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New fluoroindate glass compositions

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Fluoroindate glasses are potential new materials for the fabrication of IR fibers with extended spectral range. InF_3–SrF_2–BaF_2–ZnF_2–X glass compositions, where X = PbF_2, CdF_2, NaF and CaF_2, have been prepared in a glove box using a conventional method and their phase diagrams have been determined. The addition of small quantities of GdF_3 improves the stability of these compositions. Optical and thermal properties of these glasses are reported.

1. Introduction

Since the discovery of fluoride glasses [1], the optical properties of these glasses have served as catalysts for much of the research to find more stable compositions for drawing optical fibers. Until now only fluorozirconate fibers have been manufactured with losses lower than 1 dB/km [2]. The intrinsic limit of fluorozirconate glasses is a barrier for future applications.

Recently, it was found that InF_3-based systems have more stable compositions and present better optical properties [3]. Various ternary, quaternary and multicomponent systems containing InF_3 as a major component have been investigated [4,5]. Specimens thicker than 10 mm have been manufactured. Unfortunately, it has not been possible to draw fibers from the preforms of these glasses.

In this paper, we investigate new InF_3-based systems containing Pb, Cd, Na and Gd fluoride. The glass stability has been improved and found to be adequate for the fabrication of optical fibers.

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2. Experimental

The starting materials used for this study are: ZnF_2 and SrF_2 from BDH, BaF_2 and CaF_2 from Prolabo, CdF_2 from Fluka and In_2O_3 supplied by Preussag. The indium oxide was first fluorinated at 400°C with $NH_4F \cdot HF$ in a platinum crucible. The powders used to prepare the derived compositions were then mixed and heated at 700°C for melting and 800°C for fining, both processes being performed in a dry box under argon atmosphere. The melt was poured into a preheated mold consisting of two brass plates.

3. Results: glass-forming systems

We have investigated several compositions in the InF_3–ZnF_2–BaF_2–SrF_2–CdF_2 system [3]. Samples were fabricated with a thickness of 8 mm. A comparative study of the influence of CaF_2, PbF_2 and NaF on the glass formation ability was performed. The results are exemplified in fig. 1. The size of the vitreous area of maximum stability increases for CaF_2 and PbF_2. It was noted that PbF_2 may substitute BaF_2 at a higher concentration than SrF_2. Thick samples up to 15 mm were prepared in some cases, but it was

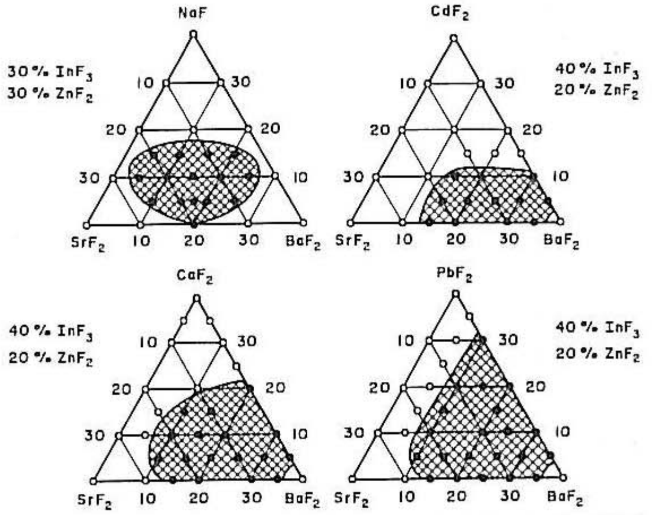

Fig. 1. Limits of glass formation for InF_3–ZnF_2–BaF_2–SrF_2–XF_n (X = Na, Cd, Pb, Ca and $n = 1$ or 2). ○, Quenched glasses; ●, cast glasses.

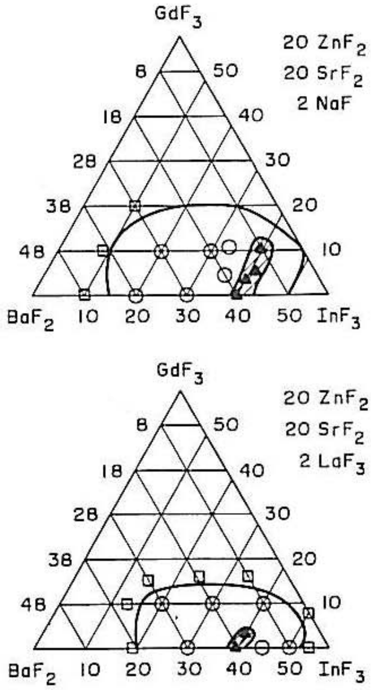

Fig. 2. Limits of glass formation of InF_3–BaF_2–GdF_3–$20ZnF_2$–$20SrF_2$–$2NaF$ (or $2LaF_3$). ■, No glass formation; ○, quenched glasses; ▲, cast glasses.

difficult to find more stable compositions for fiber drawing based on this system.

Further systematic investigations have been performed in this system with the incorporation of GdF_3 in order to obtain more stable glasses. The diagrams of the glass formation are shown in fig. 2. The preparation of large bulk samples has been obtained only with the addition of small quantities of GdF_3. The maximum stability was observed for glasses containing less than 4% GdF_3.

4. Characterization

We have chosen the best compositions reported in table 1 for the determination of their physical properties.

Table 1
Best In-based compositions (mol%)

Acronym [a]	InF_3	ZnF_2	SrF_2	BaF_2	MF_n
IZSBCd	40	20	20	15	$5CdF_2$
IZSBPb	40	20	5	25	$10PbF_2$
IZSBC	40	20	20	15	$5CaF_2$
IZSBNa	30	30	20	15	5NaF
IZSBGdNa	40	20	20	16	$2GdF_2$, 2NaF
IZSBGdL	40	20	20	17	$2GdF_3$, $1LaF_3$

[a] The acronyms are labelled according to the following elements: I = In, Z = Zn, S = Sr, B = Ba, C = Ca, L = La.

Table 2
Physical properties of the best compositions

Acronym	T_g (°C)	T_x (°C)	T_p (°C)	$T_x - T_g$ (°C)	n_D	α (10^{-7} K^{-1})
IZSBCD	291	383	400	92	1.4980	182
IZSBPb	277	366	372	89	1.5300	189
IZSBC	295	385	390	90	1.1950	186
IZSBNa	290	380	389	90	1.4870	192
IZSBGdNa	289	390	401	101	1.4930	–
IZSBGdL	294	390	410	96	1.5080	–

T_g, glass transition temperature; T_x, onset of crystallization; T_p, exotherm maximum temperature; n_D, refractive index at $\lambda = 584.9$ nm; α, expansion coefficient.

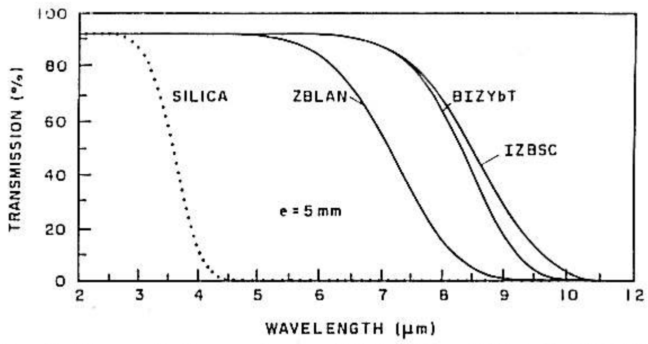

Fig. 3. Transmission of 5 mm thick silica, ZBLAN, BIZYbT and IZBSC glasses.

The characteristic temperature were determined by differential scanning calorimetry using a Dupont 2000 instrument with a 10°C/min heating rate and are given in table 2: T_g, glass transition temperature; T_x, onset of crystallization temperature; T_p, exotherm maximum temperature. The table also shows the difference (T_x–T_g) which reflects the glass stability, the refractive index, n_D, at $\lambda = 584.9$ nm and the expansion coefficient, α.

The infrared transmission of a 5 mm thick fluoroindate glass is reported in fig. 3 together with other glasses for comparison. This glass is more transparent in the infrared region compared with fluorozirconate glass (ZBLAN) and slightly better than BIZYbT glasses.

5. Discussion

Various components have been incorporated in the InF_3–ZnF_2–BaF_2–SrF_2 basic system in order to decrease the devitrification rate. According to table 2, CaF_2, CdF_2, PbF_2 and NaF improve the glass stability and provide numerous possibilities of compositions. The preparation of large bulk samples can be obtained only with the addition of small quantities of GdF_3. However maximum stability is only observed for compositions containing less than 4% GdF_3.

The study of the multiphonon absorption shows that a level of 100 dB/km should be obtained at 5 μm. Therefore this new family of glasses is highly promising for the preparation of optical fibers for coupling to infrared emitting sources such as the CO laser and, when doped with rare earths, for optical amplification. Recently, it has been reported that the phonon energy in this materials is lower than that in ZBLAN glass and the radiative quantum efficiency in the Pr^{3+}-doped glass is approximately twice that of ZBLAN-doped glasses [6].

6. Conclusion

New fluoroindate glass compositions have been investigated. The incorporation of small amounts of GdF_3 strongly increased their thermal stabilities. Large bulk samples and preforms, with 10 mm diameter and 12 cm length, have been prepared. These glasses appear very stable against atmospheric moisture as compared with fluorozirconate glasses. Fibers have been successfully drawn and their characterization will be presented elsewhere. This new family appears therefore very promising for the fabrication of special fibers for coupling to CO lasers for high power beam delivery, thermal measurements and the realization of optical amplifiers.

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