NEW FLUORIDE GLASSES FOR THE PREPARATION OF INFRARED OPTICAL FIBERS (U) RENNES-1 UNIV (FRANCE) J LUCAS MAR 87 R/D-5477-M5-01 DAJA45-86-C-0050
Title of research project: NEW FLUORIDE GLASSES FOR THE PREPARATION OF INFRARED OPTICAL FIBERS

Principal investigator: Professor J. LUCAS, University of Rennes

Contractor: CENTRE REGIONAL ETUDES BRETAGNE SCIENCES, CREBS PRESIDENCE DE L'UNIVERSITE, Rue du Thabor - 35000 RENNES (France).

Contract number: DAJA 45-86-C-0050


The research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. This report is intended only for the internal management use of the contractor and the U.S. Government.
New indium-based fluoride glasses called BIZYT, resistant to devitrification, have been investigated in order to measure their chemical durability versus humidity. The corrosion mechanism has been studied and the molar absorption coefficient of the OH parasitic peak has been evaluated. Also the evolution of the refractive index and the material dispersion versus λ have been investigated. In order to design a core-clad structure, the variation of refractive index with chemical composition has been measured for LiF and PbF₂ containing glasses.
SECOND PERIODIC REPORT

In the first periodic report, we described a new family of fluoride glasses based on indium fluoride and called BIZYT, acronym related to the five component composition $\text{BaF}_2$, $\text{InF}_3$, $\text{ZnF}_2$, $\text{YF}_3$ or $\text{YbF}_3$, $\text{ThF}_4$.

These glasses are of special interest because of their broad transmission range from 0.2 $\mu$m to 8 $\mu$m in bulk sample. Drawn into fiber, a reasonable transmission could be estimated in the 5 $\mu$m region where the $\text{ZrF}_4$ based fibers are opaque due to multiphonon absorption.

This report is relative to two independent investigations:

1. the study of the corrosion by humidity of these glasses and the measurement of the molar absorption coefficient of OH
2. the evolution of the refractive index with the chemical composition and versus wavelength.

First, a sample of polished BIZYT glass has been exposed to the atmosphere of the lab during many weeks and examined time to time; microscopic observation of the surface indicates no alteration of the surface. These glasses are very stable in the atmospheric humidity at room temperature.

Then parallelepiped samples have been treated by Ar gas carrying water vapor at different temperatures around $T_g$. The corrosion occurs slowly at this temperature according to the reaction:

$$\text{MF}_x \text{ glass} + y \text{H}_2\text{O gas} \rightarrow \text{MF}_{x-y}\text{OH}_y + \text{HF gas}$$

The evolved HF was trapped and analysed after the steam treatment and the intensity of the OH peak was measured for different steps of corrosion. Consequently, the relation between the OH concentration measured by HF analysis and the absorption coefficient at 2.9 $\mu$m was established.

The spectral analysis of the 6.2 $\mu$m region indicates also that the presence of water molecule is much less important in BIZYT glass compared to $\text{ZrF}_4$ glass treated in the same conditions.
Finally, using the Beer-Lambert law, the molar absorption coefficient $\varepsilon$ of OH at 2.9 $\mu$m has been measured for the glass BIZYT having a $T_g = 324^\circ$ C and gives the value $\varepsilon = 24$ l/mol/cm. Note that for SiO$_2$ based glasses, $\varepsilon$ is in the range 80-180. The corresponding attenuation loss introduced by 1 ppm of OH in the 2.9 $\mu$m region is $\beta$ (dB/km/ppm) = 7850 for the BIZYBT glass.

The second part of the report is related to the evolution of the refractive index $n$. First, in collaboration with A. BRUCE from A T & T, the variation of $n$ versus $\lambda$ and the corresponding material dispersion have been measured. The zero material dispersion is located close to 1.7 $\mu$m. For these measurements shown on figures 1 and 2, a sample of few cubic centimeters volume with good optical quality has been prepared.

The BIZYT glass can be easily doped by LiF or PbF$_2$ which has been used for changing the refractive index in order to select two glasses suitable for a core-clad structure.
The figure 3 represents the variation of $n$ with the molar fraction of LiF or PbF$_2$ in the glass BIZYT. It must be noted that the tendency towards crystallization increases with the doping contents and becomes very severe after 5%. The compromise to obtain optical quality glasses with different $n$ values will be probably to combine both glasses.

![Figure 3: Variation of refractive index versus $\lambda$ LiF or PbF$_2$ content in the glass.](image)

We now focussed our attention on this important problem which consists in keeping the position of the IR edge and the resistance to devitrification when additional fluoride favorable to $n$ variation is introduced in the glass.

The next report will also mention our first attempts in preform tube preparation.
END
DATEO
FILM
8-88
DTIC