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New multicomponent fluoride glasses

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New glass compositions have been investigated in the barium-, indium- and gallium-based glass system (BIG). Radioactive thorium has been completely removed and replaced by gadolinium, and these new glasses have been stabilized by substituting barium by alkali ions. Characteristic temperatures T_g, T_x and T_l, and the Hruby factor, H_r, have been determined for each glass. The most significant critical cooling rates, R_c, are also given: both the highest H_r and the lowest R_c values for BIG thorium-free glasses were obtained by coupling two alkali ions. Some attempts have also been made to replace thorium by cerium (IV), leading to cerium(III)-containing glasses. The synthesis of cerium(IV)-containing fluoride glasses seemed to be impossible. Nevertheless, CeF_4 has been synthesized, the knowledge of its lattice parameters being improved.

1. Introduction

The most studied fluoride glasses remain the ZrF_4–BaF_2-based ones. These studies have shown that the best glass in this family, called ZBLAN, was obtained by substituting Ba^{2+} by Na^+. ZBLAN is, to date, the best fluoride glass with respect to its thermomechanical properties, but its cut-off occurs at 6 μm, compared with 8 μm for BaF_2–InF_3-based glasses. During the last 5 years, the stability of these last glasses has been greatly improved, resulting in the so-called BIG glasses [1], which are nearly as stable as ZBLAN but still contain 10% radioactive Th^{4+}, which must now be suppressed. Th^{4+} must be substituted by a cation able to fill its place in the vitreous network without injuring the optical characteristics of the glass. Two ways seem to be possible: the first is the substitution of Th^{4+} by Gd^{3+}, which has the same ionic radius (0.105 nm in coordination VIII [2]) and, though paramagnetic, does not exhibit any absorption peak above 310 nm [3]. The second is the substitution of ThF_4 by an isostructural fluoride MF_4 (with M = Zr, Hf, or Ce); Zr^{4+} and Hf^{4+} being too small, the only non-radioactive candidate appears to be CeF_4. In this paper, we examine the effects of Th^{4+} removal and Ba^{2+} substitution by alkali ions on the stability of the glass.

2. Experimental procedure

Both ThF_4- and GdF_3-containing glasses were synthesized as follows: the starting materials, metallic fluorides and oxides, were mixed with NH_4F, HF and heated at 300 °C for 3 h. The excess of NH_4F, HF was then sublimated at 500 °C, and the mixture was melted in a dry box between 800 and 850 °C. The melt was poured at 700 °C into a brass mould preheated at 260 °C, and the glass was then annealed at this temperature. Each sample was obtained as a 5 mm thick bulk.

As cerium(IV) fluorides are reduced by NH_4F, HF, CeF_4 and $BaCeF_6$ were added to the mixture just before the melting of CeF_4-containing glasses in the dry box. Furthermore, CeF_4 melts incongruently at about 835–841 °C [4], leading to a $CeF_{3.78 \pm 0.03}$ liquid in an open system [5]. Consequently, some of these glasses were prepared under an oxidizing NF_3 flow.

CeF_4 and $BaCeF_6$ were prepared by treating CeO_2, CeF_3 and BaF_2 by pure gaseous fluorine (6 h, 1.5 atm, 520° C). They were characterized by weighing and by X-ray diffraction.

The glass transition, crystallization and liquidus temperatures (T_g, T_x and T_l, respectively) of each glass were measured by differential thermal analysis and differential scanning calorimetry with heating rates of 10 K min^{-1}. The Hruby factor, H_r, was calculated as $H_r = (T_x - T_g)/(T_l - T_x)$ [6]. The critical cooling rate, R_c, was calculated as previously described [7], with cooling rates ranging from 2–11 K min^{-1}.

The critical cooling rate, R_c, and the Hruby factor, H_r, are very different parameters, even though not really independent. This empirically observed fact has been mathematically demonstrated [8]. In fact, the critical cooling rate is only linked to the glass-forming ability of a system, i.e. to the ease by which a melt can be cooled to form a glass without any crystal formation. The Hruby factor measures the glass stability, i.e. the resistance of the glass towards devitrification upon reheating, and is therefore the most significant criterion for our purpose.

3. Substitution of thorium by gadolinium

We will first mention the best glasses obtained to date by substituting some components of thorium-containing BIGaZYbT ($Ba_{30}In_{18}Ga_{12}Zn_{20}Yb_{10}Th_{10}F_{260}$).

TABLE I Characteristic temperatures, Hruby factor and critical cooling rate for glasses derived from BIGaZYbT

Substitution	T_g (°C)	T_X (°C)	T_l (°C)	H_r	R_c (K min^{-1})	Ref.
None	345	472	610	0.9_2	18	[1]
$5BaF_2 \rightarrow 5LiF$	310	460	596	1.1_0	12	[9]
$12.5BaF_2 \rightarrow 12.5NaF$	302	445	601	0.9_2	7	[9]
$5BaF_2 \rightarrow 5KF$	335	474	609	1.0_3	24	[9]
$4ZnF_2 \rightarrow 4MnF_2$	350	472	610	0.8_8	5	[1]
$4ThF_4 \rightarrow 4ZrF_4$	328	460	609	0.8_9	6	[1]

TABLE II Characteristic temperatures and Hruby factor for BIGaZYbTh$_{10-x}$Gd$_x$ glasses

Th	Gd	T_g(°C)	T_x(°C)	T_l(°C)	H_r
10	0	345	472	610	0.9_2
7.5	2.5	343	484	601	1.2_1
5	5	343	489	598	1.3_4
2.5	7.5	341	478	622	0.9_5
0	10	349	468	631	0.7_3

The stability of each glass is characterized both by determinating its Hruby factor, H_r, and critical cooling rate, R_c. The results, collected in Table I, show the great ability of BIGaZYbT to be stabilized by variations of its nominal composition.

Consequently, we tried to stabilize in this way a GdF_3-containing thorium-free BIG glass. First, thorium has been gradually removed from BIGaZYbT and replaced by gadolinium. Table II shows that the thorium-free glass, called BIGaZYbGd, remains stable enough to be regarded as a quite interesting glass which can be stabilized by subsequent substitutions. In addition, its critical cooling rate is 23 K min^{-1}, which means it is almost as convenient as BIGaZYbT. The intermediate composition shown here is noticeable by its widely improved H_r.

It has been shown [1] that the substitution of 4% YbF_3 by GdF_3 induces a significant decrease of the critical cooling rate of $Ba_{30}In_{30}Zn_{20}Yb_{10}Th_{10}F_{260}$ glass (BIZYbT), i.e. from 120 K min^{-1} to 74 K min^{-1}. Consequently, BIGaZYb$_x$Gd$_{20-x}$ glasses have been synthesized for $x = 6, 8, 10, 12$ and 14. But the most stable glass remains BIGaZYbGd.

Many attempts have therefore been made to improve the stability of BIGaZYbGd by substituting some of its components. For that purpose, cations such as Mn^{2+}, Zr^{4+}, Na^+, Li^+, K^+ and Cd^{2+} have successively been used, separately or together.

3.1. Incorporation of Mn^{2+} or Zr^{4+}

It is obvious from Table I that Mn^{2+} and Zr^{4+} induce the most spectacular decrease of the critical cooling rate of thorium-containing glass, without injuring its Hruby factor. Because it is too small, Zr^{4+} cannot replace totally Th^{4+} without destabilizing the glass and shifting the cutoff towards shorter wavelengths, but up to 4% ZrF_4 can easily be incorporated in thorium-containing BIGaZYbT. Table III shows the Hruby factors for the analogous thorium-free glasses and for two others obtained by different distributions of ZrF_4. It is unmistakable from both the H_r value and more significant the shape of the experimental DTA curves that MnF_2 is prejudicial to the stability of BIGaZYbGd. However, ZrF_4-containing glasses seem to be slightly stabilized as shown by the increase of their H_r values. In fact, their critical cooling rates are higher than 50 K min^{-1}. The synthesis of a glass containing both 4% ZrF_4 and 4% MnF_2 requires a quenching step.

3.2. Substitution of Ba^{2+} by an alkali ion–influence of Cd^{2+}

Among the alkali-containing glasses displayed in Table I, the best R_c and H_r belong, respectively, to those containing sodium and lithium.

Several glasses have been made by substituting Ba^{2+} by Na^+ in BIGaZYbGd. Table IV reveals that the best H_r is obtained for 10% Na^+. This BIGaZYbGdNa10 glass also exhibits a quite good R_c close to 15 K min^{-1}. However, an attempt to synthesize a 50 g bulk failed, resulting in a partial devitrification.

The 5% LiF-containing glass was not much stabilized ($T_g = 314$ °C, $T_x = 443$ °C, $T_l = 610$ °C; $H_r = 0.77$) compared to BIGaZYbGd, and the 5% KF-containing was slightly destabilized.

Cadmium has been found [1] to decrease the stability of BIZYbT when substituted for barium. But, as Ga^{3+}/In^{3+} or Zr^{4+}/Th^{4+}, which are pairs of analogous cations, it is hoped that Cd^{2+} will stabilize a glass when substituted for Zn^{2+} instead of Ba^{2+}. This latter hypothesis is unambiguously confirmed here: 3% CdF_2 widely improved the Hruby stability factor of the 5% lithium-containing glass presented in the previous paragraph: for the Li–Cd-containing glass, $T_g = 293$ °C, $T_x = 437$ °C, $T_l = 604$ °C; $H_r = 0.86$.

TABLE III Characteristic temperatures and Hruby factor for MnF_2- and ZrF_4-substituted thorium-free BIG glasses

Ba	In	Ga	Zn	Mn	Yb	Gd	Zr	T_g(°C)	T_x(°C)	T_l(°C)	H_r
30	18	12	20	–	10	10	–	349	468	631	0.7_3
30	18	12	16	4	10	10	–	343	453	628	0.6_3
30	18	12	20	–	10	6	4	336	458	616	0.7_7
28	18	12	20	–	10	7	5	333	458	618	0.7_8
25	18	12	20	–	10	10	5	324	460	625	0.8_2

TABLE IV Characteristic temperatures and Hruby factor for $Ba_{30-x}Na_xIn_{18}Ga_{12}Zn_{20}Yb_{10}Gd_{10}$ fluoride glasses

x	T_g (°C)	T_x (°C)	T_l (°C)	H_r
0	349	468	631	0.7_3
2	339	454	620	0.6_9
4	337	462	617	0.8_1
6	334	463	611	0.8_7
8	326	464	604	0.9_9
10	307	448	584	1.0_4
12	312	444	580	0.9_7
14	313	418	605	0.5_6
15	300	414	601	0.6_1
16	301	415	606	0.6_0

TABLE V Characteristic temperatures and Hruby factor for $Ba_{30-x}Na_xIn_{18}Ga_{12}Zn_{20-y}Cd_yYb_{10}Gd_{10}$ fluoride glasses

x	y	T_g (°C)	T_x (°C)	T_l (°C)	H_r
10	4	314	441	596	0.8_2
13	4	308	424	576	0.7_6
15	4	291	420	566	0.8_8
12	3	308	440	582	0.9_3
14	3	300	452	575	1.2_4
15	3	290	438	563	1.1_8
16	3	295	435	566	1.0_7

Because Na^+ is better than Li^+ for our purpose; several glasses, displayed in Table V, have been synthesized in order to add the beneficial effects of Na^+ and Cd^{2+}. The first glasses, which contain 4% CdF_2, are more stable than BIGaZYbGd, but less stable than BIGaZYbGdNa10. Nevertheless, it is obvious from the 15% sodium-containing glass that Cd^{2+} allows the glass to admit much more Na^+ than it could without CdF_2 (see Table IV). Consequently, other glasses have been synthesized, containing 3% CdF_2 and much NaF. In this last system, two glasses exhibit a spectacular increase of H_r. The shapes of the experimental DTA curves suggest that the 15% sodium-containing glass should be at least as stable as the 14% one. But its critical cooling rate ($R_c = 32\ K\ min^{-1}$) remains too high. So it is still necessary to continue to stabilize these glasses, in order to improve both their H_r and R_c.

3.3. Incorporation of Na^+, Li^+ and Cd^{2+}

It was then reasonable to next investigate the lithium-, sodium- and cadmium-containing system.

TABLE VI Characteristic temperatures and Hruby factor for $(Ba, Li, Na)_{30}In_{18}Ga_{12}Zn_{17}Cd_3Yb_{10}Gd_{10}$ fluoride glasses

Ba	Li	Na	T_g (°C)	T_x (°C)	T_l (°C)	H_r
15	0	15	290	438	563	1.1_8
14	2	14	277	434	571	1.1_5
13.5	3	13.5	271	427	582	1.0_1
13	4	13	270	431	580	1.0_8
12.5	5	12.5	264	430	561	1.2_7
12	6	12	265	417	584	0.9_1
11	8	11	263	391	577	0.6_9
27	3	0	320	450	610	0.8_1
22	3	5	291	428	585	0.8_7
19.5	3	7.5	275	432	591	0.9_9
17	3	10	284	446	581	1.2_0
15	3	12	281	435	572	1.1_2
13.5	3	13.5	271	427	582	1.0_1
12	3	15	268	435	585	1.1_1
10	3	17	267	403	576	0.7_9
25	5	0	293	437	604	0.8_6
20	5	5	279	419	577	0.8_9
17.5	5	7.5	283	426	579	0.9_3
15	5	10	278	419	569	0.9_4
13.5	5	11.5	273	426	570	1.0_6
12.5	5	12.5	264	430	561	1.2_7
10	5	15	268	419	566	1.0_3

TABLE VII Characteristic temperatures and Hruby factor for $(Ba, Li, Na)_{30}In_{18}Ga_{12}Zn_{16}Cd_4Yb_{10}Gd_{10}$ fluoride glasses

Ba	Li	Na	T_g (°C)	T_x (°C)	T_l (°C)	H_r
20	2.5	7.5	303	437	596	0.8_4
17.5	2.5	10	302	436	580	0.9_3
15	2.5	12.5	299	434	569	1.0_0
12.5	2.5	15	278	432	566	1.1_5
13.5	3	13.5	281	430	569	1.0_7
12.5	5	12.5	275	428	568	1.0_9
15	5	10	276	432	574	1.1_0

The main attempts, presented in Table VI, deal with 3% CdF_2 glasses. The first series taken into account, with equal amounts of Ba^{2+} compared to Na^+, clearly shows that the best glasses in this system contain 5% or less LiF. Consequently, two more series have been studied, containing respectively 3% and 5% LiF with increasing NaF amount. Eventually, the best glass in this whole system seems to be that containing $12.5BaF_2$–5LiF–12.5NaF, for which the Hruby factor (1.27) is the highest so far obtained, and which also exhibits the best critical cooling rate ($R_c = 13\ K\ min^{-1}$) among the thorium-free glasses so far discussed in this paper; nevertheless, other compositions are of great interest in this system, including the $14BaF_2$–2LiF–14NaF, the critical cooling rate of which is equal to $20\ K\ min^{-1}$. This system includes many glasses which exhibit better Hruby factors than the thorium-containing ones.

Next, few glasses containing 4% CdF_2 were synthesized (Table VII). They remain quite stable even if none is better than the best previously obtained.

This study has indicated the lack of affinity between thorium-free BIG glasses and Mn^{2+} or, to a lesser degree, Zr^{4+}, cations which are, however, of great interest to increase the glass-forming ability of BIGaZYbT. Although quite difficult to explain, this fact is not that surprising. In fact, such selective affinities have already been shown; for instance, Na^+ and Li^+, which improve both the glass-forming ability and the glass stability of BIG glasses, are injurious to gallium-free BIZYbT [10].

Results such as those presented in Table VII reveal that the corresponding eutectic well is of noticeable width, which is significant in discussing the interest of a glassy system.

TABLE VIII Lattice parameters of monoclinic CeF_4 in the space group $C_{2/c}$

	a (nm)	b (nm)	c (nm)	β (deg)
Zachariasen [12]	1.26 ± 0.01	1.06 ± 0.01	0.83 ± 0.01	126 ± 1
Present work	1.260 (0.001)	1.063 (0.001)	0.825 (0.001)	126.31 (0.06)

TABLE IX Starting materials used to try to prepare cerium-containing glasses analogous to stable BIG glasses (mol %)

Name	BaF_2	NaF	InF_3	GaF_3	ZnF_2	YbF_3	YF_3	ThF_4	CeF_4	$BaCeF_6$	CeF_3
BIGaZYbT	30	–	18	12	20	10	–	10	–	–	–
BIGaZYbTNa	20	10	18	12	20	10	–	10	–	–	–
C1	30	–	18	12	20	10	–	–	10	–	–
C2	20	–	18	12	20	10	–	–	–	10	–
C3	30	–	18	12	20	10	–	5	5	–	–
C4	25	–	18	12	20	10	–	5	–	5	–
C5	20	10	18	12	20	10	–	5	5	–	–
C4Y	25	–	18	12	20	–	10	5	–	5	–
C5Y	20	10	18	12	20	–	10	5	5	–	–
C6Y	30	–	18	12	20	–	10	5	–	–	5

4. Substitution of thorium by cerium

Cerium(IV)-containing fluorides have been prepared, respectively, from CeO_2, CeF_3, and a mixture of $CeF_3 + BaF_2$. The purity of each final product is equal to the efficiency of the oxidant fluorination performed by F_2: each has been found higher than 99%. $BaCeF_6$ has also been identified by its X-ray diffraction pattern, which is similar to that previously described [11]. The structure of CeF_4 had been announced [12], from its well-known isostructural fluorides such as ZrF_4 or UF_4 which crystallize in a monoclinic system with the space group $C_{2/c}$. From our experimental data, knowledge of these lattice parameters has been improved (Table VIII).

Compounds C1 to C5 (Table IX) were first prepared in the dry box, under an argon atmosphere. During their fusion, these compositions were expected to remain close to their original definitions or, at least, a moderated reduction of CeF_4 to $CeF_{3.78}$, such as previously reported [5], was not expected to be very harmful for the stability of the resulting glasses. Nevertheless, each composition resulted in a white translucent glass-ceramic. Similar glass-ceramics resulted from the preparation of five other samples having the same composition under an N_2/NF_3 flow. None of these solids is sufficiently well crystallized to exhibit a usable X-ray diffraction pattern.

Two different reasons could explain these failures. First, CeF_4 might simply be unable to replace efficiently ThF_4 in the vitreous structure. Second, the reduction of CeF_4 might be too important. This question has been answered thanks to a simple magnetic method. Glass-ceramics C4Y, C5Y and C6Y, containing YF_3 instead of YbF_3, have been prepared by the same method as compounds C1 to C5. None of these three solids contains any paramagnetic ion except Ce^{3+}, at the rate of 5% for C6Y and 0%–5% for C4Y and C5Y. Each one has been characterized by measuring the influence of a magnetic field on its apparent mass. The measured effective moment-per-ion, μ_{eff} (in μ_B), for global cerium in these solids is, respectively, 1.91 ± 0.20, 1.99 ± 0.17 and 1.90 ± 0.19 for C6Y, C5Y and C4Y.

Although clearly lower than the usual values of μ_{eff} for Ce^{3+} (ranging from 2.28–2.5 [13]), these are clearly identical. Indeed, the maximum value for measured μ_{eff} is inevitably reached when all cerium is Ce^{3+}, i.e. in the solid C6Y. μ_{eff} being obviously the same in C4Y and C5Y but not in C6Y, shows unambiguously that C4Y and C5Y are cerium(IV)-free. The reduction of Ce^{4+} has been complete.

This complete reduction should have been predicted earlier, because each sample from C1 to C5 lost between 1 and 2 wt% during the preparation of the respective solid, when the loss due to this complete reduction theoretically represents 1.4% for samples C1 and C2, and 0.7% for C3 to C5. Nevertheless, this fact was not absolutely sufficient because an evaporation and/or a sublimation of InF_3 is often believed to occur during the preparation of fluoride glasses.

It should have been possible to stabilize cerium(IV) by making the glass in a sealed tube: there, the decomposition of CeF_4 is reported to be lessened, leading to $CeF_{3.95}$ instead of $CeF_{3.78}$ in an open system [5]. Nevertheless, this method has not been carried out: a composition requiring such a glass-formation method will not lead to a good glass liable to supplant the gadolinium-containing BIG glasses, nor even the thorium-containing ones.

5. Conclusion

New thorium-free fluoride glasses have been synthesized by substituting ThF_4 by GdF_3, and stabilized by substituting partly BaF_2 and ZnF_2 by NaF/LiF and CdF_2 from BIGaZYbT glass. The best composition found in this new system, $Ba_{12.5}Li_5Na_{12.5}In_{18}Ga_{12}Zn_{17}Cd_3Yb_{10}Gd_{10}F_{232.5}$, exhibits a quite good glass-forming ability ($R_c = 13\ \mathrm{K\ min^{-1}}$), and its glass stability, measured by the Hruby factor, is widely improved ($H_r = 1.27$) compared to the previously known BIG glasses. A large field of very stable glasses has also been found around this composition.

CeF_4 and $BaCeF_6$ have been synthesized at 520 °C by the use of pure gaseous fluorine. X-ray diffraction patterns have been drawn for the samples of CeF_4, leading to a knowledge about one order of magnitude improved of the lattice parameters previously announced by Zachariasen [12].

After many attempts, the feasibility of BIG glasses containing CeF_4 or $BaCeF_6$ remained impossible. These failures have been demonstrated to be due to a complete reduction of cerium(IV) to cerium(III) during the fusion of the starting powders. Consequently, this impossibility has definitely been demonstrated as an intrinsic phenomenon.

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