PHYSICAL PROPERTIES OF MULTICOMPONENT FLUOROHAFNATE GLASSES

S. CHAGUETMI [a,c], A. BOUTARFAIA [b], M. POULAIN [c*]
[a] *Laboratoire LSPN, Université du 08 Mai 45, Guelma, Algérie*
[b] *Laboratoire de Chimie Appliquée, Université d'Ouargla, Algérie*
[c] *Matériaux photoniques, UMR Sciences Chimiques, Université de Rennes1, F-35042 Rennes*

Fluoride glasses based on HfF_4 have been synthesized in the HfF_4-SrF_2-BaF_2 system. In order to decrease the crystallization rate, various fluorides (PbF_2, ZnF_2, AlF_3 and YF_3) have been introduced in the $66HfF_4$-$22SrF_2$-$12BaF_2$ composition as substituent of alkali earth cations. Glass transition temperature is close to 320 °C, and coefficient of thermal expansion is 155 10^{-7} K^{-1}. Microhardness and elastic moduli have been measured. Values of refractive index are given for wavelengths ranging from 633 nm to 1551 nm. By comparison to fluorozirconates, fluorohafnate glasses exhibit larger density, lower refractive index, lower phonon energy and extended transmission in the mid-infrared spectrum. Potential applications relate to active optical fibres and supercontinuum generation.

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1. Introduction

Heavy metal Fluoride Glasses (HMFG) offer a set of attractive features for optical applications based on optical fibres [1]. While most developments are centered upon fluorozirconates, mainly ZBLAN glass, other HMFGs could be prefered when this standard glass has reached its limits. This is the case for the cut-off wavelength in the infrared spectrum or equivalently the phonon energy. Trivalent fluoride glasses –fluoroindates and fluorogallates- can be used for this purpose. However, fluorohafnate glasses offer the advantage of a better compatibility with fluorozirconates with identical processing.

Previous studies were implemented on fluorohafnate glass compositions obtained by the Hf/Zr substitution [2, 3]. More recently, we reported new glass forming systems based on the HfF_4-SrF_2 association [4]. However, these glasses are prone to devitrification and require a large cooling rate. More stable glasses may be obtained in multicomponent systems. According to the so-called "confusion principle", the stability against nucleation increases with the number of glass components.

This short paper reports thermal and optical properties of new fluorohafnate glass compositions.

2. Experimental

Samples are prepared by the conventional method that includes melting, fining, casting and annealing [1]. Synthesis is implemented at room atmosphere in long platinum crucibles. Pro analysis reagents are used and typical sample size is 5 grams.

Thermal properties have been investigated using a TA DSC 2010 differential scanning calorimeter, at 10 K/min heating rate under Ar atmosphere. The estimated temperature accuracy is

[*]Corresponding author: marcel.poulain@univ-rennes1.fr

± 2 K for the temperatures of glass transition Tg and onset of crystallization Tx Thermal expansion is measured using a TMA TA 2840 set-up, at 2 K/min heating rate, between 100°C and 250°C. The density of some samples was determined using a helium picnometer (Micromeritics, AccuPyc 1330), with ± 0.001 g/cm^3 accuracy. Micro-hardness values were taken by Matzuzawa MXT 70 digital micro hardness tester, and the charge was 100 g. Infrared transmission was recorded on a Brucker Vector 22 spectrometer. Room temperature ultrasonic measurements were performed by the pulse-echo method with a Panametrics model 5800 pulser/receiver with a quartz transducer. Both X-cut transducer and Y-cut transducer (with 10 MHz frequency) were employed for longitudinal modes and for shear modes. Refractive index was measured by the prism coupling method, using a Metricon 2010 apparatus. Taking into account the optical quality of the samples, the estimated accuracy on n value is ± 10^{-3}.

3. Results

3.1 Thermal properties

Three series of samples have been synthesized from the ternary composition 66 HfF_4-22 SrF_2- 12 BaF_2, with introduction of selected additives, as shown in table 1.

Table 1- Glass compositions (mol %)

Acronym	HfF_4	SrF_2	BaF_2	AlF_3	PbF_2	YF_3	ZnF_2
HSBAY	66	20	8	2	2	2	-
HSBAPYZn	66	18	8	2	2	2	2
HSBAPZn	66	20	8	2	2	-	2

Characteristic temperatures are rather close, with glass transition occurring around 320°C. Table 2 reports the respective values of Tg, Tx and Tp corresponding respectively to glass transition, onset of crystallization and maximum of exothermic peak. Glass forming ability is estimated from semi-empirical parameters: the value of the stability range $\Delta T = T_x - T_g$ [5] and the S factor defined as $S = (T_x - T_g)(T_p - T_x)/T_g$ [6] with temperatures expressed in Kelvin. These data suggest that zinc fluoride does not enhance resistance to devitrification, which is consistent with similar observations in fluorozirconates. The coefficient of thermal expansion CTE is smaller than that of standard zirconium fluoride glasses [1].

Table 2. Coefficient of thermal expansion CTE and characteristic temperatures: T_g for glass transition, T_x for onset of crystallization, T_p for maximum of exotherm. T_x-T_g and S factor are stability criteria

Acronym	T_g (°C)	T_x (°C)	T_p (°C)	T_x- T_g (°C)	S(K)	CTE (10^{-7} K^{-1})
HSBAY	323	384	403	61	3.6	155.4
HSBAPYZn	322	370	389	48	2.8	155.2
HSBAPZn	318	359	378	41	2.5	155.6

3.2 Mechanical properties.

As one could expect, density ρ is nearly constant for the three glasses, ranging from 5.87 to 5.89 $g.cm^{-3}$. This large value results from the large atomic weight of hafnium.

The values of Young’s modulus E, bulk modulus K, shear modulus G and Poisson ratio μ have been calculated from the measured longitudinal and transverse sound velocities V_L and V_T.

Table 3 reports the corresponding values to the zinc-free composition. The experimental microhardness measured by Vickers indentation is given in table 4.

Table 3. Density, sound velocity and elastic moduli

Acronym	ρ (Kg/m^3)	V_L (m/s)	V_T (m/s)	E (GPa)	G (GPa)	K (GPa)	μ
HSBAPY	5873	3826	2115	67.3	26.3	50.9	0.281

Table 4. Vichers microhardness

Acronym	HSBAPY	HSBAPYZn	HSBAPZn
Hv(Kg/mm^2)	310	302	297

3.3 Optical Properties

Refractive index has been measured for various wavelengths. Experimental values appear in table 5.

Table 5. Refractive index at different wavelengths

λ (nm)	n_{HSBAPY}	$n_{HSBAPYZn}$	$n_{HSBAPZn}$
632.8	1.507	1,500	1.496
825	1.502	1.495	1.492
1060.7	1.500	1.494	1.490
1311	1.499	1.492	1.489
1551	1.497	1.491	1.488

Experimental data have been fitted to the Cauchy's relation: $n(\lambda) = A + B/\lambda^2 + C/\lambda^4$. The computed constants A, B and C are given in table 6

Table 6. Values of A, B and C parameters

Parameter	HSBAPY	HSBAPYZn	HSBAPZn
A	1.497	1.491	1.496
B	$3.451.10^3$	$2.135.10^3$	$3.575.10^3$
C	$2.941.10^8$	$6.475.10^8$	$1.532.10^8$

A typical infrared transmission curve is reported in figure 1 for a sample 2.5 mm thick. A residual OH band is observed around 3400 cm^{-1}. The tiny band around 1600 cm^{-1} results from surface molecular water.

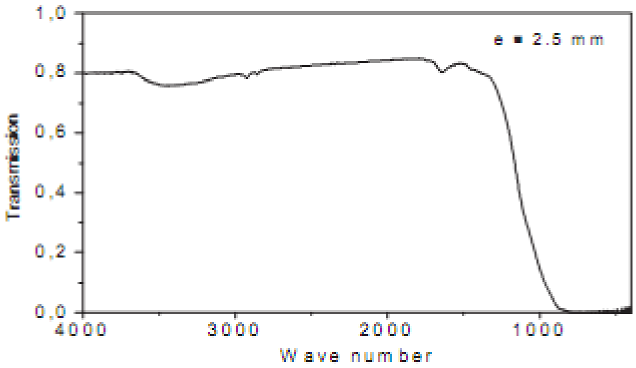

Fig. 1 Infrared transmission of a HSBAPY glass, 2.5 mm in thickness.

4. Discussion-Conclusion

Multimillimeter glass samples can be obtained with alkali earth fluorohafnates stabilized by the small addition of AlF_3, YF_3 and PbF_2. Zinc fluoride is not active in this respect. Main physical and optical properties have been investigated. Refractive index is close to 1.50, which is smaller than that of alkali-free fluorozirconates. Spectral dispersion has been determined. However, data are not accurate enough to calculate material dispersion $d^2n/d\lambda^2$. As one could expect, these HfF_4 based glasses exhibit large density (>5.8 g.cm^{-3}) and extended transmission in the IR spectrum. In this respect, they push ahead the limits of the stadard fluorozirconate glasses. Because of their low phonon energy, they make promising materials for rare earth-doped active fibres, and also for supercontiuum generation [7]. It is expected that fibres with optical losses lower than those of ZBLAN fibres could be drawn from optimized compositions.

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