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New fluoroindate glass compositions

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The limits of glass formation of new fluoroindate glass compositions have been determined for the basic systems $InF_3-BaF_2-GdF_3-20ZnF_2-20SrF_2-2XF_n$ where X = Na, La and $InF_3-BaF_2-20ZnF_2-20SrF_2-2GdF_3-XF_n$, where X = Ca and Y. The incorporation of small amounts of GaF_3 and/or GdF_3 increases strongly the thermal glass stability. All the fluoroindate compositions studied are highly transparent in the mid-infrared range; their transmission edge is shifted beyond 7 μm and the theoretical attenuation coefficient, extrapolated at the CO laser wavelength emission, is typically $\alpha = 100$ dB/km. Large bulks and preforms have been prepared allowing the drawing of optical fibers.

I. INTRODUCTION

Among the many compositions tested to improve the physical properties of Heavy Metal Fluoride Glasses (HMFG), it was found recently that InF_3-based systems allowed glasses with better forming ability and better optical properties to be prepared.[1,2] These new compositions are emerging as one of the major groups of the HMFG glass family. These glasses present a theoretical minimum value of the optical attenuation in the infrared region lower than that of the fluorozirconate compositions, and their absorption edge is shifted toward longer wavelength, beyond 7 μm. Therefore, they offer potential applications for the realization of optical fibers for the power delivery of CO laser which emits at ~ 5 μm.

Various ternary, quaternary, and quinternary systems with indium fluoride as the main constituent have already been investigated. The most stable compositions were initially found in the $InF_3-ZnF_2-BaF_2-SrF_2-CdF_2$ system,[2,3] which allows the casting of rather large samples.

Although these glasses show enhanced thermal stability compared to the standard fluorozirconate [e.g., ZBLAN ($ZrF_4-BaF_2-LaF_3-AlF_3-NaF$)], it was not possible till now to draw fibers due to crystallization of the preform during the process. Consequently, better InF_3-based compositions with lower devitrification rates are necessary. Mitachi *et al.*[4] have studied the effect of small (up to 3%) GdF_3 addition to fluorozirconate standard compositions and found a drastic improvement of the stability and devitrification process for these glasses, making these compositions the best for fiber drawing.

Using a similar approach, we investigated the thermal stability and the optical properties of several InF_3-based compositions containing a small amount of GdF_3. The glass stability has also been drastically improved and the crystallization rates reduced significantly. Some compositions are shown to be adequate for the fabrication of optical fibers.

II. EXPERIMENTAL

The basic starting materials used for this study were ZnF_2 from Merck, BaF_2 and SrF_2 from B.D.H., GdF_3 from Alfa, In_2O_3 and Ga_2O_3 supplied by Prussag, and ammonium bifluoride from Riedel de Häen.

Indium and gallium compounds were first fluorinated with NH_4F, HF for 1.5 h at 400 °C in a platinum crucible in air. The fluoride powders used to prepare the desired compositions were then mixed together and heat-treated first at 700 °C for melting and then at 800 °C for refining. The melt was finally either poured between two preheated brass plates to allow the preparation of samples with different thicknesses (hereafter called casting under normal cooling) or rapidly quenched. The melting, refining, and sample preparation procedures were all realized in a dry box under argon atmosphere. NF_3 was also added during the refining process.

III. GLASS-FORMING SYSTEMS

Two InF_3-based systems have been studied: (a) $InF_3-BaF_2-GdF_3-20ZnF_2-20SrF_2-2NaF$ and (b) $InF_3-BaF_2-GdF_3-20ZnF_2-20SrF_2-2LaF_3$. Figure 1 shows the limits of their glass formation obtained by melt

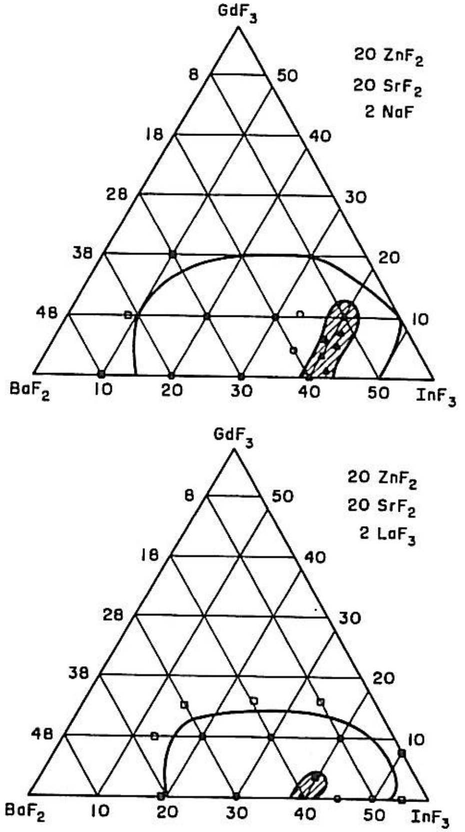


FIG. 1. Limits of glass formation of InF_3–BaF_2–GdF_3–$20ZnF_2$–$20SrF_2$–$2NaF$ (or $2LaF_3$) compositions: (□) no glass formation, (○, ▲) glass formation by melt quenching, and (▲) glass formation by normal casting.

quenching (○, ▲) and by casting under normal cooling only (▲, dashed area). The preparation of large bulk samples (up to a few cm^3) can be obtained only with the addition of small quantities of GdF_3 (up to 12 and 5 mol %) in the base compositions (a) and (b), respectively. However, maximum stability is observed only for glasses containing less than 4% GdF_3. Using these criteria the best composition was found to be $40InF_3$–$20ZnF_2$–$20SrF_2$–$16BaF_2$–$2GdF_3$–$2NaF$ (or $2LaF_3$).

Further systematic investigations have been performed with this system by substituting NaF by YF_3 or CaF_2. YF_3 is known as a glass-former for HMF glasses, and its incorporation should improve the glass stability; on the other hand, CaF_2 is known to reduce the glass corrosion. The diagrams of the glass formation are shown in Fig. 2. The incorporation of CaF_2 enlarges the region of glass forming for casting under normal cooling. The incorporation of YF_3 is limited to 4 mol % and does not improve the thermal stability (see below).

Substitution of a small amount of InF_3 by GaF_3 has also been studied and also improves the glass stability.[5]

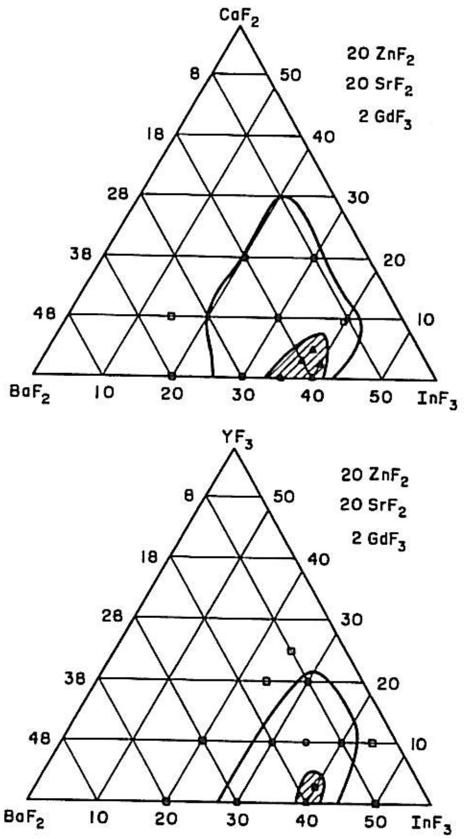


FIG. 2. Limits of glass formation of the composition shown in Fig. 1 where NaF (or LaF_3) has been substituted by YF_3 or CaF_2. (□) No glass formation, (○, ▲) glass formation by melt quenching, and (▲) glass formation by normal casting.

IV. GLASS CHARACTERIZATION

Among the best glass-forming regions shown in Figs. 1 and 2, we have chosen the compositions given in Table I in order to determine their characteristic temperatures T_g: glass transition temperature, T_x: onset of crystallization temperature, and T_p: temperature of the maximum of the DSC exotherm, their stability parameters $(T_x - T_g)$ and $S = (T_x - T_g)(T_p - T_x)/T_g$,[6] as well as their bulk density and refractive index at λ_D = 584.9 nm. The characteristic temperatures have been determined by differential scanning calorimetry using a Dupont 2000 instrument with a 10 °C/min heating rate. The results are shown in Table II.

The bulk densities are almost constant 5 g/cm^3 and the refraction indices, n_D, remain around 1,5. For all compositions, except the one containing lead, the glass transition temperature is of the order of 295 °C. The temperature of the onset of crystallization is around 390 °C for the first four compositions and shifted toward lower temperature when Pb is incorporated; it is slightly higher than 400 °C for the last two compositions containing Na and Ga or Na and Ca. The temperature of the maximum of the DSC exotherm is particularly high (400 °C) for the composition containing Na and Ga.

It is known that the higher the value of the stability parameters, the more stable is the composition. According to this criterion, the last two compositions IZSBNGaGd (InF_3–ZnF_2–SrF_2–BaF_2–NaF–GaF_3–GdF_3) and IZSBCNGd (InF_3–ZnF_2–SrF_2–BaF_2–CaF_2–NaF–GdF_3) present the best performances with $(T_x - T_g)$ = 115 °C and S = 15 °C. These values are by far superior to those obtained for ZBLA (ZrF_4–BaF_2–LaF_3–AlF_3) $(T_x - T_g = 80$ °C) and ZBLAN (ZrF_4–BaF_2–LaF_3–AlF_3–NaF) $(T_x - T_g = 92$ °C), and are comparable to those of BIZYT (BaF_2–InF_3–ZnF_2–YF_3–ThF_4) $(T_x - T_g = 112$–123 °C).[7] Therefore these new compositions should be good candidates for fiber drawing.

In order to draw optical fibers from a preform, it is also important to know the temperature behavior of the viscosity in order to determine the temperature range at which the preform should be drawn.

The glass viscosity was determined with a parallel plate rheometer[8,9] (Dupont 1090 Thermal Analyser with a model 934 TMA cell) measuring the deformation of a cylindrical sample under an applied axial load. Measurements were performed every second at a 10 °C/min heating rate. Figure 3 shows the temperature dependence of the viscosity obtained for two IZSBGdGaN glass compositions (Table I). From the slopes of the curves, the extent of the working range of the glasses for optical fiber drawing is of the order of 380–400 °C. The activation energy for viscous flow has been calculated from the Arrhenius behavior of the curves and lies in the range 580–700 kJ/mol; this value is similar to that found for BIZYbT (BaF_2–InF_3–ZnF_2–YbF_3–ThF_4) glass.[10]

The optical transmission of several InF_3-based compositions has been measured at room temperature in the near and mid-infrared range using a Bomem DA8 spectrophotometer. Figure 4 shows the spectrum obtained for a 5 mm thick IZSBC (InF_3–ZnF_2–SrF_2–BaF_2–CdF_2)

TABLE I. Standard In-based compositions (mol. %).

	InF_3	ZnF_2	SrF_2	BaF_2	GdF_3	MF_n
IZSBC	40	20	20	15	...	$5CaF_2$
IZSBGdN	40	20	20	16	2	2NaF
IZSBGdL	40	20	20	17	2	$1LaF_3$
IZSBGdY	40	20	20	16	2	$2YF_3$
IZSBPbCCd	40	20	10	15	...	$10PbF_2$, $3CaF_2$, $2CdF_2$
IZSBGdGaN	34	20	20	16	2	2NaF, $6GaF_3$
IZSBGdCN	40	20	10	20	2	2NaF, $6CaF_2$

TABLE II. Physical properties of the standard compositions T_g: glass transition temperature, T_x: temperature of the onset of crystallization, T_p: temperature of the maximum DSC exotherm, d: density, n_D: refractive index at λ_D = 584.9 nm, $T_x - T_g$, and $S = (T_x - T_g)(T_p - T_x)/T_g$ are stability parameters.

	T_g (°C)	T_x (°C)	T_p (°C)	d (g/cm^3)	n_D	$T_x - T_g$ (°C)	S (°C)
IZSBC	295	385	390	4,94	1,4950	90	1,53
IZSBGdN	289	390	401	...	1,4930	101	3,84
IZSBGdL	294	390	410	...	1,5080	96	6,53
IZSBGdY	298	388	419	...	1,4948	90	9,36
IZSBPbCCd	272	376	390	...	1,5300	104	5,35
IZSBGdGaN	292	406	450	...	1,4885	114	17,18
IZSBGdCN	290	408	417	...	1,4934	118	12,94

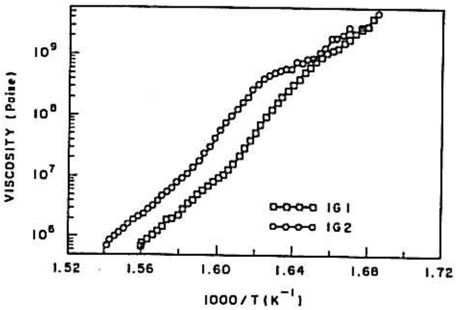


FIG. 3. Temperature dependence of the viscosity for glasses of composition IZSBGdGaN (see Table I) with two different concentrations of gallium.

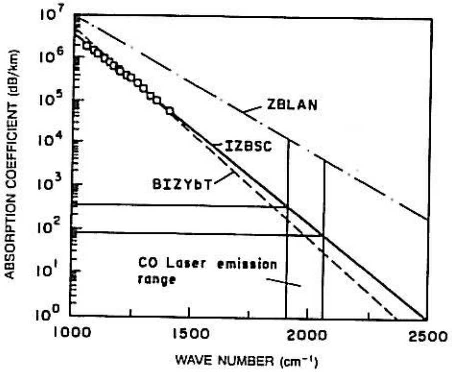


FIG. 5. Absorption coefficients α(dB/km) of IZBSC, BIZYbT,[14] and ZBLAN[13] compositions versus wave number (cm^{-1}). The straight lines have been extrapolated to show the values of α in the CO laser emission range.

glass composition (Table I). This glass is highly transparent, and the other fluoroindate compositions present identical behavior.

These compositions have In atoms in octahedral coordination (InF_6^{3-}) with active glass modes around 261 cm^{-1} and 462 cm^{-1}; however, small contributions of Zn–F–Ba or Ba–F–Ba modes may not be excluded.[11] These modes are drastically shifted toward lower wave numbers compared to fluorozirconate glasses and BTYGZ (BaF_2–ThF_4–YF_3–GaF_3–ZnF_2) and slightly shifted in the same direction compared to the BIZYT composition. This explains the better infrared transition observed for our fluoroindate compositions. Figure 4 shows also a comparison of the optical transmission of this glass with silica, ZBLAN, and BIZYT whose thickness was normalized to the same 5 mm value.[12] This new fluoroindate family presents the best IR optical transmission.

The attenuation coefficient α of the IZBSC glass was calculated in dB/km, and is shown in Fig. 5 as a function of the wavelength. The extrapolation of the straight line to higher wave numbers gives an indication of the intrinsic optical attenuation of this composition in the optical range of CO laser emission. The value is of the order of 100 dB/km. The same figure shows also the results of the attenuation coefficient obtained for ZBLAN[13] and BIZYbT glass.[14] The IZBSC and BIZYbT compositions present a similar behavior with an attenuation at ~5 μm, 50 times lower than the one of ZBLAN glasses. In this optical region the loss due to Rayleigh diffusion and UV absorption is negligible and the attenuation coefficient is given by $\alpha = C \exp(-c/\lambda)$. The values of C and c are given in Table III.

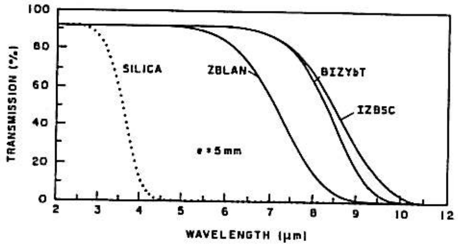


FIG. 4. Mid-infrared transmission of HMF glasses of compositions: silica, ZBLAN, BIZYbT, and IZBSC. The thickness is 5 mm for all glasses.

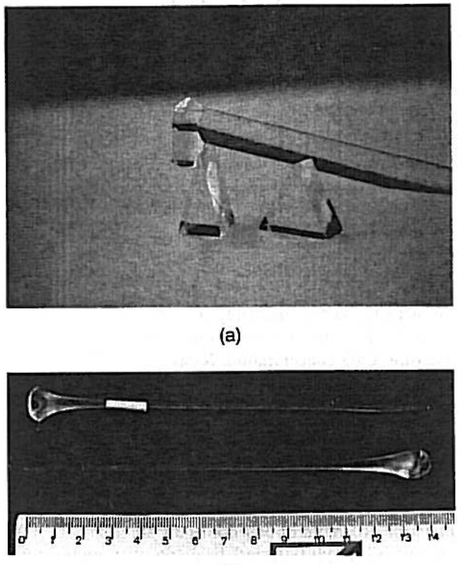
Large bulk samples and simple preforms with 10 mm diameter and 15 cm length have been prepared (Fig. 6). Fibers have been successfully drawn with simple preforms and their characterizations will be presented elsewhere.[15]

V. CONCLUSION

New In-based composition has been investigated in the basic systems InF_3–ZnF_2–BaF_2–SrF_2–GdF_3–NaF (or LaF_3). The glass-forming diagrams have been determined. These glasses are highly transparent in the mid-infrared spectral region, and their transmission edges are shifted beyond 7 μm. Small additions of GdF_3 and GaF_3 drastically improve their thermal stability. This new family appears very promising for the fabrication of optical fibers, especially for applications with CO laser emitting around 5 μm. Preforms have been fabricated and fibers have been successfully drawn from simple preforms.

TABLE III. Values of the coefficients C and c of the attenuation coefficient $\alpha = C \exp(-c/\lambda)$ for ZBLAN, BIZYbT, and IZBSC glasses.

Glasses	ZBLAN[13]	BIZYbT[14]	IZBSC
C (db/km)	$1.22 \cdot 10^{10}$	$3.75 \cdot 10^{11}$	$7.31 \cdot 10^{10}$
c (μm)	71.6	112	100



(a)

(b)

FIG. 6. Top: large bulk samples of IZSBGdGaN composition cast by normal cooling. Bottom: preforms of the same composition. (a) With core only and (b) tip of a preform after drawing showing no crystallization.

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