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NEW FLUORIDE GLASSES FOR THE PREPARATION
OF INFRARED OPTICAL FIBERS

by
Jacques LUCAS
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Gilles FONTENEAU
Catherine PLEDEL

UNITED STATES ARMY
EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY
London England

N° : DAJA 45-86-C-0050
CREBS - University of RENNES - FRANCE

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A new class of zirconium-free fluoride glasses having a broad optical window lying from 0.2 to 8 μm have been optimized in order to prepare core-clad preforms and then optical fibers. The conditions of fiber drawing have been investigated versus several important parameters such as viscosity, glass and crystallization temperatures, moisture corrosion, glass composition, critical cooling rates . . . The molar extinction coefficient of OH impurities have been measured in this new type of glasses showing the influence of these fundamental impurities on the optical attenuation in the 2.9 μm region.

Finally the feasibility of fiber drawing has been demonstrated and it appears that these new glasses are good candidates for obtaining optical fibers operating in the 0.2-5 μm optical window.

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KEYWORDS

Study of new fluoride glasses for the preparation of infrared optical fibers.

- Fluoride glasses
- Optical fibers
- I. R. transmission
- Moisture corrosion
- Indium fluoride
- Zr-free glasses
- Devitrification
- Core-clad preform
- Critical cooling rate
- OH absorption
- Viscosity
- I. R. guide
- Scattering

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INTRODUCTION - MOTIVATIONS OF THE STUDY

Heavy metal fluoride glasses HMFG belong to a new family of vitreous materials which have been discovered at the University of Rennes, ten years ago. The two interesting features of these new glasses are their broad transmission from the U. V. $0.2\ \mu\text{m}$ to the mid I. R. $7\ \mu\text{m}$ and their potential ultratransparency with estimated losses as low as $0.01\ \text{dB/Km}$ in the $3\ \mu\text{m}$ region.

Two families of HMFG have been described and developed : both of them have been discovered in the Rennes laboratory. The first is the ZrF_4 based group called fluorozirconate glasses, the second is a multicomponent glass based on the association of thorium, rare-earth and zinc fluorides. The ZrF_4 glasses are more stable, but the transmission range is limited to the $6\text{-}7\ \mu\text{m}$ region. The thorium - rare-earth fluoride glasses show a greater tendency to devitrify but their optical window is broad lying from $0.2\ \mu\text{m}$ to $8\text{-}9\ \mu\text{m}$.

In this contract we will discuss a new family of fluoride glasses recently discovered in Rennes, and protected by composition patents. These glasses are multicomponent materials based essentially on the interesting glass forming properties of indium fluoride InF_3 .

The optimized composition discovered after a systematic investigation of the characteristic temperatures, T_g glass temperature, T_c crystallization temperature, is the so called BIZYbT glass having the composition :

BaF_2 : 30 %

InF_3 : 30 %

ZnF_2 : 20 %

YbF_3 : 10 %

ThF_4 : 10 %

Because of an infrared edge shifted of about $1\ \mu\text{m}$ towards longer wavelengths compared to Zr-based fluoride glasses, the BIZYbT glass ($\text{Ba}_{30}\text{In}_{30}\text{Zn}_{20}\text{Yb}_{10}\text{Th}_{10}$) is theoretically a good candidate for optical fibers operating until $5\ \mu\text{m}$, where the predicted multiphonon absorption is about $100\ \text{dB/Km}$. Fig. 1 shows the infrared transmission curve for an indium based fluoride glass compared to other glasses.

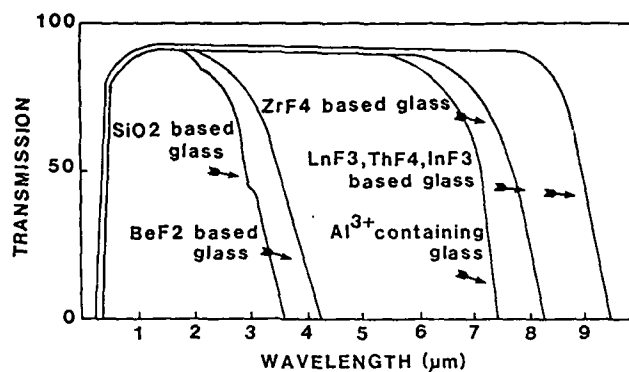


Figure 1 : Infrared transmission spectra of several fluoride glasses compared to SiO_2

Furthermore the predicted minimum loss for a BIZYbT glass optical fiber is about 0.001 dB/Km at 3.2 μm , which is slightly lower than for the ZBLAN glass (Figure 2). For these reasons, it was decided to begin a project concerning the investigations of the different technical steps leading to an optical fiber of the BIZYbT glass, and this report presents the very first results.

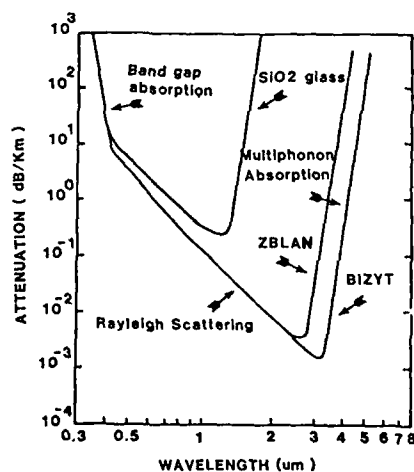


Figure 2 : Low loss regions for two fluoride glasses - ZBLAN is a ZrF_4 based glass - BIZYbT is an indium based glass selected and investigated in this report

The ZrF₄ based optical fibers have a transmission limited at about 4 μm by the multiphonon absorption mechanisms associated to the Al-F and Zr-F vibrational modes.

In this new InF₃ based composition the shift of the I. R. edge towards the long wavelengths permits a good transmission until 5-5.5 μm .

This opening of the optical window with an extension in the I. R. is very important for at least two reasons. First, it allows the collection and guiding of a larger spectrum of I. R. light for thermal imaging or pyrometry and will give much more informations. Secondly, it allows to extend the I. R. remote spectrometry to the C-O vibrational mode and also to realize a coupling between the CO laser operating at 5-5.3 μm and these new BIZYbT optical fibers. This new energy transfer through an original waveguide is specially important for application such as laser surgery, laser marking, printing. . . .

II. Summary of the results obtained in the first part of the research

The beginning of the research was essentially devoted to the optimization of the glass composition (ref. 1).

Many four-component compositions were examined by Differential Scanning Calorimetry DSC in order to find a composition with a large difference between the crystallization temperature T_c , and the glass temperature T_g . The maximum $\Delta (T_c - T_g)$ was around 100°C leading to glass samples having a thickness of about 10 mm without crystallization.

Finally the composition of this four-component glass was also optimized in replacing a part of the ZnF₂ by YF₃.

The final glass was the so called BIZYT with the molar composition : BaF₂ 30%, InF₃ 30 %, ZnF₂ 20%, YF₃ 10 %, ThF₄ 10 %. The characteristic temperatures are for a this glass $T_g=326$ °C and $T_c=447$ °C.

The Time-Temperature-Transformation curves have been measured and for the results it is concluded that the critical cooling rate for this composition is around 80 °C/mn.

III. Summary of the results obtained in the second part of the research

During this period of the research we investigated two different fields : corrosion of the glass by humidity and refractive index versus composition.

1) The study of the corrosion of the glass at room temperature in normal humidity conditions shows no alteration of the glass surface after several months in the laboratory atmosphere.

2) The corrosion of the glass surface by a flow of argon saturated by H₂O vapour was systematically investigated versus time and temperature.

The corrosion reaction is :



From this, the corrosion mechanism has been elucidated : the OH concentration profile and the molar extinction coefficient have been measured. It is concluded for example that one part per million (1 ppm) of OH was introducing a parasitic absorption at 2.9 μm and that the corresponding attenuation loss was $\beta=7800 \text{ dB/Km/ppm}$ (ref. 2).

3) The study of the refractive index n of the glass has been made in collaboration with A. BRUCE from AT & T USA. From this investigation we measured the evolution of n versus λ and determined the material dispersion. It was concluded from the figure 3 and figure 4 that the zero material dispersion was at 1.7 μm .

4) We also measured the evolution of the refractive index versus glass composition in replacing Ba by Li or Ba by Pb. The results are presented on figure 5.

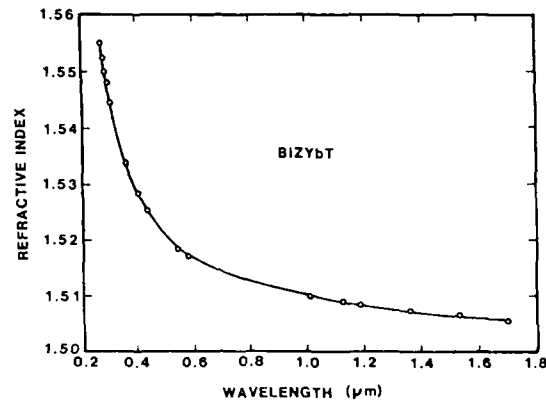


Figure 3 : Evolution of the refractive index versus λ for the BIZYbT glass

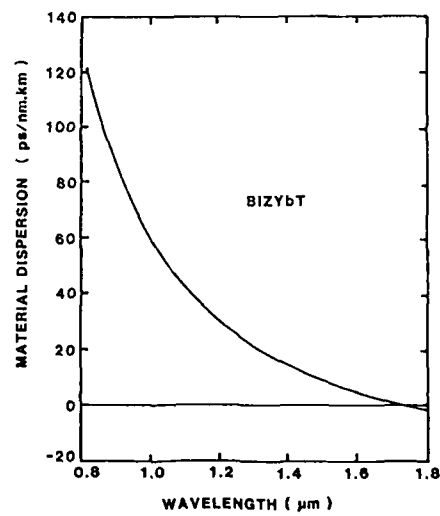


Figure 4 : Evolution of the material dispersion versus λ for the BIZYbT glass

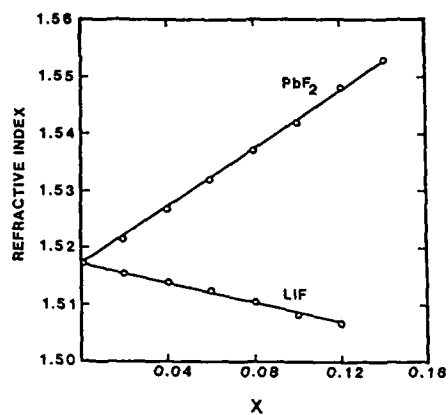


Figure 5 : Evolution of the refractive index versus glass composition, respectively Ba/Li and Ba/Pb substitution

IV. Summary of the results obtained in the third part of the research

This third part of our research was devoted to the first attempts on preforms preparation and influence of transitions metals impurities on absorption.

1) Preforms preparation

This critical step in the preparation of optical fiber is still in progress and can be summarized as follows :

- a) The preparation of a rod having a good optical quality is possible .

b) The preparation of a glass tube by the so called rotational technique is also possible.

c) The most difficult parameter to control is the crystallization of the interface when the core glass is introduced in the tube. This observation will be reexamined in the last part of the report.

2) Metallic impurities

Impurities such as V^{3+} , Cr^{3+} , Fe^{3+} , Ni^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , have been introduced in the glass and the molar extinction coefficient ϵ were measured.

V. Summary of the results obtained in the fourth part of the research

Four points related to viscosity, fibering conditions, fibers characterization, and fluorides purification were examined.

1) For the viscosity measurements, it was a collaboration work with Professor C. T. MOYNIHAN from RPI USA. We concluded that the ideal fibering conditions corresponding to viscosity of about 10^6 poises were obtained around $415^\circ C$ not far from the beginning of the crystallization temperature $T_c=447^\circ C$.

2) Fibering conditions

The fibering experiments were made in collaboration with the Centre National d'Etudes des Télécommunications CNET at Lannion located 150 km West Rennes and with the laboratoire of Marcoussis CGE group near Paris.

Rods and preforms were made in Rennes. The core-clad preforms were obtained from the rotational casting technique and the difference in refractive index was due to NaF addition in one case and to $BaF_2/BaCl_2$ substitution in the other case.

It was observed that the preforms had to be teflon-jacketed to avoid corrosion and devitrification.

In these conditions it was concluded that the Na doped preforms were successively

fibered (more than 200 m) without apparent crystallization. Nevertheless, the CI containing preforms and fibers showed some tendencies to devitrify.

VI. Results obtained in the last part of the contract

A) Optimization of the glass compositions

As indicated before the key points for improving the fibering conditions are the following :

1) Preparation of a good glass with a low critical cooling rate R_c . For memory the best Zr based glass ZBLAN has a R_c close to 1 °C/mn. The BIZYbT glass depending on the purity in oxygen O or hydroxyl group OH in the starting materials has a R_c around 120 °C /mn.

2) Modification of the refractive index of about 0.5 to 1 percent in keeping the same quality of the glass versus devitrification. The good compatibility between the core and the clad glass is an essential parameter : this means that the two glasses must have the same thermal expansion coefficient to avoid any break and also the same characteristic temperatures specially T_g to be fibered in the same heating conditions.

From the preliminary fibering results it was clear that the first parameter to be improved was the critical cooling rate R_c .

These investigations have been done in changing systematically the composition of the BIZYbT glass by different substitutions.

The following experiments have been carried out : substitution of Ba by Sr with the ratio 26 Ba-4 Sr, Yb by Gd with 6 Yb-4 Gd, In by Ga with 26 In-4 Ga, Zn by Mn with 16 Zn-4 Mn, Ba by Ca with 26 Ba-4 Ca, Th by Hf with 6 Th-4 Hf, In by Al with 26 In-4 Al, Ba by Cd with 26 Ba-4 Cd, Ba by Pb with 26 Ba-4 Pb, In by Al with 20 In-10 Al, Th by Zr with 6 Th-4 Zr, and also the addition of CaF_2 or NaF to the BIZYbT glass in the respective proportions 3.69 CaF_2 or 7.69 and 14.8 NaF.

Glass Sample	Rc(k/min)			Observed Homogeneity	
	1st	2nd	3rd	Scattering*	Crystallites
(BYZYbT -non doped)	122				
BIZYbT(Ba-26, Sr-4) No 6	71	102		Very small	0
BIZYbT(Yb-6, Gd-4) No 11	74	58		Very small	1
BIZYbT(In-26, Ga-4) No 12	44	37	34	Very small	1
BIZYbT(Zn-16, Mn-4) No 20	115	94		Small	0
BIZYbT(Ba-26, Ca-4) No 5	174	149		Large	7
BIZYbT(Na-7.69) No 8	108	110		Very small	1
BIZYbT'(Ca-3.69) No 4	103			Large	3
BIZYbT(Th-6, Hf-4) No 10	112				
BIZYbT(In-26, Al-4) No 13	150				
BIZYbT(Ba-26, Cd-4) No 15	159				
BIZYbT(Ba-26, Pb-4) No 16	250				
BIZYbT(In-20, Al-10) No 14	260				
BIZYbT(Th-6, Zr-4) No 7	73	330		Large	Foggy
BIZYbT(Na-14.8) No 9	158			Large	5

* The impression of the observation by He-Ne laser at Rennes Lab.

** The impression of crystallite amount contained in glass.
(1: very few - 10: large amount)

-Table 1-

The table I give the results of the Rc values observed in one run and when necessary and possible two or three runs.

The following comments can be made on these results :

- 1) The starting materials BIZYbT used as the basic sample had a $R_c=122$ °C/mn value which is considered as relatively high.
 - 2) It is observed that some substitutions have no beneficial effect on the Rc ; sometimes it is going on the other way like for the Ba/Pb or In/Al case.
 - 3) On the other hand it is clear that the In/Ga, Ba/Sr and Yb/Gd substitutions lead to significant decrease of the Rc ; it is for instance around 40 °C/mn for the In/Ga.
 - 4) From these observations and measurements, we decided to focus our attention on the In/Ga BIZYbT glass and it is clear that this new composition is leading to glasses which are much easier to obtain in large transparent samples specially in the rod shape.
- The actual optimized glass must be denominated BIGaZYbT having an In/Ga ratio being close to 24 In-6 Ga.

B) Attempts on fiberizing indium based fluoride glasses

- Glass compositions

The BIZYbT glass was chosen as the base composition and in order to decrease and increase the refractive index, LiF and PbF₂ respectively were substituted for BaF₂ in the base glass, but it is not possible to prepare large glass samples because the stability of these glasses is very poor. After several attempts, three compositions were selected, and Table II shows these compositions together with some physical properties.

Compositions	T _g (°C)	T _c (°C)	n
30 BaF ₂ -30 InF ₃ -20 ZnF ₂ -10 YbF ₃ -10 ThF ₄	326	447	1.5170
25 BaF ₂ -30 InF ₃ -20 ZnF ₂ -10 YbF ₃ -10 ThF ₄ -5 NaF	305	410	1.5075
26 BaF ₂ -30 InF ₃ -20 ZnF ₂ -10 YbF ₃ -10 ThF ₄ -4 BaCl ₂	310	407	1.5230

-Table II-

- Preform preparation

Starting materials were oxides (In₂O₃, Yb₂O₃, ThO₂) and fluorides (BaF₂, ZnF₂, NaF) in 99.9 to 99.99 % purity and fluorination was carried out in air or in argon and in gold or vitreous carbon crucibles using NH₄HF₂, but a reduction of In³⁺ seems to take place in argon atmosphere. After fluorination and elimination, the raw glass is melted for 1/2-1 hour at about 750 °C in a r. f. furnace in connection with a dry box and under an atmosphere consisting of 10 % NF₃ in nitrogen.

Thereafter the temperature was raised to about 820 °C for 30 minutes and finally lowered until the pouring temperature was reached.

Both built-in and rotational casting preform fabrication have been tried. Because of the BIZYbT glass is highly viscous, built-in casting was difficult to control and rotational casting was used preferentially.

Because of a critical cooling rate of 120 °C/mn for the BIZYbT glass, compared to 0.8 °C/mn for the ZBLAN glass, large glass samples are difficult to prepare. Different mould dimensions were tried and a rod of 10 cm in length and 0.9 cm in diameter was the largest sample prepared without visible crystallization.

Finally, for preform preparation, the 25 BaF₂- 30 InF₃- 20 ZnF₂- 10 YbF₃ - 10 ThF₄- 5 NaF glass was chosen as cladding glass and the base BIZYbT glass as core glass. The mould was preheated to a temperature around T_g, the cladding glass was poured at 740 °C and rotated for 20 seconds at 10,000 rpm, and finally the core glass was poured.

The preform preparation had to be finished within 2 minutes, otherwise the core glass crystallized and/or the cladding glass broke. At present, at least two bubbles always

occur in the preforms and always at the same position in the core glass. Furthermore the operating parameters such as glass quantities, operating temperatures and operating times can not be changed very much due to the poor stability of the BIZYbT glass. NaF was added in order to try to stabilize the base glass, but when the NaF content exceeds 10 % (molar), crystallization is always present and the thermal expansion coefficients between the core and cladding glasses are getting too different.

The second type of preform has the BIZYbT glass as cladding and a 26 BaF₂- 30 InF₃- 20 ZnF₂- 10 YbF₃- 10ThF₄- 4 BaCl₂ as core. The operating conditions are similar to the first type of preform, and bubbles are always present . Figure 6 shows a photo of the first type of preform.

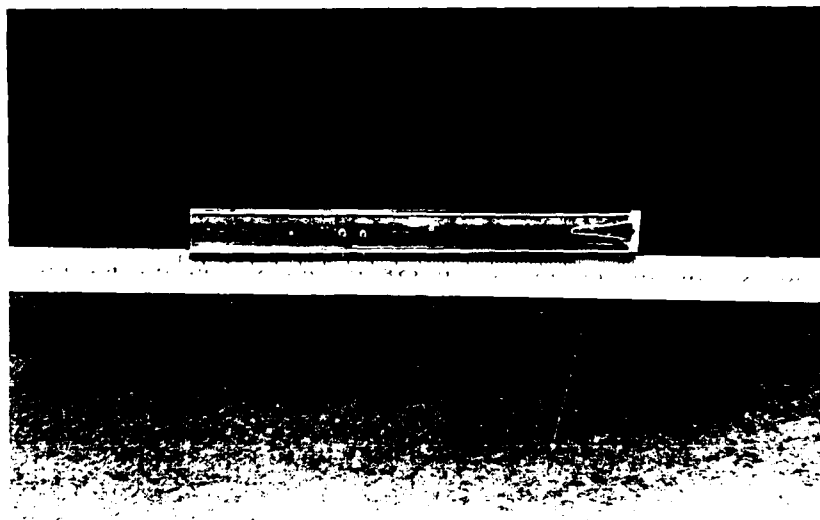


Figure 6 : Photograph of a BIZYbT glass preform

- Fiber drawing

Fiber drawing was carried out in a conventional tower in a r. f. furnace with a sharp temperature gradient and in a He atmosphere. Fiber drawing attempts on nude preforms resulted in a black colouring of the surface followed by crystallization. Therefore, all preforms were protected with a Teflon FEP jacket before fiber drawing. From a rod of BIZYbT, 20 meters of optical fiber were drawn at 384 °C and at a speed of 1m/mn. Fiber diameter was 180 μm . The attenuation curve shows a nearly constant attenuation of about 15 dB/m from 2 to 5.5 μm . From a preform of BIZYbTNa/BIZYbT, 45 meters of optical fiber were drawn at 375 °C and at a speed of 3 m/mn. Fiber diameter was 160 μm (core 110 μm), and the fiber broke at a drawing force of 44 MPa. Figure 7 shows the attenuation curve for 1 meter of optical fiber from 1.5 to 6.25 μm .

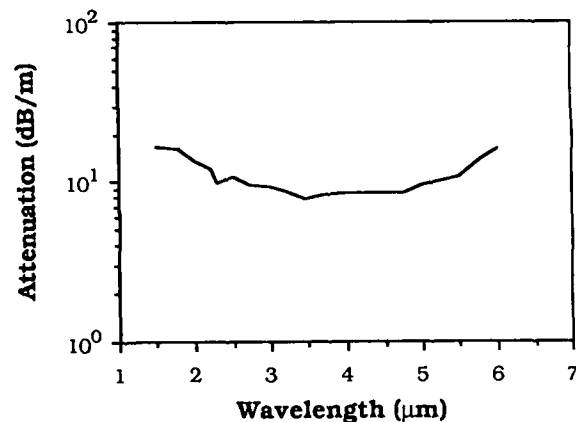


Figure 7 : Attenuation curve for a BIZYbTNa/BIZYbT optical fiber

The preform of BIZYbT/BIZYbTCl was impossible to draw into an optical fiber, probably due to the evaporation of InCl_3 from the melt. When the BaCl_2 containing core glass was poured, white fumes did appear, and in trying fiber drawing this type of preform the interface core cladding crystallized followed by crystallization of the core glass probably due to the deposition of crystalline InCl_3 during pouring.

The fiber drawing experiments have shown that the drawing temperature must be controlled within 1 °C to avoid rupture of the fiber, and furthermore if fiber drawing does not take place within about 10 to 15 minutes the preforms crystallize, which indicates that the fiber drawing temperature is close to the crystallization temperature.

The attenuation curve for the NaF containing preform shows a rather constant attenuation of about 10 dB/Km. This wavelength independent scattering can only be explained by the presence of bubbles and crystals in the preform and in the fiber.

- Conclusion

For the first time, a fluoride glass based on indium has been drawn into an optical fiber. The attenuation curve shows a high scattering due to bubbles and crystals.

Attempts to stabilize this glass will continue and furthermore the possibilities of making a fiber laser from a BIZYT glass (YF₃ instead of YbF₃) have begun. Recently, 150 m of optical fiber have been drawn from a rod of 30 BaF₂- 30 InF₃- 20 ZnF₂- 10 YbF₃- 10 ThF₄ doped with 2 % of NdF₃.

The results of fiber drawing of the BIZYbT glass are similar to the results for some of the first optical fibers drawn from the ZBLAN glass. This work will be continued, not for telecommunication, but for analytical purposes.

VII. Discussions - Conclusions

From these investigations it appears clearly that we have developed a new generation of fluoride glasses, not containing Zr⁴⁺ but based on a complex composition where InF₃ is the main glass former fluoride.

The first preliminary results obtained on imperfect optical fibers show that the positions of the U.V. and I.R. edges are at the expected position determined on bulk samples. From these results we verified that the expected transmission range for the BIZYbT optical fibers is lying from 0.3 to 5-5.5 μm. This demonstrates the superiority of the BIZYbT glass versus the ZrF₄ based glass for transmitting informations in the mid I.R. , the extension of the optical window in the I.R. side being approximatively 1 μm better.

The main target of this research was to demonstrate the feasibility of optical fiber preparation from an exotic original fluoride glass and we consider that this goal has been reached. Therefore the following points need to be discussed in order to emphasize the technological difficulties and the limitations of such technology.

The first difficulty for obtaining good optical fibers is obviously associated with the tendency to devitrification. The fibering results presented here are referred to a classical BIZYbT glass with a critical cooling rate R_c of about $100\text{ }^{\circ}\text{C/mn}$. Note that the first generation of ZrF₄ based glass developed few years ago had almost the same R_c values and that the best R_c are now in the range of few degrees/mn. At this time the optical fibers prepared from Zr based glasses were very comparable to our BIZYbT fibers.

At the end of the contract we just discovered the potentiality of getting a much more better critical cooling rate of about $40\text{ }^{\circ}\text{C/mn}$ by In/Ga substitution. It was immediately verified that the quality of these new glasses was obviously superior to the standard composition.

Unfortunately, at the time of this report writing we are not able, due to the lack of time, to prepare preforms and fibers. But we can assume reasonably that the difficulties associated to crystallization, which was very severe before, will be less with these new glasses. We hope that we will be able to continue this work if new fundings are available.

The second point which must be emphasized is related to the core-clad structure of the preforms. By definition a good optical guide with a large numerical aperture is associated to a large difference between the refractive index of the core glass and the clad glass. This situation can be realized by different dopings but the immediate consequence is that the two glasses become also different by their glass temperature T_g , their thermal expansion coefficient, . . . and are no more compatible for a core-clad structure. We very often observed some cracking of the double index preform during cooling after the rotational casting operation. For the moment this appears to be the most difficult factor to solve. Consequently we decided in a first approach to work with two glasses slightly different in compositions giving difference in the refractive index which is in the range of few 10^{-3} .

We hope in a near future to be able to produce optical fibers with attenuation in the range of 0.1 dB/m . This value will be reached in decreasing the devitrification mechanisms which occur essentially during the preform fabrication.

REFERENCES

Ref. 1 : A. BOUAGGAD, G. FONTENEAU, J. LUCAS, Mat. Res. Bull. 22, p. 685, 1987.
New zirconium free multicomponent fluoride glasses.

Ref. 2 : S. MITACHI, G. FONTENEAU, P. S. CHRISTENSEN, J. LUCAS
Molar extinction coefficient of OH in fluoride glasses considering molecular
water influence. J. of non cryst. solids, 92, p.313, 1987.