Fluoride glass fiber sources: Problems and prospects

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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
21 Glass composition

Initial system (1975)
Fluoride glass families

Most studies focused on fluorozirconates based on ZrF$_4$ and HfF$_4$

Other fluoride glasses are formed with AlF$_3$, GaF$_3$ and InF$_3$ as main glass formers

Significant differences are observed in:
- Chemical durability
- Glass stability
- Mechanical strength & hardness
- Phonon energy
## Typical glass compositions

<table>
<thead>
<tr>
<th>Glass</th>
<th>COMPOSITION (mol %)</th>
<th>$n_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZBLA</td>
<td>57 ZrF$_4$, 34 BaF$_2$, 5 LaF$_3$, 4 AlF$_3$</td>
<td>1.519</td>
</tr>
<tr>
<td>HBLA</td>
<td>57 HfF$_4$, 34 BaF$_2$, 5 LaF$_3$, 4 AlF$_3$</td>
<td>1.504</td>
</tr>
<tr>
<td>ZBLAN</td>
<td>53 ZrF$_4$, 20 BaF$_2$, 5 LaF$_3$, 4 AlF$_3$, 20 NaF</td>
<td>1.498</td>
</tr>
<tr>
<td>ZBSFCI</td>
<td>60 ZrF$_4$, 20 BaFCl, 20 SrFCl</td>
<td>1.542</td>
</tr>
<tr>
<td>YABC</td>
<td>20 YF$_3$, 40 AlF$_3$, 20 BaF$_2$, 20 CaF$_2$</td>
<td>1.440</td>
</tr>
<tr>
<td>IZBS</td>
<td>40 InF$_3$, 20 ZnF$_2$, 20 SrF$_2$, 15 BaF$_2$, 5 CaF$_2$</td>
<td>1.495</td>
</tr>
<tr>
<td>PGICZ</td>
<td>30 PbF$_2$, 22GaF$_3$, 13 InF$_3$, 18 CdF$_2$, 13 ZnF$_2$, 2 GdF$_3$, 2 NaF</td>
<td>( $n = 1.595$ )</td>
</tr>
</tbody>
</table>
# General physical properties

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>HMFG</th>
<th>ZBLAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature (°C)</td>
<td>200-450</td>
<td>260</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion (10^-7 K^-1)</td>
<td>140-210</td>
<td>180</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>4-6</td>
<td>4.14</td>
</tr>
<tr>
<td>Young Modulus (GPa)</td>
<td>50-60</td>
<td>54</td>
</tr>
<tr>
<td>Vickers hardness (kg/mm²)</td>
<td>200-270</td>
<td>210</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.25 – 0.35</td>
<td>0.30</td>
</tr>
<tr>
<td>Refractive index n_D</td>
<td>1.45 – 1.60</td>
<td>1.500</td>
</tr>
<tr>
<td>Non linear refractive index n_2 (10^-13 esu)</td>
<td>0.8 – 0.9</td>
<td>0.85</td>
</tr>
<tr>
<td>Abbe Index ν</td>
<td>60 – 80</td>
<td>75</td>
</tr>
<tr>
<td>dn/dT</td>
<td>1.10^-5 - 2.10^-5</td>
<td>1.5 .10^-5</td>
</tr>
<tr>
<td>Cp (J / g at.K)</td>
<td>24.9</td>
<td></td>
</tr>
</tbody>
</table>
Optical transmission

Optical transmission of samples 4 mm thick
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 MF$_6$ or MF$_8$ polyhedra with large cations Na$^+$, Ba$^{++}$ as modifiers.

The vacancy model offers an alternative description: A disordered packing of large ions (F$^-$ and Ba$^{++}$) in which small cations are inserted. This packing contains vacancies that are mobile in the liquid state.
Bidimensional picture
GLASS PROCESSING
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 (Δn < 10⁻⁶) is difficult and time consuming.

Several parameters must be considered and optimized.
23 Fiber manufacturing

Core
- BaF₂
- NaF
- ZrF₄
- PbF₂
- AlF₃
- LaF₃

Cladding
- BaF₂
- NaF
- ZrF₄
- AlF₃
- LaF₃

Powders

Melting

Preform

Fiber
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

Diagram showing energy levels and transitions in Ho$^{3+}$.
Rare earths for mid IR emission
Rare earths for mid IR emission

\[ \begin{align*}
\text{Er}^{3+} & \quad 4I_{15/2} \\
& \quad 4I_{13/2} \quad 2.7 \ \mu m \\
& \quad 4I_{11/2} \quad 1.6 \ \mu m \\
& \quad 4I_{9/2} \quad 0.975 \ \mu m \\
& \quad 0.79 \ \mu m \\
& \quad 0.655 \ \mu m \\
\end{align*} \]
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

Wavelength (µm)

Attenuation (dB/km)
Type of fibers

- Multimode
- Single mode
- Polarization maintaining
- Low bireringence
- Rare earth-doped
  - Double-clad
  - D-shapred,
- Ring-core (M-shaped)
- High NA
ZBLAN fiber lasers

Intense activity in the 80’s (CNET, BT…)


ZBLAN fibers have hugely increased the number of laser lines

Marketing issues are heavier than technical problems
ZBLAN fiber lasers: Up conversion

![Graph showing output power vs wavelength for different elements in ZBLAN fiber lasers.](image)
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
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
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
Molar volume of ZBLAN glass is 8.10 cm³ and \( \Delta C_p = 14.2 \text{ J.mol}^{-1}.\text{K}^{-1} \) while I have measured \( \Delta \alpha = 1.2 \times 10^{-4} \text{ K}^{-1} \) (dilatometry), which leads to \( e_v = 132 \text{ KJ. mole}^{-1} \).

The rate of vacancy formation is \( 8 \times 10^{18} \text{ K}^{-1} \text{ cm}^{-3} \).

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 \( T_g \).