STRONTIUM FLUOROHAFNATE GLASSES

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New fluorohafnate glasses have been synthesized in ternary systems based on the HfF_4-SrF_2 association. The compositional limits for glass formations are reported in the HfF_4-SrF_2-NaF, HfF_4-SrF_2-MF_2 (M= Ca, Ba, Cd), HfF_4-SrF_2-LaF_3 systems. The general trend is that HfF_4 content exceeds 60 mol %. Characteristic temperatures, optical transmission and densities are reported. The physical properties of these glasses are discussed by comparison to fluorozirconates. In most cases glass transition occurs above 300 °C.

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1. Introduction

Since the discovery of the first fluorozirconate glasses[1], Heavy Metal Fluoride Glasses (HMFG) have been the subject of numerous studies[2-6]. Their intrinsic physical properties –high transparency and low phonon energy - make them attractive materials for a set of photonic applications [7]. These applications have been developed in optical fiber technologies, when silica fibers have reached their limits. This is the case for optical transmission in the mid-infrared beyond 2 μm, and active fibers for which low phonon energy is required. In practice, most commercial components are based on the ZBLAN glass that is one of the most stable fluorozirconate glass compositions[8,9]. In the early research stage, the large similarities between the chemistry of zirconium and that of hafnium suggested that fluorohafnate glasses should form. Indeed, this assumption was confirmed[10-13], but the use of fluorohafnates was limited, mainly because high purity HfF_4 was rare and expensive. Nevertheless, it appears as a convenient way to adjust the physical properties of core and cladding glasses for optical fibers. Fluorohafnate glasses have also been investigated as high density scintillating materials[14].

While most fluorozirconate systems are based on the ZrF_4-BaF_2 association, other fluorides have lead to binary vitreous fluorozirconates: CaF_2, SrF_2, PbF_2 [15], LaF_3[16]. Some fluorohafnate glass compositions were identified from the mere HfF_4/ZrF_4 substitution[5]. Strontium fluorozirconates have also been studied[17].

This paper reports new vitreous compositions of fluorohafnate glasses based on the HfF_4-SrF_2 association. The aim of this study is to collect information about glass formation and the composition/properties relations. Characteristic temperatures, optical transmission and density are measured.

2. Experimental

Glass synthesis includes a series of classical steps: mixing of starting materials, melting, fining, casting and annealing. Glass samples are prepared from chemical grade reagents according to a method reported elsewhere [5]. Process must be adjusted to take into account the specific features of the fluoride glass melts: melt viscosity is very low at liquidus temperature and these melts are sensitive to hydrolysis. An additional difficulty lies in their devitrification tendency. Depending on glass stability, cooling rate must be adjusted to prevent crystallization upon cooling. Starting materials are analytical grade HfO_2, CaF_2, SrF_2, BaF_2, CdF_2, LaF_3 and NH_5F_2. Fluorination and melting are carried out in a long platinum crucible that limits the exchange with atmosphere. The limits for glass formation reported here correspond to quenched glasses: melt is poured onto a brass mould and squeezed by a metallic plate. The estimated quenching rate is in the 100 to 1000 $K.s^{-1}$ range, which results in thin samples, 0.5 to 0.8 mm in thickness.

Characteristic temperatures were determined by differential scanning calorimetry (DSC) (Seiko DSC 220) at a standard 10 K/min heating rate. They encompass glass transition temperature (Tg), temperatures for onset of crystallization (Tx) and exothermic maximum (Tp). The absolute temperature error on Tg and Tx is less than ± 2°C and relative errors between compositions are expected to be < ±1 °C. The stability of the glasses with respect to devitrification is evaluated using the stability factors ΔH[18] and S[19], defined as follows:

$\Delta H = Tx-Tg$ $S = (Tx-Tg)(Tp-Tx)/Tg$.

Optical transmission spectra were recorded using a Varian spectrometer in the UV-visible range and a Bomem Michelson 100 IR spectrometer operating between 400 and 4000 cm^{-1}.

3. Results

3.1 Glass formation

Five ternary systems were investigated: HfF_4-SrF_2-NaF, HfF_4-SrF_2-CaF_2, HfF_4-SrF_2-BaF_2, HfF_4-SrF_2-CdF_2, HfF_4-SrF_2-LaF_3. Figure 1 reports the various compositions investigated in these systems and the corresponding limits of the vitreous domains. This study encompasses the binary HfF_4-BaF_2 and HfF_4-SrF_2 binary systems. Glass forming range is narrower with barium than with strontium. However, in the ternary systems, calcium and cadmium fluorides lead to smaller vitreous areas than barium fluoride. In a general way, vitreous zone extends beyond 60 mol % HfF_4. In most cases, fast cooling rate in necessary to avoid crystallization and consequently glass samples are usually thin (< 1 mm). Obtaining thick samples in these systems will require both composition and processing adjustments to control crystal growth and extrinsic nucleation.

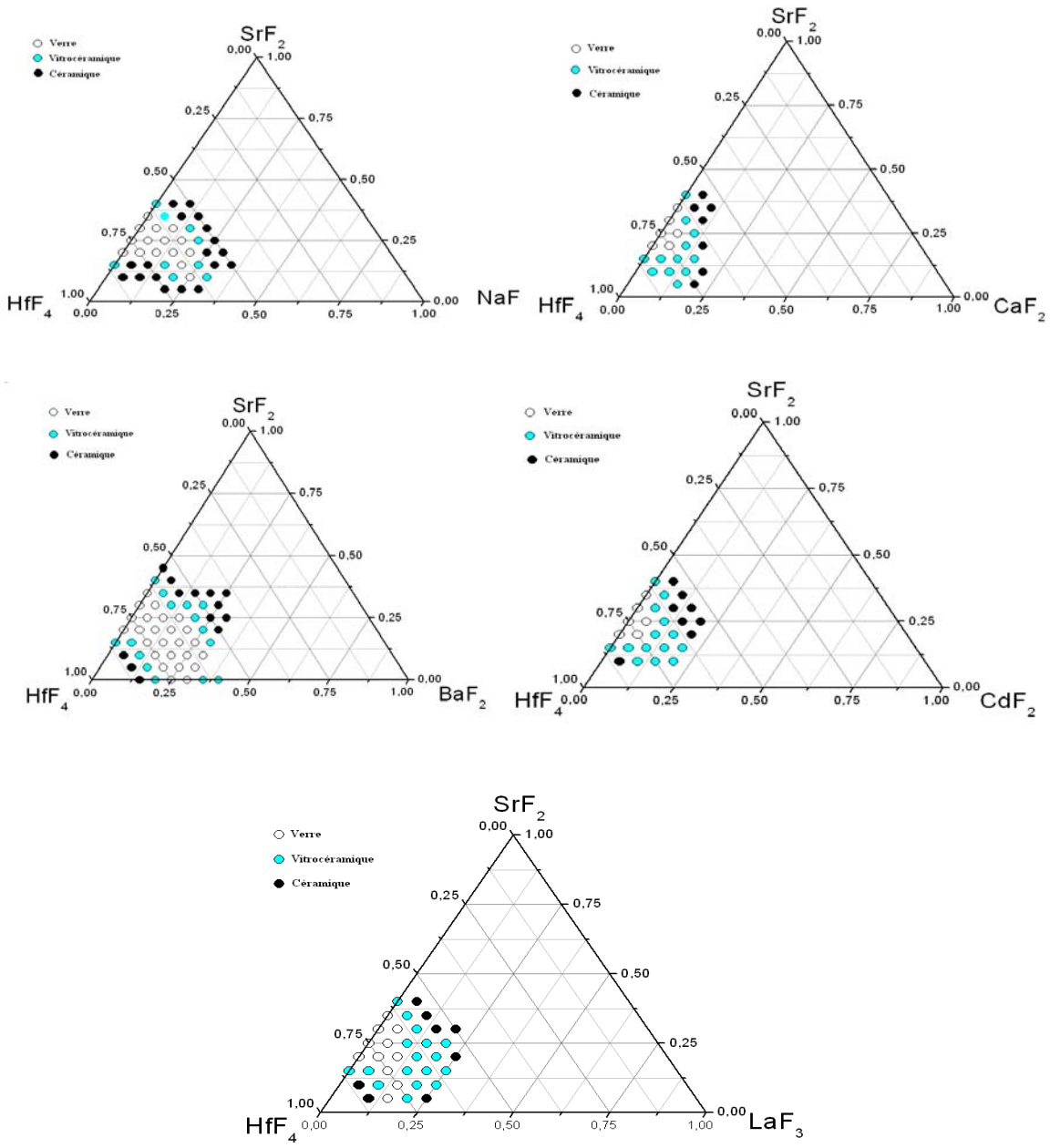

Fig. 1. Glass forming areas in the HfF_4- SrF_2-NaF, HfF_4- SrF_2-CaF_2, HfF_4- SrF_2-BaF_2, HfF_4- SrF_2-CdF_2 and HfF_4- SrF_2-LaF_3 ternary systems.

3.2 Thermal properties

3.2.1 Binary glasses

Characteristic temperatures – Tg for glass transition, Tx for onset of crystallization, Tp for maximum of crystallization exotherm – have been measured for HfF_4-SrF_2 and HfF_4-BaF_2 glasses. Corresponding values are given in table 1 that also reports the stability factors ΔH and S. Figure 2 shows the evolution of the characteristic temperatures versus composition in the HfF_4-SrF_2 system. Glass transition temperature increases with hafnium content. The same trend is observed with the barium fluorohafnate glass. Note that Tg increases as SrF_2 replaces BaF_2 (table 1).

Table 1. Thermal properties of binary fluorohafnate glasses. Tg, Tx and Tp are temperatures for glass transition, onset of crystallization, maximum of exotherm respectively. Tx-Tg and S are stability factors.

Glass composition	Tg(°C)	Tx(°C)	Tp(°C)	Tx-Tg(°C)	S(K)
$75HfF_4$-$25BaF_2$	314	354	363	40	1.06
$70HfF_4$-$30BaF_2$	311	350	359	39	1.12
$80HfF_4$-$20SrF_2$	323	375.5	393	42.5	2.26
$75HfF_4$-$25SrF_2$	323.5	370.5	388	47	2.58
$70HfF_4$-$30SrF_2$	316	369	382	53	2.11
$65HfF_4$-$35SrF_2$	311.5	352	362	40.5	1.29

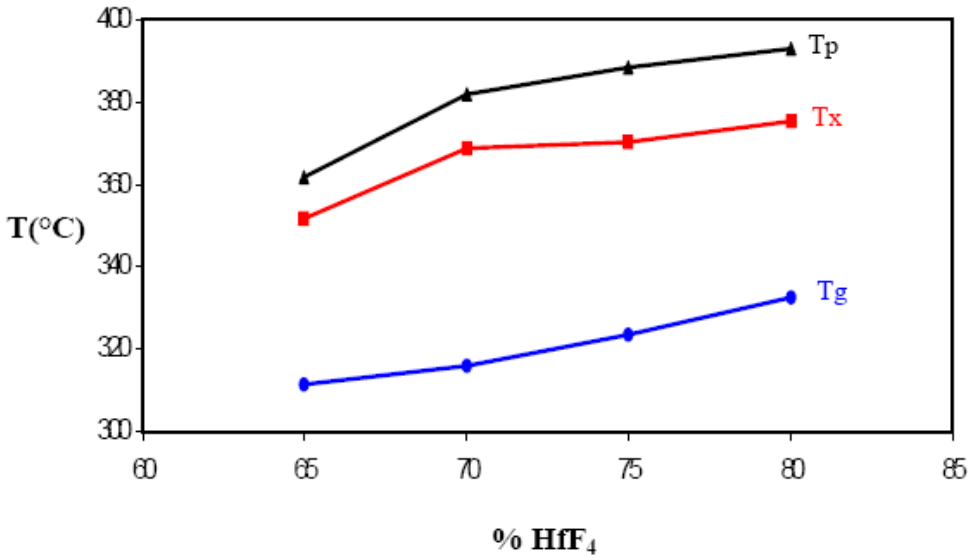

Fig. 2. Evolution of characteristic temperatures versus HfF_4 content in the HfF_4 –SrF_2 binary system. Tg for glass transition, Tx for onset of crystallization and Tp for the maximum of exothermic peak

3.2.2 Ternary glasses

Thermal measurements have been carried out in a systematic way on the glasses from the five diagrams studied. They are reported in tables 2 to 5. Glass transition occurs above 300 °C, except for glasses containing 10 mol % NaF or more. A maximum value of 412 °C is observed for the 80 HfF_4-5 SrF_2-15 LaF_3 ternary glass. The third fluoride added to the HfF_4-SrF_2 binary glass increases Tg according to the sequence Cd < Ca < Ba < La, while sodium fluoride has the reverse effect.

The influence of the SrF_2 / HfF_4 substitution on Tg is illustrated by figure 3. Higher Tg are observed when HfF_4 content increases.

Table 2. Thermal properties of HfF_4- SrF_2-NaF glasses.

Glass composition	Tg(°C)	Tx(°C)	Tp(°C)	Tx-Tg(°C)	S(K)
$75HfF_4$- $20SrF_2$-5NaF	305	361	370	56	1.65
$70HfF_4$- $25SrF_2$-5NaF	304	359	373	55	2.53
$65HfF_4$- $30SrF_2$-5NaF	303	356	366	53	1.75
$70HfF_4$- $20SrF_2$-10NaF	298	353	364	55	2
$65HfF_4$- $25SrF_2$-10NaF	288	342	355	54	2.44
$60HfF_4$- $30SrF_2$-10NaF	284	329	342	45	2
$65HfF_4$- $20SrF_2$-15NaF	278	320	331	42	1.66
$60HfF_4$- $25SrF_2$-15NaF	277	319	332	42	1.97
$65HfF_4$- $15SrF_2$-20NaF	280	331	345	51	2.55
$60HfF_4$- $20SrF_2$-20NaF	275	330	345	55	3
$65HfF_4$- $10SrF_2$-25NaF	265	309	325	44	2.65

Table 3. Thermal properties of ternary glasses in the HfF_4- SrF_2-CaF_2 and HfF_4- SrF_2-CdF_2 systems.

Glass composition	Tg(°C)	Tx(°C)	Tp(°C)	Tx-Tg(°C)	S(K)
$75HfF_4$- $20SrF_2$-$5CaF_2$	330	369	386	39	2
$70HfF_4$- $25SrF_2$-$5CaF_2$	320	370	387	50	2.65
$75HfF_4$- $20SrF_2$-$5CdF_2$	325	374	389	49	2.26
$70HfF_4$- $25SrF_2$-$5CdF_2$	318	366	385	48	2.87

Table 4. Thermal properties of HfF_4- SrF_2-LaF_3 glasses.

Glass composition	Tg(°C)	Tx(°C)	Tp(°C)	Tx-Tg(°C)	S(K)
$75HfF_4$- $20SrF_2$-$5LaF_3$	332	390	398	58	1.40
$70HfF_4$- $25SrF_2$-$5LaF_3$	331	376	384	45	1.10
$65HfF_4$- $30SrF_2$-$5LaF_3$	322	366	378	44	1.64
$75HfF_4$- $15SrF_2$-$10LaF_3$	353	406	412	53	0.90
$70HfF_4$- $20SrF_2$-$10LaF_3$	341	382	392	41	1.20
$80HfF_4$- $5SrF_2$-$15LaF_3$	412	448	464	36	1.40
$75HfF_4$- $10SrF_2$-$15LaF_3$	362	404	413	42	1.04

Table 5. Thermal properties of HfF_4- SrF_2-BaF_2 glasses.

Glass composition	Tg(°C)	Tx(°C)	Tp(°C)	Tx-Tg(°C)	S(°C)
$75HfF_4$- $20SrF_2$-$5BaF_2$	322	371	386	49	2.28
$70HfF_4$- $25SrF_2$-$5BaF_2$	328	373	387	45	1.92
$65HfF_4$- $30SrF_2$-$5BaF_2$	291	340	354	49	2.36
$75HfF_4$- $15SrF_2$-$10BaF_2$	323	367	381	44	1.91
$70HfF_4$- $20SrF_2$-$10BaF_2$	314	360	373	46	1.90
$65HfF_4$- $25SrF_2$-$10BaF_2$	312	365	379	53	2.38
$75HfF_4$- $10SrF_2$-$15BaF_2$	321	368	381	47	1.90
$70HfF_4$- $15SrF_2$-$15BaF_2$	315	359	371	44	1.67
$65HfF_4$- $20SrF_2$-$15BaF_2$	276	320	331	44	1.75
$60HfF_4$- $25SrF_2$-$15BaF_2$	310	353	365	43	1.66
$75HfF_4$- $5SrF_2$-$20BaF_2$	319	363	373	44	1.38
$70HfF_4$- $10SrF_2$-$20BaF_2$	312	360	370	48	1.54

Glass composition	Tg(°C)	Tx(°C)	Tp(°C)	Tx-Tg(°C)	S(°C)
$65HfF_4$- $15SrF_2$-$20BaF_2$	310	355	366	45	1.60
$60HfF_4$- $20SrF_2$-$20BaF_2$	309	345	362	36	1.98
$70HfF_4$- $5SrF_2$-$25BaF_2$	312	354	362	42	1.07
$65HfF_4$- $10SrF_2$-$25BaF_2$	310	350	361	40	1.42
$60HfF_4$- $15SrF_2$-$25BaF_2$	324	382	396	58	2.50
$65HfF_4$- $5SrF_2$-$30BaF_2$	315	369	377	54	1.37
$60HfF_4$- $10SrF_2$-$30BaF_2$	310	348	364	38	1.96

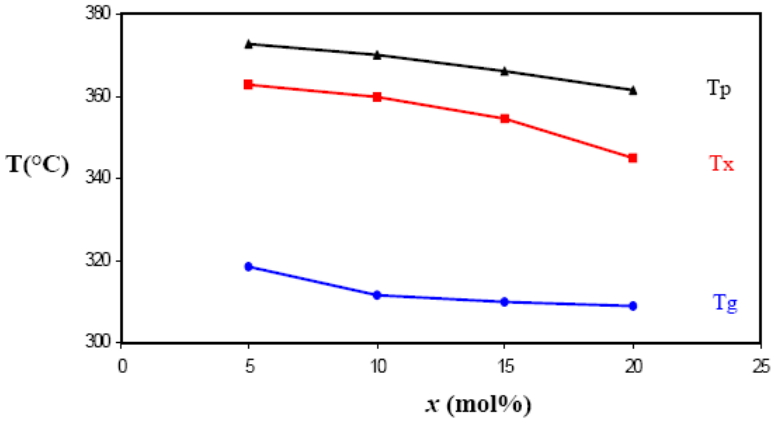

Fig. 3. Evolution of characteristic temperatures versus composition in the (80-x) HfF_4 x SrF_2 20BaF_2 ternary system.

3 3 Other physical properties

The density of these glasses is rather large -close to 6 g/cm^3- by comparison to common HMFG. Typical values appear in table 6. As shown in figure 4, the evolution of density in the (80-x) HfF_4 - x SrF_2 - 20 BaF_2 (5 < x < 20) series of glasses is linear.

Optical transmission has been recorded for thin samples (< 1 mm). It ranges from 210 nm in the UV spectrum to 8 µm in the infrared spectrum, without extrinsic absorption band. Thicker samples are required for more accurate optical measurements.

Table 6. Density of fluorohafnate glasse

Glass composition	d(g/cm^3)
$65HfF_4$- $25SrF_2$-10NaF	5.95
$65HfF_4$- $30SrF_2$-5NaF	5.63
$70HfF_4$- $25SrF_2$-5NaF	5.53
$70HfF_4$- $20SrF_2$-$10BaF_2$	6.19
$70HfF_4$- $25SrF_2$-$5BaF_2$	5.97
$70HfF_4$- $25SrF_2$-$5LaF_3$	5.43
$70HfF_4$- $25SrF_2$-$5CaF_2$	5.07
$75HfF_4$- $5SrF_2$-$20BaF_2$	6.30
$70HfF_4$- $10SrF_2$-$20BaF_2$	6.24
$65HfF_4$- $15SrF_2$-$20BaF_2$	6.20
$60HfF_4$- $20SrF_2$-$20BaF_2$	6.15
$70HfF_4$- $25SrF_2$-$5CdF_2$	5.57

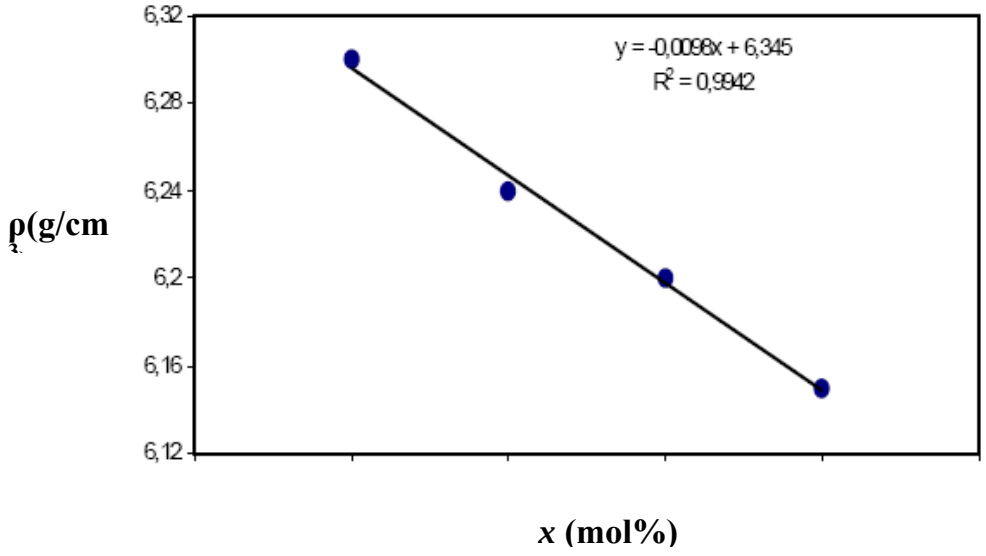

Fig. 4. Evolution of density versus composition in the (80-x) HfF_4 x SrF_2 20BaF_2 ternary system.

4. Discussion

The vitreous areas in these fluorohafnate systems compare with those reported for the strontium fluorozirconate glasses [17]. In a general way, glass transition temperature is slightly larger with HfF_4 and the correlation between the value of Tg and the chemical composition is consistent with current network model. On may assume that glass structure is constructed from the network of HfF_8 or HfF_7 polyhedra sharing corners and edges. Large cations such as Sr^{2+} and Ba^{2+} act as modifiers. As a consequence, network connectivity increases with hafnium concentration. The influence of the modifying cations is ruled by size and charge. Thus lower Tg is observed with Na^{+} and higher with La^{3+}. For earth alkali cations, Tg decreases as ionic radius increases, which is consistent with the following values (in Å) for a VIII coordination number[20]: 1.12 (Ca), 1.26 (Sr), 1.42 (Ba).

High density of fluorohafnate glasses arises first from the large atomic weight of hafnium (178.5), almost twice that of zirconium. In addition, there is a small size effect: because of the lanthanidic contraction, ionic radius is smaller for Hf^{4+} than for Zr^{4+}.

By comparison to standard fluorozirconates, fluorohafnate glasses offer a set of attractive features that may compensate their higher cost. It has been stated that their refractive index is smaller for the same nominal composition, with facilitates the adjustment of numerical aperture in optical fibers. From a chemical point of view, the reduction of tetravalent hafnium to form Hf^{3+} is more difficult than the reduction of Zr^{4+}. Therefore, one may expect smaller concentration of defects associated to trivalent zirconium. The most interesting aspect concerns the IR multiphonon absorption edge that is shifted to larger wavelengths by reference to ZBLAN glass[21], because of hafnium mass. In these conditions, fluorohafnate glass fibers free of zirconium and aluminium should allow transmission up to 4.8 □m (at 1 dB/m loss). However, fiber drawing requires that glass stability is improved, which implies additional work on glass compositions. The lower phonon energy that is associated to fluorohafnate glasses [22] increases the quantum efficiency of some transitions in rare earths, e.g. the 1.3 μm emission of Pr^{3+}.

5. Conclusion

New Heavy Metal Fluoride Glasses based on hafnium tetrafluoride have been synthesized in the HfF_4-SrF_2-NaF, HfF_4-SrF_2-CaF_2, HfF_4-SrF_2-BaF_2 , HfF_4-SrF_2-CdF_2 , HfF_4-SrF_2-LaF_3. systems. The limits for glass formation have been determined in these ternary systems and HfF_4 concentration ranges from 60 to 80 mol % for quenched glasses. Glass transition occurs above 300 °C, except for glasses containing sodium. The evolution of characteristic temperatures and glass stability versus composition has been studied in the HfF_4-SrF_2 and HfF_4-BaF_2 binary systems and the HfF_4-SrF_2-BaF_2 ternary system.

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