Fluoride glass research in France: fundamentals and applications

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Abstract

The paper reviews research activities on fluoride glasses in France over the last 10 years. Glass compositions for industrial applications as well as new glasses from academic research are presented. They include heavy-metal fluoride glasses, fluorochloride glasses and oxyfluoride glasses. Besides physico-chemical properties, special attention is paid to the optical characteristics of heavy-metal fluoride glasses. They exhibit broader infrared transparency than oxides, which results in unique optical properties and applications, especially in the fields of fiber lasers and optical amplifiers operating at wavelengths not accessible with silica. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The discovery of zirconium-based heavy-metal fluoride glasses at the University of Rennes in the 1970s [1], was the starting point of intensive worldwide research. Since then, laboratories at the Universities of Rennes, Le Mans, and Lyon have been pursuing large-scale research on new glass compositions, on their optical properties as well as on the elaboration of optical structures such as fibers and planar waveguides.

Rapidly, research on fluoride glass became telecom-oriented and French organizations such as *CNET — France Telecom* (National Center for Telecommunication Studies) and *Alcatel* were strongly active in this initially-fundamental research.

Today, some French companies and industries are still directly involved in the manufacture of fluoride glasses and related devices. Those are *Alcatel*, which produces and characterizes rare-earth-doped fibers for optical amplification, *Photonetics*, which develops specific optical amplifiers for telecommunication in the second window of transmission — these amplifiers are based on praseodymium-doped fluoride glass fibers — and *Le Verre Fluoré* which manufactures customized fibers and windows.

This paper reviews research activities in France in the 1990s essentially. Glass compositions for industrial applications as well as new glasses from academic research are presented. Optical properties along with present and future applications of fluoride glasses are discussed.

2. The various types of fluoride and oxyfluoride glasses

2.1. Glass compositions and physical properties

2.1.1. Heavy-metal fluoride glasses

Besides the optimization of first-generation fluorozirconates that ultimately lead to the well-known ZBLAN glass, new glasses such as fluoroindates [2,3] and transition-metal fluoride glasses [4,5] have been synthesized. Typical compositions and some fundamental physical properties are listed in Table 1.

The glass transition temperature, T_g, of heavy-metal fluoride glasses is in the 300°C range, and melting occurs at temperatures T_m between 450 and 600°C. An estimate of the glass stability is given by the Hruby ratio $((T_x - T_g)/(T_m - T_x))$ where, T_x is the crystallization temperature — which must be as large as possible. On this basis, ZBLAN is very stable against devitrification. In addition, thermal analysis shows that the crystallization exotherm is weak for that glass. These favorable conditions are experimentally confirmed by a better ability of ZBLAN for fiber drawing, as compared to other fluoride glasses.

Some exotic fluoride glasses have been synthesized as well. Thus, ZnSB, which contains 80–90% Zn–Sr–Ba, is an example of divalent, zirconium-free glass. It was essentially

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Table 1
Chemical compositions and physical properties of some fluoride and oxyfluoride glasses. Refractive indices (n_D) are given at sodium D-line. α: linear expansion coefficient

Glass	Composition	T_g (°C)	T_x (°C)	T_m (°C)	n_D	α (10^{-7} K^{-1})
ZBLAN	53 ZrF$_4$–20 BaF$_2$–4 LaF$_3$–3 AlF$_3$–20 NaF	262	352	455	1.498	200
BIG	30 BaF$_2$–18 InF$_3$–12 GaF$_3$–20 ZnF$_2$–10 YbF$_3$–6 ThF$_4$–4 ZrF$_4$	332	460	576	1.505	171
PZG	39 PbF$_2$–29 ZnF$_2$–32 GaF$_3$	266	304	543	1.574	–
ZnSB	47 ZnF$_2$–24 SrF$_2$–10 BaF$_2$–5 CdF$_2$–6 InF$_3$–4 GaF$_3$–2 LaF$_3$–2 NaF	303	377	615	1.498	227
CNBZn	18 CdF$_2$–22 CdCl$_2$–30 NaF–20 BaF$_2$–10 ZnF$_2$	158	259	–	1.570	276
CNBK	17 CdF$_2$–33 CdCl$_2$–34 NaF–13 BaF$_2$–3 KF	137	249	296	1.650	215
NBLn (Ln = Tb)	58 NaPO$_3$–11 BaF$_2$–31 TbF$_3$	300	506	–	1.526	194
NAsBY	40 Na$_4$As$_2$O$_7$–30 BaF$_2$–30 YF$_3$	277	390	–	1.555	–
BOF	BO$_{1.3}$F$_{0.4}$	$\approx$50	–	–	–	–

developed for its potential as a broad transmitter of mid-infrared light [6].

The refractive indices of fluoride glasses are typically around 1.5 at the sodium D-line, except for PZG that shows an index of 1.6 because of the large PbF$_2$ content. Highly polarizable lead ions are common dopants for increasing the refractive index of core glass in fluoride glass optical fibers.

2.1.2. Chlorofluoride glasses

In the same logic of expanding the infrared transparency, glass formation was investigated in chlorofluoride systems. CNBZn and CNBK glasses shown in Table 1 are two representatives of the chlorofluoride glass family [7,8]. These glasses contain 22 and 33 mol% CdCl$_2$, respectively, in addition to divalent and monovalent fluorides. Because of the presence of chloride ions, these materials are usually moisture-sensitive. Corrosion is due to a preliminary ionic exchange between OH$^-$ and Cl$^-$ at the glass surface followed by a diffusion of the hydroxyl groups inside the glass. Addition of chloride ions induces the main physical alterations, namely lower glass transition temperatures and increased refractive indices, as compared to pure fluoride glasses. This is due to the weaker strength of M–Cl bonds and higher polarizability of Cl$^-$ ions. A systematic study showed that, in the chlorofluoride glass family, CNBZn was the best compromise between glass thermal stability, resistance to moisture and ability to accept rare-earth ions.

2.1.3. Oxyfluoride glasses

In the last 10 years, special efforts were dedicated to the search of novel, non-conventional glasses based on both fluorides and oxides. Thus, new fluorophosphate, fluoroarsenate and boron oxyfluoride glasses were discovered [9–11].

Table 1 shows compositions of fluorophosphate and fluoroarsenate glasses with high concentrations of rare-earth fluorides, up to 31 mol% in NBTb, which make them good candidates for luminescence and magneto-optic studies. Like pure fluorides, NBTb exhibits a glass transition temperature in the 300°C range. NBTb fluorophosphate glass is very stable with a temperature difference (ΔT) between

crystallization and glass transition greater than 200°C and a weak crystallization exotherm. Therefore, fiber pulling with NBTb glass is straightforward. Conversely, and despite a favorable ΔT of >110°C, NAsBY fluoroarsenate glass is suitable for the synthesis of bulk samples only.

Boron oxyfluoride glasses can be synthesized in the BO$_{(1.5-0.5x)}$F$_x$ system with $0.2 < x < 0.6$. Within this composition range, glass transition temperatures vary from 120 to −15°C, respectively. Their structure, as investigated by molecular dynamics computer simulations and NMR spectroscopy, is based on chains of BO$_{2/2}$F units where the fluorines are non-bridging [12]. Boron oxyfluoride glasses are degraded by atmospheric moisture, so that they need to be prepared and kept in sealed evacuated silica ampoules.

2.2. Passive optical properties

Optical transmission is an essential physical characteristic of heavy-metal halide glasses, in the sense that this property differentiates easily halide glasses from traditional oxide glasses.

Except for BeF$_2$-based glasses, fluoride glasses are transparent at wavelengths greater than or equal to 5 μm, depending on the nature of the main cation in the glass. Infrared transmission spectra are shown in Fig. 1 for typical tetra-valent-, trivalent-, and divalent-based fluoride glasses. Glasses with large, heavy and lightly-charged elements possess lower phonon energies and a consequent extended infrared transparency.

For ZBLAN, the IR edge is in the 5–8 μm range with 50% transmission at $\approx$7 μm for a 2 mm-thick sample. This is to be compared with silica glass whose transparency starts decreasing at $\approx$3 μm. The IR edge is due to multiphonon absorption processes related to the fundamental vibration frequencies of the host. For ZBLAN, Zr–F vibrations around 580 cm^{-1} account for the multiphonon absorption, while, for silica, the position of the IR edge is due to Si–O vibrations at 1100 cm^{-1}.

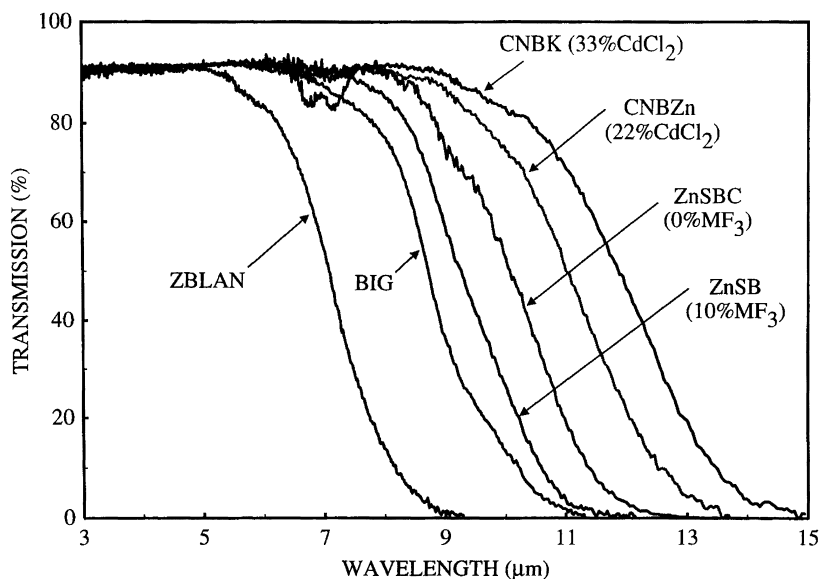A shift by more than 1.5 μm in the IR is observed for trivalent BIG glass as compared to standard ZBLAN [13].

Fig. 1. Infrared transmission spectra of fluoride glasses. M: trivalent metal ions.

This is due to the lower frequency of In–F bonds ($\approx$510 cm^{-1}) with respect to Zr–F.

Glasses based on divalent fluorides show a broader IR transparency than glasses based on indium or zirconium, as reported for ZnSB and ZnSBC in Fig. 1. They exhibit a full transparency up to 9 μm for the former and 10 μm for the latter which is a pure MF$_2$ fluoride glass containing Zn, Sr, Ba, and Cd.

On the contrary, a poor infrared transparency limited to 2.5–3 μm characterizes fluorophosphate and fluoroarsenate glasses. This is because of the presence of oxygen in the glass, which induces high-energy vibration modes (P–O; As–O) resulting in strong absorptions at 4.5 μm in fluorophosphates and at 3.6, 4.2, and 5.65 μm in fluoroarsenates.

Intrinsic light scattering is of major concern for obtaining fluoride glass optical fibers with low optical attenuation. Attaining the theoretical level of intrinsic Rayleigh scattering necessitates, at first, stringent glass preparation conditions. Especially, the melting conditions play an important role. In order to avoid the particle contamination associated with the use of crucibles for glass melting, Baniel et al. at *Alcatel* have developed a containerless gas film levitation technique [14]. They obtained a low Rayleigh coefficient of 0.66 dB km^{-1} μm^4 for a ZBLAN bulk glass, a value comparable to that of silica.

2.3. Active optical properties

Most fluoride glasses accept rare-earth ions in quite large quantity. They are hosts of prime interest for spectroscopy, due to low phonon energies that induce high quantum efficiencies for rare-earth emissions. Thus, a number of transitions, which cannot be detected in silica-based rare-earth-doped glasses, are observed in fluoride glasses.

Extensive research including the study of radiative and non-radiative properties of almost any rare-earth ion has been carried out in France and worldwide. An exhaustive list of results can be found in [15]. Only a few typical examples will illustrate this broad field of fluoride glass research.

Rare-earth emissions in fluoride glasses range from the UV to the mid-infrared. One of the most widely studied is the 1.3 μm emission of Pr^{3+} ions because of its suitability for optical amplification in the second telecommunication window. This emission, which occurs from the $^1G_4$ excited state to the $^3H_5$ level, peaks at 1.31 μm. Because of an energy gap of about 3000 cm^{-1} between $^1G_4$ and its next lower level $^3F_4$, this transition is observed exclusively in low-phonon energy materials such as fluorides, chlorides, sulfides and so on. It shows a favorable branching ratio of nearly 0.65 in fluoride glasses [16] and excited-state absorption of the emission wavelength, located in the long-wavelength side of the band, is by far not as severe as for the 1.3 μm emission of Nd^{3+} ions [17]. A main drawback is the weak oscillator strength of the $^1G_4$ absorption, which results in poor pumping conditions. This can possibly be improved by codoping with Yb^{3+} whose $^2F_{5/2}$ level coincides with $^1G_4$.

Laser-induced cooling is another domain of investigation for fluoride glasses, because of their low-phonon energy. The fundamental principle of laser-induced cooling is anti-Stokes luminescence, that is luminescence that occurs at a wavelength shorter than that of the pump laser. The energy mismatch is then provided by absorption of phonons from the glass host, which results in a cooling of that host. The cooling efficiency is quite low, so radiative transitions with quantum efficiencies near unity are to be used. From this point of view, best combinations are obtained with Yb^{3+} ions in fluoride glasses [18].

With a high content of lanthanide ions, oxyfluoride glasses such as NBLn and NAsBY, are also of interest for rare-earth studies. Thus, because of a high concentration of Tb^{3+} ions, which show a large paramagnetic Verdet constant, NBTb fluorophosphate glasses were studied for their magneto-optic properties, for Faraday rotator applications [19]. In the field of spectroscopy, it was shown that in (Yb, Tb) co-doped NBLn glass, a two-step up-conversion process involving 982 nm photons was capable of exciting the $^5D_4$ level of Tb^{3+} ions. This was due to a cooperative effect between two Yb^{3+} ions that transfer their energy to one Tb^{3+} ion. The process led to the characteristic $^5D_4 \rightarrow {}^7F_5$ green emission. In absence of terbium, the cooperative effect between Yb^{3+} ions still occured leading to a short-lifetime blue emission [20].

Concerning NAsBY fluoroarsenate glasses, Nd^{3+} spectroscopy and energy transfer mechanisms have been investigated [21].

3. Optical applications of fluoride glasses

3.1. Lasers and optical amplifiers

Because of the exceptional guiding properties and confinement provided by optical fibers, lasing has been obtained for a large number of rare-earth transitions in fluoride glasses, including several three-level systems that hardly lase in bulk configuration. The suitable fiber structure for most applications is close to single mode, that is a core radius in the 2–10 μm range for an outside fiber diameter around 150 μm. The rare-earth concentration in the core of the fiber is typically 100–1000 ppm, possibly one percent. Usually, the length is from a few centimeters to several meters.

Fluoride glass fiber lasers operate at discrete wavelengths from the blue to the mid-infrared, especially at wavelengths not achievable with oxide glasses [22–29]. Those are, for example, the up-conversion blue and green lasers, with Tm^{3+} and Ho^{3+}, and the Er^{3+} laser at 2.714 μm. A complete review can be found in [15].

In these fiber laser experiments, the optical cavity was typically made of two external mirrors butted against the fiber input and output ends. More sophisticated systems will take advantage of Bragg gratings written directly inside the fiber. Thus, scientists at the University of Lille have demonstrated that permanent Bragg gratings could be photo-induced in cerium-doped fluorozirconate glass plates and fibers by means of conventional holographic interferometry of 246 nm light from a pulsed UV laser [30,31]. Refractive index changes up to 4×10^{-4} and reflectivity of nearly 100% were achieved. Similar experiments have been conducted with Eu^{2+} and Ce^{3+}-doped PZG thin films illuminated by a CW laser at 244 nm. Photo-induced modifications of the refractive index were as high as 1.3×10^{-2} and 3.9×10^{-3}, respectively [32].

Scientists at ENSSAT engineering school (University of Rennes) have demonstrated low-threshold, up-conversion lasing at 540 nm in Er^{3+}-doped ZBLAN microspheres [33].

Current activity in fluoride glass research in France is still strongly telecommunication-oriented with research devoted to broadband optical amplifiers, within the 1.2–1.6 μm spectral domain. The need for such amplifiers is crucial by now with the implementation of new highly-transparent silica fibers for trunk lines. The 1.5–1.6 μm band can be covered with erbium-doped fiber amplifiers (EDFA) based on silica. However, fluoride EDFA's remain of practical interest because they possess a flat and broad gain bandwidth as a function of signal wavelength [34]. This property, which is fundamental for wavelength division multiplexing (WDM), is depicted in Fig. 2. This figure shows the optical spectrum of 16 channels at the output of four cascaded fluoride or silica EDFA's without any spectral filtering [35]. One may note that all channels, which range from 1533.7 to 1558.2 nm, are quasi-equally amplified by fluoride EDFA's with a maximum gain variation of 3 dB only. With silica EDFA's, on the other hand, large discrepancies are observed as shown in Fig. 2b. The gain variation between minimum and maximum amplified channels is as high as 23 dB in that case. Laboratory tests have demonstrated the transmission of such 16 channels at 10 Gbits/s over 531 km with seven fluoride EDFA's [36].

Despite spectroscopic parameters that are much less favorable than for EDFA's, praseodymium amplifiers
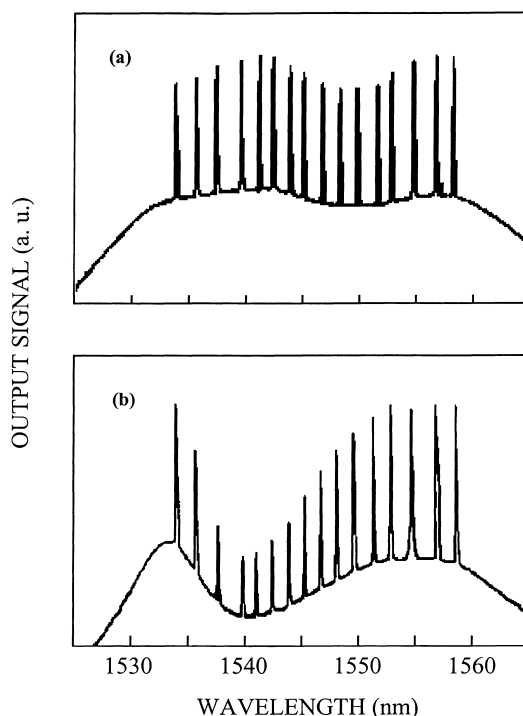

Fig. 2. Optical spectrum of 16 channels at the output of four cascaded EDFA's: (a) fluoride amplifier; (b) silica amplifier (after [35]).

(PDFA) have been extensively studied for application in the second telecommunication window at 1.3 μm. High-gain (>20 dB) and high-output power PDFA's have been demonstrated [37]. PDFA's are of special importance for Central-Antenna-TV signal distribution.

3.2. Integrated optics

The feasibility of fluoride glass channel waveguides has been demonstrated by using two different techniques: ionic exchange developed at the University of Rennes and physical vapor deposition implemented at the University of Le Mans.

Fluoride glass planar waveguides can be obtained by F^-/Cl^- ionic exchange. Substituting chloride ions for small and light fluoride ions results in an increase of the refractive index. The best results were obtained with optically polished ZBLA fluoride glasses, treated by a gas flow composed of a mixture of argon and HCl. The samples were maintained in this reactive atmosphere for several hours, depending on the desired number of guided modes, at a temperature below the glass transition temperature [38]. Chloride ions were found to partially substitute for fluorine down to a depth of 10 μm from the glass surface after a 10 h treatment at 250°C. The chlorine concentration profile was constant from the surface down to 1 μm depth, and then, obeyed a normal diffusion profile. Five propagation modes at 632.8 nm were measured for such a sample. Channel waveguides were prepared by creating a silica mask at the fluoride glass surface by using photolithography techniques. Then, the guide was formed by ionic exchange as described above, and the silica mask was removed by reactive ion etching (RIE). The near-field pattern recorded at the output of a channel waveguide with 830 nm light from a laser diode showed that propagation was single-mode at this wavelength.

Physical vapor deposition techniques can be applied to PZG glass because the main components of that fluoride glass — PbF_2, ZnF_2, and GaF_3 — show similar vapor pressures, contrary to ZBLAN and BIG glasses [5]. Thus, a congruent vaporization of PZG melts is possible, and films can be obtained by deposition of the vapor phase on a cleavable CaF_2 substrate. A preliminary coating of the substrate with a negative photoresist allows the elaboration of channel waveguides as narrow as 5 μm [39].

Active waveguides are obtained by evaporating simultaneously the glass composition and a given rare-earth fluoride or rare-earth chloride. Recently, researchers at the University of Lyon have demonstrated 1.6 dB/cm signal amplification (internal gain) at 1530 nm with an Er^{3+}-doped PZG channel waveguide. Absorbed pump power was 3 mW at 1485 nm [40]. Similarly, Er^{3+}-doped ionic-exchanged ZBLA channel waveguides showed a 1.1 dB/cm internal gain with ≈16 mW absorbed pump power [41]. Spectroscopy and optical amplification with Nd^{3+} ions were also studied in both types of waveguides [42,43].

4. Conclusions

More than 25 years after the discovery of fluoride glasses, fundamental and applied research in this field is still very active in France. By now, several universities and companies are involved and collaborate on specific research programs.

As far as future work is concerned, it will be oriented essentially towards applications in active optics. Thus, scientific and technological breakthroughs can be expected in the fields of rare-earth-doped fibers and channel waveguides for broad-band optical amplification, rare-earth-doped fluoride glasses for microcavity lasers, and laser-induced cooling.

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