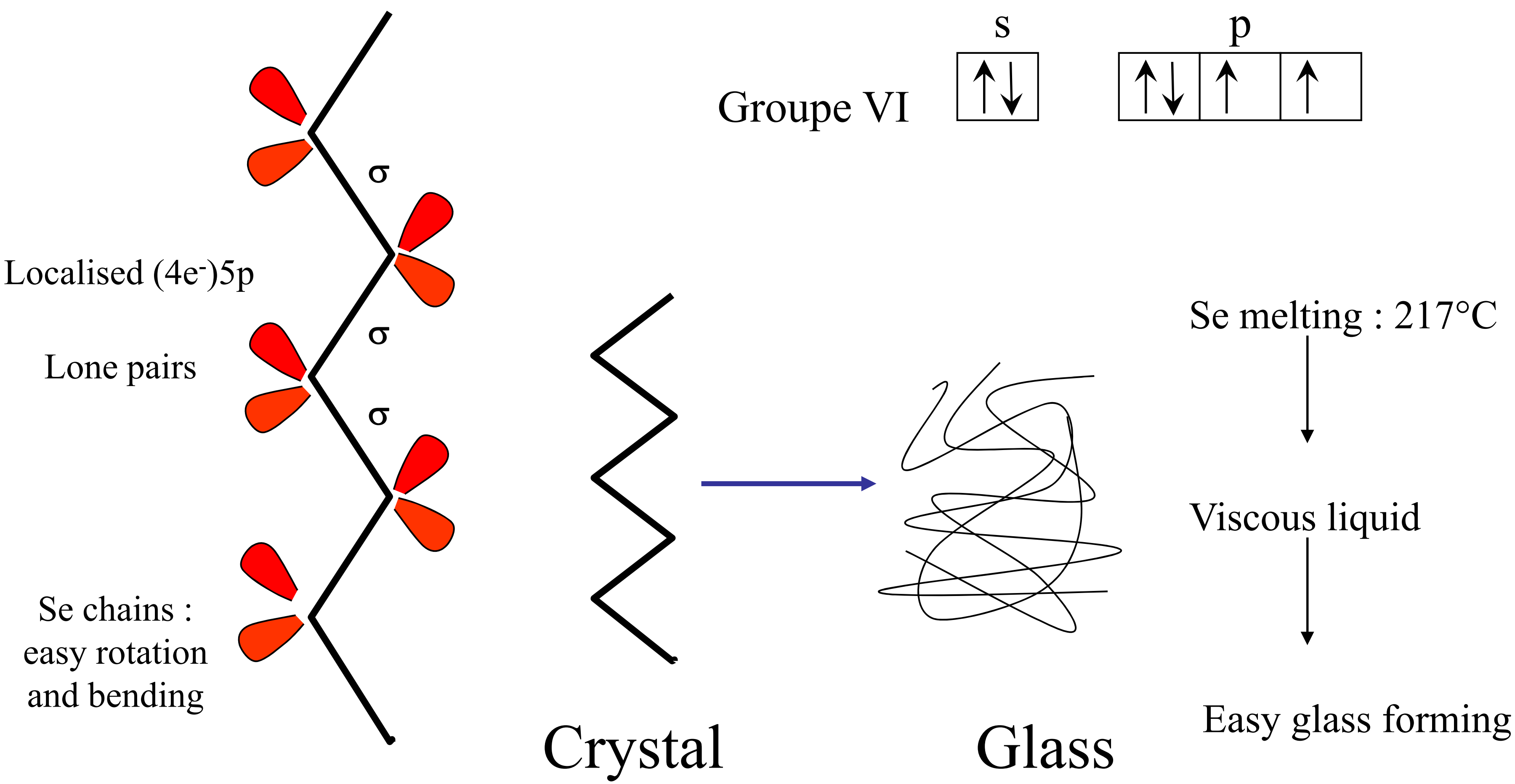
CHALCOGENIDE GLASS SAMPLE



Se : a key atom in chalcogenide glasses

- Good glass former
  - low phonon characteristics
  - technical glasses such as AMTIR (Amorphous materials Inc) and GASIR (Umicore IR Glasses) based on combination of Se, Ge, As, Sb.
- Excellent local probes for NMR spectroscopy

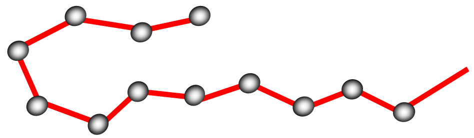
Se



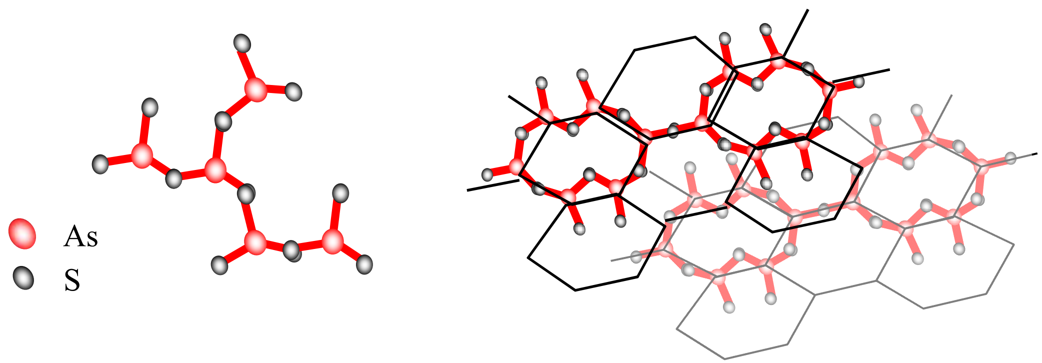
Groupe VI
s
p
Localised (4e-)5p
Lone pairs
σ
σ
σ
Se chains :
easy rotation
and bending
Crystal
Glass
Se melting : 217°C
Viscous liquid
Easy glass forming

Chalcogenide glasses structural models

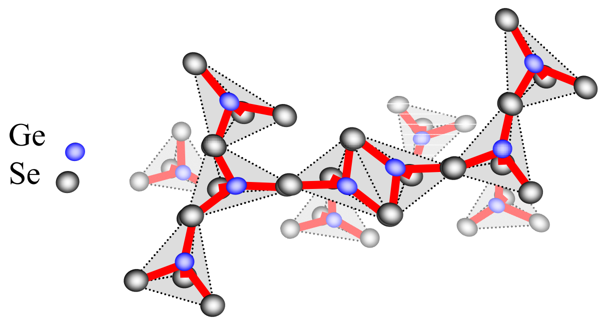
1) 1D spaghetti-type, such as vitreous Se

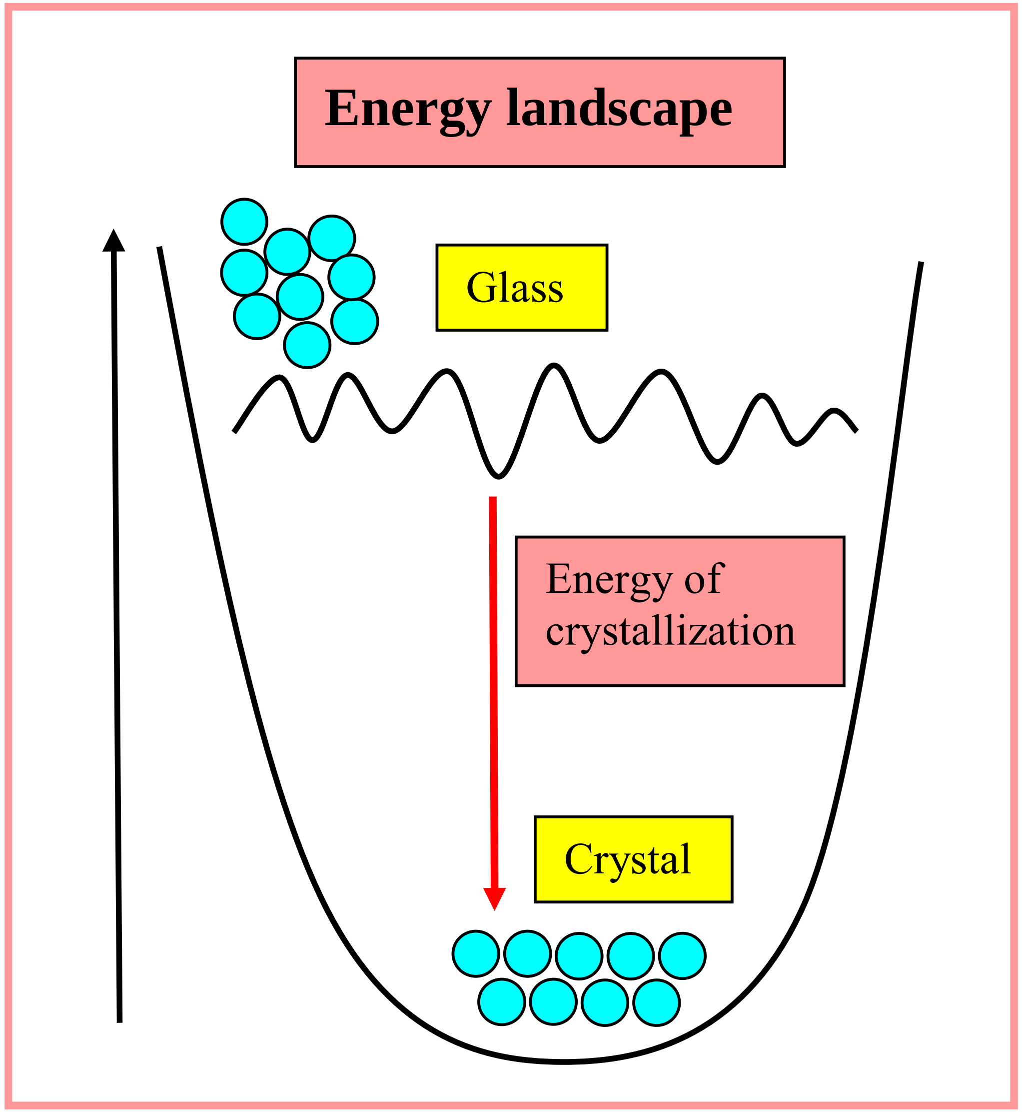


2) 2D distorted planar glasses such as As_2S_3



3) 3D glasses, such as GeS_4

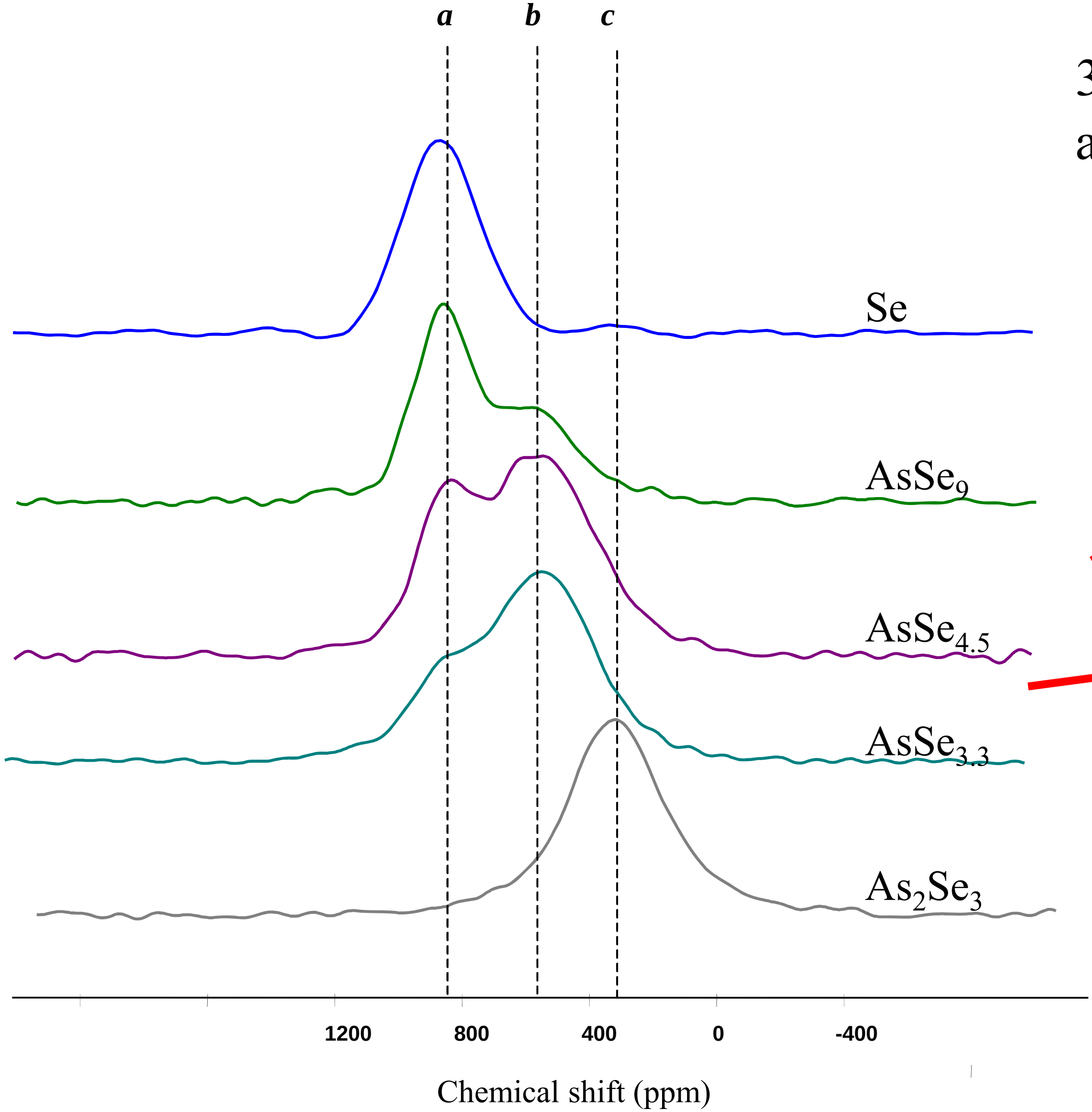




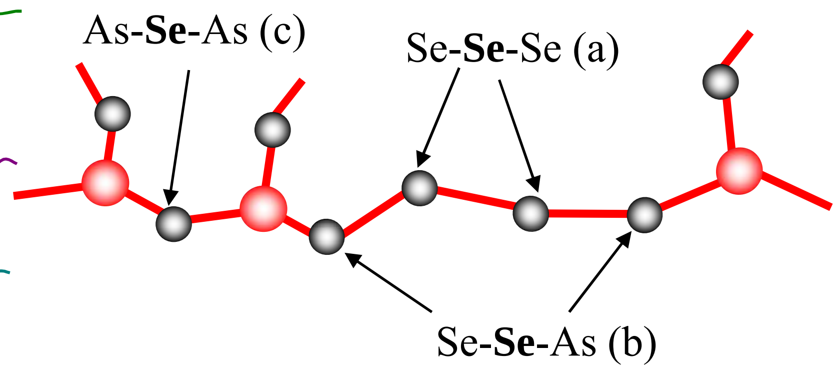
Energy landscape
Glass
Energy of crystallization
Crystal

Se/As/Ge GLASS SAMPLE

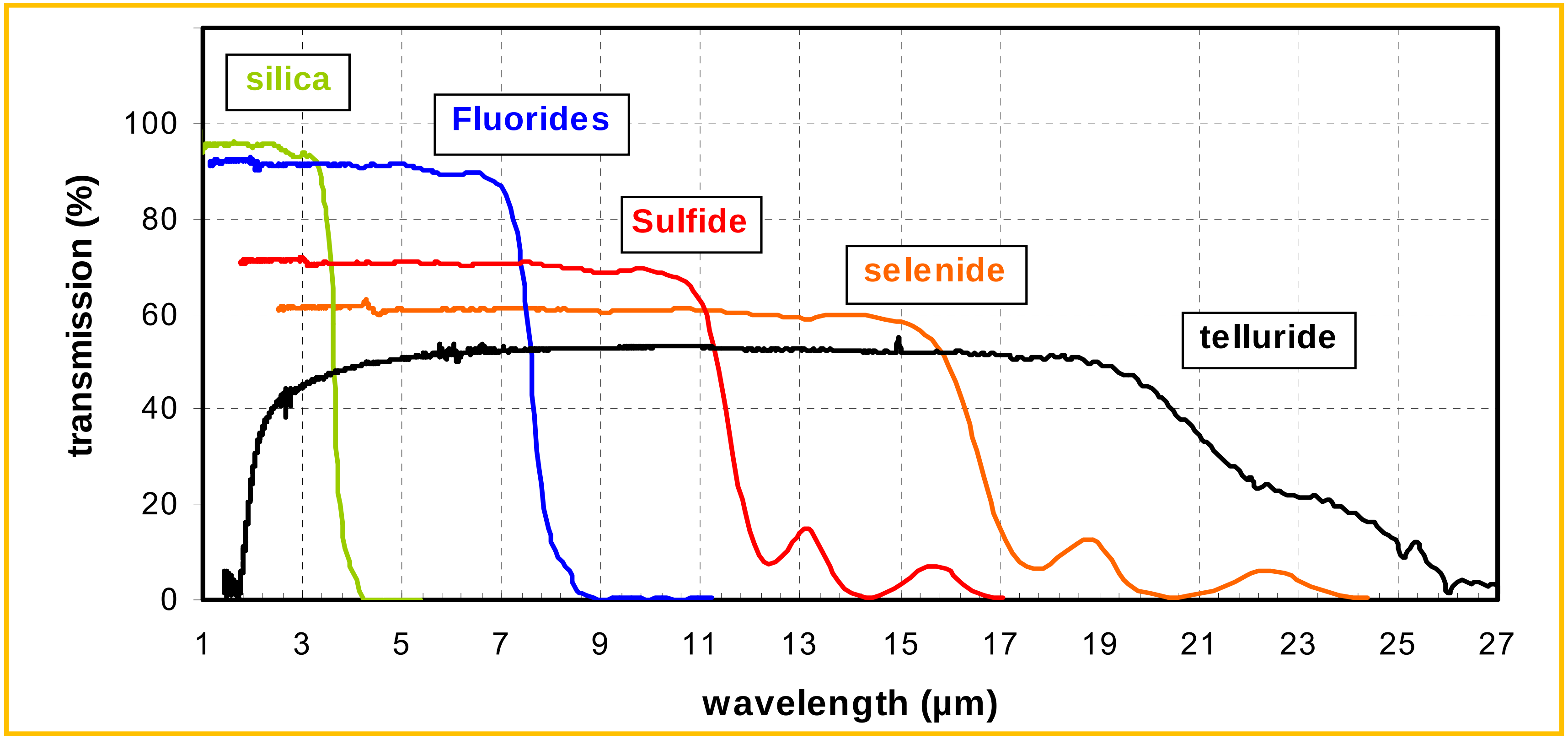
Se NMR spectra of As/Se chains ramified glasses (1D/2D)



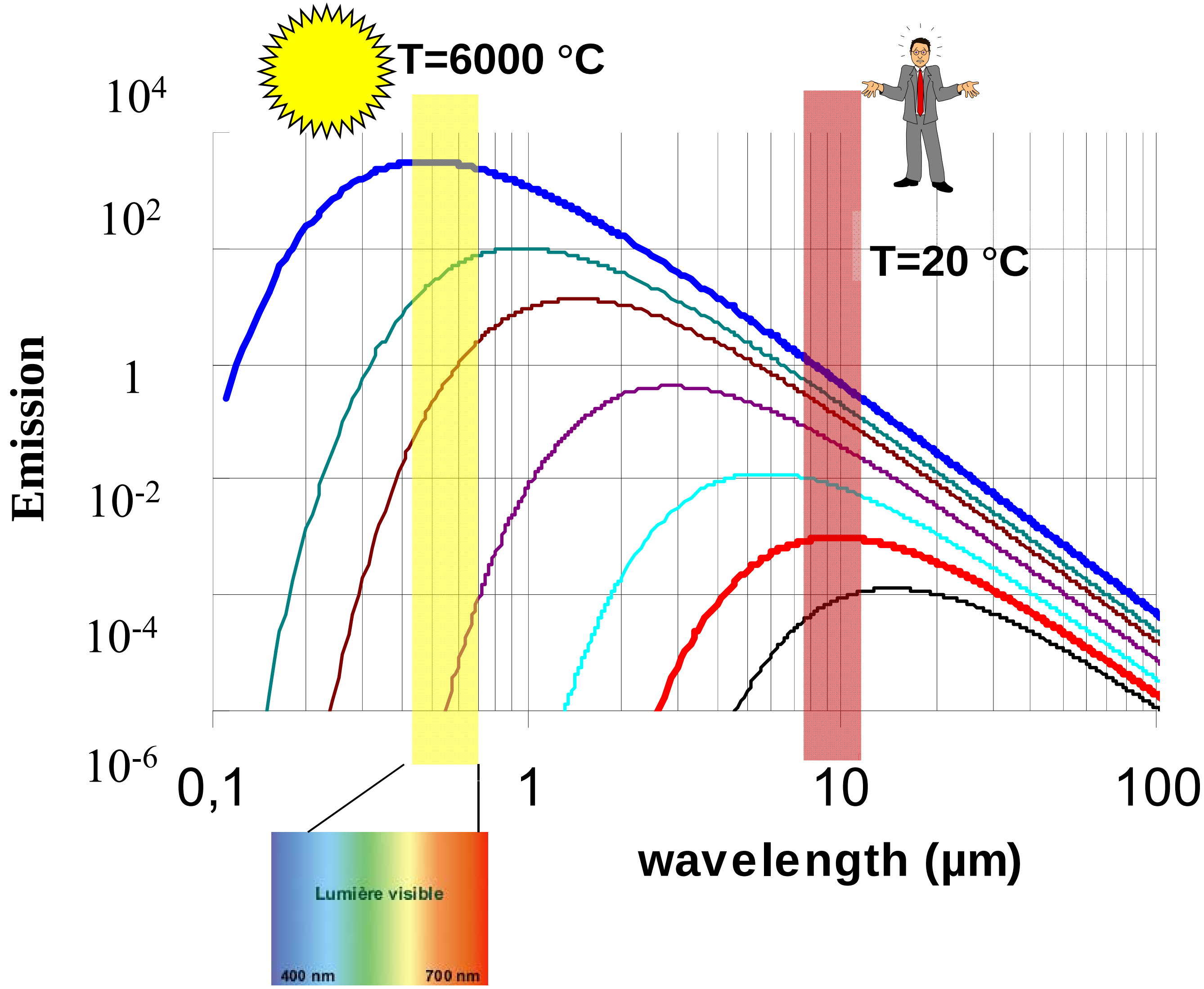
3 types of Se: (a) at 850 ppm , (b) at 550 ppm and (c) at 380 ppm



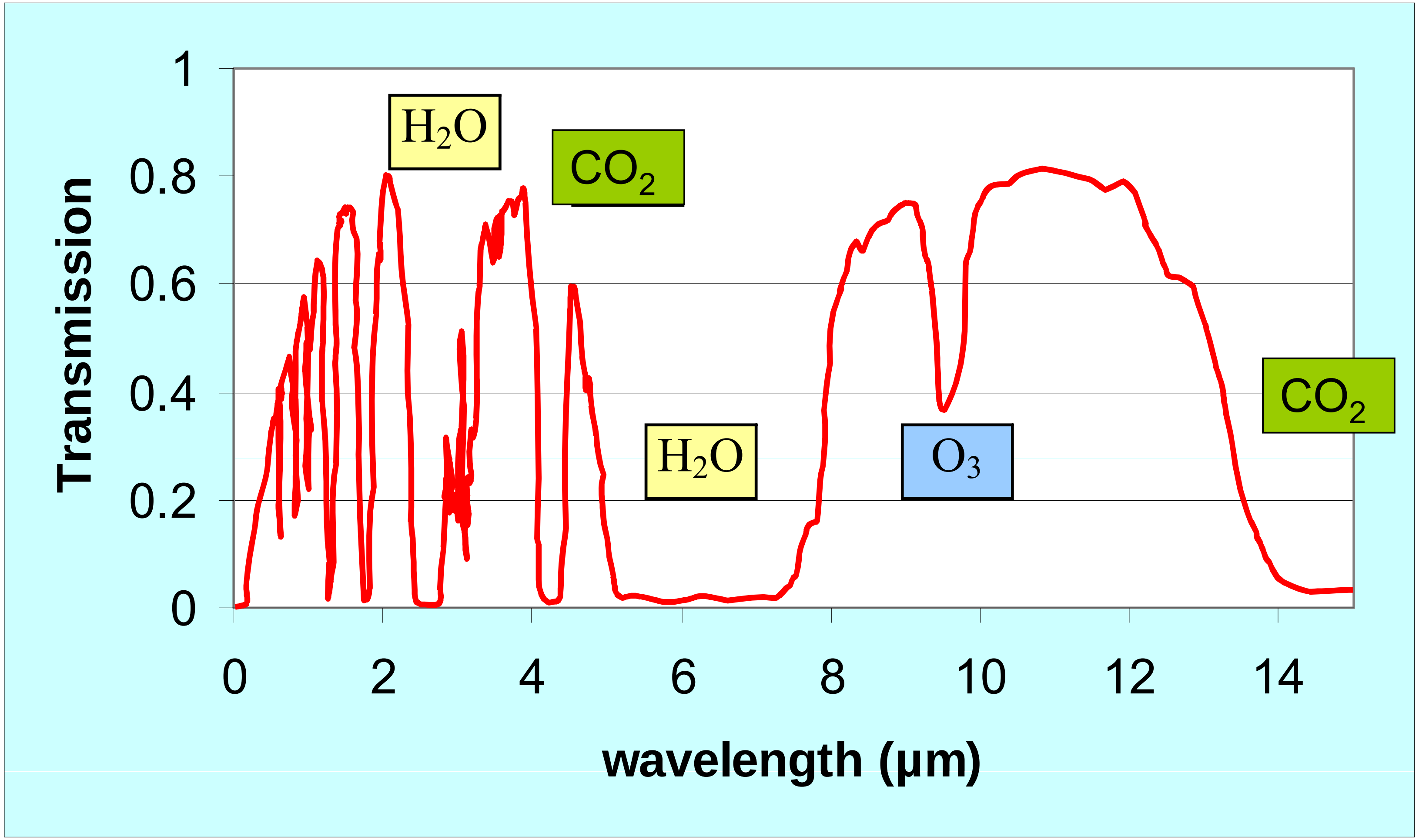
IR transparency range of different glasses



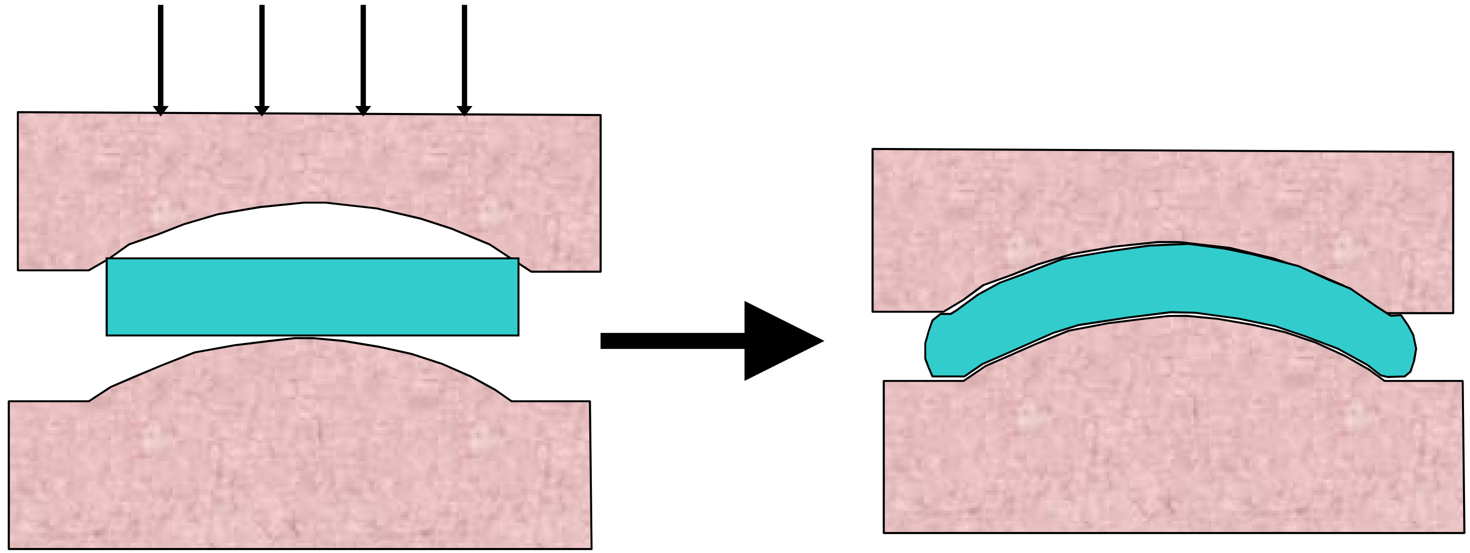
Spectral emission of black body



Transmission of atmosphere



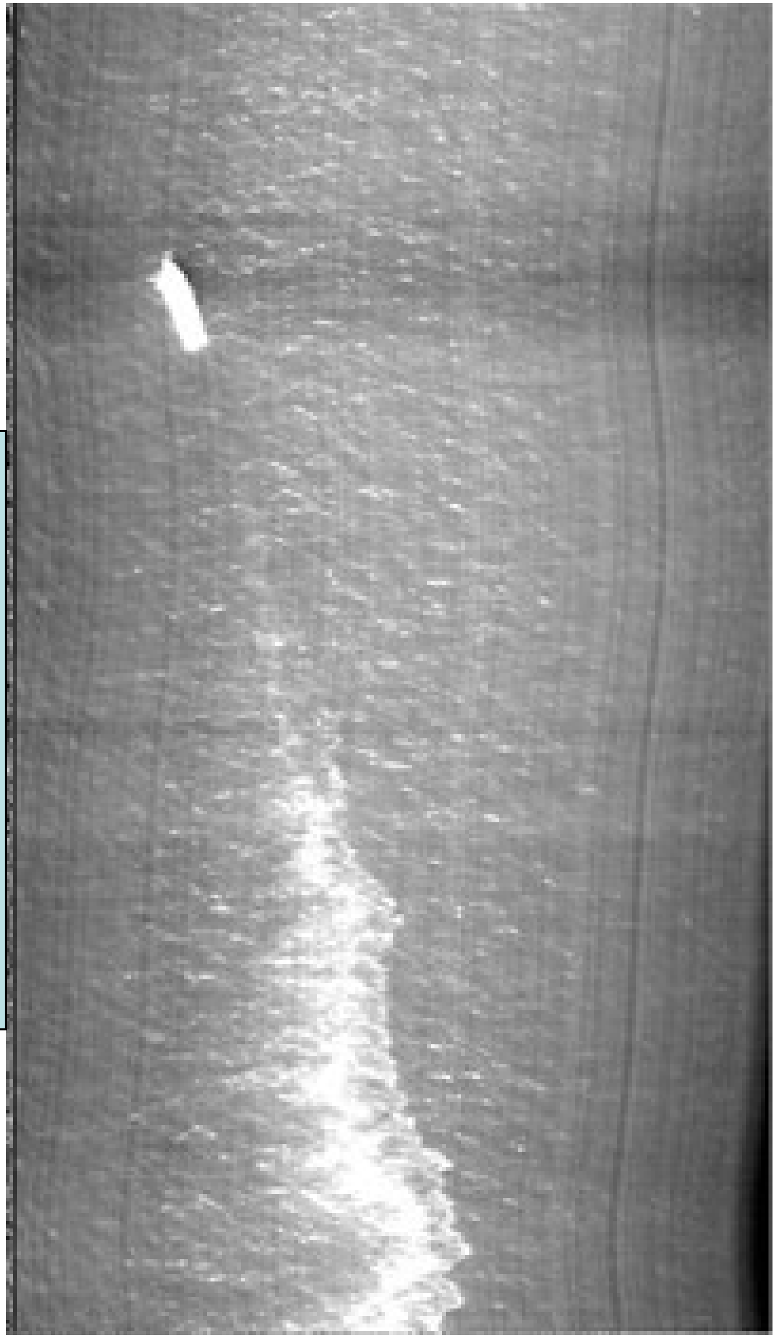
OPTICS MOULDING for THERMAL IMAGING IR CAMERAS

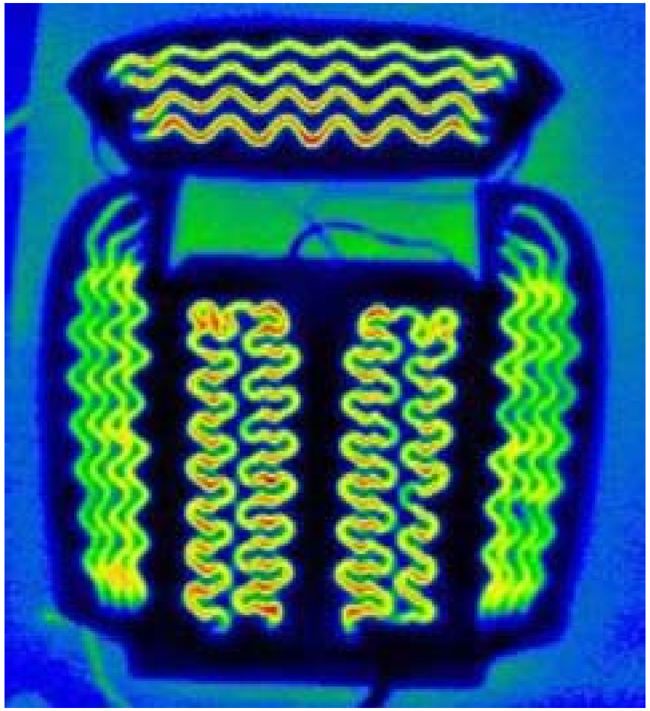


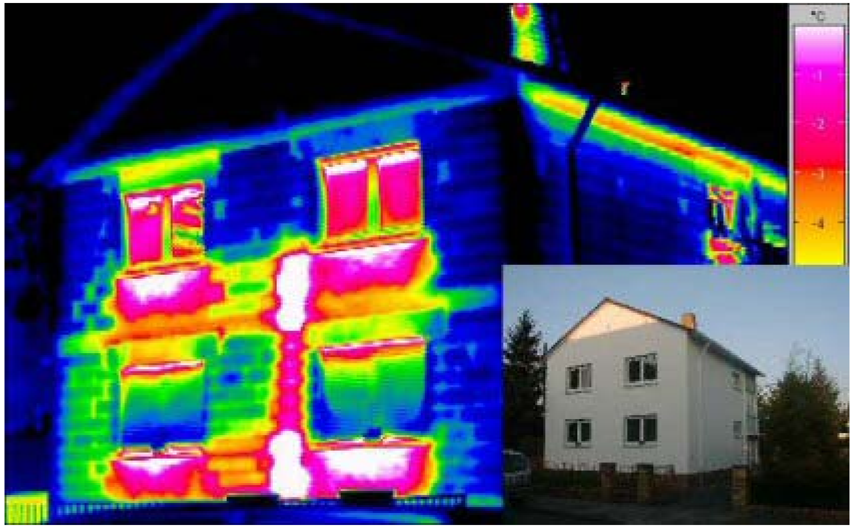
CHALCOGENIDE MOULDED LENSES
(left) DIFFRACTIVE
(right) ASPHERIC

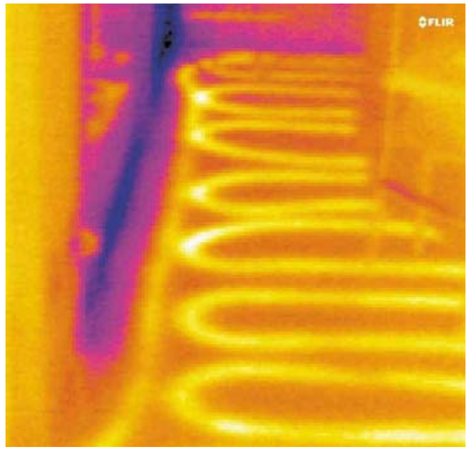
THALES ELVIR INFRARED CAMERA equiped with molded chalcodenide glass optics

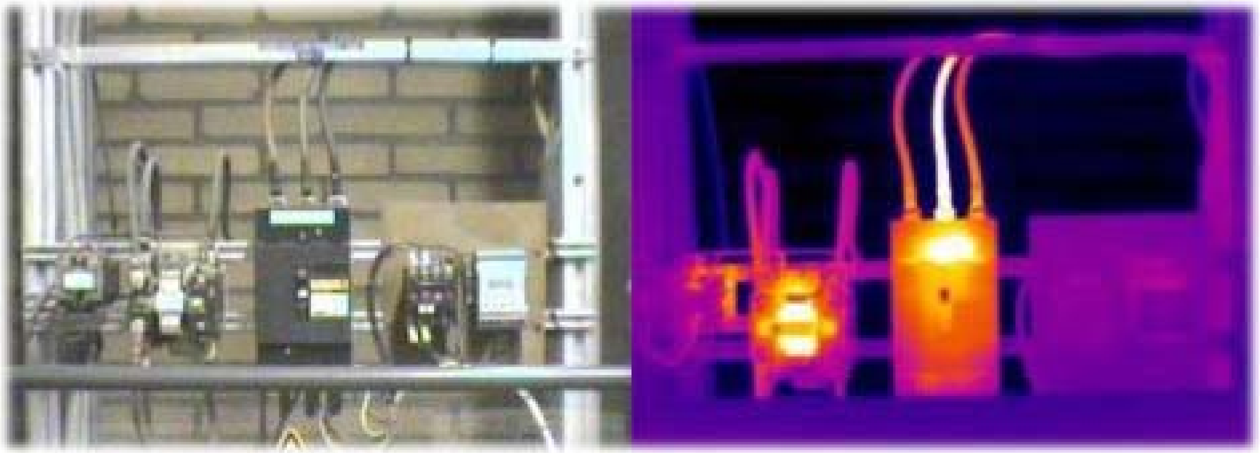
Détection infrarouge de jour ou de nuit d’une nappe d’hydrocarbures rejetés par un Pétrolier. L’émission thermique de l’eau est différente de celle du polluant

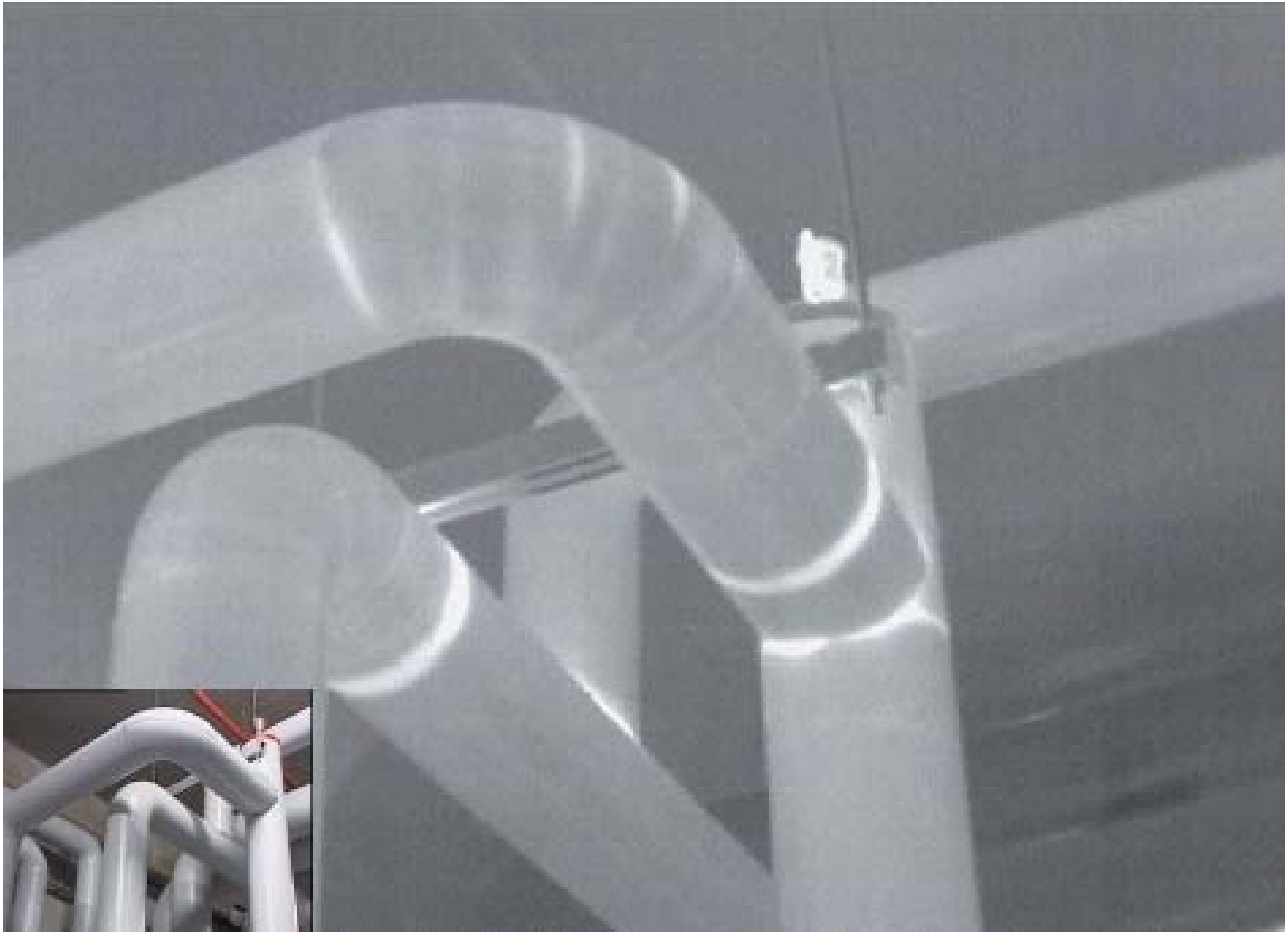


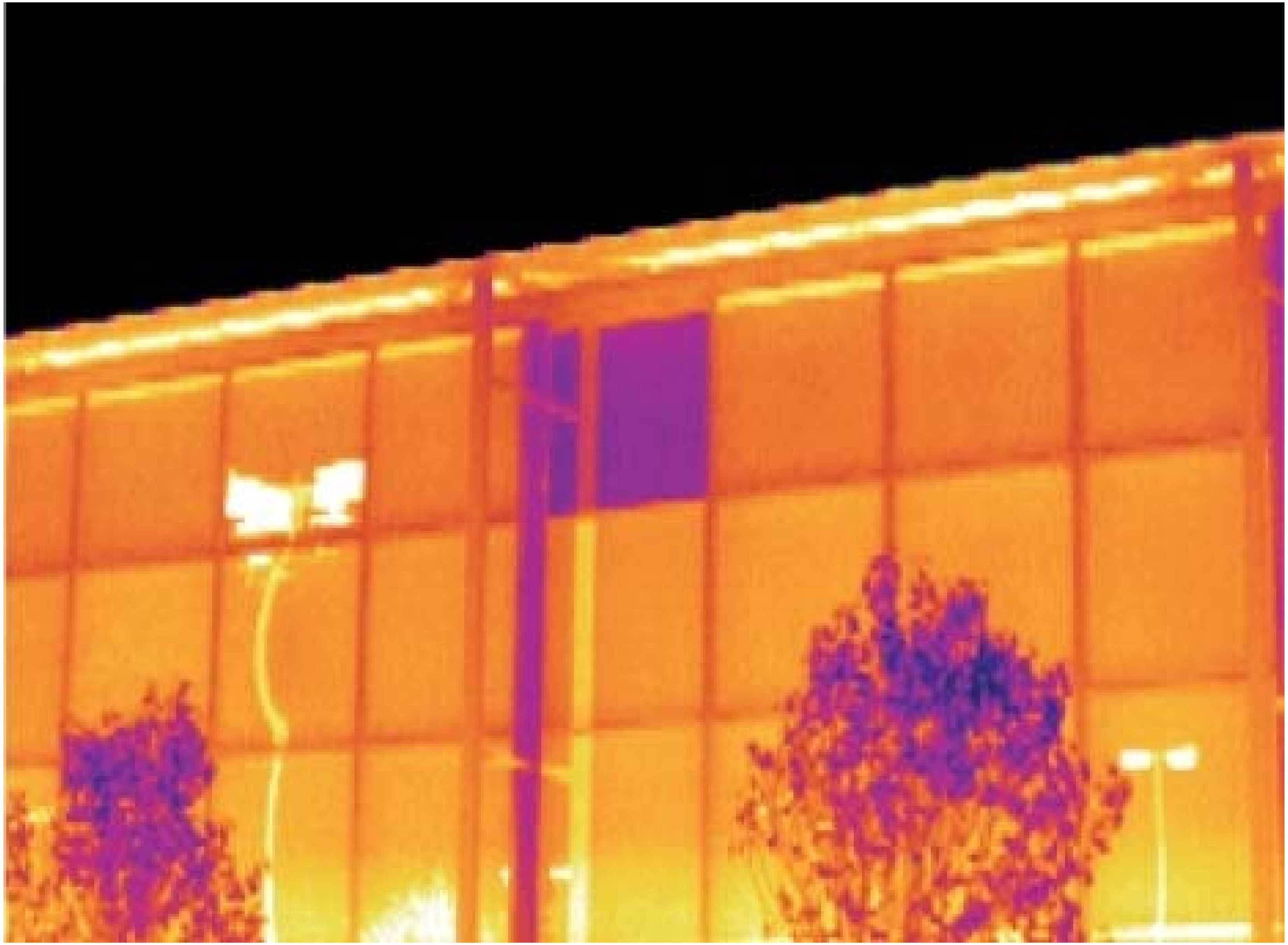



°C

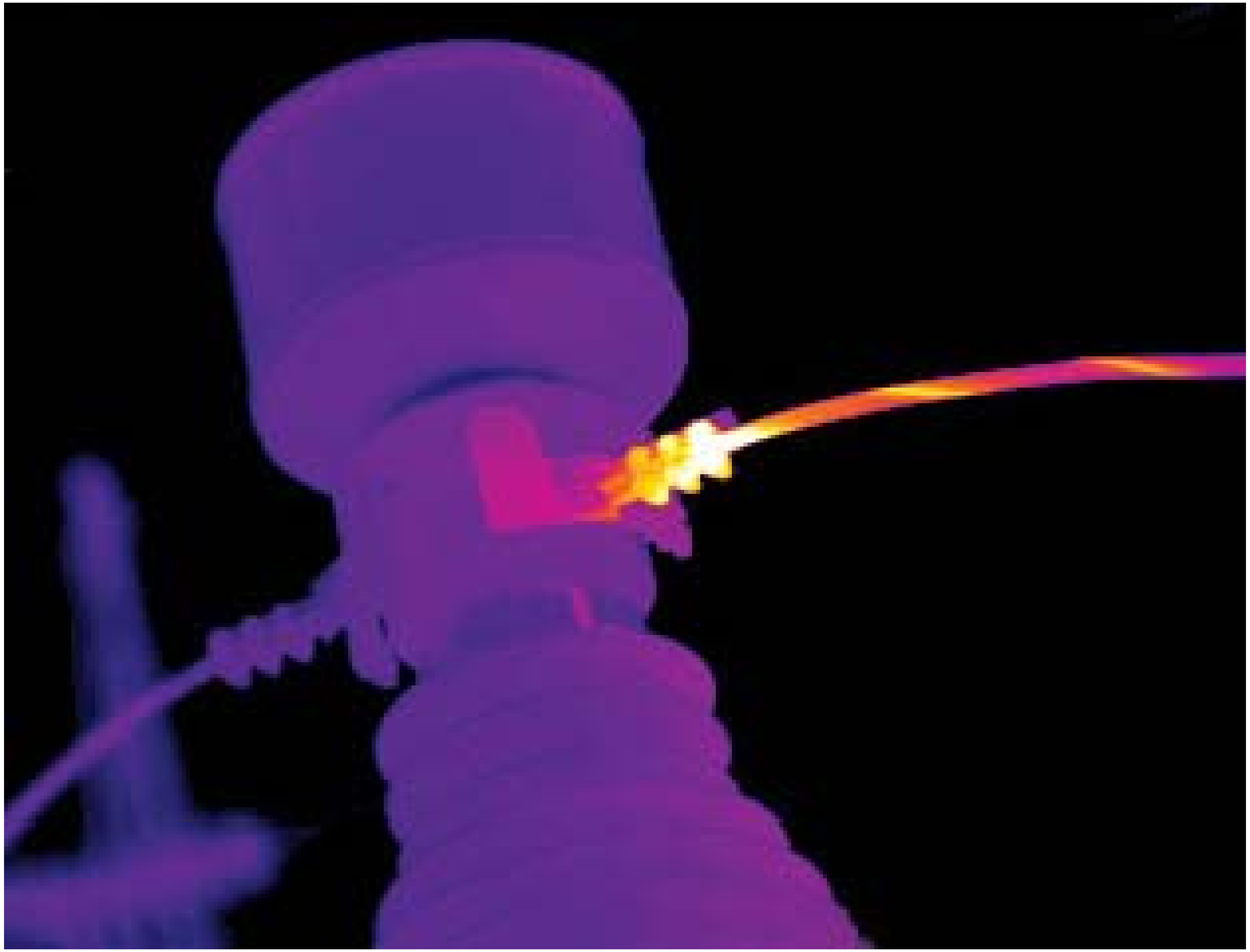








Detection of overheating on elecrical lines



Night vision camera
For car driving assistance

Chalcogenide glass
optics

Camera IR
Pour assistance
a la conduite de
nuit.

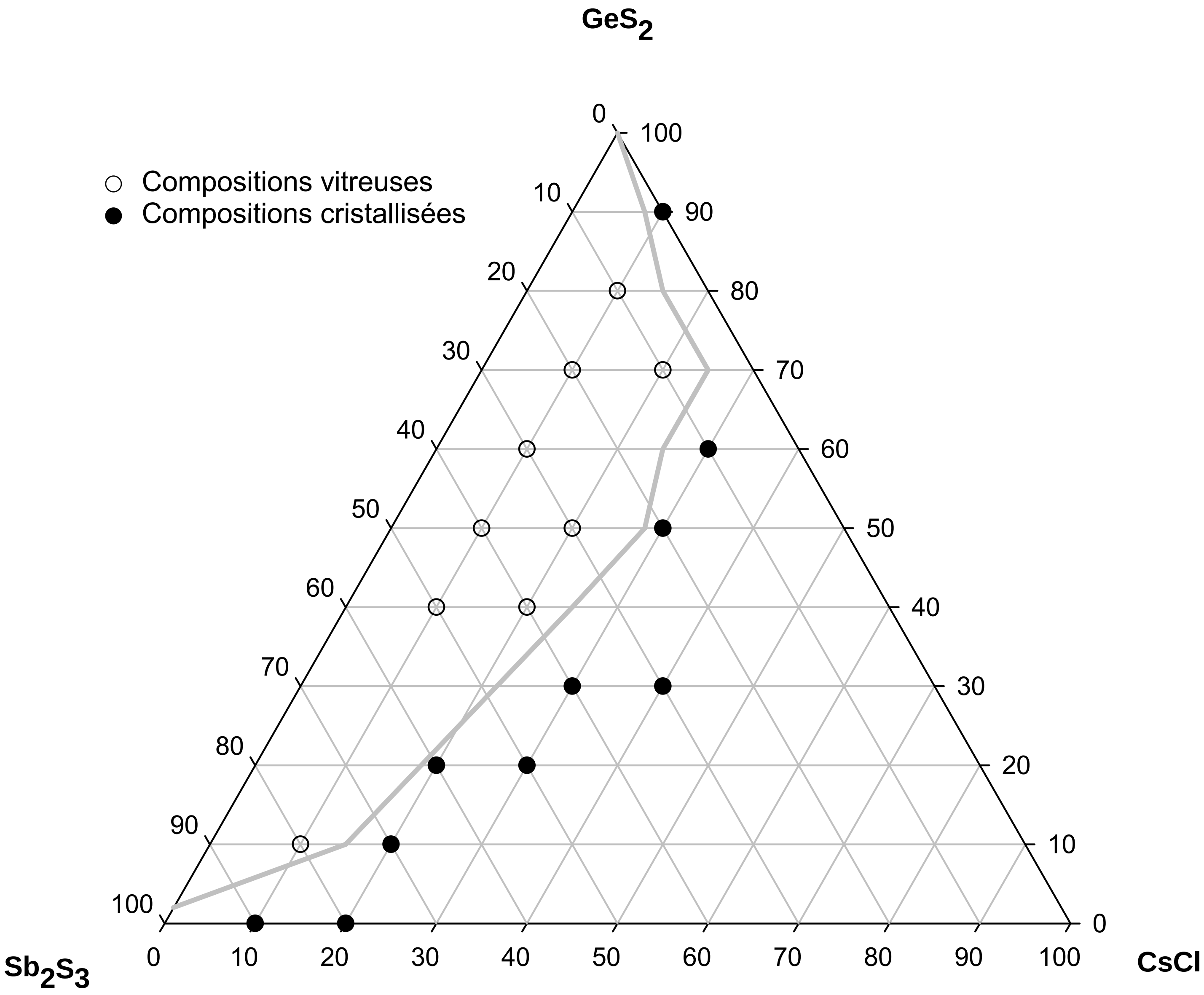
Image in the visible →

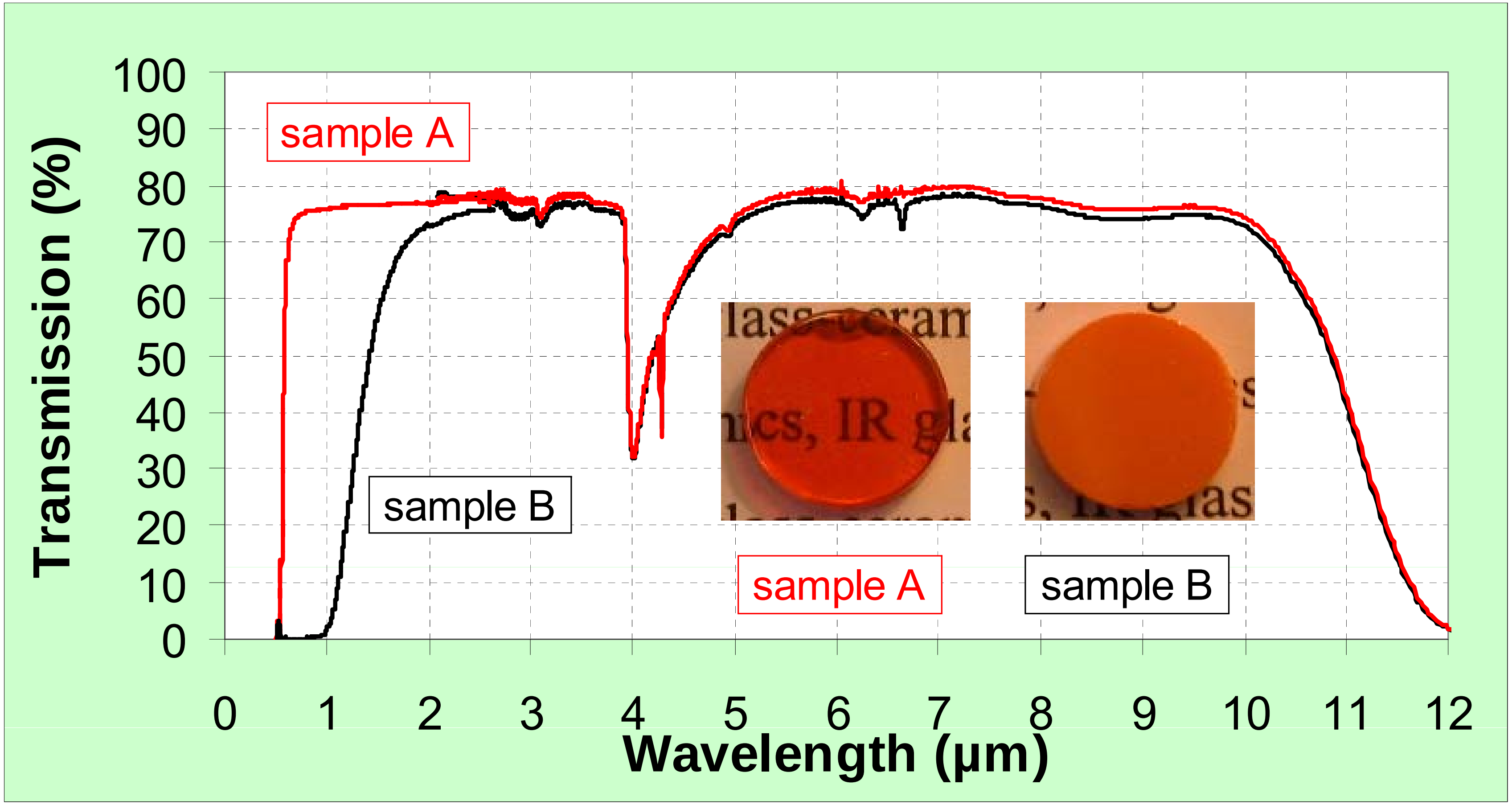
Thermal image in the
Infrared →


20

Infrared transmitting glass ceramics (Zhang, Laurent Calvez Uof Rennes)

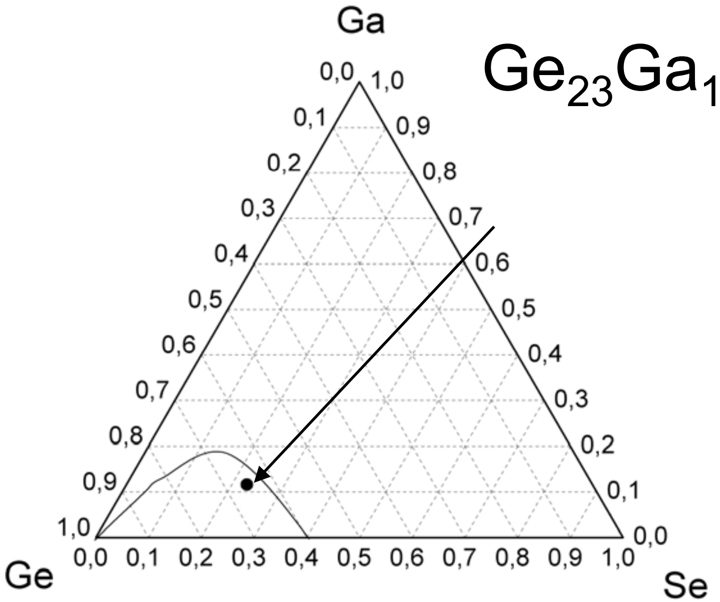
The basic glass is :GeS2/Sb2S3/CsCl. By heating → nucléation then growth of CsCl particles.


GeS2
Compositions vitreuses
Compositions cristallisées
Sb2S3
CsCl
0
10
20
30
40
50
60
70
80
90
100

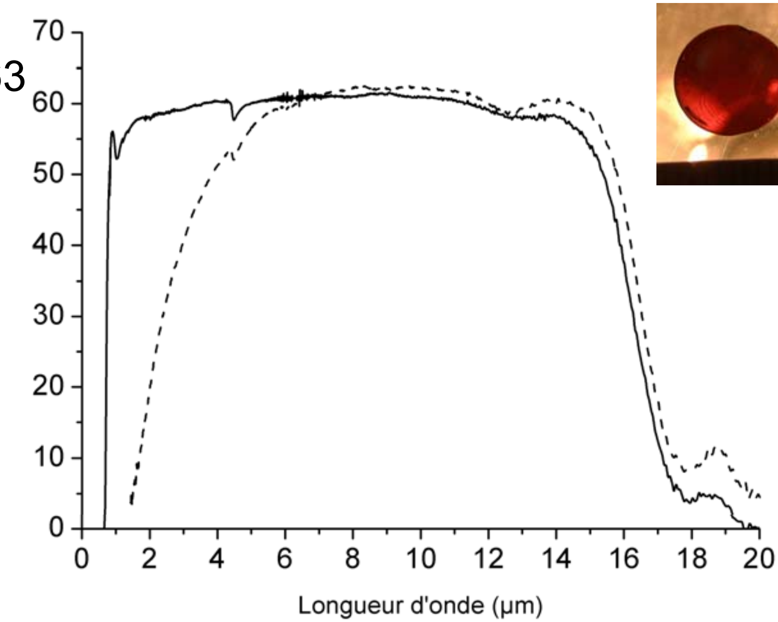


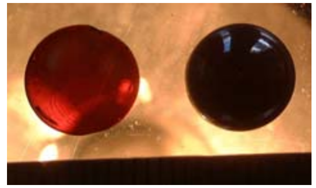
Transmission (%)
100
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
9
10
11
12
Wavelength (µm)
sample A
sample B
sample A
sample B

Verres et vitrocéramiques à base de séléniures: Système Ge-Ga-Se



$Ge_{23}Ga_{12}Se_{63}$



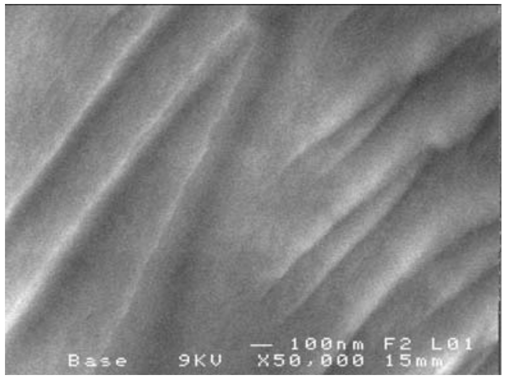


$Ge_{23}Ga_{12}Se_{63}$

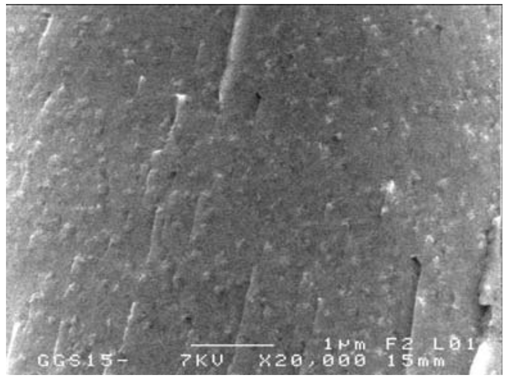
T_g = 370°C

T_x = 460°C

λ_{gap}= 690 nm



Verre de base



Vitrocéramique

M. Rozé, L. Calvez, Y. Ledemi, X.H Zhang

Advantages of glass ceramics

Glass ceramic

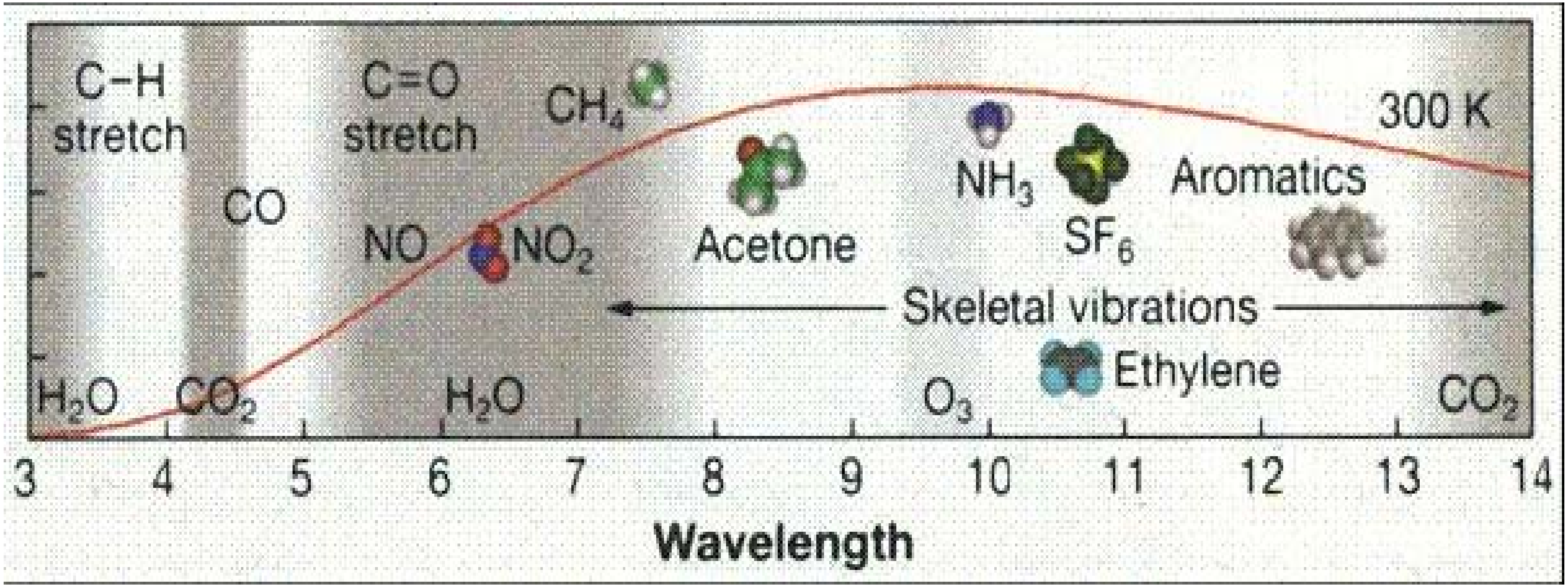
Glass

Resistance to fracture propagation

Collaboration with LARMAUR, Rennes

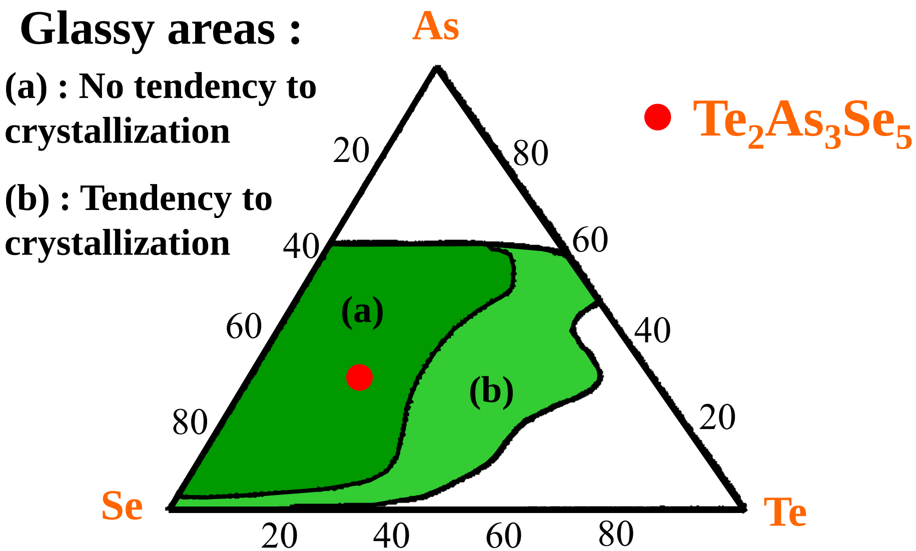
Tellurium based glasses for biosensors and space

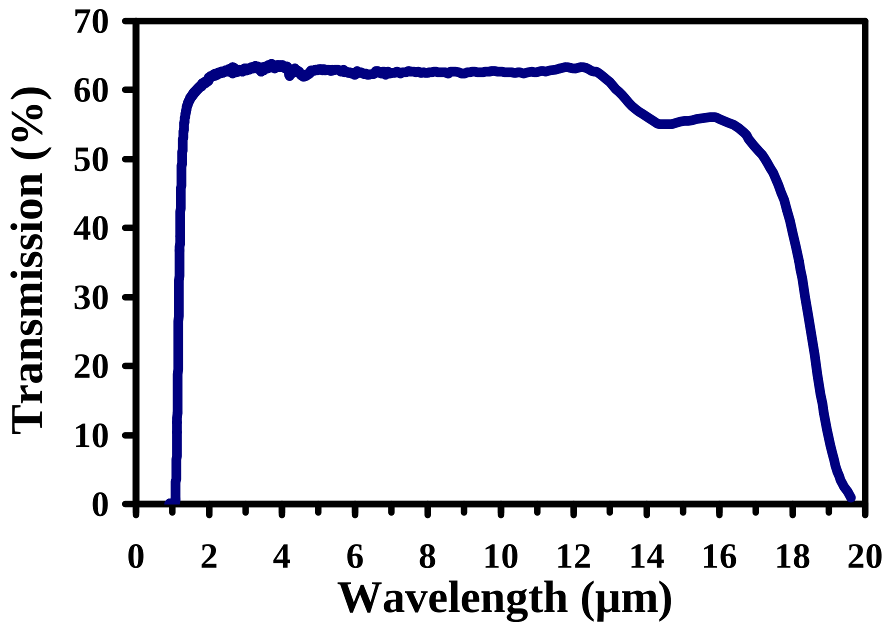
Optical fibers needed
stable glass candidate
TAS glass: Te/As/Se



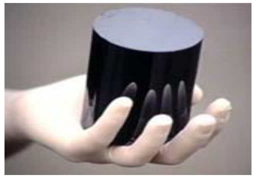
C–H stretch
CO
C=O stretch
CH_4
300 K
NO
NO_2
Acetone
NH_3
SF_6
Aromatics
Skeletal vibrations
Ethylene
H_2O
CO_2
H_2O
O_3
CO_2
3
4
5
6
7
8
9
10
11
12
13
14
Wavelength

TAS glass properties



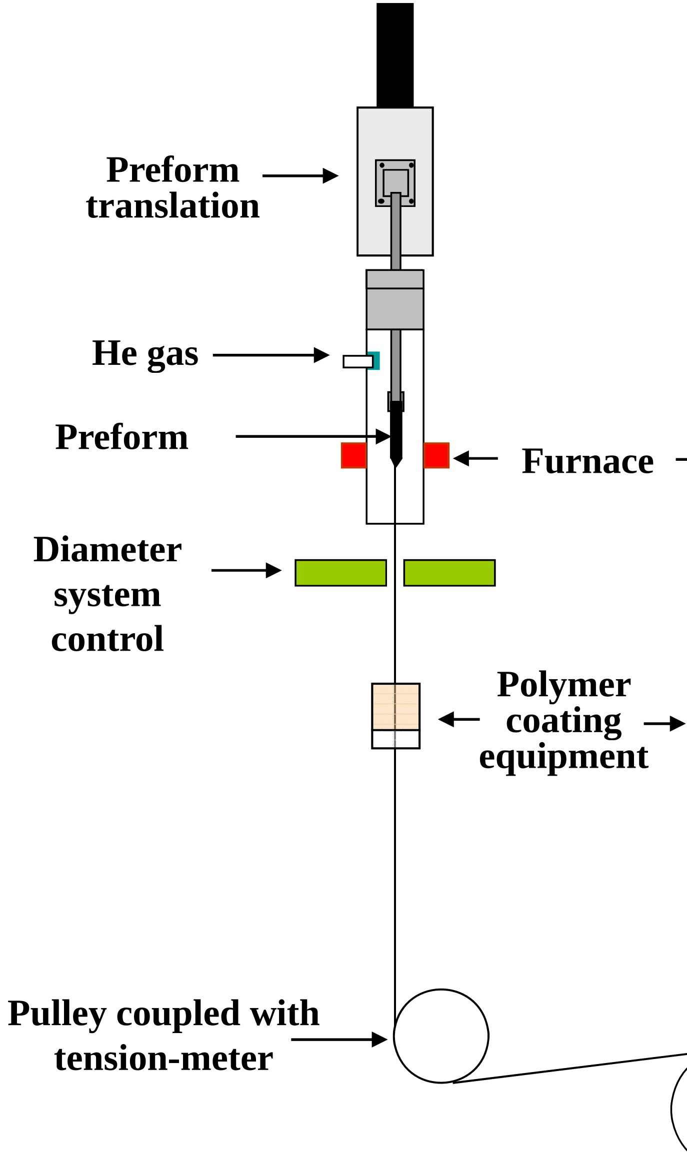


- **Large optical window lying from 2 to 18 µm**
- **Excellent resistance to devitrification during the fibering process**
- **Good durability towards water and solvent corrosion**
- **High refractive index (ex. $Te_2As_3Se_5$: n ~ 2.8)**
- **Good candidate for the first window: 4 to 12µm**

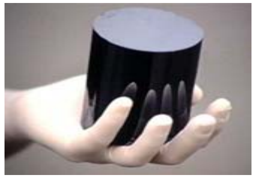


Optical fiber preparation

- Glass temperatures Tg ~ 135 °C
- Fibering temperature T_f ~ 270 °C

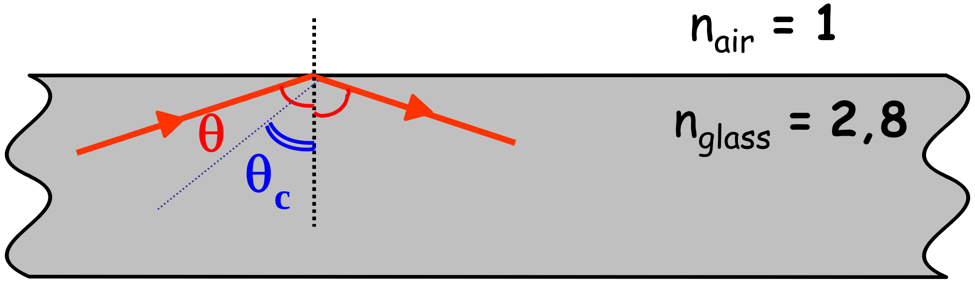


Drawing tower



Fiber Evanescent Wave Spectroscopy Principle

Wave λ

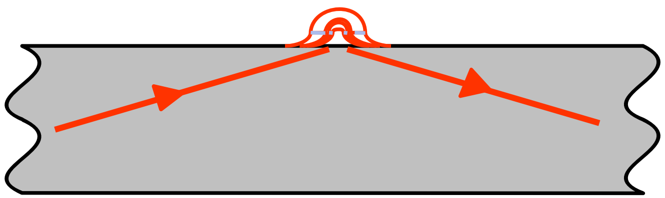


θ = incident angle of the λ wave

θ_c = critical angle

Medium which does not absorb λ

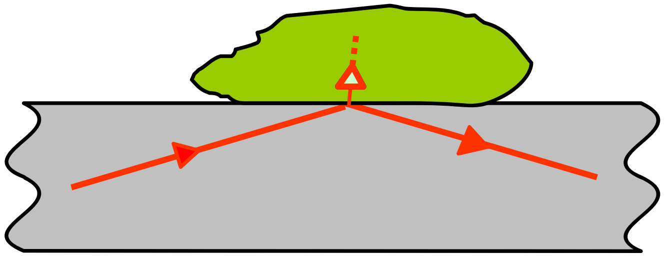
evanescent field without energy loss



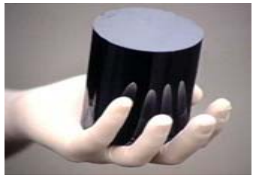
Total Internal Reflection

Medium which absorb λ

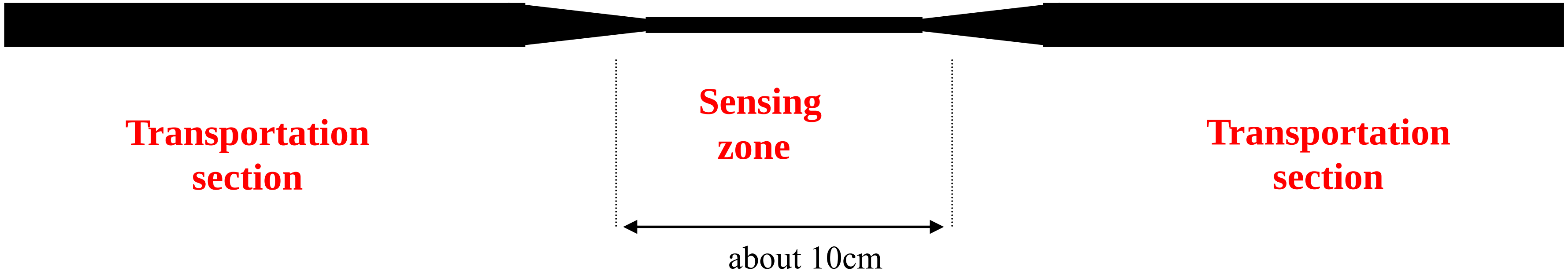
wave attenuation by absorption



Attenuated Total Reflection : ATR



Tapered fibers (2)

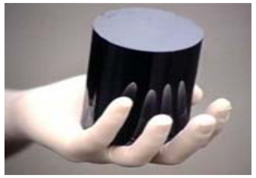


Two routes for tapering locally the fibre :

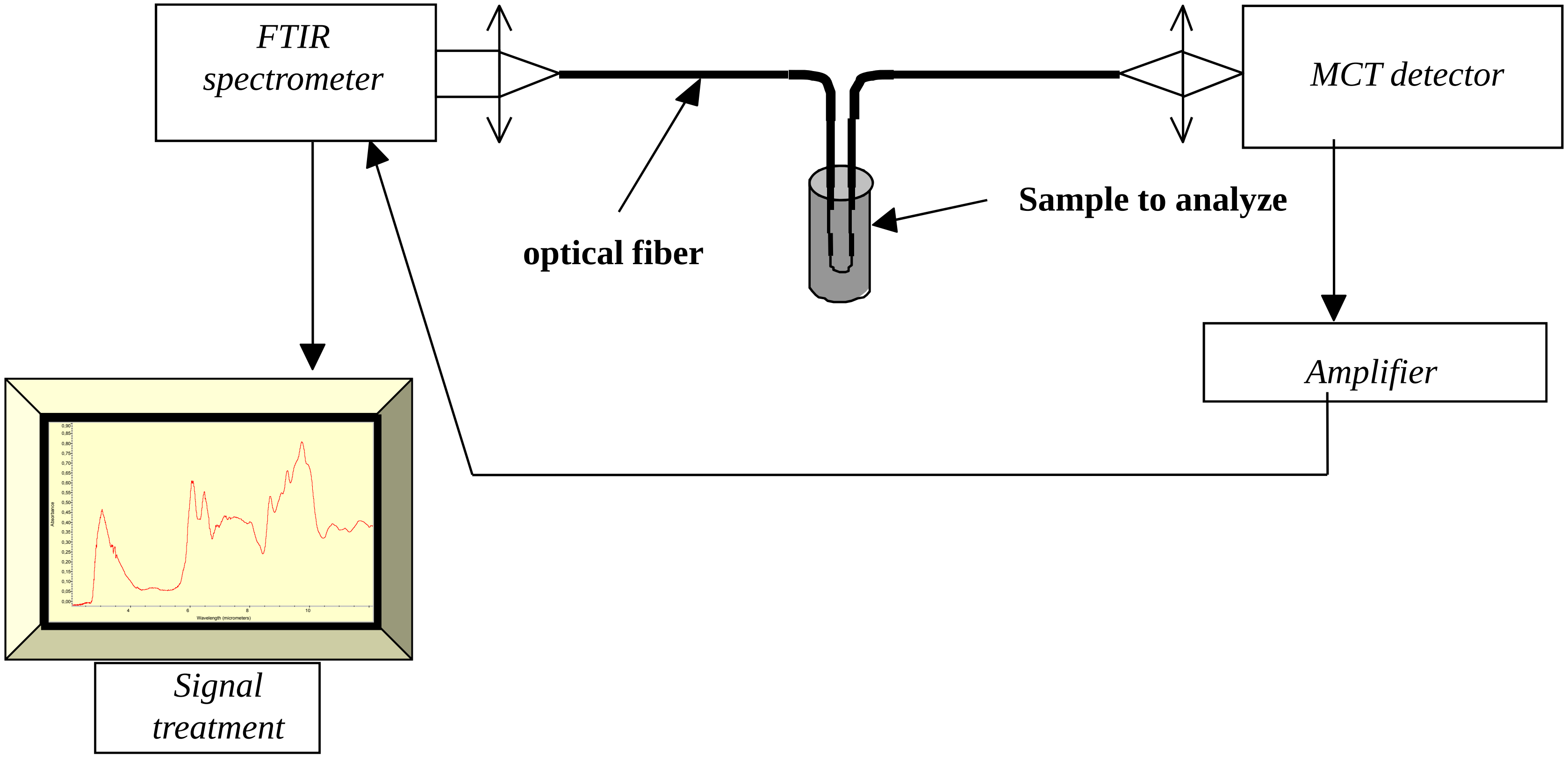
Strong increase of the fibering speed during the drawing process

Chemical etching using $H_2SO_4 + H_2O_2$ solutions

⇒ 

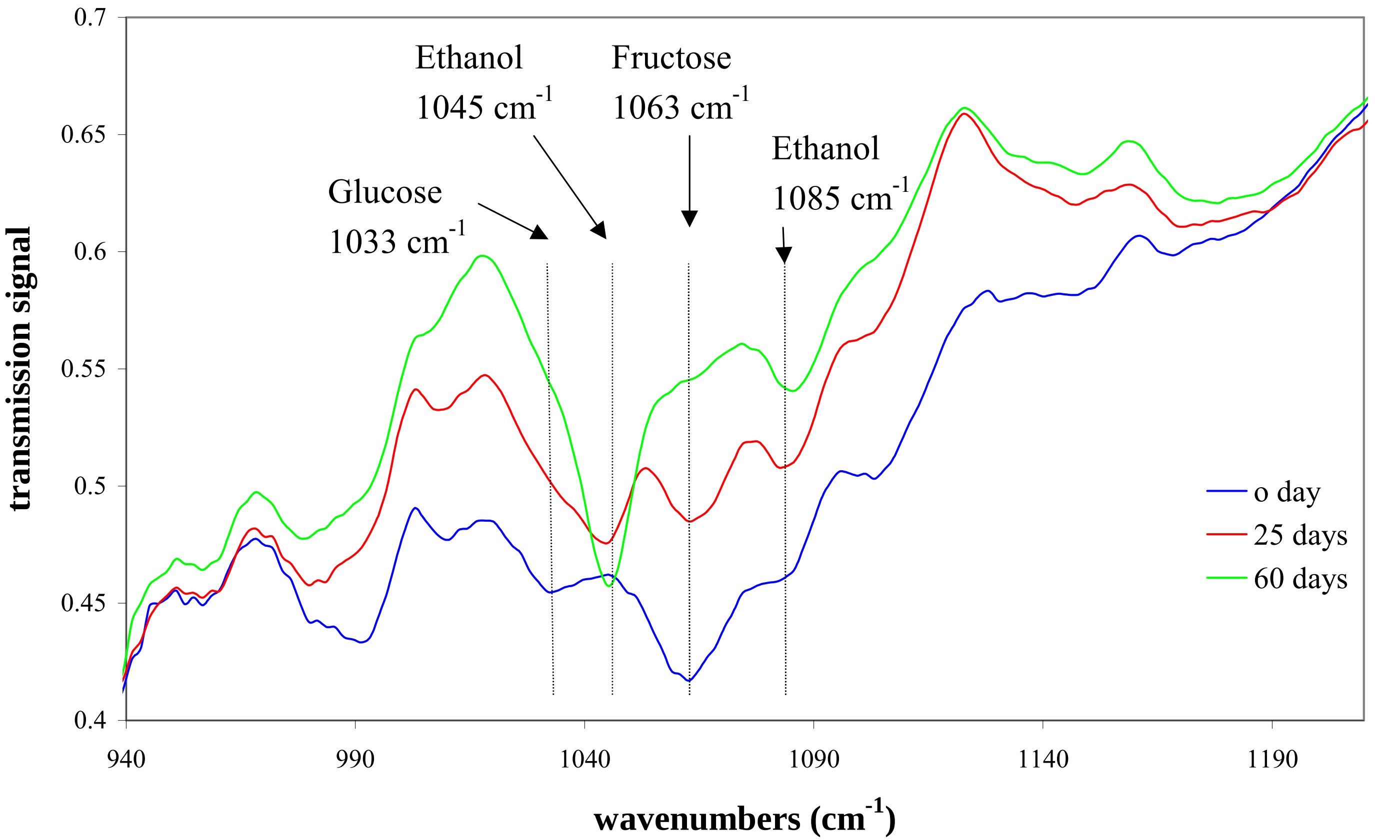


Experimental set-up

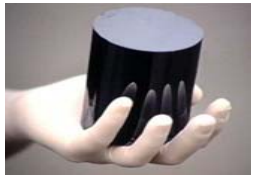


A unique chalcogenide glass fiber aimed at transmittting the beam and at probing the sample.

Alcoholic fermentation



Cider fabrication process from apple juice fermentation, in situ control of the transformation of glucose and fructose into ethanol

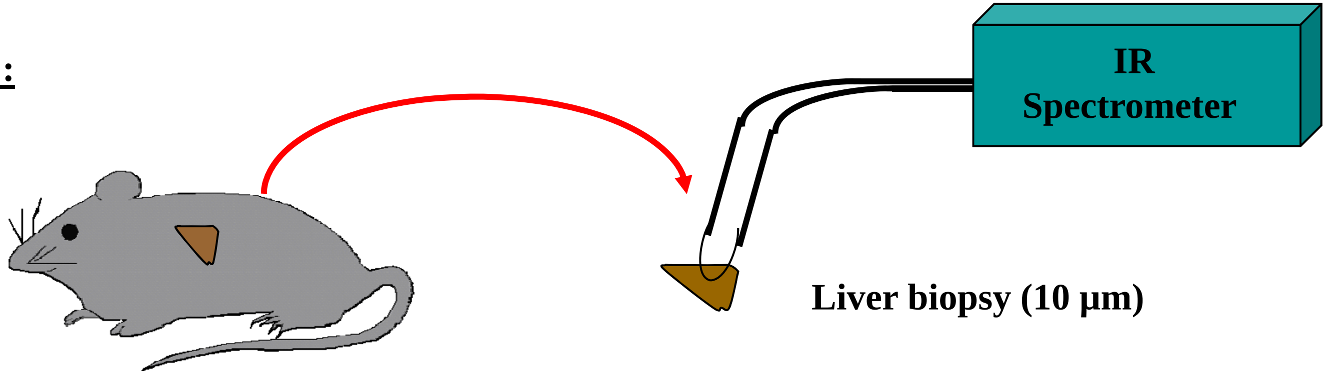


Study of a biological tissue : mouse liver (1)

Inserm
Institut national
de la santé et de la recherche médicale

OBJECTIVE : Following the effect of a starvation in the liver cells

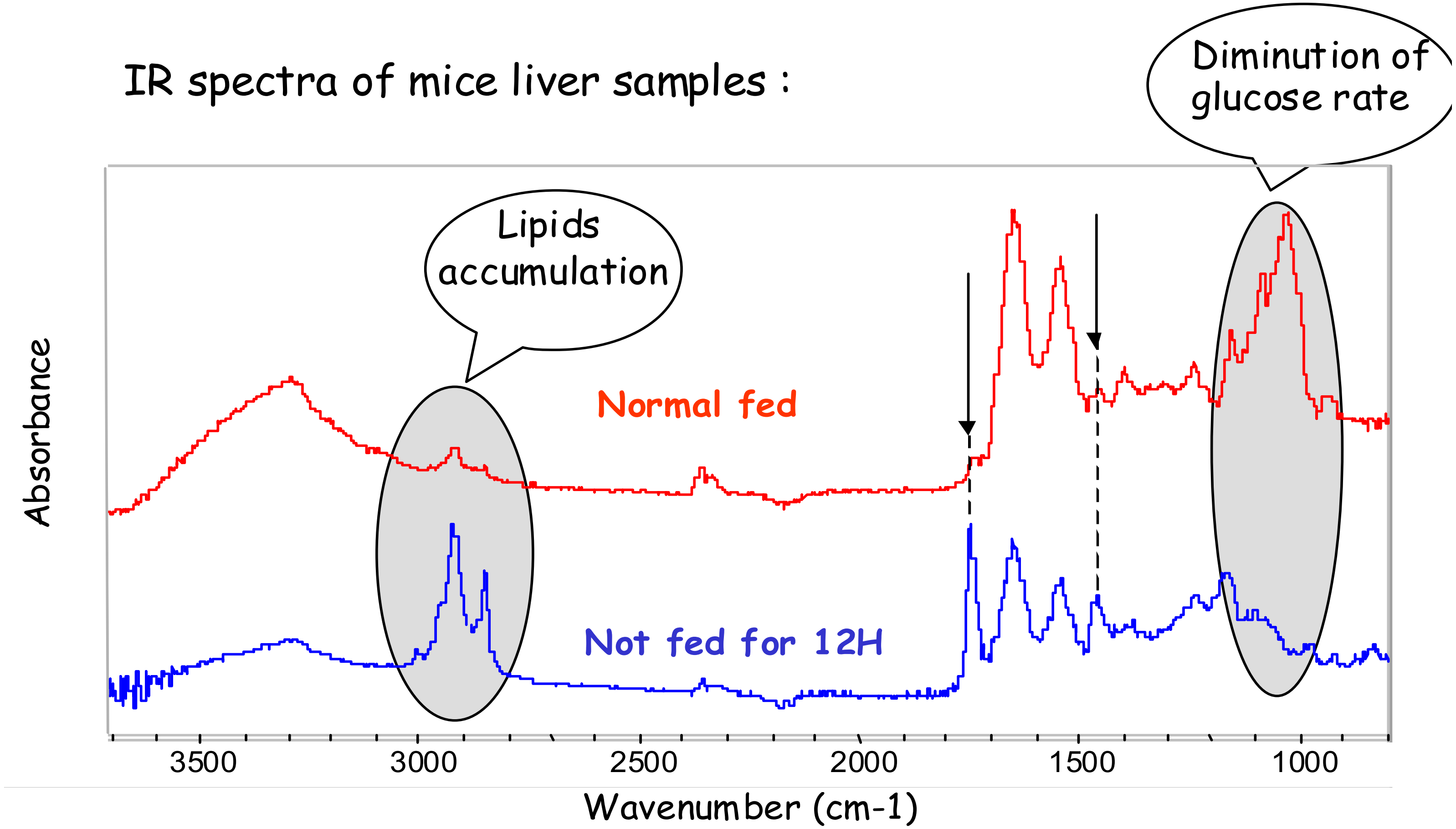
PRINCIPLE :



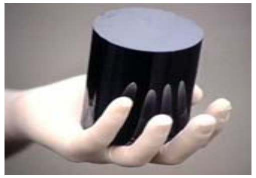
The tissues were merely deposited on the tapered part of the fibre to ensure an optimal contact between the fibre and the tissue

Study of a biological tissue : the liver

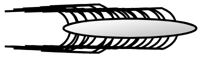
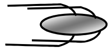
IR spectra of mice liver samples :

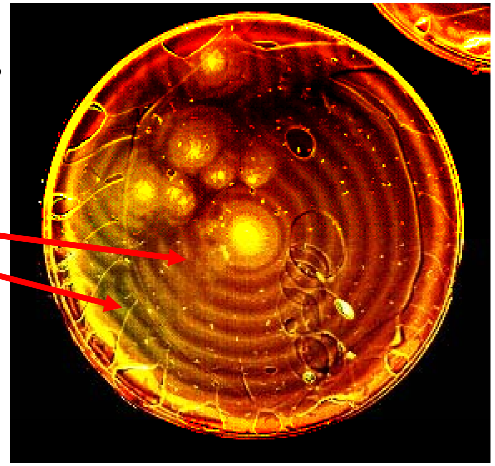


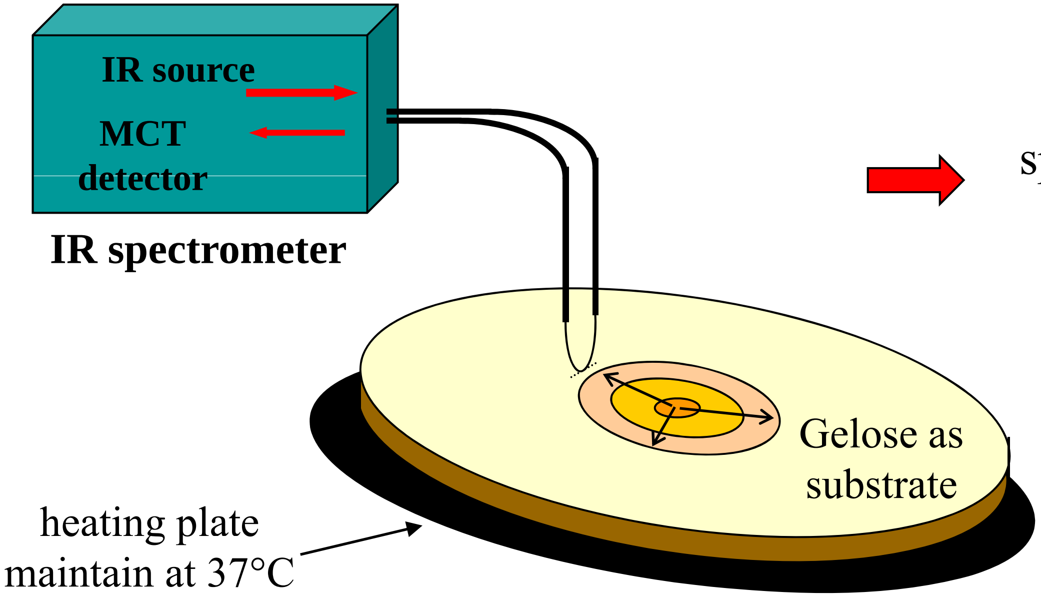
Possibility to detect metabolic variations in the liver.



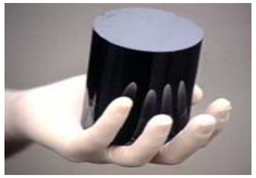
Study of a bacterial biofilm : Proteus mirabilis (1)

- **Opportunist pathogen agent of the human urany tract**
- **Presents two phenotypes : swarming**  **and vegetative** 
- **Their spreading from innoculum exhibit some terraces**

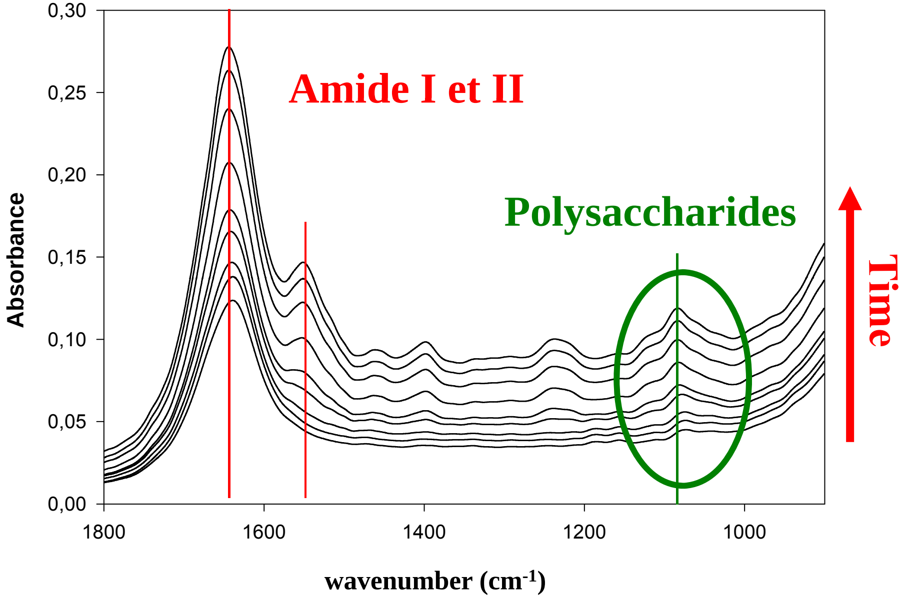


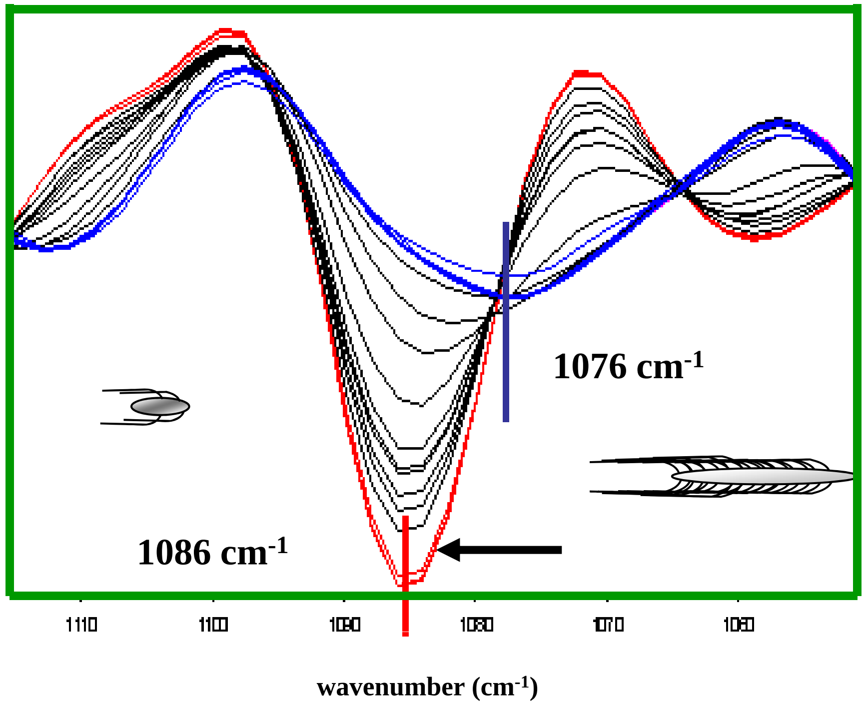


spectra recorded in situ every 15 min.
during the migration process
in the Petri plate.



Study of a bacterial biofilm : Proteus mirabilis (2)





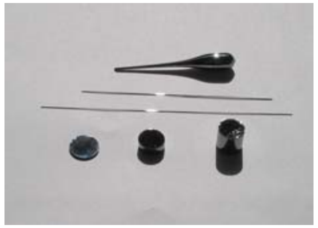
- Increase of the absorbency in agreement with the bio-mass growth

Detection in real time of the bacteria-sensor contact

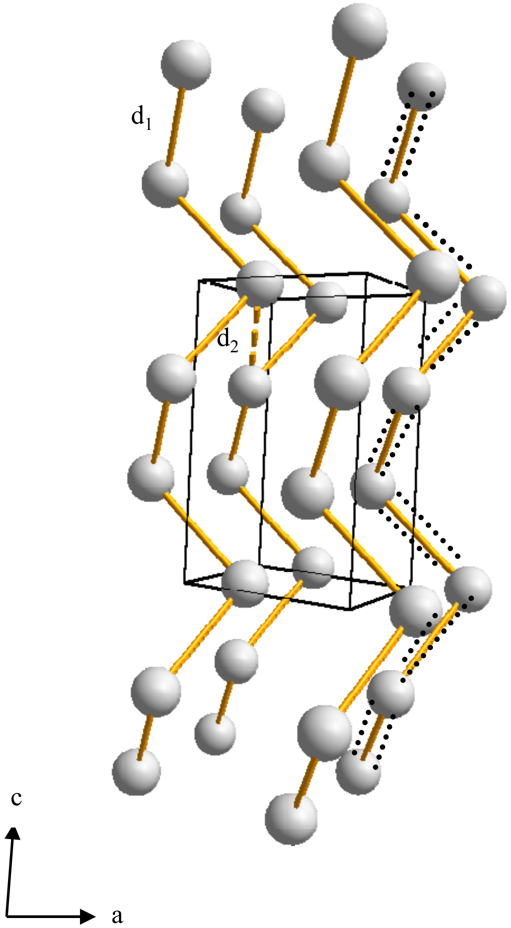
- Shift of the polysaccharides absorption bands

IR signatures of the both phenotypes

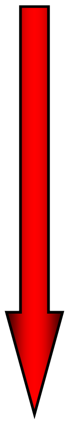
Te structure and bonding, seven order of magnitude in conductivity between Se and Te



Crystalline structure of metallic Te

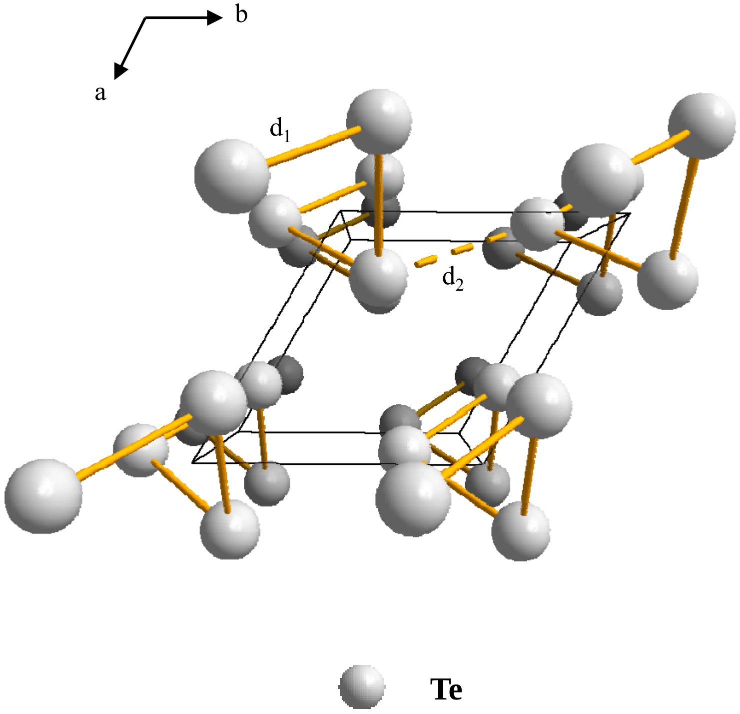


π metallic bonding



RIGIDITY

- Pure Te → no glass
- Te is not a glass former
- Tm = 450°C, fluid melt



Hexagonal structure

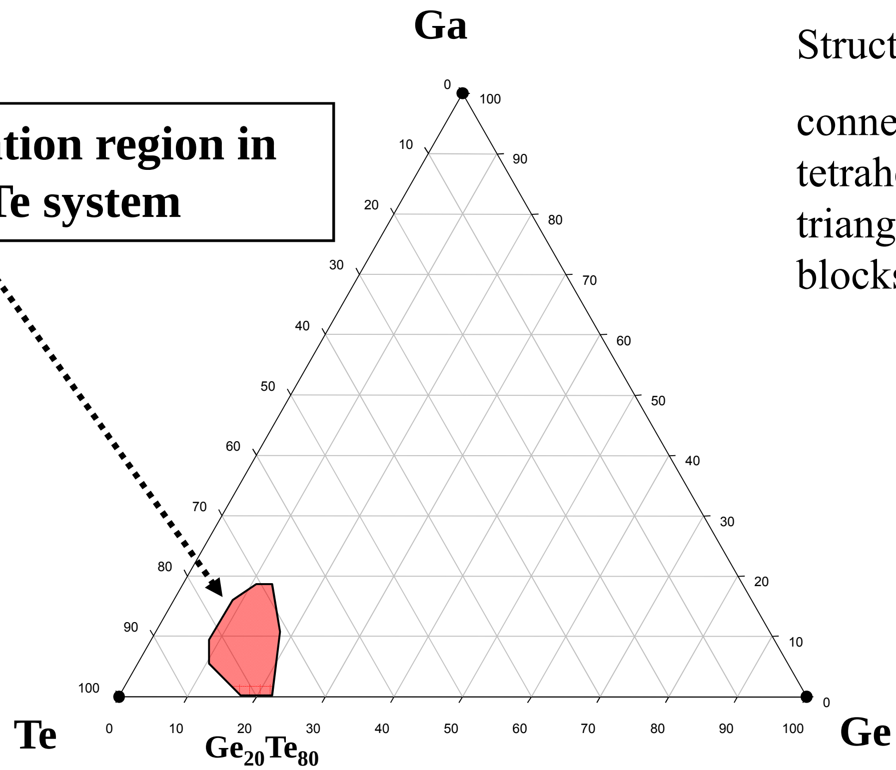
d_1: 2.83 Å

d_2: 3.49 Å

New optical Tellurium based glasses: Ga-Ge-Te

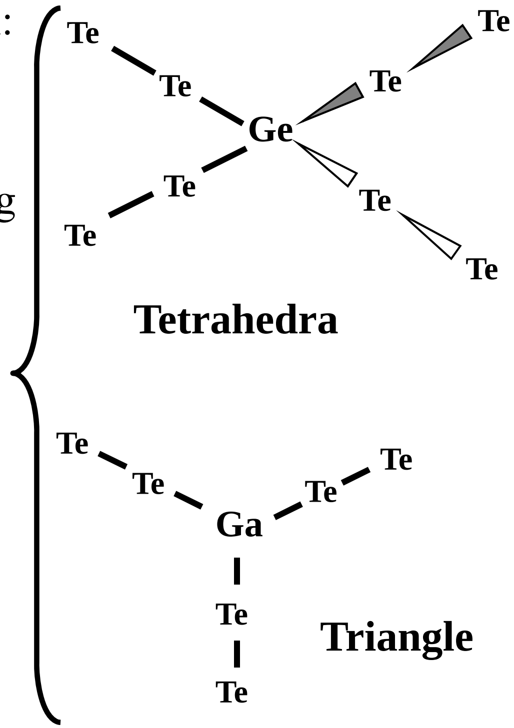
<u>Strategy:</u> suppress the possibility of metallic bond to allow flexibility

Glass formation region in the Ga-Ge-Te system



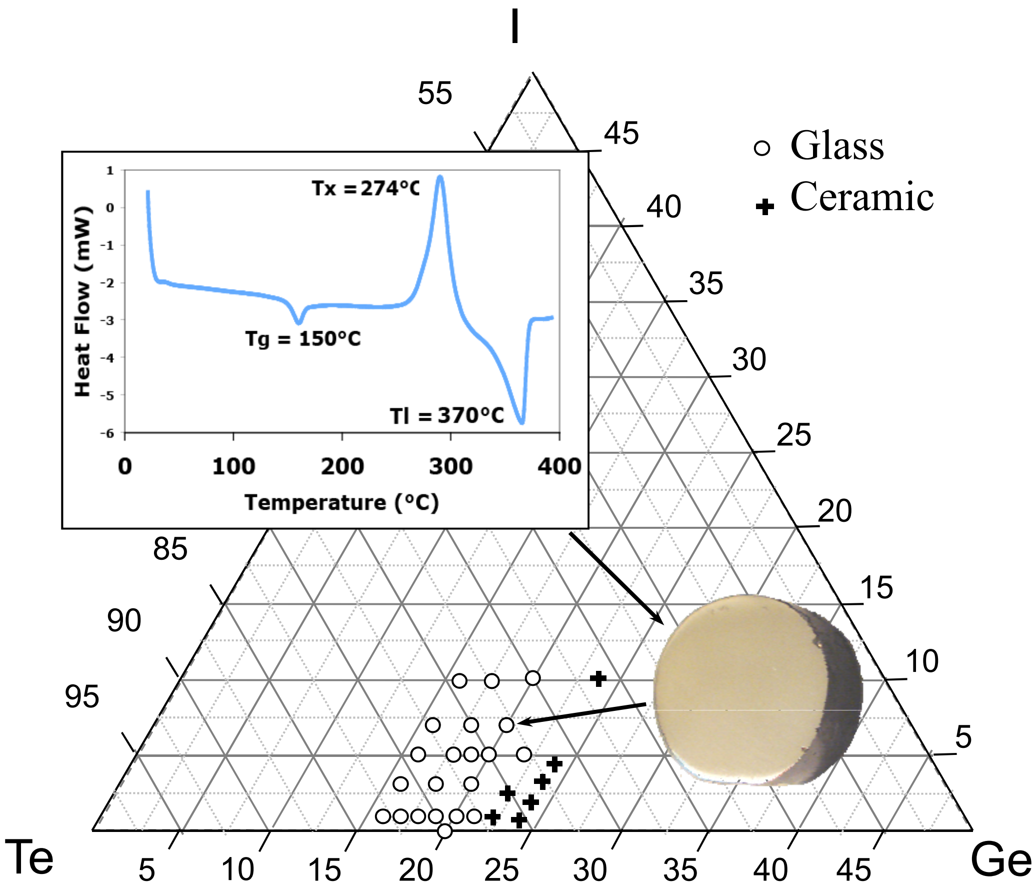
Structural model:

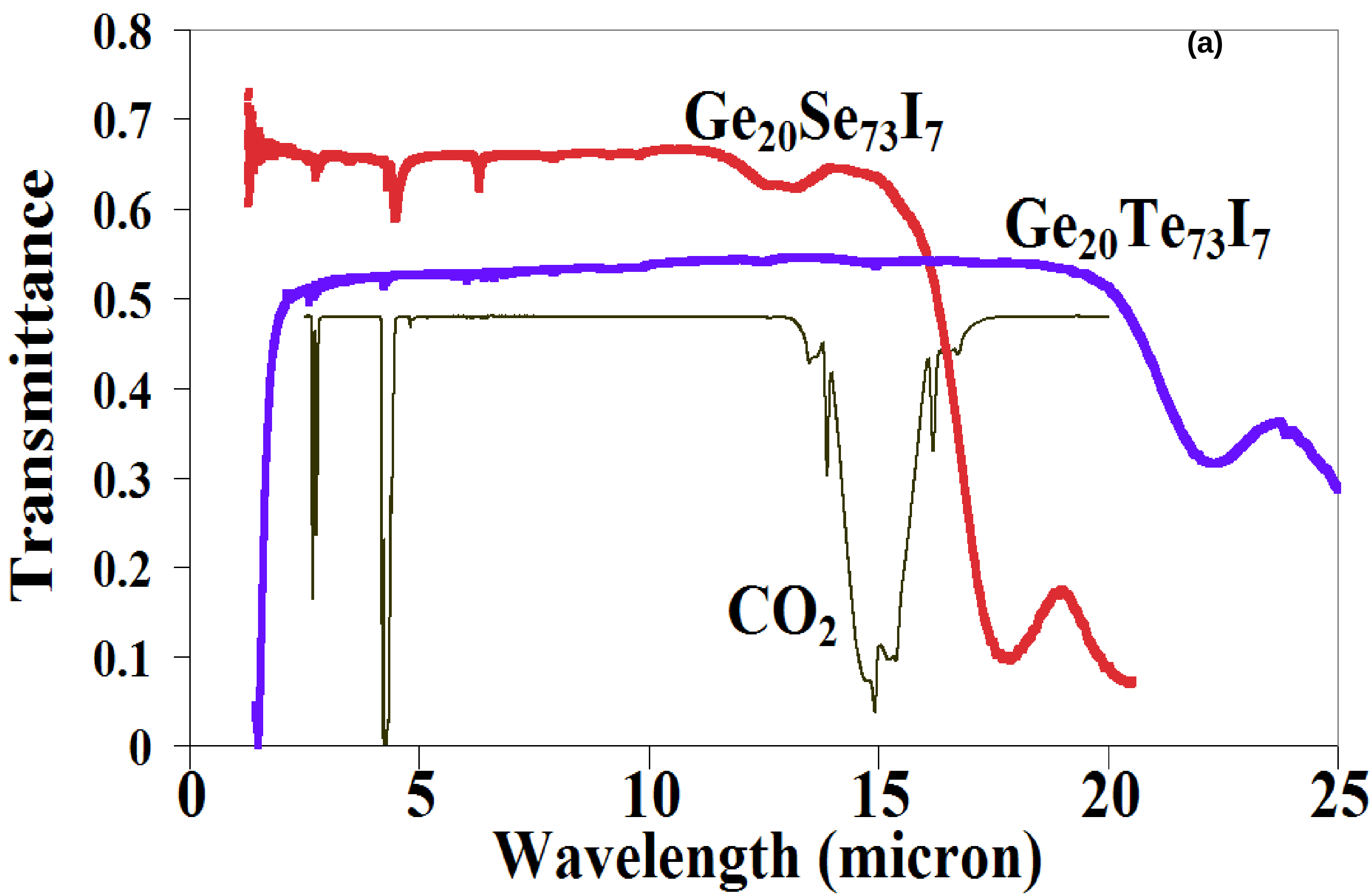
connection of tetrahedra and triangles building blocks



⇒ bulk glasses with 70% to 80% of Te

Glass formation domain in the Ge/Te/I system
The glass to crystal competition is strong
Tg= 150°C   Tx= 274°C





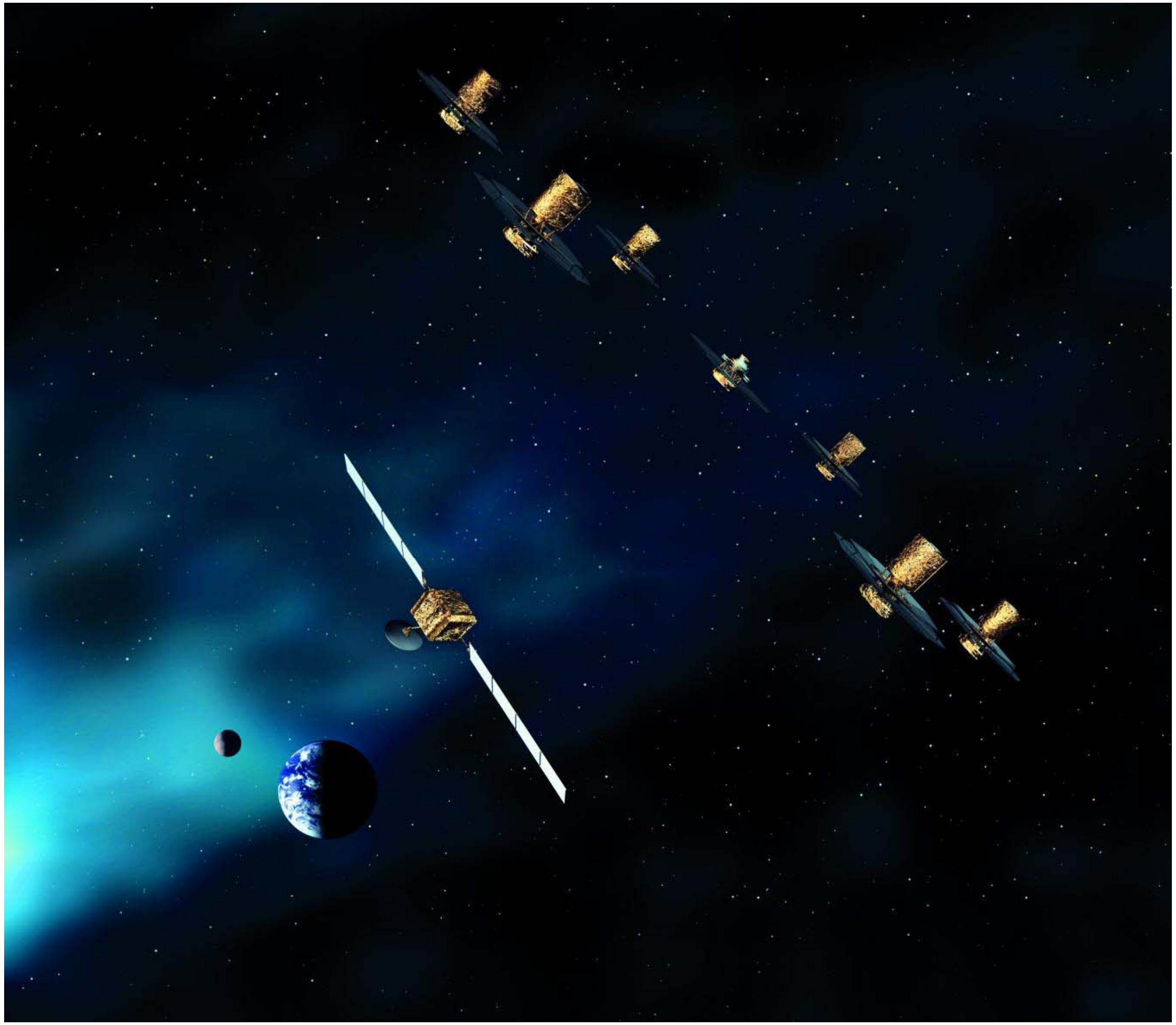
Optical transmission of a Te glass compared to an equivalent Se based glass

The 15µm CO_2 absorption band is in the middle of the transparency window

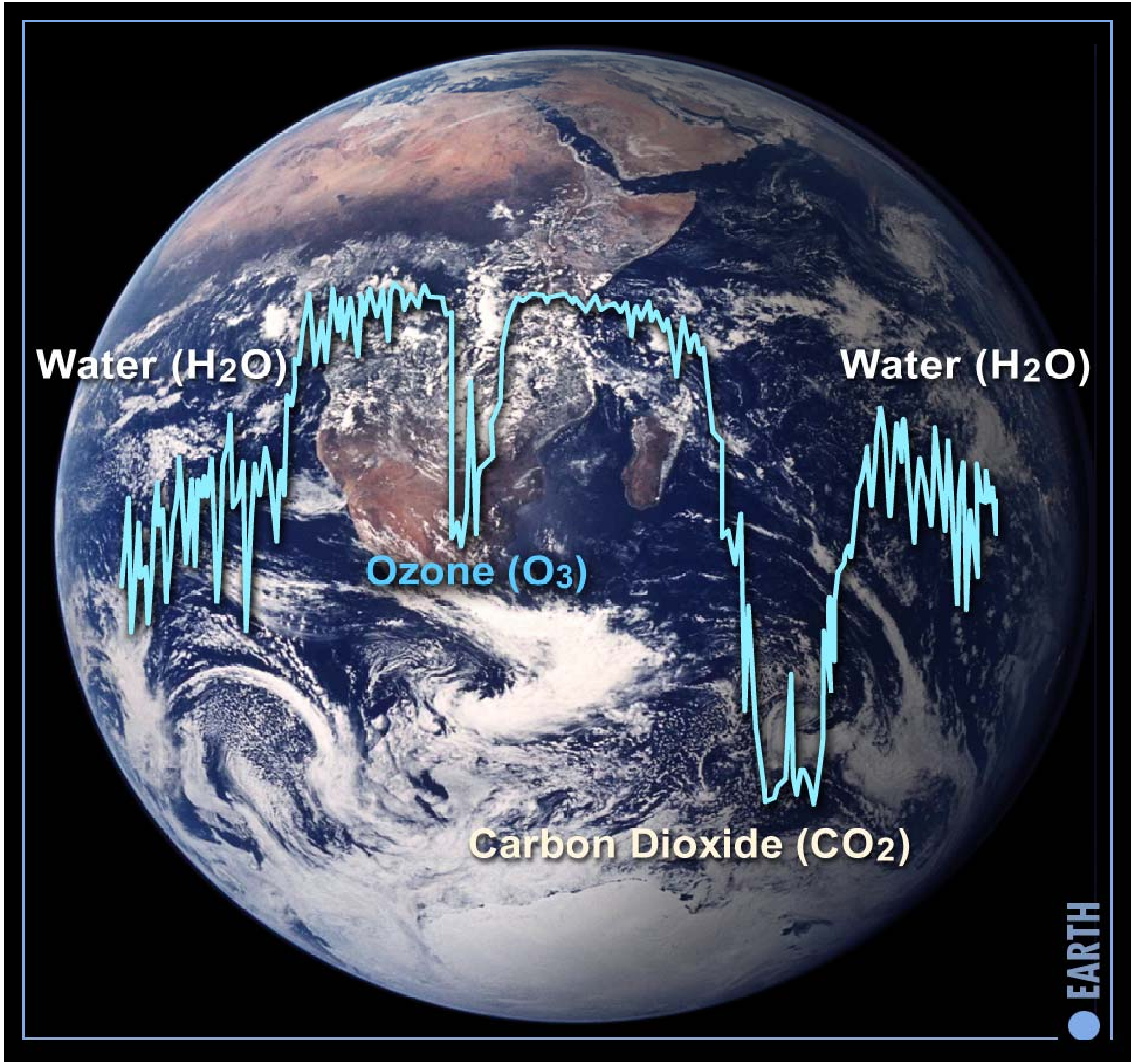
DARWIN MISSION

ESA, European Space Agency

Target: detection of biological of biological life on exoplanets, out of the solar system→ markers are H_20, O_3 and CO_2 having their signature in the IR: 6µm, 10µm, 15µm

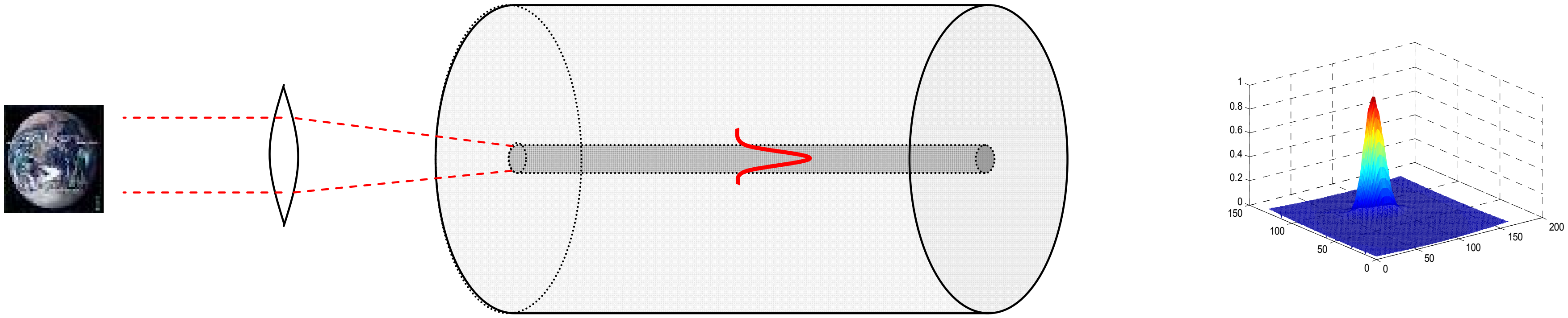


Two windows: 6-10 µm for water (vibration) and ozone detection 10-20µm for carbon dioxide and water (rotation) detection.



Water (H_2O)
Water (H_2O)
Ozone (O_3)
Carbon Dioxide (CO_2)
EARTH

Infrared single mode fibre for wavelength filtering



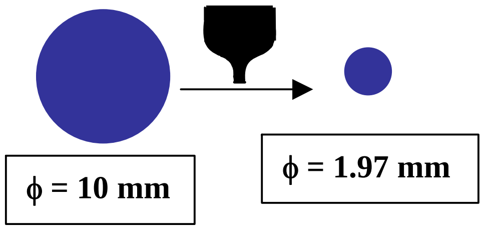
Planet emitting IR light

Gaussian IR light output

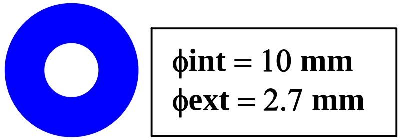
Rod in tube vacuum method (RTVM)

Preparation of a core glass rod

Reducing the diameter of the core glass by fiber drawing

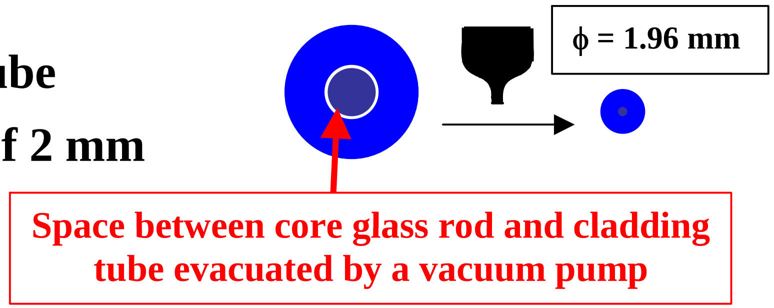


Preparation of a cladding tube of 10 mm

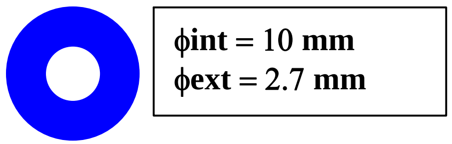


Fixation of the core rod inside the cladding tube

Drawing an intermediate core-cladding rod of 2 mm

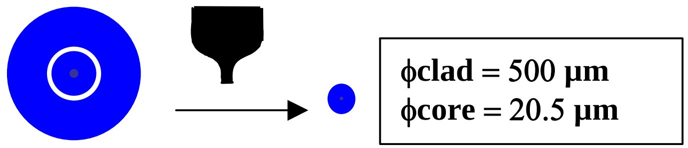


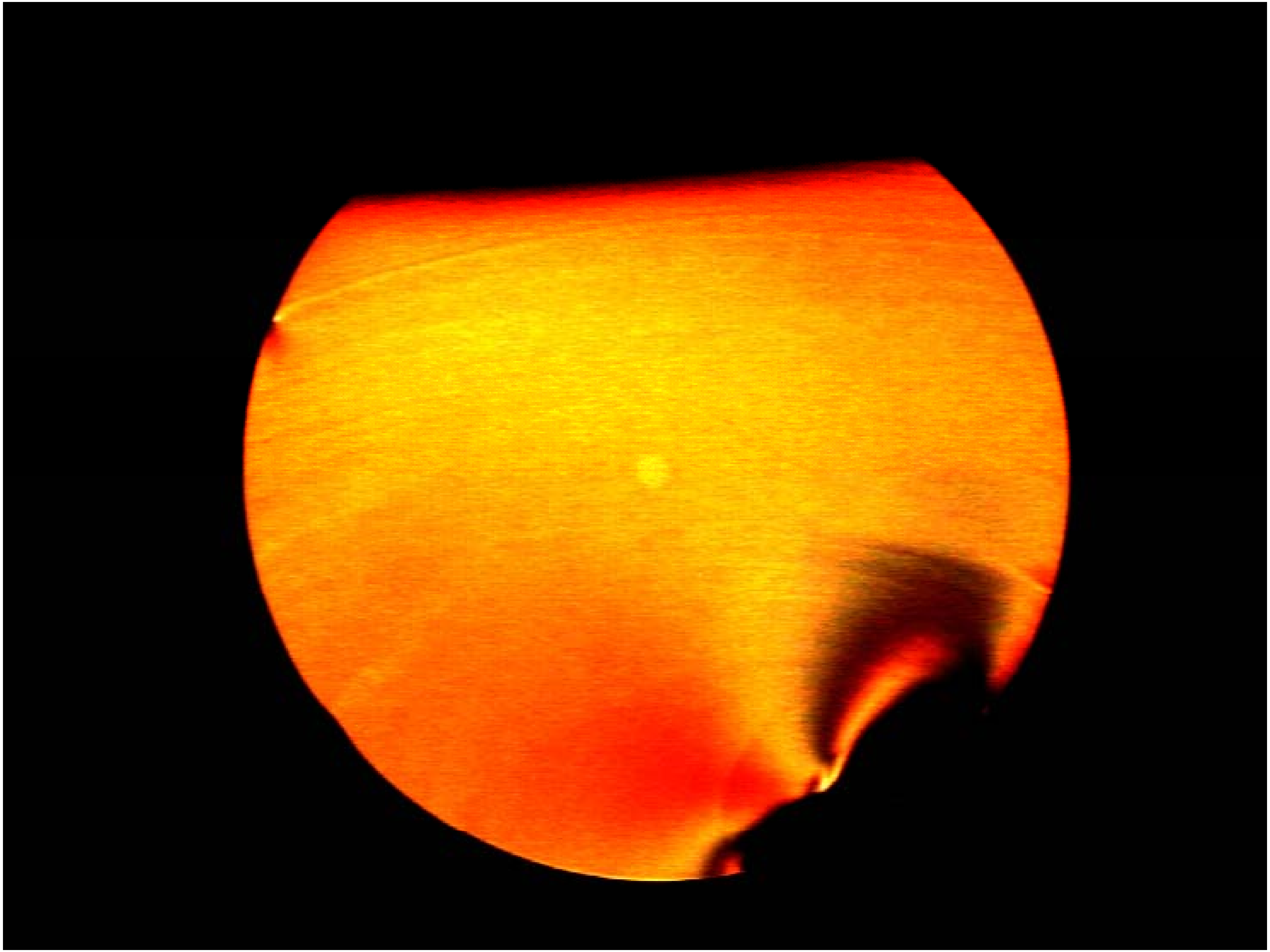
Preparation of a cladding tube of 10 mm



Fixation of the core-cladding rod in the cladding tube

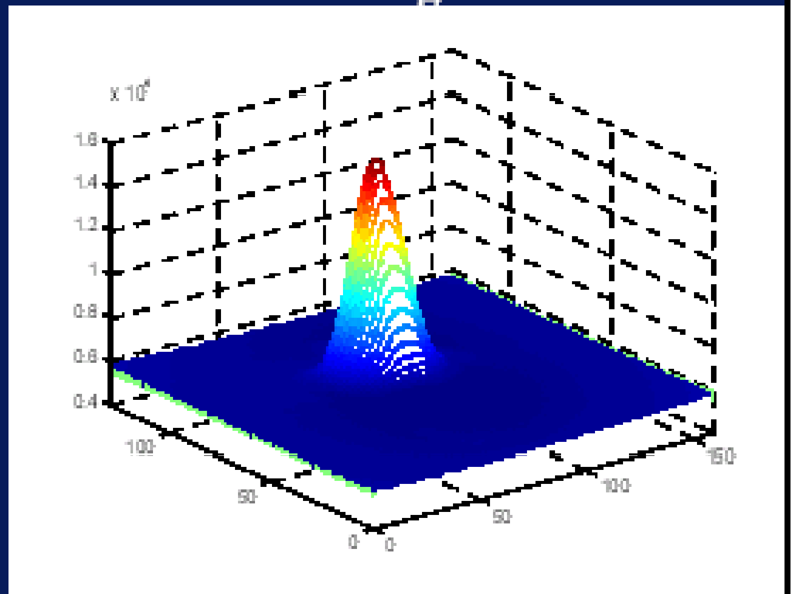
Final fibering process leading to the final fiber : TAS#2



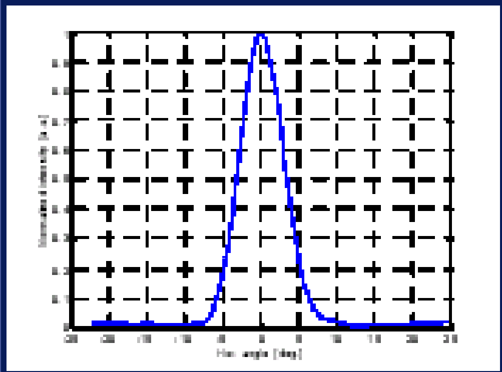


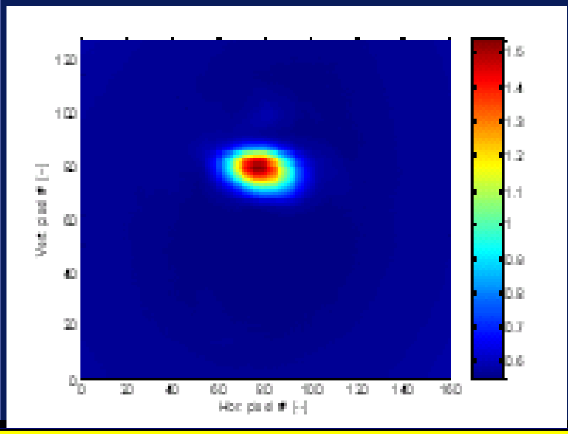
D: Fiber in single mode operation (1)

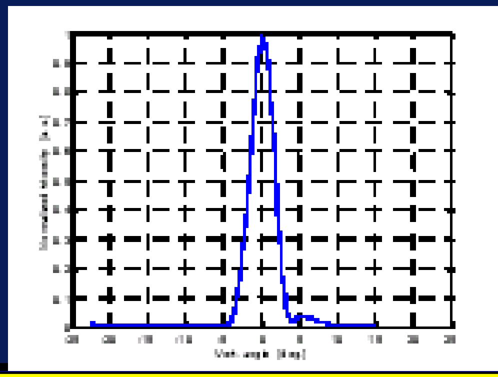
- TAS fiber of 23cm. Extra attention for the Gallium coating
- Detector at 10mm from fiber end



Horizontal NA = 0.12







Vertical NA = 0.06

Single mode fibre at 10µm (CO_2 laser)