Fluoride Glasses: Synthesis and Properties

M. Poulain and A. Soufiane

Centre d'Etude des Matériaux Auancés, Rennes, France

Y. Messaddeq and M. A. Aegerter

Instituto de Física e Química de São Carlos, Universidade de São Paulo

Caixa Postal 369, São Carlos, 13560-970, SP, Brasil

The discovery of heavy metal fluoride glasses has opened new prospects for fiber optics operating beyond 2 μm with expected losses less than 10^{-2} dB/Km. The main interest of fluoride glasses lies in their infrared transmission up to 8 μm in the bulk form and 4.5 μm for optical fibers. We have reported here the preparation, the glass forming systems and properties of heavy metal fluoride glasses.

I. Introduction

The development of optoelectronic devices and systems for telecommunications, sensing and miscellaneous applications has stimulated intense research on vitreous materials. Insofar as it becomes possible to reach the theoretical limits of silica-based glasses, further improvements in performances depend only on the discovery of new glasses and their optimization. The discovery of unexpected glasses at Rennes University in 1974[1] was the beginning of numerous researches on fluoride and, more generally, halide glasses, resulting in the description of hundreds of new glass forming systems. Fluor de glass fiber technology was investigated, especially in its specific aspects. Glass formation, which was considered as an exceptional event, appears now as a common feature in many fluoride systems. This development has expanded the horizons of the traditional field of glass science. Also, infrared fibers are now available for various technical purposes. Prospects for long haul repeaterless telecommunications are promising, in spite of extrinsic scattering losses which keep the actual losses above the theoretical limits. The closest applications of fluoride glasses in this field of telecommunications relate to optical amplification, as they offer possibilities at the 1.31 micrometer wavelength[2].

II. Glass synthesis and processing

II.1. Genera aspects of fluoride glass preparation

The classical way to prepare a glass sample consists in mixing the basic glass components, heating, cooling, casting and annealing. Although the synthesis of a fluoride glass encompasses this sequence of operations, it requires some special processing in relation with the chemical reactivity of fluoride powders and melts, and also with the relatively low stability of fluoride glasses

with respect to divitrification. Consequently, processing may be critical for the quality of the final material. It starts with batch preparation and ends with sample polishing.

II.1.1. Starting materials

The manufacturing of high quality optical components such as optical fibers implies that starting materials meet severe purity requiremerits. However, they are different from current chemical specifications because one may tolerate significant amounts of diamagnetic cations, while trace levels of optically abscrbent impurities must be reduced drastically. As an example, there is no need to remove alkali or alkaline earth elements from starting rnaterials.

Fluoride glasses may contain a small amount of anionic oxygen which reduce slightly glass forming ability in most cases, but is believed to generate wavelength independent scattering. Anionic impurities, such as nitrates, carbonates, and sulfates may be chemically active and should be avoided since they are a source of anionic oxygen in the final glass even when a fluoridating step is carried out. Chlorine anions have less influence upon optical transmission, except in the UV spectrum.

Another group of insidious impurities consists in gaseous species because they are usually neglected. Carbon dioxide may be present in fairly large amounts in lanthanum oxide. The most drastic impurity is water which is common both in many so-called anhydrous fiuorides and also in reportedly non-hydroscopic compounds. Depending on the process, water contamination may largely determine the final level of hydroxyl and anionic oxygen.

Processing atmosphere is critical for achieving an optimum glass quality. For example, hydrogen fluoride

HF is commonly contaminated by H_2 and H_2O, and most pressured gases contain traces of water.

In summary, the selection and the handling of starting materials require much attention. Oxides should preferentially be reheated at 1000°C before use. Alkali and alkaline earth fluorides may also be dehydrated by heating them in an oven. Other fluorides, e.g. those of zirconium, aluminum and rare-earth, cannot be easily dehydrated. For this reason, the ammonium bichloride process which works with oxides or hydrated materials, has been widely used for current preparations.

II.1.2. Melting and fining

Melting is usually implemented in platinum, gold or vitreous carbon crucibles. When there is no fluorination step, the heating rate may be fast. The critical point of this step is the dryness of the working atmosphere. Flowing a dry gas into the melting enclosure may not be always sufficient because water can remain adsorbed on the walls.

A raw glass is obtained at the end of the initial melting process. It appears often grey or black and exhibits a rather high divitrification rate. Consequently, batches cooled within the crucible may be crystalline. Also, optical scattering and hydroxyl absorption at 2.9 micrometers may be significant.

Most of these defects are removed during the finingstage. It consists in heating the melt above the liquids temperature in an oxidizing atmosphere. The viscosity decreases and the melt is homogenized without stirring. Volatile species are eliminated, and reduced phases which give rise to scattering are oxidized and dissolved. Most of hydroxyl decompose into gaseous HF and anionic oxygen. Time and temperature are adjusted according to glass composition, batch size and crucible geometry. With fluorozirconate glasses, care must be taken regarding ZrF_4 volatilization which occurs at high temperature.

II.1.3. Casting, cooling and annealing

After fining, glass melt is cooled at a temperature for which nucleation rate is still low. It must not be kept in this situation for a too long time. It is poured onto a metallic mold - usually brass - which has been preheated around glass transition temperature. Graphite may also be used as a mold material although its surface is easily contained.

Most fluoride glass samples are prepared in this way. By comparison with classical glasses, the low melt viscosity makes it possible to fill molds of small size or complex shape. The large difference between the solid and liquid volumes implies that the volume of the melt poured is larger than that of the final sample. There may be some problems at the end of the solidification process when the entire outer surface has just solidified but the inside has not. For example, "vacuum" bubbles may be formed along the axis in cylindrical samples.

However, there are some limitation and problems associated with the casting method. First, atmospheric contamination is enhanced as the melt surface is increased during casting. Hydrolysis can occur and more volatile fluorides such as ZrF_4 go into the vapor phase which locally modifies the chemical composition. Moreover, there may be some condenses around the upper part of the crucible, leading to oxides or oxyfluoride phases which can be incorporated into the melt flow and resulting in microcrystalline phases. Finally, the liquid motion may generate small bubbles which do not always reach the sample surface before the glass is frozen.

It is also possible to manufacture homogeneous and defect-free glass samples using the "mold-crucible" method: in this method, the molten glass is simply cooled inside the crucible in which it was melted. Thus, the sample replicates the crucible shape and has much more limited exchange with the atmosphere because the melt remains static. Indeed homogeneous, cord and defect-free samples have been obtained in this way. By comparison with the casting method, lower cooling rates must be used and it is difficult to avoid bubbles on the walls. Therefore, the outer part of the glass sample has to be removed by polishing.

When glasses exhibit high divitrification rate, rapid quenching is needed. This may be achieved simply by squeezing the melt between two metal plates or by using classical quenching devices such as cooled rollers or splat quenching.

In order to get samples free of internal stresses, an annealing stage is usually needed, especially before cutting and polishing. Temperature is adjusted empirically, commonly around the glass transition temperature, T_g. For current (i.e. small) samples, annealing time appears to be less important than slow cooling to room temperature in order to avoid the formation of new thermal stresses.

11.2. Chemical reactivity

In laboratory conditions, oxide materials appears much more inert than fluorides. Chemical reactions between fluorides and water are the most important. The reaction rates are critically dependent on temperature and also on cation nature. For example, alkali and alkaline earth fluorides which may adsorb water at room temperature are easily dehydrated. On the contrary, niobium pentafluoride is hygroscopic even at low temperature giving rise to oxyfluoride and gaseous HF. In standard fluoride glasses, there are two possible reactions between molten glass and water[3]
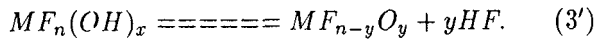
$$MF_n + xH_2O ======= MF_{n-x}(OH)_x + xHF \quad (1)$$

$$MF_n + xH_2O ====== MF_{n-2x}O_x + 2xHF \quad (2)$$
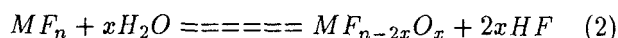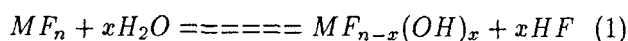
Reaction 1 occurs at lower temperatures, for example around T_g, while reaction 2 becomes predominant

at higher temperatures. Then, in the molten state, hydroxyl groups become reactive with fluorine anions, according to the relation

$$OH^- + F^- ====== O^{2-} + HF \qquad (3)$$

or equivaleiitly

$$MF_n(OH)_x ====== MF_{n-y}O_y + yHF. \qquad (3')$$
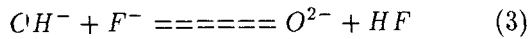
Reaction 3 occurs easily in the melt since each hydroxyl group is surrounded by 8 to 12 fluorine anion in the liquid state. Conversely, the probability of two hydroxyl being close becomes very small as OH concentration decreases. The chemical equilibrium

$$(OH)^- + (OH)^- ======== O^{2-} + H_2O, \qquad (4)$$
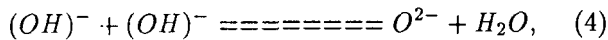
which makes the basis of the hydroxide elimination in oxide melts becomes highly unlikely in high temperature fluoride melts, where reaction (2) applies.

Oxidation reduction processes form the second group of chemical reactions. This concerns first zirconium which may be reduced to lower oxidation states. The main cliaracteristic of these reduced phases is their insolubility in the glass melt, which gives rise to intense scattering. Similar reduced phases may be observed in Zr-free fluoride glasses and this could make the subject of further chemical studies. Reduction may arise from traces of ainmonium, hydrocarbons, solvents, grease, dust or plastic impurities contained in the starting material~. Ox dizing reagents may be gases such as O_2, NF_3, Cl_2, CCl_4, SF_6..., or ions such as In^{3+} or SO_4^{2-}.

Various other chemical reactions may occur in fluoride melts. They correspond to liquid/gas, liquid/liquid and liquid/solid reactions. Direct reaction between oxygen and fluorides is very limited in current conditions. Gases may be dissolved[4] as well as various salts. Reactions with oxides result either in limited dissolution, e.g. with alumina or zirconia, or in double decomposition: for example, silica reacts strongly and produces gaseous SiF_4.

II.3. Ammonium bifluoride processing (ABP)

K. H. Sun[20] who was the pionneer of fluoroberyllate and fluoroa'uminate glasses used ammonium fluoride for the current synthesis of his samples. In this case, it was used only for preventing melt hydrolysis and not for the oxide to fluoride conversion.

The origin of the ammonium bifluoride processing (ABP) is economical: at the early stage of investigation of the glass forming systems, it was difficult to find anhydrous fluorides in quantities rather large at the laboratory scale. For this reason, it appeared interesting to use oxides as starting materials and to convert them into fluorides using NH_4HF_2. With experience and adjustnients in the fluorination conditions - time, temperature, quantities - this process could lead to high quality fluoride glasses.

The chemical reaction between oxides and ammonium bifluoride follows the general scheme:

$$MO, + (n + x/2)NH_4HF_2 \rightarrow MF_{2n}xNH_4F +$$
$$(2n + x/4)H_2O + (n - x/2)NH_3. \qquad (5)$$
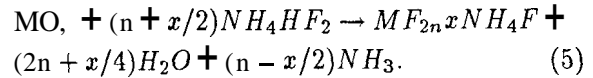
The fluorination reaction produces gaseous water, which may be a source of contamination. Reactions may start at low temperature and it is advantageous to keep temperature as low as possible in order to prevent hydrolysis. Metallic amrnonium fluoride complexes are further decomposed by heating and the last traces of volatile NH_4F are generally removed during melting. In practice, the batch is heated up between 200 and 400°C for a time which may vary from a few minutes to several hours. The optimum time and temperature depend on many factors such as the quantity and the quality of the starting materials or the processing atmosphere.

When a very low OH level is not necessary, the fluorination, fining and casting process may be carried out in less than 15 minutes for small samples. On the other hand, fluorination requires **3** to 15 hours for preform glass fabrication using ABP. Processing time is reduced when the amount of oxides in the batch is small. In the limiting case of starting materials consisting of pure fluorides, the ABP serves simply to remove water adsorbed in powdered reagents, according to Sun's experimental procedure.

This process has some disadvantages. First, it is time consuming. It also leads to large changes in batch volume. Furthermore, ammonium ions may induce some chemical reduction and remain at some trace level in the final glass. Moreover, ammonium bifluoride contain some cationic impurities which will stay in the glass, and consequently limit the purity of the final material. In some cases, it may even be significantly hydrated, which in turn results in hydroxyls and anionic oxygen.

II.4. Reactive atmosphere processing (RAP)

The reactive atmosphere processing (RAP) was first used for halide crystal growth. Robinson and Pastor implemented the first application to fluoride glass synthesis[6]. The basis of RAP lies in the processing of the melt by a gaseous active chemical component. In these conditions, anionic impurities such as oxygen and hydroxyl groups may be removed. Carbon tetrachloride is the most common reagent. It reacts according to the following chemical equations:

Oxidation
$$2CCl_4 \rightarrow C_2Cl_6 + Cl_2 \qquad (6)$$

Deoxygenation
$$O^{2-} + CCl_4 \rightarrow 2Cl^- + COCl_2 \qquad (7)$$
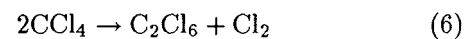
Dehydroxydation
$$OH^- + CCl_4 \rightarrow Cl^- + COCl_2 + HCl \qquad (8)$$
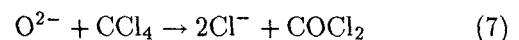
Very positive results have been reported by various researches. By comparison with the synthesis of fluoride glasses under neutral atmosphere, RAP leads to more clear samples, and the OH content seems to be significantly lower. Comparative studies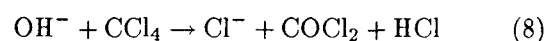 indicate than the multiphonon absorption edge is shifted toward longer wavelengths[7] which suggest that the residual oxygen content is lowered. One of the drawbacks of RAP is chlorine incorporation which may influence nucleation rate and decreases UV transmission. Other reactive atmospheres have been experimented: chlorofluorocarbons, sulfur hexafluoride, CF_4, CS_2, XeF_2, BrF_3 and NF_3.[8-12] It appears that RAP is only one element in a complex set of operations which are ruled by several chemical equilibria. Most researchers, especially those involved in ultralow loss fluoride glass optical fibers have emphasized the reduction of the OH content. This has led to the development of a dry processing in which all synthesis operations are carried out in a very dry air. Atmospheric oxygen has an oxidizing action on the reduced species contained in glass melt, while the very low water concentration - generally below 5 ppm - enhances the elimination of hydroxyls. Of course, it also produces anionic oxygen which may be a severe limitation on the way toward ultra low optical losses.

11.5. New processes

It is largely assumed that new synthesis processes are needed for the achievement of very low optical losses. Among various possibilities, vapor phase processes appear attractive because of the success of chemical vapor deposition (CVD) in silica fibre technology. Some preliminary results appear to be encouraging[13,14]. However, the practical achievement of fluoride glasses through CVD appears as a difficult challenge. The control of fluorinating reactions associated with corrosion problems impose severe limitations to the parameters of reaction: temperature, deposition rate, volume, etc. As they are multicomponent glasses, it is more difficult to achieve complete chemical reaction with all the elements. Finaly, devitrification problems still increase the difficulty of the task. A first convincing step could be the synthesis of beryllium fluoride glasses for which chemical parameters are more favourable.

Another possible approach is based on evaporation and condensation of fluoride melts. There are some examples of fluoride glass films prepared in this way. Further developments are needed for the manufacturing of glass tubes with a low contamination level. One of the problems relates to the control of glass composition.

More recently, attempts for applying the Sol-Gel techniques to the synthesis of fluoride glasses proved to be successful[15-17]. There are two different processes: either in non aqueous medium with strong fluorinating reagents, or the fluorination of wet gels by gaseous hydrogen fluoride. Amorphous powders with characteristics DSC traces are obtained, and transparent bulk

samples may be prepared by melting these powders under anhydrous atmosphere. Some researchers assuming that crucible makes a major soirce of nucleation have suggested the use of microgravity for containerless processing[18]. Among other possibilities, one may quote laser processing, microwave assisted chemical reactions, hot or cold plasma and molecular beam deposition. These ways and other processes could be tried in the future if the need for lower loss fluoride glasses is confirmed.

III. Glass forming systems

111.1. Introduction

Glass formation in fluoride systems has been considered for long as a marginal and exceptional phenomenon. Berylium fluoride glasses made the classical example of such glasses: because of the four-fold coordination of Be and the isostructural forms of crystalline SiO_2 and BeF_2, it was assumed that both glasses were similar in their structure and their formation. While vitreous BeF_2 was reported more than 90 years ago[19], fluoroberylate glasses were more extensively studied later, especialy by K. H. Sun who discovered some unexpected fluoroaluminate glasses[20].

The seredipendous discovery of the first fluorozirconate glasses in 1974[1] was the starting point of numerous researches on heavy metal fluoride glasses (HMFG). Although it was first assumed that glass formation in theses systems was related to the specific crystal chemistry of zirconium, it became rapidly clear that glass formation was a rather common event in numerous multicomponent fluoride systems.

The description of the various groups of fluoride glasses requires a classification which may be difficult to define. Quite naturally, fluoride glasses were described by reference to oxide glasses, that is from an implicit structural criterion. It is generally assumed that oxide glasses consist of a random network of tetrahedra sharing corners and trapping large cations. In this scheme, glass forming ability is correlated to the possibility of constructing a tetrahedral disordered network. Glass families may be defined according to the nature of the cations of the network: silicates, germanates, phosphates, borates, etc. The same approach may be used for fluoride glasses, and, indeed, it has been. However, the physical existence of a vitreous network based on the coordination polyhedra of the smaller cations in the complex structure of the fluoride glasses is far from being obvious. Insofar as they may also be described as a random ionic packing, the contribution of large cations to the vitrification process cannot be neglected. For example, it is rather arbitrary to claim that, in the ZnF_2-SrF_2 binary glass, zinc fluoride is the vitrifier.

While the separation of fluoride glasses into distinct groups may suffer from a lack of structural basis, it is
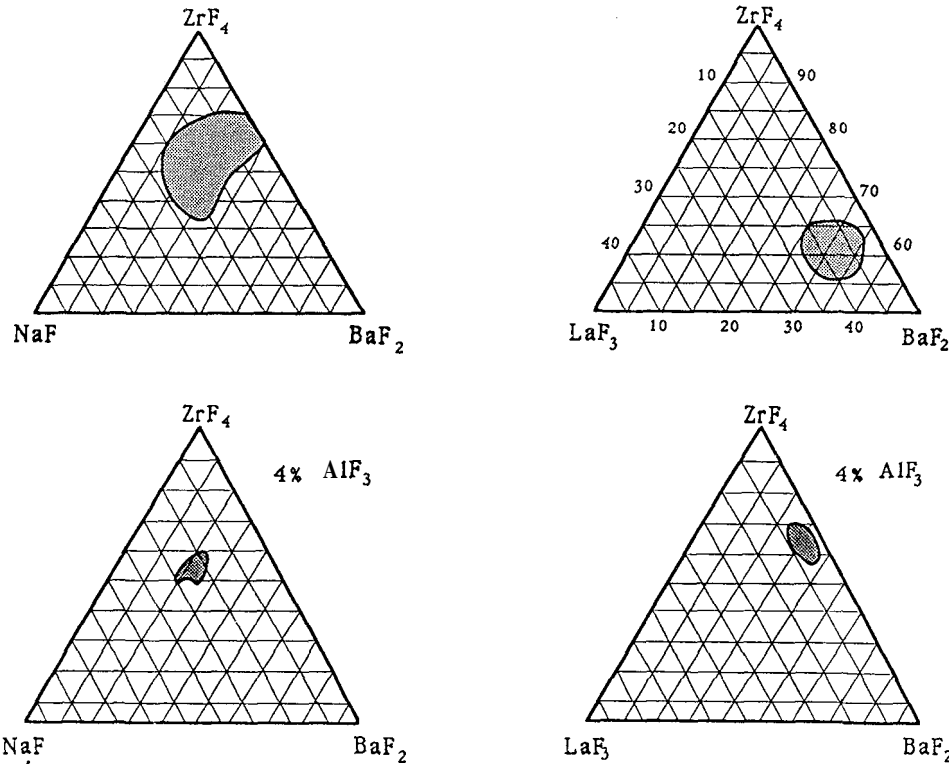
Figure 1: Limit of glass formation in various fluorozirconate glass forming systems. The ZrF_4-BaF_2-NaF ternary system was the first diagram investigated and it corresponds to quenched glasses. Aluminum incorporation leads to an increase in glass forming ability.

still the easiest and probably the most convenient, even when it is no; possible to define a major glass former.
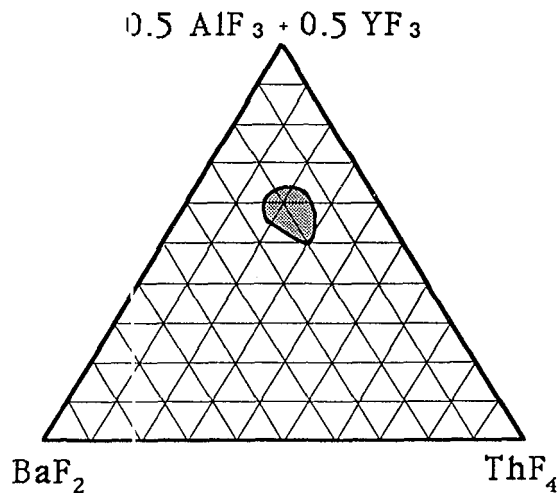

Figure 2: Glass forming area in the AlF_3-BaF_2-YF_3-ThF_4 systerns.

III.2. Fluorozirconate and fluorohafnate glasses

Fluorozirconates are still forming the main group of fluoride glasses, both for historical and practical reasons: discovered 18 years ago, they have been devel-

oped for a longer time; also, they exhibit a good resistance against devitrification and their technology is well defined. Because of the close chemical behaviour of zirconium and hafnium, this family encompasses both fluorohafnates and fluorozirconates. Zirconium fluoride does not exist in the vitreous form, but it forms binary glasses in association with BaF_2, SrF_2, ThF_4, LaF_3 and probably other fluorides. These binary glasses are not very stable and require a fast cooling of the melt. Ternary combinations are needed in practice to obtain samples thick enough for physical and optical characterization. The first fluorozirconate glasses were observed in the ZrF_4-BaF_2-NaF ternary system[1] and large samples could be obtained in the ZrF_4-BaF_2-ThF_4-NaF systems[21]. Various ternary diagrams based on the ZrF_4-BaF_2 association have been investigated, for example the ZrF_4-BaF_2-LaF_3 system[22]. Similar vitreous areas are observed when hafnium substitutes zirconium, but there may be some differences in the optimum compositions of fluorozirconate and fluorohafnate glasses.

Glass composition suitable for the casting of large samples or the drawing of fibers must exhibit a minimum stability against devitrification. Optimization may be achieved by composition adjustments arid by increasing the number of glass components, according to the well known "confusion principle". Various standard multicomponent glasses have been defined. They include aluminum trifluoride as a stabilizer[24]. Some
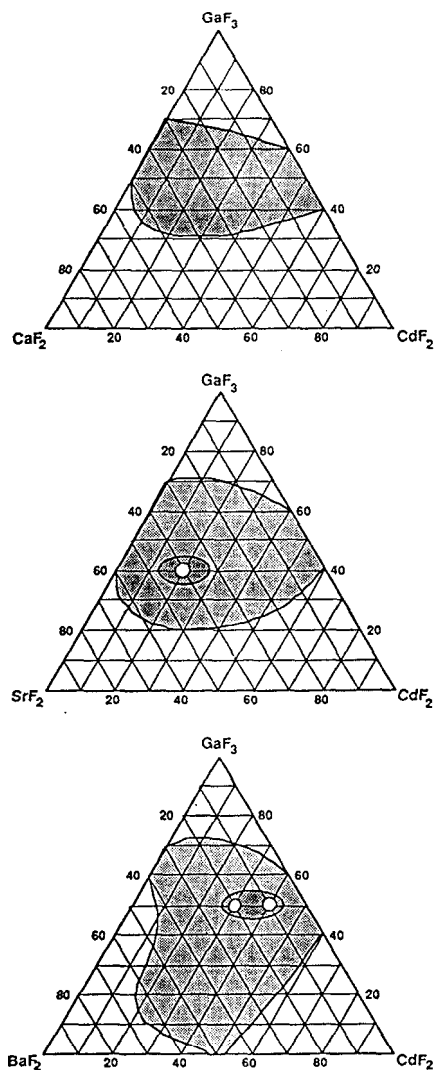
Figure 3: Glass forming areas in the GaF_3-CdF_2-MF_2 systems, (M=Ca,Sr,Ba). Inner limits correspond to more stable glasses.

typical glass forming areas are displayed in figure 1, while standard glasses are reported in Table I. This table includes some less common glasses such as ZrF_4-ThF_4-LaF_3 or barium-free fluorozirconate glasses.

In practice, standard compositions are often modified by the incorporation of selected additives aiming at the adjustment of physical properties. For example, alkali cations will decrease T_g and refractive index, while rare earths or thorium have a reverse effect[25]. While there is still room for further improvements in glass stability, the present compositions seem stable enough for current needs, including large optics and optical fibers.

III.3. Fluoroaluminate glasses

The first fluoroaluminate glasses were reported by Sun in 1946 in the AlF_3-PbF_2-SrF_2-MgF_2 system,

but systematic studies started only after the development of fluorozirconate glasses. Typical systems are AlF_3-BaF_2-CaF_2, AlF_3-BaF_2-YF_3-CaF_2 and AlF_3-BaF_2-YF_3-ThF_4[26-28], as shown in figure 2. Thick samples could be prepared, and rods could be drawn into fibers. Numerous other fluoroaluminate glasses have been synthesized in multicomponent systems including zinc, alkali, magnesium and rare earths[29].

III.4. Fluorogallate and fluoroindate glasses

Glasses based on the association of InF_3 and GaF_3 with divalent fluorides appear now as a group of emerging importance. While the occurrence of such glasses was reported more than then years ago, they remained for a long time in the field of basic science. Various glass forming systems were investigated and glass stability was gradually improved. Tables II-IV summarize the main systems reported in the literature before 1991.

In a general way, fluoroindate glasses are more stable than fluorogallates, which makes possible the manufacturing of thick samples or fiber drawing. Progress in the stabilization of fluorogallate glasses has been made recently[31,32]. Further improvements could allow fiber drawing.

The practical interest of these glasses lies in their extended IR transmission by comparison with fluorozirconate glasses. Their lower phonon energy should increase the performances of active fibers, and their lower optical losses in the mid IR could make possible power delivery from CO_2 laser.

An interesting feature is the occurrence of numerous binary glasses:

- InF_3-BaF_2, -SrF_2, -PbF_2
- GaF_3-CaF_2, -SrF_2, -BaF_2, -PbF_2, -CdF_2, -YF_3

From these binary associations, numerous ternary and multicomponent systems have been investigated. As an example, figures 3 and 4 show typical vitreous areas in ternary or quartenary systems based on gallium or indium trifluorides. It was found that fluoroindate glasses could be stabilized by In/Ga substitution and by the incorporation of Cd, Gd, Ca and Na. From glasses belonging to the vitreous area displayed in figure 5 it is possible to cast samples more than 15 mm thick.

A set of investigations implemented with fluorogallate glasses has led to a significant increase in stability. Sample thickness may reach 11 mm, which should enhance the practical use of these glasses. A representative glass forming system is described in figure 6.

Some glass compositions are displayed in Table III.

III.5. Other fluoride glasses

As outlined previously, glass formation is rather common in fluoride systems. The three groups described previously -fluorozirconate, fluoroaluminate, fluoroindate- are emerging because of their applications. Many other glasses have been reported and investigated. Most of them originate from studies prior

Table I - Fluorozirconate glass compositions (mole %)

	HfF$_4$	ZrF$_4$	BaF$_2$	LaF$_3$	ThF$_4$	NaF	LiF	MF$_n$	AlF$_3$
ZBL		62	33	5					
3BL	62		33	5					
HBT	60		33		7				
ZBNT		50	20		7.5	20			
ZBLN		58	15	6		21			
ZTL		60		10	30				
ZTA		50			43				7
ZBLA		57	34	5					4
HBLA	58		33	5					4
ZBCA		60	32					4 CaF$_2$	4
ZBYA		45	36					11 YF$_3$	4
ZBGA		60.5	31.7					3.8 GdF$_3$	4
ZBTA		57	29		10				4
ZBNA		52	24			20			4
ZBLiA		52	26				18		4
ZBLiLA		52	21	5			19		3
ZBLAN		53	20	4		20			3

Table II - Fluoroaluminate glass compositions (mole %)

	AlF$_3$	YF$_3$	ThF$_4$	BaF$_2$	CaF$_2$	PbF$_2$	CdF$_2$	LiF	SrF$_2$	ZrF$_4$	NaF	MgF$_2$
AB	50			50								
APMS	40					24			12			2
BATY	28.7	28.7	22.6	20								
YABC	40	20		20	20							
ABCYS	40	16		12	22				10			
CLAP	30.6					33.3	26.1	10				
BACSZNM	30.2			10.6	20.2				13.2	10.2	3.8	3
BATYN	30	30	15	5							10	
BATYLi	30	10	15	15				30				
ATYMLN	25	25	15					5			20	1
BAMYNC	30	30		20	2						5	1
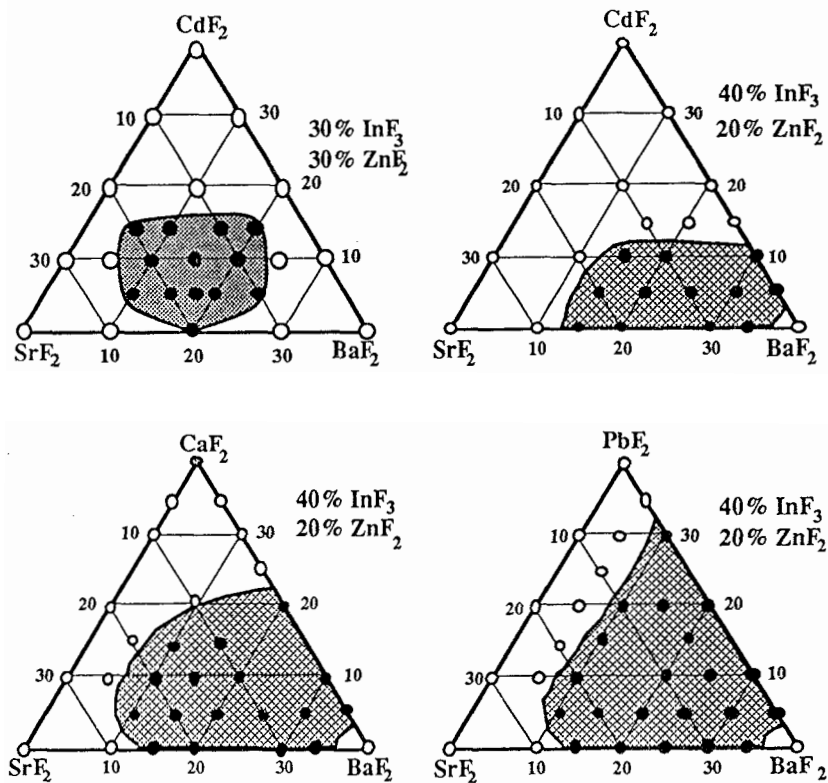
Figure 4: Glass forming areas in the InF_3-BaF_2-SrF_2-ZnF_2-CdF_2 systerns, (M=Cd,Ca,Pb). Open circles correspond to quenched glasses.

Table III - Trivalent fluoride glass compositions (mole %)

	GaF$_3$	InF$_3$	YF$_3$	BaF$_2$	SrF$_2$	PbF$_2$	CdF$_2$	ZnF$_2$	MgF$_2$	NaF	MF,
GNP	45					25				30	
GKP	45					25					30 KF
GCB	50			20			30				
CGI	35	15					50				
GSY	50		20		30						
GYB	45		45	10							
GYC	50		20				30				
GYSBM	50		16	13	15				6		
GYSBIMP	45	4	16	14	15	2			4		
GYCBI	45	5	17	16							17 CaF$_2$
GCCBSY	50		10	10	10		10				10 CaF$_2$
GZnBSCN	40			10	10		10	20		10	
IPB		50		20		30					
ISB		15				50		35			
IBG		20	45		35						
IBM		55		40					5		
PIZn					32					46	22
BIY		40	17	43							
IBYP		40	17	32		11					
BIZnYT		30	10	30				20			10 ThF$_4$
BIGaZYbT	12	18	10(Yb)	30				20			10 ThF$_4$
IZnSBC		40		15	20		5	20			
IBZnPS		40		20	5	15		20			
IBZnCN		40		25			5	20		10	
PZnIGL	17	17			43			19			4LaF$_3$
IBZnSGL	4	36		20	19			20			1LaF$_3$
ISZnBGGN	6	34		16	20			20		2	2GdF$_3$

Table IV - Miscellaneous glass compositions (mole %)

	ZnF_2	CaF_2	BaF_2	SrF_2	CdF_2	PbF_2	ThF_4	LiF	NaF	UF_4	YbF_3	YF_3	ScF_3	FeF_3
ZnS	60			40										
CdB			50		50									
ZnBCd	20		40		40									
ZnBSC	60	10	10	20										
ZnSCBCd	50	5	12.5	20	12.5									
BZnYbT	28.3		15				28.3				28.3			
TL							30	70						
TLB			10				30	60						
TLNB			8				20	36	36					
TBZn	40		20				40							
UNL1								30	20	50				
ULN2								60	10	30				
FNP						25		30						45
FPZn	33					33								33
SBY			40									20	40	
SBNY			30						20			5	45	

Table V - Mixed anion fluoride glasses (mole %)

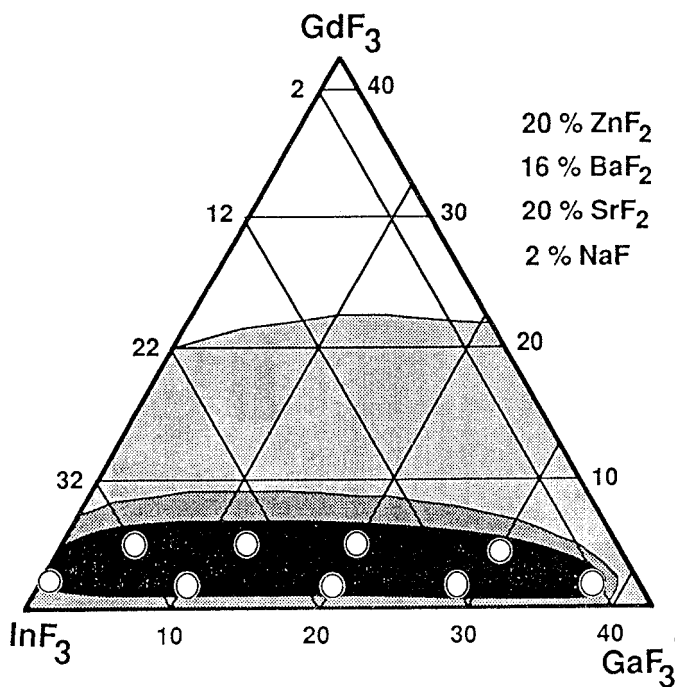|	CdF_2	$CdCl_2$	BaF_2	$BaCl_2$	NaCl	KCl	$PbCl_2$
CBX2	65	2		33			
CBNX2	49	4		11	36		
CKPX	40				40		20
CBX1	40	30	**30**				
CBN1	42	11	11		36		
CKX	15	45				40	
AgAlF	40 AgI		45 AgF	10 AlF3			
NbBCOF	30 NbO_2F		40 BaF_2	30 CdF_2			
NbBCKOF	30 NbO_2F		30 BaF_2	30 CdF_2	10 KF		
NbTiBCOF	20 NbO_2F	10 $TiOF_2$	40 BaF_2	30 CdF_2			
TiBNCOF	30 $TiOF_2$		30 BaF_2	20 NaF	20 CdF_2		

Figure 5: Vitreous fluoroindates in a multicomponent glass forming system. Darker area corresponds to very stable glasses allowing the synthesis of thick samples.
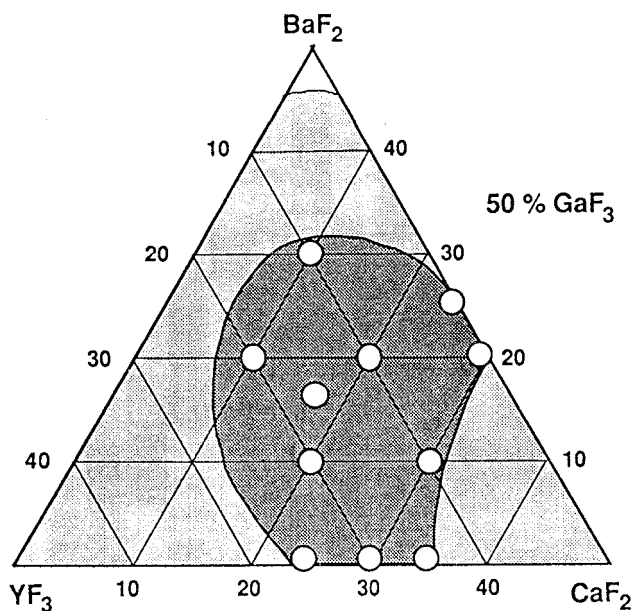

Figure 6: Glass forming area in the quartenary GaF_3-BaF_2-YF_3-CaF_2 system. Thick samples may be obtained in the inner area.

to 1980 which made the basis of two patents. These fluoride glasses may be described as follows.

III.5.1. Transition metal fluorides

Vitreous phases based on the association of transition metals with alkali cations, silver and lead, were reported by Miranday et al.[34]. This concerns trivalent cations: V^{3+}, Cr^{3+}, Fe^{3+} and also Ga^{3+} and divalent transition metals: Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}. Most of these glasses must be prepared by fast cooling.

Among these materials, fluorozincate glasses were more studied because they are colorless. It was found that they could be stabilized by the incorporation of higher charged cations: Al, Ga, In, Yb, Th. Also, large similarities were observed between fluorozincate and fluoromanganate glasses.

III.5.2. Fluoroscandate glasses

Several systems involving ScF_3 and BaF_2 have been reported, for example ScF_3-YF_3-BaF_2[45]. Such studies are limited because of the scarcity of scandium compounds. These glasses exhihit good chemical durahility and fair glass forming ability

III.5.3. Thoriuin fluoride glasses

Because of the clear stabilizing effect of thorium fluoride in numerous glasses, it is not surprising that it could form glass in association with various fluorides. A binary ThF_4-LiF glass exists around 70% LiF, and ternary glasses deriving from this association have been reported[46]. Vitreous phases have been prepared in the ThF_4-BaF_2-LnF_3 ternary systems.

III.5.4. Miscellaneous fluoride glasses

Various fluoride glasses have been reported in different systems. First, numerous glasses may be obtained from UF_4 and presumably from actinide tetrafluorides[33]. Rinary CdF_2-BaF_2 glasses may be prepared by quenching[45]. Also heavy alkali fluorides may be stabilized in the vitreous form by a limited addition of ZnF_2. In spite of its volatility, TiF_4 may also form vitreous glasses[33].

III.6. Mixed anion fluoride glasses

While most studies focus on fluoride glasses, numerous glasses may be formed in polyanionic systems. The most classical group is that of oxyfluoride glasses, mainly fluorophosphates. It could also encompass fluorosilicate glasses. As the scope of this review is restricted to IR transmitting glasses, only heavy metal oxyfluoride glasses are described. They derive from the oxyfluorides of niobium and titanium with divalent or monovalent fluorides. Typical examples are NbO_2F-BaF_2-CdF_2 and $TiOF_2$-BaF_2-CdF_2[47]. Tungsten oxyfluoride glasses make another possibility.

A much larger group is made from polyhalide glasses. Cadmium fluorohalide glasses appear as promising rriaterials because of their extended IR transmission correlated with low phonon energy. Some of these glasses may be cast as thick samples and could be good candidates as optical fiber materials.

Numerous new polyhalide glasses can be synthesized from standard fluoride glasses by tlie incorporation of heavy halides. For example, it has been shown that large amounts of alkali chlorides could be dissolved in fluorozirconate glasses. Aluminum silver fluoroiodide glasses make another example.

Some examples of such glasses are displayed in Table V.

IV. Physical properties

IV.1. Structure

Structural characterizations are a major part of solid state chemistry. While X-ray diffraction provide essential information for crystalline compounds, it is much less accurate and easy to use for glasses. Several studies have been carried out on the structure of fluoride glasses, using diffraction, spectroscopy and computer simulation[48]. Beyond the discrepancy between possible models, several features are now emerging:

1) Coordination numbers and bond lengths are close to the values observed in crystalline phases containing the same cations. In other words, short range ordering is largely the same in glass and in crystal.

2) In the case of fluorozirconate glasses, tlie average coordination number of Zr versus F is 8, which is also consistent with a high compactness.

3) The coordination number of barium varies between 10 and 12 depending on coniposition.

4) Glass structure may be described as a random network of ZrF_8, AlF_6, LnF_8 polyhedra, sharing corners and edges and trapping large cations, e.g. Na^+, Ba^{2+}.

5) Another description is that of a random packing of F^- and Ba^{2+} ions in which small cations - Zr^{4+}, Al^{3+}, Zn^{2+} - are randomly inserted[49].

IV.2. Characteristic ternperatures

For a glass, there are three temperatures which are major thernial references. They correspond to glass transition (T_g), melting (T_m) and onset of crystallization (T_x). A:; this later phenomenori depends on time, the corresponding temperature is usually measured for a heating rate of 10 K min^{-1}.

Fluoride glasses exhibit rather low T_g. It ra ges from 200°C for alkali rich fluoride glasses to 500° C for some bariurr and alkali free glasses. Melting temperature, which is roughly correlated to T_g according to the 2/3 rule nay vary between 400 and 900°C. There is some uncertitinty about melting teniperature as some authors report only tlie first onset of melting while

Table VI - PHYSICAL CHARACTERISSICS OF TYPICAL FLUORIDE GLASSES. T_g, T_x and T_m are temperatures for glass transition, onset of crystallization and melting respectivelly. Values are expressed in degrees Celsius. n_D is the refractive index, α is the coefficient of thermal expansion and d is the average density in (g/cm^3).

Glass	T_g	T_x	T_m	n_D	α $(10^{-7}K^{-1})$	d
ZBT	315	395	532	1.524	180	4.86
ZBL	315	389	547	1.529	170	4.60
ZTL	450	550	800	1.547	109	5.25
ZBLA	320	392	513	1.519	168	4.54
ZBWA	258	344	450	1.495	205	4.28
ZBLAN	262	352	455	1.498	200	4.35
HBLA	312	390	520	1.504	170	5.88
BATY	446	554	710	1.487	147	5.10
YABC	430	535	710	1.440	165	4.0
SYB	360	410	720	1.499	180	4.38
TLB	256	310	560	1.495	205	5.29
ZnSCBCd	302	348	560	1.507	185	4.91
BZnYbT	344	426	665	1.538	151	6.43
IZnSBC	292	383	409	1.498	183	5.10
BIZnYbT	324	440	650	1.517	171	5.66
NOBCN	308	348	600	1.657	190	5.10

others measure liquids temperatures from tlie last endothermic peak.

Characteristic temperatures of standard fluoride glasses are summarized in Table VI. It appears that these temperatures are higher for fluoroaluminates and fluorogallates, while InF_3-. ZrF_4- and HfF_4- and HfF_4-based glasses exhihit close values. The separation between T_g and T_x reflects the tendency of the glass to devitrify on reheating. For tliis reason, it is often used as a criterion for stability assessment.

IV.3. Optical properties

I-Ieavy metal fluoride glasses are transparent in tlie infrared (IR) spectrum beyond 7 μm, depending on sample thickness and glass composition. Tlie IR cut-off is ruled by the nature of tlie ligliter cation and its concentration. As a general rule, the position of IR edge is shifted toward longer wavelengtlis according to tlie sequence:

$$AlF_3 < ZrF_4 < HfF_4 < ScF_3 < GaF_3 < InF_3.$$

It is assumed that Mg and Li have nearly the same influence as Al. The contribution of Ba, Sr, Pb and La may be neglected. Th and Zr are equivalent to In.

UV transmission is expected to be superior to that of oxide glasses, because of a theoretical higher gap between electronic states. In practice, this may not be

tween electronic states. In practice, this may not be the case as impurity content - namely transition metals - is much higher in HMFG than in pure silica.

The measured values of refractive index are in the range 1.45 and 1.55. This medium value results for the association of heavy cations with fluorine anions which have opposite effects on polarizability. Refractive index n_D is correlated with composition. This is used for the design of fiber optics structures.

Fluoride glasses exhibit low dispersion and negative dn/dT.

IV.4. Other physical properties

Average density of HMFG lies between 4 and 6 g/cni^3 (Table VI). Denser glasses may be prepared from lead fluorohafnate glasses and lighter from lithium fluoroaluminates.

Fluoride glasses appear as rather soft materials by comparison with oxide glasses. They compare rather well with chalcogenide glasses.

Thermal expansion is rather high and ranges from 140 to 200 K^{-1} for most fluoride glasses , although some exotic glasses are outside these values. Thermal expansion is correlated with barium and alkali concentrations, and, in a more general way, with the value of T_g.

Fluoride glasses are not severely corroded by atmospheric moisture, but they undergo a surface attack when exposed to liquid water. The rate of attack depends on pH and also on glass composition. Some fluoride glasses are stable in aqueous solutions: this is the case for some fluoroaluminate and fluoroindate glasses.

V. Conclusion

After more than 15 years of development, fluoride glasses have been found to exist in numerous multicomponent systems. Major families of heavy metal fluoride glasses are fluorozirconates, fliioroaluminates and fluoroindates. The later group exhibit superior IR transmission and good chemical durability.

Significant improvements have been achieved for glass stabilization and optical quality. Correlation between composition and physical properties is being qiiantified. The important development needed for the achievement of reliable optical fibers for sensor, optical amplification and transmission may take advantage of the large number of informations collected in the study of exotic systems.

References

1. M. Poulain, M. Poulain, J. Lucas and P. Brun Mat. Res. Bull. 10, 243 (1975).
2. Y. Miyajima, T. Sugawa and Y. Fukasaku, Electron. Lett., 27, 1706 (1991).
3. M. Poulain aiid G. Maze, Chenitronics, 3, 77 (1988).
4. S. F. Carter, P. W. France and J. R. Williams, Phys. Chem. Glasses 27, 42 (1986).
5. K. H. Sun "Fluoride Glass", U. S. Patent 2, 466, 509 (5-4-49) (1946).
6. M. Robinson, R. C. Pastor, R. R. Turk, M. Braustein and R. Braunstein, Mat. Res. Bull. 15, 735 (1980).
7. M. G. Drexhage, C. T. Moynihan, B. Bendow, E. Gbogi, K. H. Chung and M. Boulos, Mat. Res. Bull. 16, 943 (1981).
8. M. Robinson, Mat. Sci. Forum 5, 19 (1985).
9. D. C. Tran, G. H. Sigel and B. Bendow, J. Lightwave Techn. **LT2,** 5, 566 (1984).
10. D. Trégoat, G. Fonteneau and J. Lucas, Mat. Res. Bull. 20, 179 (1985).
11. G. G. Devyatykh, M. F. Cherbanov and E. M. Dianov, Mat. Sci. Forum, 19-20, 187 (1987).
12. T. Nakai, Y. Mimura, H. Tokiwa and 0 . Shinbori, J. Lightwave Techn. **LT4**, 87 (1986).
13. N. Mitachi, T. Shindo and S. Shibata, Jap. Patent Application 124042-1980 (1982).
14. K. Fujiura, Y. Ohishi, S. Sakagushi and Y. Terunuma, Mat. Sci. Forum 32-33, 25 (1988).
15. P. J. Melling and M. A. Thomson, J. Mater Res. 5, 1092 (1990).
16. M. Poulain and M. Saad, Paper 31G, presented at the 94th American Ceram. Society Meeting, Minneapolis, April 1992.
17. A. M. Mailhot, R. E. Riman and A. Elyamani, Paper 29 G, presented at the 94th American Ceram. Society Meeting, Minneapolis, April 1992.
18. A. Lopez, Thèse de l'Université de Rennes, 1991.
19. P. Lebeau, Compt. Rend. Acad. Sc., **126,** 1418 (1898).
20. K. H. Sun and T. E. Callear, "Fluoride Glasses", U.S. Patent 2,466,506 (5-4-49)(1946).
21. M. Poulain and J. Lucas, Verres Réfract. 32, 505 (1978).
22. **A.** Lecoq and M. Poulain, J. Non-Cryst.Solids, **34,** 101 (1979).
23. M. G. Drexhage, B. Bendow, and C. T. Moynihan, Laser Focus, 10, 62 (1980).
24. A. Lecoq and M. Poulain, Verres Réfrac. 34, **333** (1980).
25. M. Poulain, Compositional dependence of physical properties in fluoride glasses, in *The Physics of non-Cystalline Solids, L.* David Pye, W. C. LaCourse and H. J. Stevens Eds., (Taylor & Francis, London, 1992).
26. J. J. Videau, J. Portier and B. Piriou, Rev. Chim. Min., 16, 393 (1979).
27. T. Kanamori, K. Oikawa, S. Shibata and T. Manabe, Jap. J. Appl. Phys., 20, L326 (1981).
28. M. Poulain, M. Poulain and M. Matecki, Mat. Res. Bull., 16, 555 (1981).
29. M. Poulain, M. Poulain and M. Matecki, J. Non-Crys.Solids, 51, 201 (1982).

30. P. A. Tick, Mat. Sci. Forum, 32-33, 115 (1988).

31. T. Izumitani, T. Yamashita, M. Tokida, K. Miura and H. Tajima, Mat. Sci. Forum, 19-20, 19 (1987).

32. M. R. Shahriari, T. Tqbal, G. H. Sigel and G. Merberg, Mat. Sci. Forum, 32-33, 99 (1988).

33. M. Poiilain, M. Poulain and G. Maze, Fluoride glasses, Fr. Pat. 24 78 618 (1980).

34. J. P. Miranday, C. Jacoboni and R. De Pape, Glasses containing fluorine: their preparation and application - Eur. Pat. 17 566 B1 (1980).

35. J. J. Videau, B. Dubois and J. Portier, C. R. Acad. Sci., 297, 483 (1983).

36. N. Auriault, J. Guery, A. M. Mercier, C. Jacoboni and R. De Pape, Mat. Res. Bull., 20, 309 (1985).

37. J. J. Videau, J. M. Dance, J. Portier and B. Dubois, Rev. Chim. Min., 23, 789 (1986).

38. M. Poulain and M. Poulain, Mat. Sci. Forum, 32-33, 137 (1988).

39. A. Bousggad, G. Fonteneau and J. Lucas, Rev. Chim. Min., 24, 129 (1987).

40. M. Poulain and Y. Messaddeq, J. Non-Cryst. Solids, 140, 41 (1992).

41. J. Nishii, Y. Kaite and T. Yamagishi, Phys. Chem. Glasses, 30, 55 (1989).

42. I. Chiaruttini, Thèse de l'Université de Rennes, (1990).

43. M. Matecki, M. Poulain and M. Poulain, Mat. Res. Bull., 16, 749 (1981).

44. G. Fonteneau, H. Slim and J. Lucas, J. Non Cryst. Solids, 44, 31 (1982).

45. M. Poulain, M. Poulain and M. Matecki, Mat. Res. Bull., 17, 661 (1982).

46. M. Poulain and M. Poulain, J. Non-Cryst. Solids, 56, 57 (1983).

47. M. Poulain and M. Poulain, Mat. Sci. Forum, 67-68, 129 (1991).

48. J. H. Simmons, C. J. Simrnons, R. Ochoa and A. C. Wright in *Fluoride glass fiber optics,* I. Aggarwal and G. Lu Eds., (Academic Press, NY, 1991) pg. 37-84.

49. M. Poulain, Nature, 293, 279 (1991).