



*Fluoride glass fiber sources:  
Problems and prospects*

*Marcel Poulain and Gwenael Mazé*

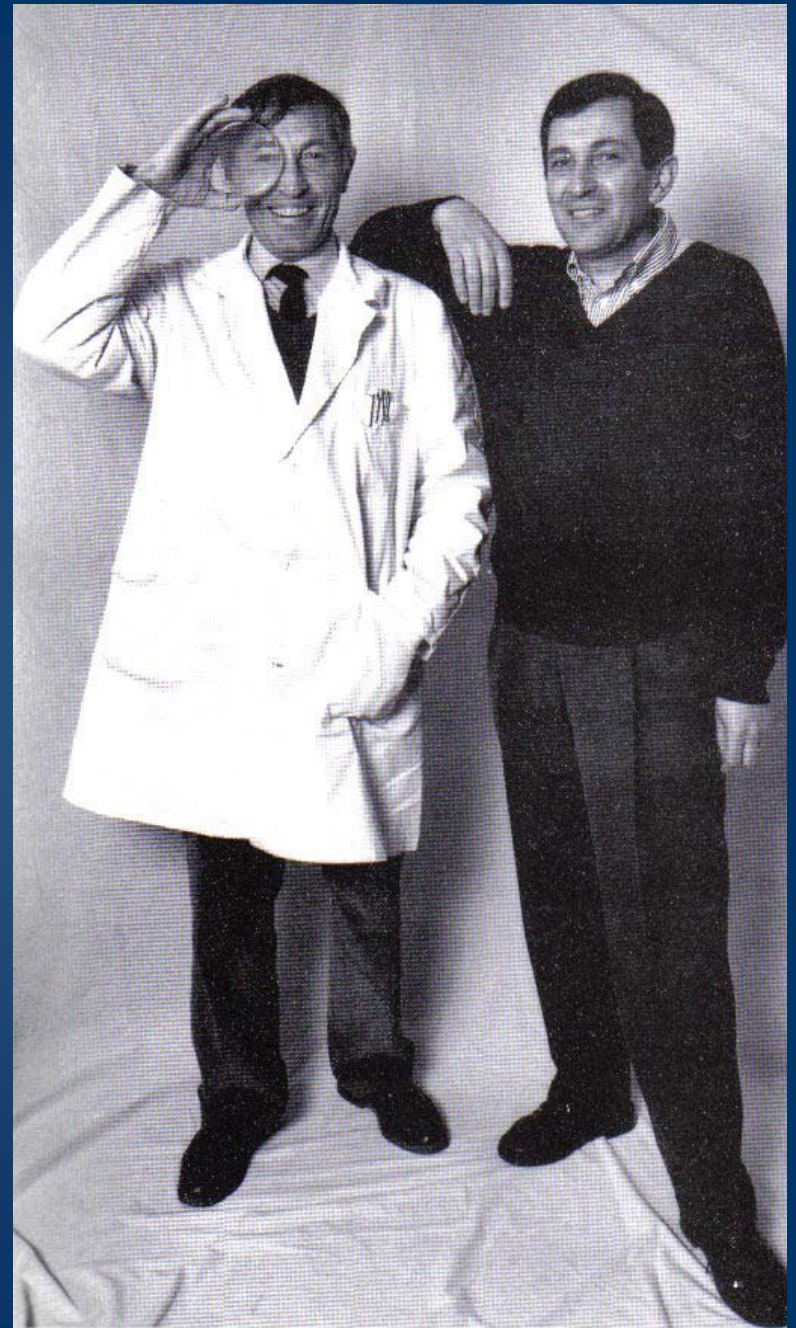
*Rennes University and Le Verre Fluoré*



| Report Documentation Page                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                    |                                     |                                             | Form Approved<br>OMB No. 0704-0188          |                                    |
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## **Outline :**

- 1 Introduction**
- 2 Fluoride glass technology**
- 3 Specifications of active fibers**
- 4 Achievements**
- 5 Problems and prospects**
- 6 Conclusion**





# INTRODUCTION



# The privilege of experience...



36 years of continuous activity in fluoride glasses, from the discovery to the industrial development



Pioneering achievements



Interaction and collaborations with major actors of fiber lasers, optical amplifiers and active devices for more than 20 years



Very large (and often unexpected) field of expertise.

# Pionnering achievements



Numerous results were not released (confidentiality)



ZBLAN glass compositions were characterized in 1980.  
[Furukawa (Shibata & Oshawa) paper appeared in 1984]



The first ZBLA:Nd laser was made in 1978 in collaboration with P.Brun's laboratory at Rennes University



Lasing effect was accidentally observed in 1984 in a Nd-doped fiber supplied to the French CEA



Low loss optical fibers ( $< 1$  dB/km) have been obtained.  
Development steps have been identified

# This talk intends



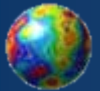
To outline some achievements (Not an exhaustive review!)



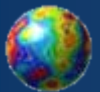
To discuss problems in relation to fiber lasers, amplifiers and sources.



To complete ambiguous or misleading informations



To draw prospects for future realizations



To make the ground for possible interactions

# Interactions, collaborations



JPL (NASA), large NA fibers (1985)



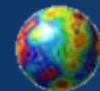
France Telecom (CNET), ORC



Various German companies and universities



Large astronomic observatories (VLT, Hawaii)



Researchers and groups from this audience



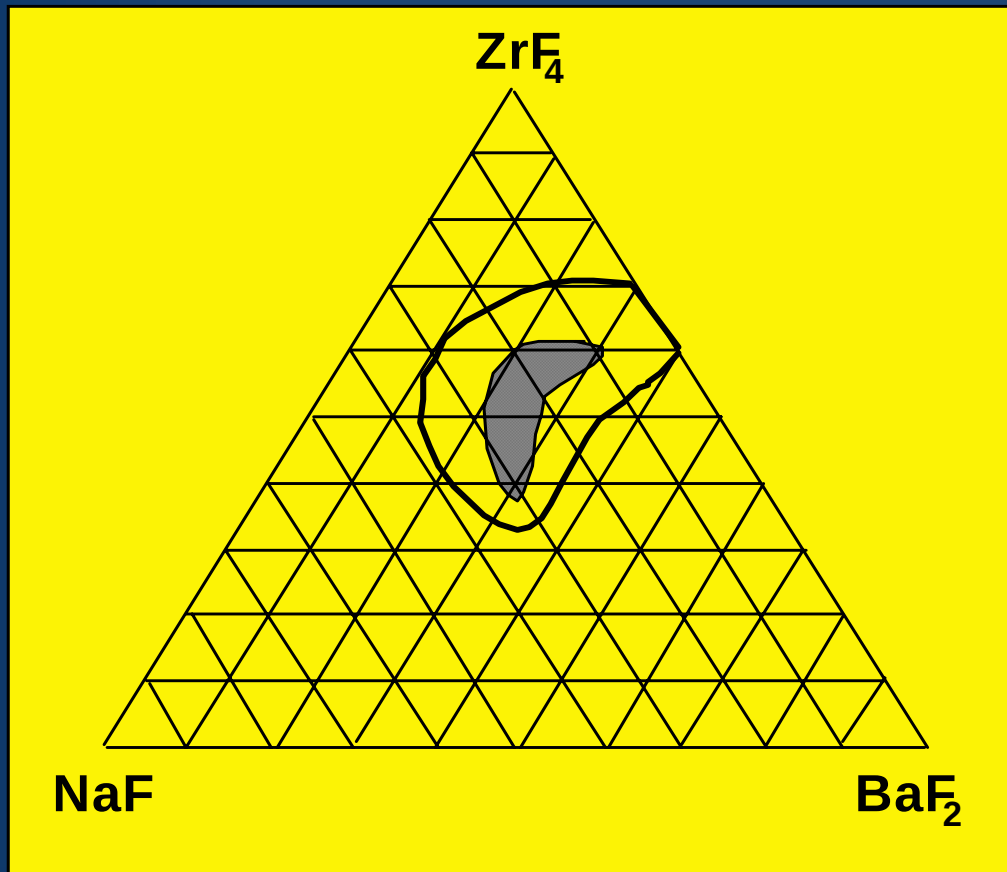
Close collaboration with COPL, Laval Univ, Québec



# **FLUORIDE GLASS TECHNOLOGY**

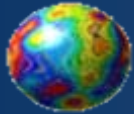


# 21 Glass composition



Initial system  
(1975)

# Fluoride glass families



**Most studies focused on fluorozirconates based on  $\text{ZrF}_4$  and  $\text{HfF}_4$**



**Other fluoride glasses are formed with  $\text{AlF}_3$ ,  $\text{GaF}_3$  and  $\text{InF}_3$  as main glass formers**



**Significant differences are observed in:**

- Chemical durability**
- Glass stability**
- Mechanical strength & hardness**
- Phonon energy**

# Typical glass compositions

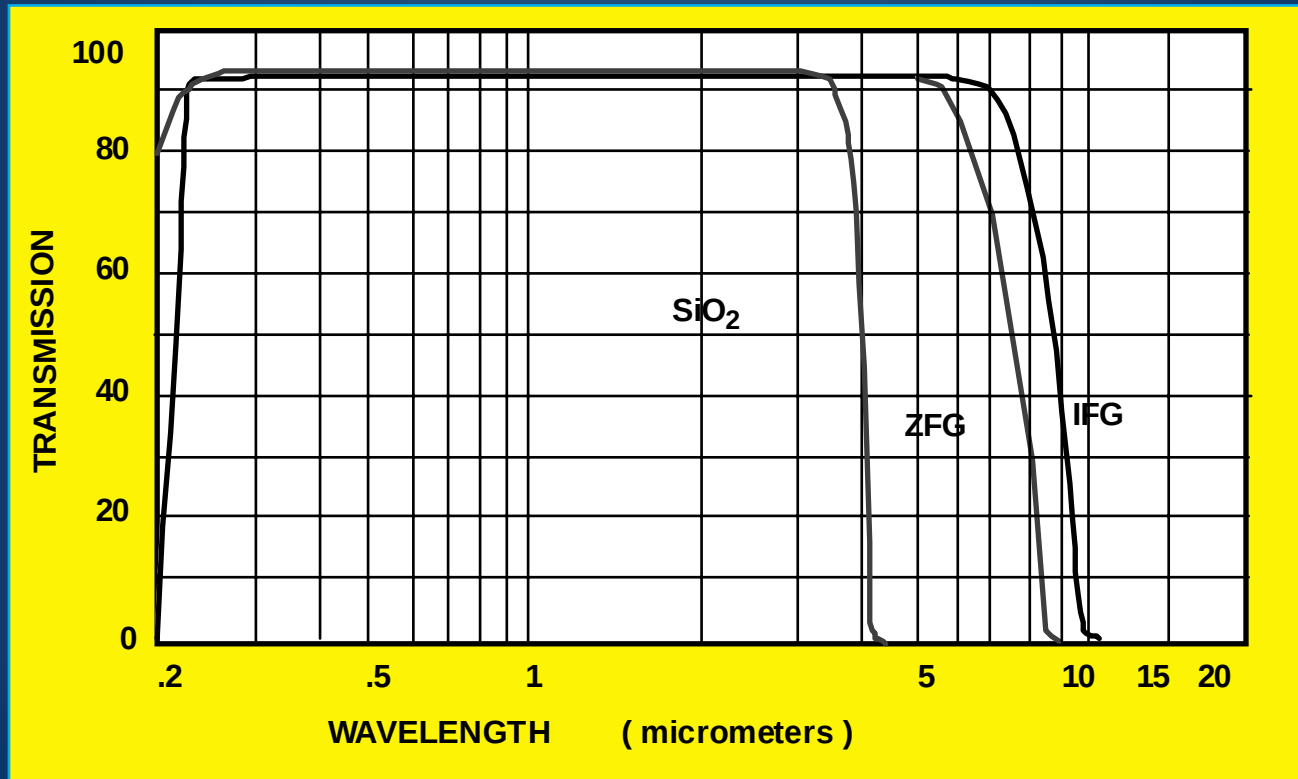
| Glass  | COMPOSITION (mol %)                                                                                                                                        | $n_D$ |
|--------|------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| ZBLA   | 57 ZrF <sub>4</sub> , 34 BaF <sub>2</sub> , 5 LaF <sub>3</sub> , 4 AlF <sub>3</sub>                                                                        | 1.519 |
| HBLA   | 57 HfF <sub>4</sub> , 34 BaF <sub>2</sub> , 5 LaF <sub>3</sub> , 4 AlF <sub>3</sub>                                                                        | 1.504 |
| ZBLAN  | 53 ZrF <sub>4</sub> , 20 BaF <sub>2</sub> , 5 LaF <sub>3</sub> , 4 AlF <sub>3</sub> , 20 NaF                                                               | 1.498 |
| ZBSFCl | 60 ZrF <sub>4</sub> , 20 BaFCl, 20 SrFCl                                                                                                                   | 1.542 |
| YABC   | 20 YF <sub>3</sub> , 40 AlF <sub>3</sub> , 20 BaF <sub>2</sub> , 20 CaF <sub>2</sub>                                                                       | 1.440 |
| IZBS   | 40 InF <sub>3</sub> , 20 ZnF <sub>2</sub> , 20 SrF <sub>2</sub> , 15 BaF <sub>2</sub> , 5 CaF <sub>2</sub>                                                 | 1.495 |
| PGICZ  | 30 PbF <sub>2</sub> , 22GaF <sub>3</sub> , 13 InF <sub>3</sub> , 18 CdF <sub>2</sub> , 13 ZnF <sub>2</sub> , 2 GdF <sub>3</sub> , 2 NaF<br>( $n = 1.595$ ) |       |

# General physical properties

| PROPERTY                                                      | HMFG                                  | ZBLAN               |
|---------------------------------------------------------------|---------------------------------------|---------------------|
| Glass transition temperature (°C)                             | 200-450                               | 260                 |
| Coefficient of Thermal Expansion ( $10^{-7} \text{ K}^{-1}$ ) | 140-210                               | 180                 |
| Density ( g/cm <sup>3</sup> )                                 | 4-6                                   | 4.14                |
| Young Modulus (GPa)                                           | 50-60                                 | 54                  |
| Vickers hardness (kg/mm <sup>2</sup> )                        | 200-270                               | 210                 |
| Poisson ratio                                                 | 0.25 – 0.35                           | 0.30                |
| Refractive index $n_D$                                        | 1.45 – 1.60                           | 1.500               |
| Non linear refractive index $n_2$ ( $10^{-13}$ esu)           | 0.8 – 0.9                             | 0.85                |
| Abbe Index $\nu$                                              | 60 – 80                               | 75                  |
| dn/dT                                                         | $1 \cdot 10^{-5}$ - $2 \cdot 10^{-5}$ | $1.5 \cdot 10^{-5}$ |
| Cp (J / g at.K)                                               |                                       | 24.9                |

# Optical transmission

Optical transmission of samples 4 mm thick



# STRUCTURE: the vacancy model



Numerous structural investigations show the high coordination number of the vitrifying cations: 8 ( Zr ) or 6 ( Al, Ga, In ).

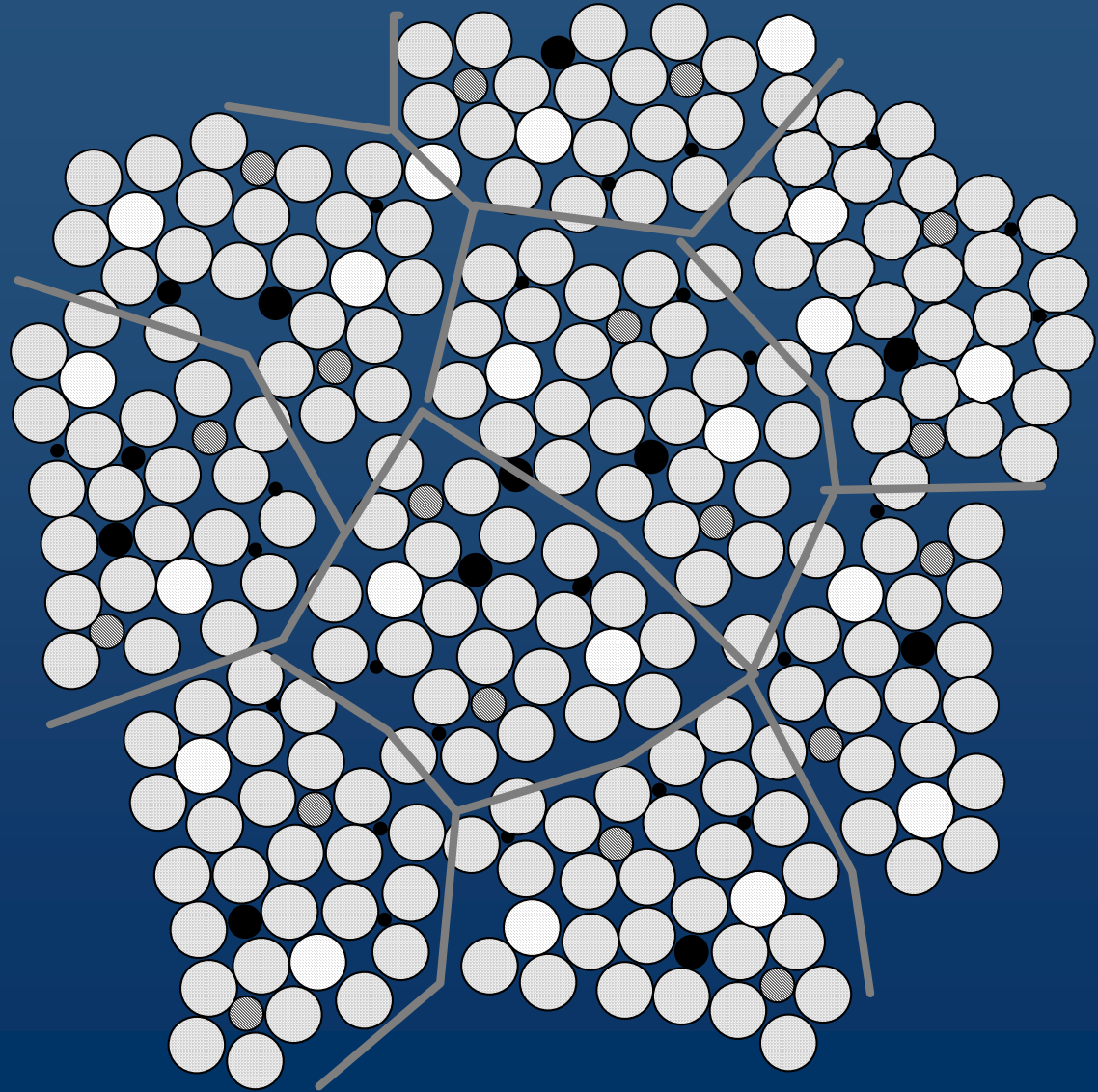


The vitrifying network is constructed from the association of the  $\text{MF}_6$  or  $\text{MF}_8$  polyhedra with large cations  $\text{Na}^+$ ,  $\text{Ba}^{++}$  as modifiers.



The vacancy model offers an alternative description:  
A disordered packing of large ions (  $\text{F}^-$  and  $\text{Ba}^{++}$  ) in which small cations are inserted. This packing contains vacancies that are mobile in the liquid state.

# Bidimensional picture





# **GLASS PROCESSING**

# 22 GLASS SYNTHESIS

- Fluoride glass synthesis includes melting, fining, casting and annealing steps
- Specific features are low melt viscosity, volatilization, devitrification and hydrolysis.
- Water action is critical. To overcome the problem various solutions have been reported:
  - Reactive atmosphere processing
  - Ammonium bifluoride processing
  - Dry processing



# Optical quality samples



Samples prepared at room atmosphere from current starting materials exhibit numerous defects:

- Cords and syrups
- « Stones » and inclusions
- Bubbles
- Crystals
- Composition fluctuations



Manufacturing of optical quality samples ( $\Delta n < 10^{-6}$ ) is difficult and time consuming.



Several parameters must be considered and optimized

# 23 Fiber manufacturing

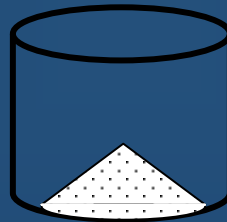
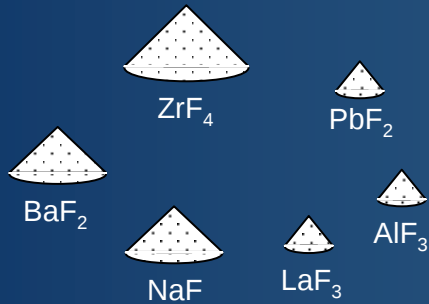
Powders

Melting

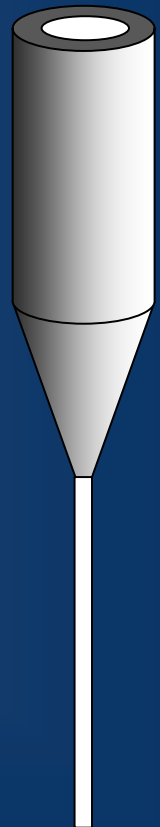
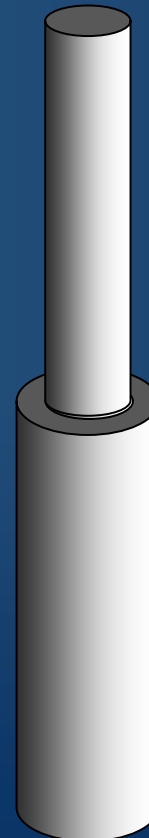
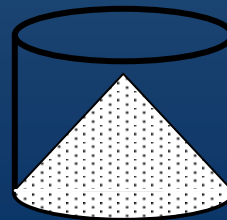
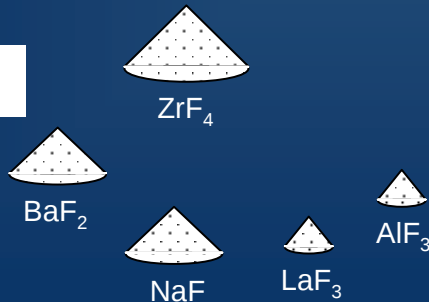
Preform

Fiber

Core

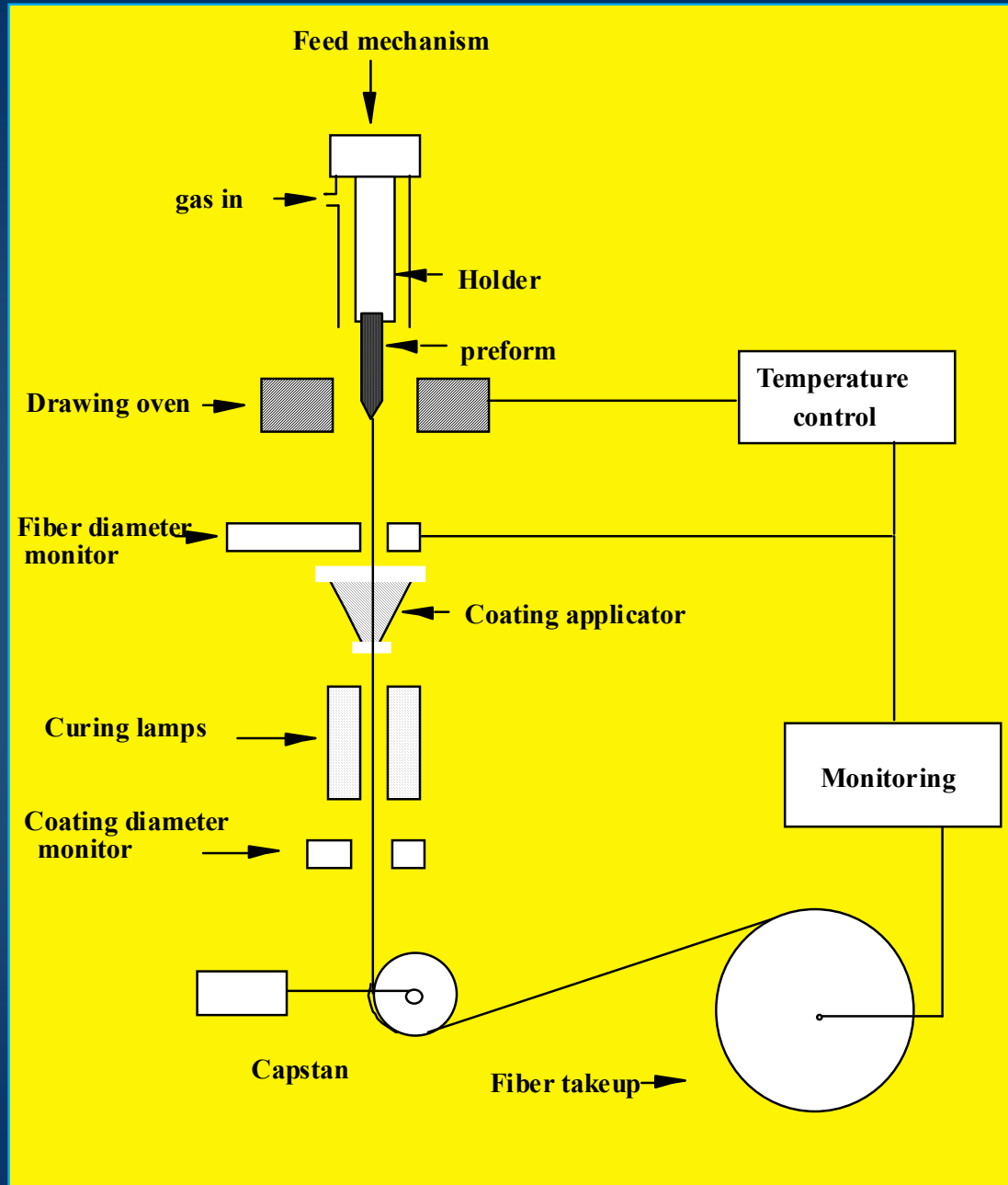


Cladding



# Fiber drawing

Fluoride glass fibers are drawn using glass preforms which are processed from high purity glasses processed in a very dry and clean atmosphere. The optical and physical characteristics of the preform determine to a large extent the structure and the optical properties of the fiber.



# Critical aspects of HMFG fibers



Fiber drawing adds defects to the preexisting defects in the preform



Various parameters must be optimized:  
Time, temperature, preform size, atmosphere  
(water, contaminants, dust)



Main contribution to optical losses arise from core defects



Quality of core/cladding interface is critical



# **SPECIFICATIONS**



# General features:

## optical fiber must be



Strong enough to survive in any case



Transparent in operating window (low optical losses)



Durable in ambient air and humidity



Stable optically and mechanically vs time and temperature



Comply with optical specifications

# Rare earth doped fibers must be



Homogeneous (no clustering)



Host the convenient amount of active ions.



Have minimum background losses

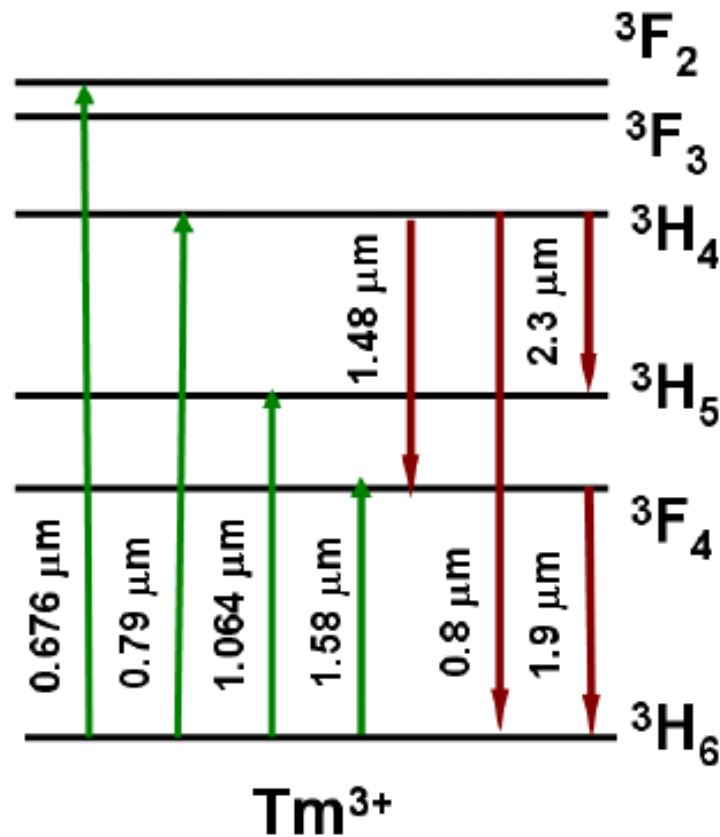


Allow co-doping (e.g. Yb/Er)

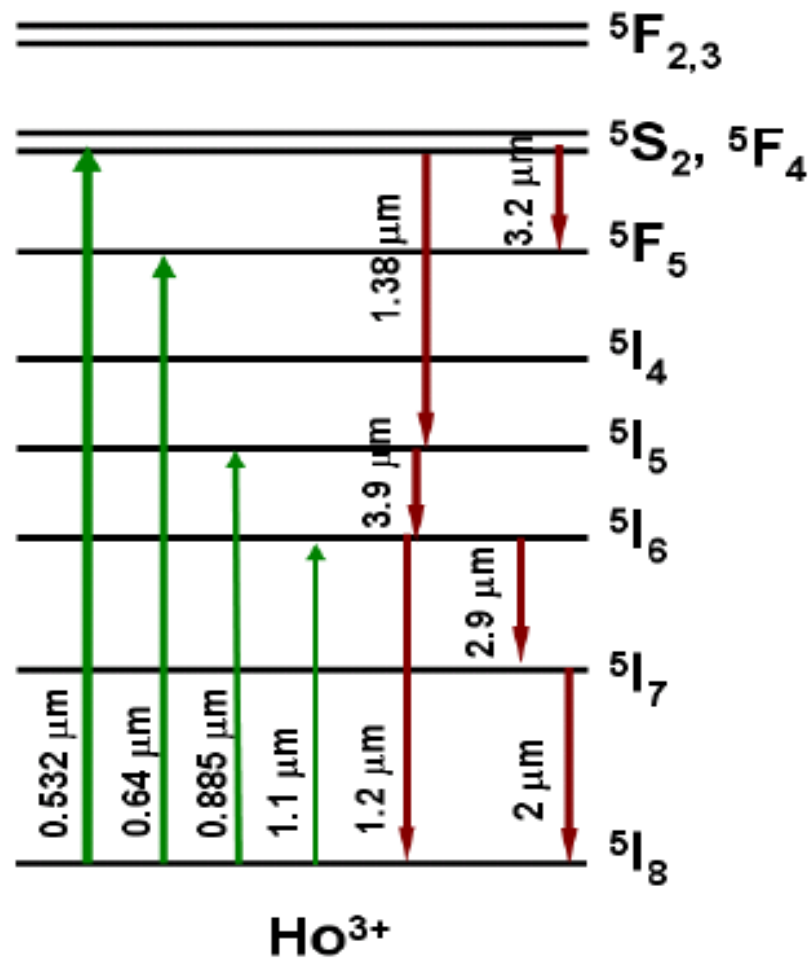


Withstand high energy pumping

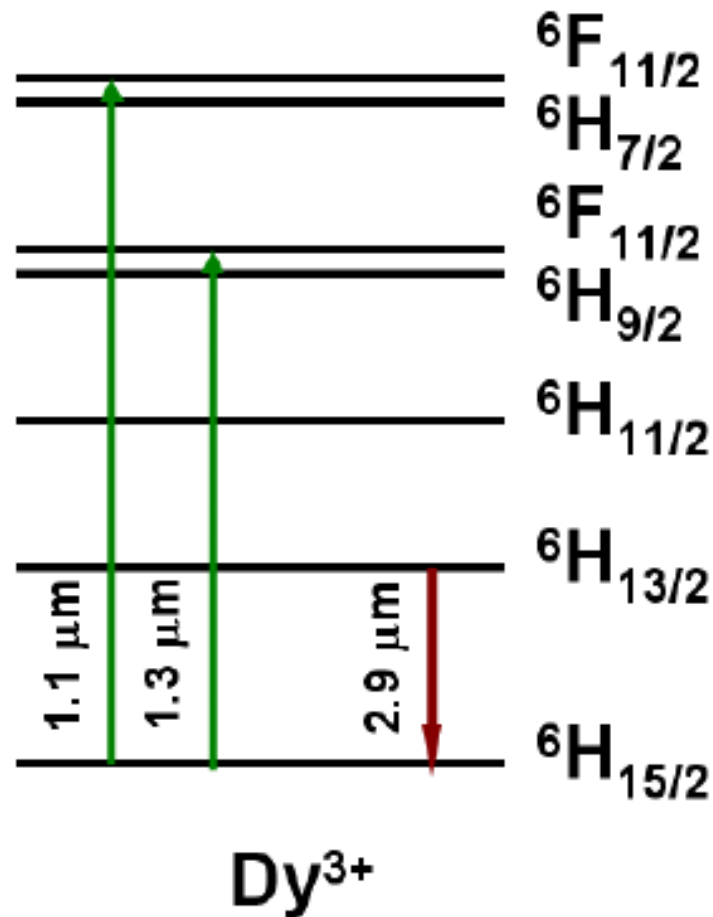
# Rare earths for mid IR emission



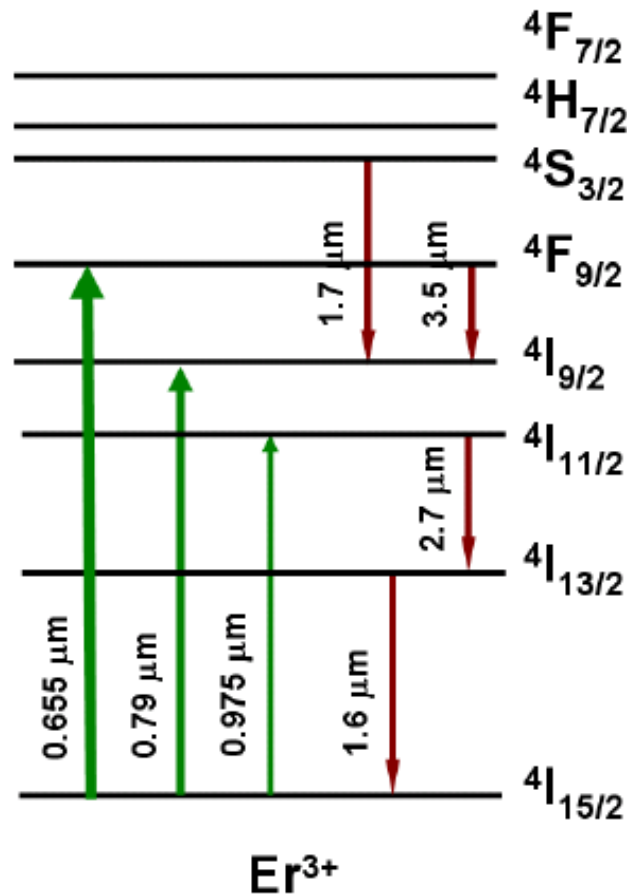
# Rare earths for mid IR emission



# Rare earths for mid IR emission



# Rare earths for mid IR emission



# High power and supercontinuum



Fiber must withstand large pump power



Limitations arise from extrinsic defects  
(Intrinsic damage threshold is largely unknown)



Power in cladding must be controlled



High non linear parameters are desirable



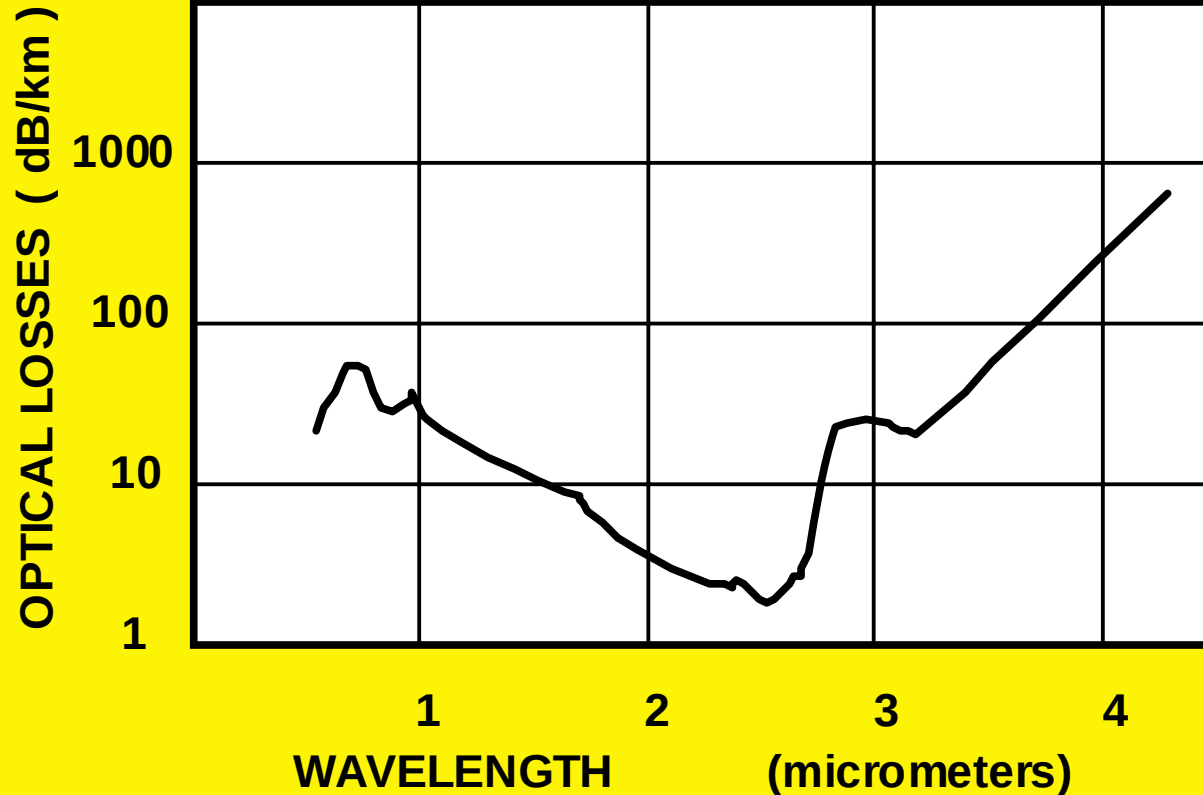
Reliability of resonator, splicing and end faces



# ACHIEVEMENTS

# Optical transmission: fibers

## Typical losses of a multimode fiber



# Optical transmission: fibers

## Typical losses of a singlemode fiber

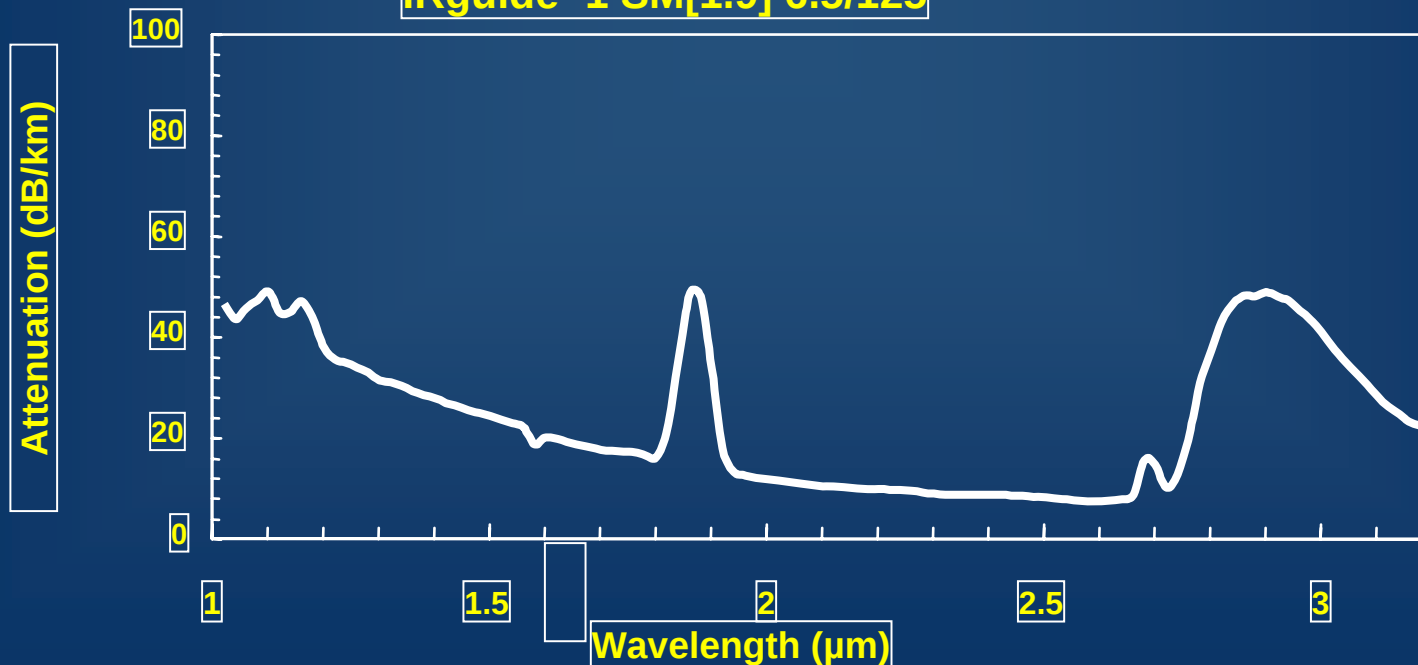
Ø core / Ø cladding : 6.5 / 125 µm

Cut-off wavelength : 1.9 µm

Attenuation at 2.5 µm : 5 dB / km

Attenuation at 3.2 µm : 20 dB / km

IRguide -1 SM[1.9] 6.5/125



# Type of fibers

Multimode

Single mode

Polarization maintaining

Low birerengence

Rare eath-doped

Double-clad

D-shasped,

Ring-core (M-shaped)

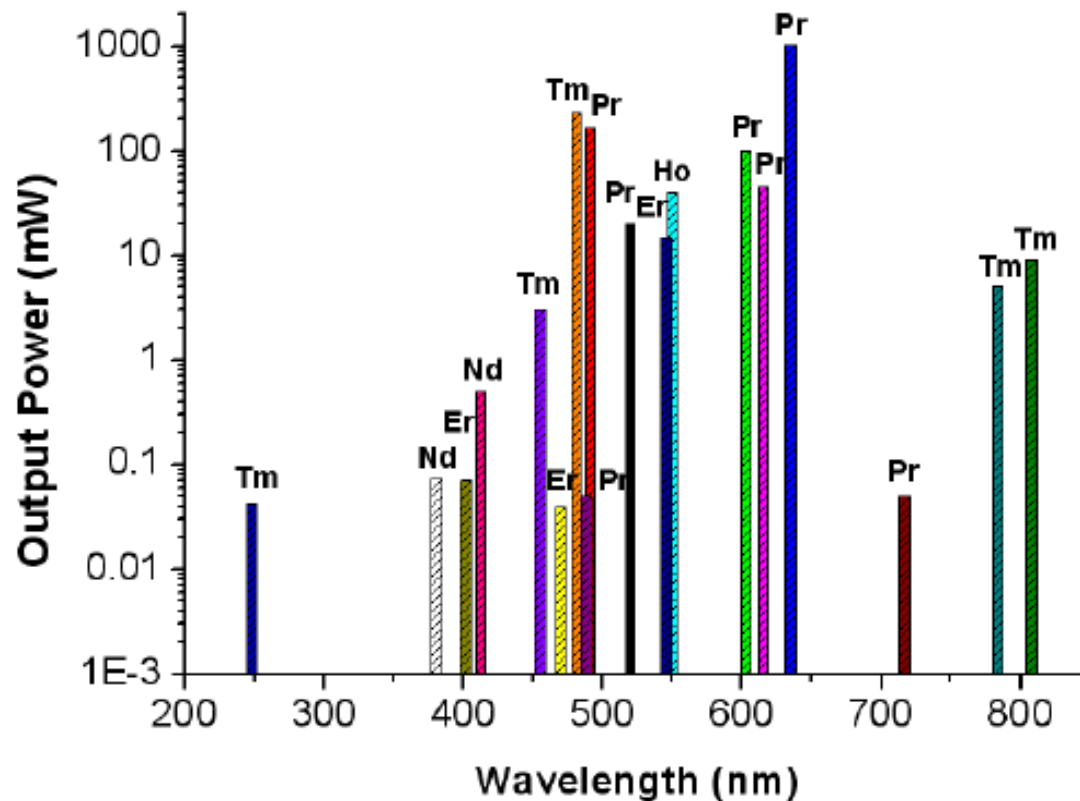
High NA



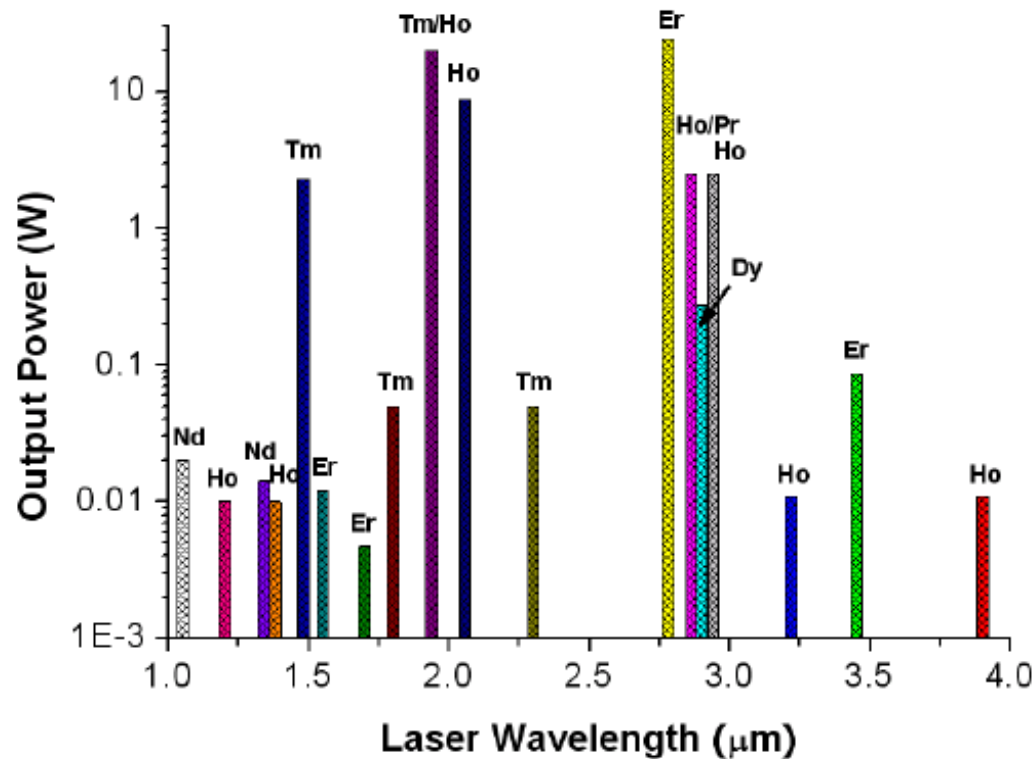
# ZBLAN fiber lasers

-  Intense activity in the 80's (CNET, BT...)
-  Development in various german labs and companies (90's):  
FSU Iena, Techn. Univ. Berlin, Laser Zentrum Hannover,  
Laser Zentrum Hambourg, Lasos, Guided Color Techn.,  
Unique Mode, Linos, Philips...
-  ZBLAN fibers have hugely increased the number of laser lines
-  Marketing issues are heavier than technical problems

# ZBLAN fiber lasers: Up conversion



# ZBLAN fiber lasers: Mid IR



# Supercontinuum



Significant achievements with ZBLAN fibers



Various parameters: fiber length, attenuation, pump power, pump frequency, pump wavelength, N.A., dispersion, fiber geometry...



Laboratory results



Available systems

# Supercontinuum using short fibers

From Toyota Technological Institute (Prof. Y. Ohishi)

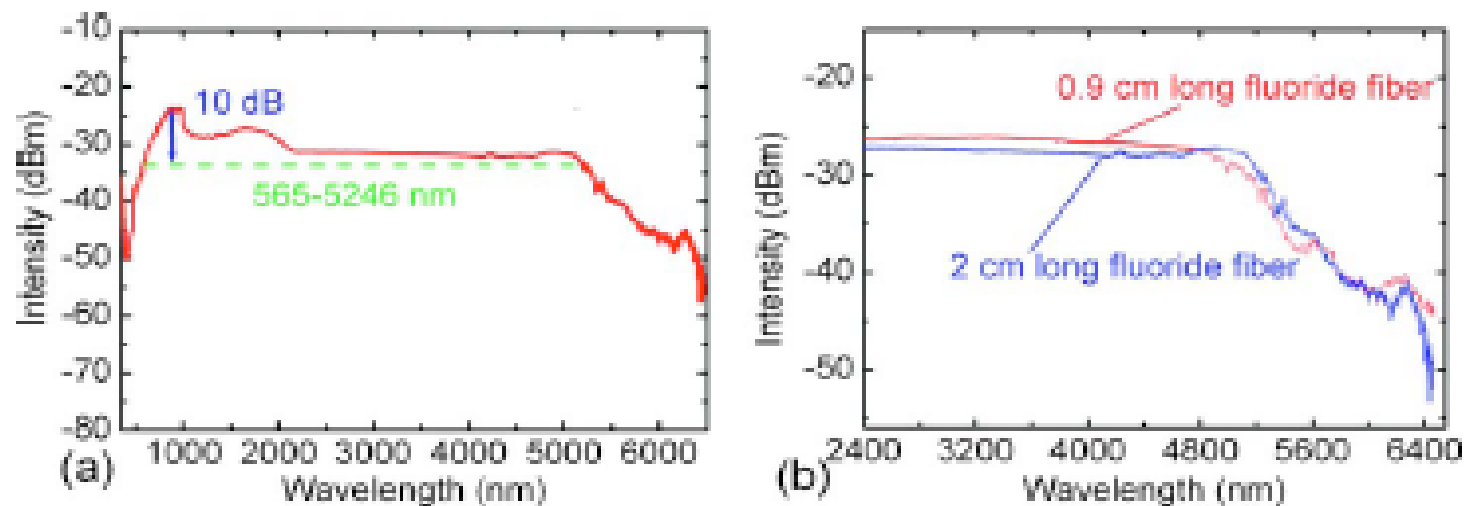


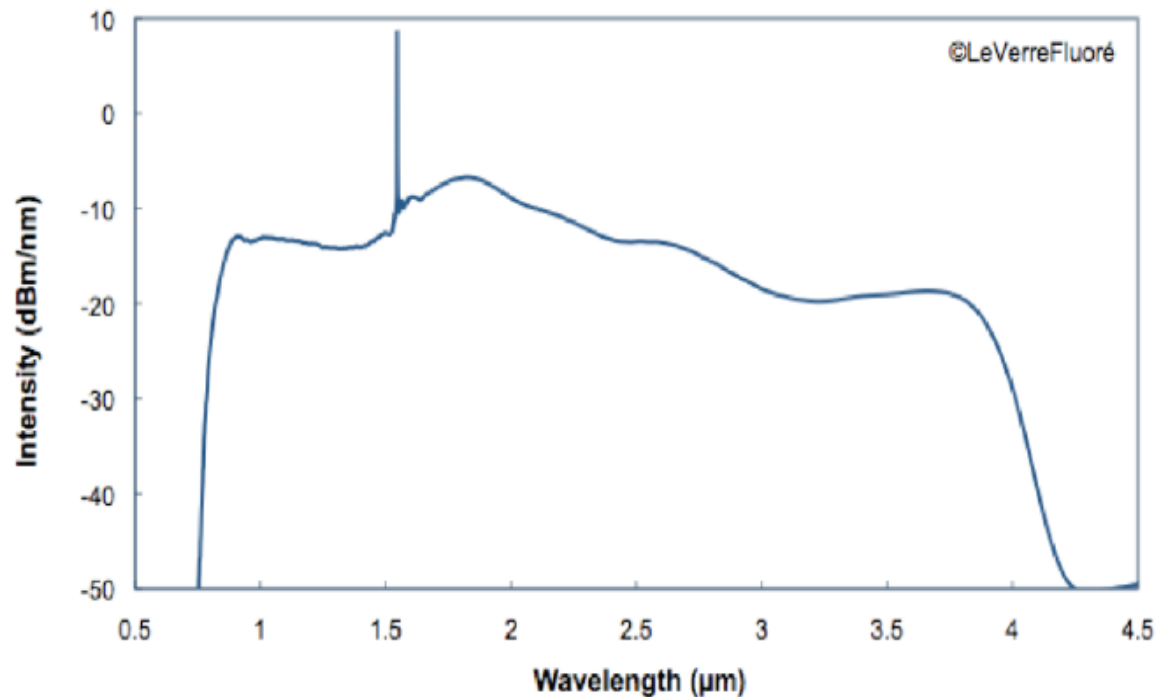
FIG. 2. (Color online) (a) The measured SC spectra from the 2-cm-long fluoride fiber when the average pump power of 1450 nm femtosecond laser was fixed at 20 mW (the corresponding peak power is about 50 MW). (b) A comparison of the long-wavelength edge of SC spectra in 0.9 or 2 cm long fluoride fiber.

# Supercontinuum

Current ZBLAN source



Typical IRguide® SC-01 Spectrum





# **PROBLEMS AND PROSPECTS**



# Practical questions



Mechanical strength.



Aging



Chemical durability



Thermal stability



Optical specifications

# Fiber strength



Failure occurs on defects, most of them extrinsic



Intrinsic strength limited by chemical bonding



Tensile strength improve by CTE adjustments



Static fatigue may be controlled by relaxation

# Chemical durability



Water, water, water ....



Liquid water must not be in contact with glass surface



Fiber is protected by coatings, jacketing, cabling.



End faces make problem. Solutions exist !



Fluoride fibers in use in industrial environment  
for more than 10 years.

# Bragg gratings in fluoride



Pioneering achievements in CNET ( FT)



But time consuming and Cerium doping



Reliable Bragg gratings obtained by femtosecond lasers  
at COPL, Laval University, Québec

# Damage threshold



Is critical for high power lasers and supercontinuum



Low values have been observed in real fibers,  
in relation to extrinsic defects



High values measured (ISL)



Femtosecond experiments implemented at Laval University,  
Suggest that intrinsic damage threshold could be higher  
in ZBLAN than in silica!

# Control of fiber defects



Identification: crystals, bubbles, metal particle, carbon...



Processing parameters to be adjusted



Contamination of interfaces



Glass stability in high NA fibers



Adjustment of thermal expansion coefficients

# Extending optical window



Requires using Indium-based glasses free of Zr and Al



Less stable compositions make more difficult to reach low background losses



Encouraging laboratory results



Development in progress

# Photonic crystal fibers



Large potential



May be achieved with ZBLAN glass



Probably more difficult than silica or chalcogenides



Thermal properties of ZBLAN offer extended possibilities

# CONCLUSIONS



The potential of fluoride fiber lasers is very large



... But FG fiber lasers are just emerging



Most technological problems are identified



Both laser and supercontinuum sources are available



Photonic crystal fibers to be developed

# ACKNOWLEDGMENTS



The scientific community for its continuous interest



All of you for your attention

# Application of lacunar model to ZBLAN glass

Molar volume of ZBLAN glass is  $8.10 \text{ cm}^3$  and  $\Delta C_p = 14.2 \text{ J.mol}^{-1}.\text{K}^{-1}$  while I have measured  $\Delta\alpha = 1.2 \cdot 10^{-4} \text{ K}^{-1}$  (dilatometry), which leads to  $e_v = 132 \text{ KJ. mole}^{-1}$ .  
The rate of vacancy formation is  $8 \cdot 10^{18} \text{ K}^{-1} \text{ cm}^{-3}$ .

With 120 K as the estimated difference between  $T_g$  and  $T_K$  the gross number of vacancies is  $N \approx 10^{21} \text{ cm}^{-3}$  at  $T_g$